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[54] **THIN FILM EVAPORATION OF A CRUDE AMIDE FEED IN MIXTURE WITH AN ALKALI METAL HYDROXIDE**

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[58] **Field of Search** ..... 203/37, 91, 89; 202/205, 202/236; 260/404, 551 R

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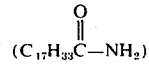
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[57] **ABSTRACT**

Oleic acid amide



and similar fatty acid amides are separated from the corresponding fatty acid impurities by neutralizing the acids with base and subjecting the neutralized reaction mixture to molecular distillation. The process also achieves an appreciable improvement in the color of the amide.

8 Claims, No Drawings

THIN FILM EVAPORATION OF A CRUDE AMIDE FEED IN MIXTURE WITH AN ALKALI METAL HYDROXIDE

BACKGROUND OF THE INVENTION

The amides of fatty acids have many uses such as mold release agents, lubricants, lusterants in the molding of synthetic resins, softeners, and waterproofing agents for textiles. Fatty acid amides are commonly produced by ammonolysis of fatty acid esters or by the dehydrative amidation of fatty acids, and the product amides contain impurities originally present in the starting materials as well as those introduced by subsequent processing. Generally, free fatty acids are the primary group of impurities. In recent years, the demand has been especially heavy for "purified" amides containing greatly reduced amounts of fatty acids and also for lighter colored amides. Fatty acid impurities are presently objected to in a wide range of industrial specifications.

A great deal of work has been directed toward separation of fatty acids. Recently in Japanese Patent Publication No. 10533/1971, a system was described whereby the amide is subjected to vacuum distillation in the presence of a basic additive such as an alkali metal hydroxide. However, the reference teaches that this method is objectionable in that the base induces decomposition of the amide to form nitriles. The reference overcomes this problem by carrying on the vacuum distillation in the presence of alkali metal phosphates; e.g., trisodium or tripotassium phosphates. By using the phosphates, the reference avoids use of bases such as the alkali metal and alkaline earth hydroxides which are described as being objectionable.

The present invention arises from the discovery that fatty acid amides can indeed be separated from the corresponding fatty acids by vacuum distillation following addition of bases such as the alkali metal hydroxides. To accomplish separation, the invention takes advantage of the theory that decomposition of the amide is related to two important factors which both outweigh base addition in their effect. The first factor is the boiling temperature (at reduced pressure) of the material to be distilled. The second factor is the "contact time" or "residence time" during which the compound is exposed to distillation temperatures. It is believed that this last factor is not adequately appreciated by the prior art and leads in large measure to the problem of nitrile formation. For example, in conventional distillation, the material to be distilled is placed in a flask and is simultaneously subjected to reduced pressure and elevated temperatures for a prolonged period of time. The average retention time of the material to be distilled is unduly long in a conventional distillation. It is believed that this prolonged exposure may be responsible for amide decomposition. A particularly important result of placing emphasis on a reduced residence time is that base addition can be employed to neutralize and separate free fatty acids as the relatively non-volatile soaps, even though the prior art recommends against the use of base as it promotes decomposition of the amide to form nitriles, at least under the conditions of vacuum distillation as these are conventionally employed.

THE INVENTION

The present invention comprises subjecting neutralized fatty acid amides to reduced pressures and simultaneously passing the amide over a distillation surface heated at or above the boiling temperature of the amide. Almost immediately upon contact with the heated distillation surface, the amide is formed into a thin film (e.g., less than 1 mm.) by gravity or by mechanical action. The thickness of the film depends on variables such as temperature, viscosity, rotor speed, and feed rate. This type of distillation process is generally known as molecular distillation; e.g., see U.S. Pat. No. 3,362,892. Film formation allows the amide to volatilize quickly under reduced pressures (0.005 to 5 mm. of Hg) after only a very short residence time (i.e., from 1 to 10 seconds) on the heated distillation surface. This short contact time with the heated surface is very advantageous because the heat exposure of the amide is greatly reduced in comparison with more conventional batch-type distillation systems where the material to be distilled is housed in a flask or other container. As the amide vaporizes, it is collected and the relatively non-volatile impurities, i.e., fatty acid salts and color bodies (some of which may also have been converted to salts) are allowed to pass over the distillation surface and are collected as a non-volatile residue. If desired, this residual fraction can be recycled to increase the yield of the amide.

By means of the invention as just described, several advantages are immediately obtained. First, relatively inexpensive and available materials such as the alkali metal hydroxides of sodium, potassium, and lithium, and alkaline earth hydroxides such as calcium and magnesium are employed to neutralize the free fatty acid content of the amide. Secondly, vacuum distillation of the fatty acid amide is accomplished without appreciable formation of nitriles and despite the fact that the above basic hydroxides are employed.

The "crude" or impurified fatty acid amide employed in the invention is generally an industrial grade C_{14} to C_{22} saturated, unsaturated, or polyunsaturated fatty acid amide such as oleic acid amide which is a mixture of fatty acid amides, predominantly oleyl amide, but also containing some saturated and unsaturated C_{14} to C_{16} amides, as well as C_{18} polyunsaturated amides. Additionally, other fatty acid amides can be employed such as commercial grade erucamide (which is largely a C_{22} unsaturated fatty amide) and stearic acid amide, a C_{18} saturated amide. The oleic and stearic acid amides generally contain some C_{16} fatty acid amides. The amides can readily be produced in commercial quantities by reacting the corresponding fatty acid with ammonia. The resulting reaction mixture obtained as product contains the desired acid amide plus varying amounts of unreacted acid, usually from 2 to 7% by weight of the reaction mixture. In addition, varying small amounts of color producing substances are also present. These are generally described simply as color bodies. Their presence is sufficient, however, to produce a color in the crude amide of from 4 to as much as 8 on the Gardner scale. Nitriles are also present in amounts of about 1% or less. It is this crude amide reaction mixture or others similar to it which are most susceptible to processing by the present invention to reduce the acid content. Processing also results in reduction in the color rating of the amide with values lower than 1 (Gardner scale) being generally obtained. There

is no increase in nitrile content over that which was present in the distillation feed stock. If the molecular distillation is carried out in the absence of added alkali metal hydroxide, the free fatty acid and part of the color bodies are not removed. This may indicate that some of the color bodies themselves are acidic and form non-volatile salts or are transformed to non-volatile substances by the addition of alkali metal hydroxides.

A preferred embodiment of the invention comprises recovering oleic acid amide wherein less than 0.5 weight percent of oleic acid is present as an impurity in the distillate. The method comprises neutralizing a reaction mixture containing 2 to 6 weight percent of industrial grade oleic acid with an alcoholic (i.e., methanol or ethanol) solution of an alkali metal hydroxide (methoxide) or calcium hydroxide. Subsequently, the alcoholic solvent is removed (e.g., by vacuum stripping) and the neutralized mixture is subjected to molecular distillation. Where the reduced pressure due to vacuum pumping is from 0.12 to 0.18 mm. Hg, the amide distills at 390° to 415° F. and is collected at a temperature from 204° to 210° F.

In neutralizing the free acid, the amount of base employed is generally in excess of that theoretically necessary. An excess of base of from 6 to 20% based on the amount theoretically necessary to neutralize the acid present in the reaction mixture is sufficient to remove the last of the free acid and prevent distillation of colored bodies. As described above, the essence of the invention is distillation of neutralized amides which have been formed into thin films. In neutralizing the amides, the particular base employed is not critical. Experimental work has been primarily restricted to inorganic bases. However, as would be apparent to one skilled in the art, other bases can be employed such as the organic quaternary ammonium hydroxides, e.g., tetraethyl ammonium hydroxide, tetramethyl ammonium hydroxide, benzyl trimethyl ammonium hydroxide, and benzyl triethyl ammonium hydroxide.

EXAMPLE I

A wiped-film evaporator of pilot plant size was used to carry out a molecular distillation of oleic acid amide containing 3 to 4 percent by weight of the sodium soap of oleic acid and no fatty acid. The evaporator had an evaporating surface area of 4 sq. ft., a condenser surface area of 19 sq. ft., and the average travel path between the two surfaces was about 3 inches. The vacuum system was provided by an oil diffusion pump having a capacity of approximately 1800 cfm. at 10 microns. This pump was backed up by a mechanical pump having a capacity of 180 cfm. at 10 microns.

The material distilled was of the following approximate composition:

1. Industrial Grade Oleic Acid Amide = 96.2 – 96.7%

$$(C_{17}H_{33}\overset{\overset{O}{\|}}{C}-NH_2)$$

2. Total Nitrile ($C_{17}H_{33}C \equiv N$) = 0.5 – 1.0%
3. Soap

$$(C_{17}H_{33}\overset{\overset{O}{\|}}{C}-ONa) = 2.8\%$$

To prepare the amide for distillation, 300 pounds of the amide were reacted with 8.0 pounds of a solution of sodium methoxide in methanol. The methanol solution contained 2.0 pounds of sodium methoxide by weight, which was an amount sufficient to neutralize all the free acid contained in the amide portion of the reaction mixture as well as to provide an excess of about 15 weight percent based on the acid present. The amide portion of the reaction mixture consisted of 288.6 pounds of total amides, 8.4 pounds of total acids, 3.0 pounds of total nitriles, and had a color rating on the Gardner scale of about 5.

The methanol solution was mixed with the molten amide and the reaction mixture was stirred for a period of about 1 hour at a temperature of about 215° F. This is sufficient time to allow the mixture to react; i.e., for the acid to be neutralized to the soap form. At the end of the reaction period, the reaction mixture was analyzed but free acid was not detected analytically.

The reaction mixture was passed into a "degassing" system to remove methanol solvent by vacuum distillation at a temperature of from about 215° F. at 1.3 mm. Hg. Subsequently, the material was subjected to molecular distillation in the wiped-film evaporator described above. Nine different portions of the reaction mixture were distilled to give a total of nine different "runs". The process conditions during distillation are set forth in Table I. Blanks indicate that a particular variable was not measured during the run in question. Particularly in run 2, malfunction of the distillation apparatus impaired production of the purified amide and data was consequently not collected on this run.

TABLE I

Run Number	1	2	3	4	5	6	7	8	9
Jacket Temperature	414		415	415	385	390	415	413	412
Condensor Temperature (° F.)	210			204	204	208	208		
WFE* Operating Pressure (Microns)	160		170	160	120	120	180	170	170
WFE Rotor Speed (R.P.M.)	280		280	280	280	280	280	280	280
Residue Rate (lbs./hr.)	48			95	31	56			
Distillate Rate (lbs./hr.)	113			113	74	90	125	118	120
WFE Feed Rate (lbs./hr.)	161			208	105	146	141	126	
Pump Pressure (microns)	11		11	12	5	6	7	6	6

TABLE I-continued

Run Number	1	2	3	4	5	6	7	8	9
Percent Distillate	70%				70.5%		89%	93.5%	

*WFE - Wiped-film evaporator

Upon analysis, the distillate contained amide, 0.5–1% nitrile, and had a color rating on the Gardner scale of much less than 1. Typical colors on the Apha scale were 20–60. The analysis indicated the absence of free acid in the distillate.

Analysis of residue was not regularly made. However, on two samples from Runs numbers 5 and 8 (Table I), the analysis was as follows:

	A		B	
Percent Distillate	70.5%		93.5%	
Amide	88.5%		86.5%	
Soap	13.6%	(0.45 meq./g.)	10.3%	(0.34 meq./g.)
Nitrile	1–2%		1–2%	
Free Fatty Acid	Nil		0.14%	

In Table I, the WFE operating pressure refers to the "top leads" pressure which is the pressure reflecting the vapor pressure contributed by the amide as it distills. The pump pressure is the WFE operating pressure less the vapor pressure from the volatilized amide. The "% distillate" is the percentage of the original feed which was distilled and collected as distillate. In carrying out the distillation, some difficulty was experienced with "freezing" of the feed before it could be distilled. Therefore, adequate measures should be taken to insure that the process lines are maintained at a suitably elevated temperature; i.e., in excess of 210° F. From Table I it can be seen that the amide was distilled at 385°–415° F. and collected at a temperature of from 204° to 210° F. (condenser temperature).

EXAMPLE II

Various batches of oleic acid amide were subjected to molecular distillation using a wiped-film evaporator of laboratory size. The distillation unit was characterized by an evaporating surface of approximately 50 sq. in., a condensing surface of 16 sq. in., and a travel path between the two surfaces of about 0.5 inch. The vacuum for the unit was provided by a rotary pump having an evacuation capacity of about 50 liters/minute.

In each Runs B and E, neutralization was accomplished by dissolving the hydroxide in the minimum amount of methanol necessary. This aides in dispersing the base in order to obtain a homogeneous mixture. Prior to neutralization and distillation, each batch of the amide contained approximately (on a weight basis) 2.5–3.4% of free acid as oleic acid and had a color rating of from 4+ to 5+ as measured on the Gardner scale.

In each run, following stripping, the amide was subjected to molecular distillation at a pressure of from 0.2 to 0.8 mm. of Hg. Under these conditions, the amide vaporized at a temperature of from 180° to 210° C. Results are set forth in Table II.

TABLE II

Run	Base	Amount of Amide Feed (g.)	Amount of Base (g.)	Free Fatty Acid % Feed	Free Fatty Acid % Distillate	Gardner Color Feed	Gardner Color Distillate	Nitrile Recovery % Feed	Nitrile Recovery % Distillate
A	CaO (Powdered)	100	.7	3.4	3.4	5+	1+	—	—
B	KOH (MeOH Solution)	100	.7	3.4	0.6	5+	<1	—	—
C	No Base	100	—	2.5	3.8	5+	2	—	—
D	$Ca(OH)_2$ (Powdered)	95	.5	2.5	0.3	5+	2	—	—
E	LiOH $.H_2O$ (MeOH Solution)	100	.7	3.4	0.06	4+	<<1	1	1

From Table II it will be noted that no reduction of acid occurred in Run A, and in Run C, the amount of acid actually increased. It is believed that the explanation of Run A is that the CaO was employed as a solid in powdered form without the aid of a solvent and did not react at the melting point of the amide. However, in Run D, calcium hydroxide did react as a dispersed powder.

In Run C, no base was employed and the free acid distilled over with the amide. In fact, in Run C, the acid content of the product actually exceeded that of the feed material.

As an illustration of the effect of the amount of base added, a sample of amide exactly neutralized in a pilot plant kettle with a solution of NaOH in methanol was first stripped of the solvent and then distilled on the laboratory molecular distillation apparatus. By this process, the acid content which was originally in excess of 3% was reduced only to about 0.2% and the distillate had a color of Gardner 1. By contrast, using the same feed, a sufficient additional amount of base was added to provide an excess of 10% based on the weight of total acids originally present in the feed. Upon analysis, free fatty acid could not be detected in the distillate. The color of the distillate was also much less than Gardner 1.

In Runs A–E, the amount of nitrile present in the feed and in the distillate was not generally determined due to the lack of a suitable method. The method employed involved thin layer chromatography and was not felt to be as precise as might be desired. However, in Run E, while the value of 1% for nitrile content in the feed and in the distillate may be subject to an error of as much as 0.5% and was not accurately determined in an absolute sense, it is significant that the nitrile content for both feed and distillate is approximately equivalent; i.e., the analysis does show that nitrile was not produced in any significant amount (if at all) by base addition.

EXAMPLE III

Purification of Erucamides

Industrial grade erucamide (56.8 g.) containing 4.8% free acids was melted and combined with 0.35 g. (10% excess) of NaOH dissolved in 10 ml. of methanol. After

mixing well, the methanol was stripped at 120° C. and 1.5 mm. of Hg using a mechanical vacuum pump. The residual amide was passed through the laboratory wiped-film evaporator described above where it was distilled at 245° C. (0.5 mm. of Hg) to yield 47 grams of product containing 0.7% acid. The Gardner color of the product was 3.5 compared with a Gardner color of 12 for the starting material. In a similar run where base was omitted, the product erucamide contained 5.6% free acid and had a Gardner color of 6.

EXAMPLE IV

Purification of Stearyl Amide

Industrial grade stearyl amide (100 g.) containing 3.98% free acids was melted and admixed with 4 g. of a 25% solution of $NaOCH_3$ in CH_3OH. This provided about 20% excess base. The methanol was stripped (150° C., 1 mm. Hg) and distilled in a wiped-film apparatus at 190° C. and 0.2 mm. Hg. The product (49 g.) contained about 0.05% of acid and had a Gardner color of less than 1.

The preceding representative examples can be varied within the scope of this total specification disclosure as it would be construed and practiced by one skilled in the art. For example, the base employed to neutralize the fatty acid as well as the temperature and pressure employed during molecular distillation can be varied within the context of the present specification and yet remain within the scope of the invention. Also, while molecular distillation using a wiped-film distillation apparatus is a preferred form of the invention, any distillation apparatus could be employed wherein the amide is subjected to a short residence time (i.e., 10 seconds or less) while being exposed to very low vacuum pressures (i.e., from 5 mm. to 0.005 mm. of Hg.). Other suitable types of distillation apparatus would include, for example, falling film and rotating disk type stills wherein the material to be distilled is spread in a thin film over a heated distillation surface by the force of gravity or by centrifugal force. Also, as would be apparent to one skilled in the art, the present invention can be employed to separate other fatty acid amides from the corresponding fatty acids. For example, C_{16}–C_{22} fatty acid amides (e.g., palmitic, stearic acid, oleic, and erucic amides) can be separated from the corresponding C_{16} to C_{22} fatty acids by means of the present invention.

What is claimed is:

1. Method for the purification of an impure fatty acid amide containing from 14 to 22 carbon atoms and containing free fatty acids as impurities, comprising the steps of:

a. neutralizing said free fatty acids with an alkali to produce a neutralized fatty acid amide;

b. subjecting the neutralized amide to molecular distillation in a wiped-film evaporator by maintaining said amide in the form of a thin film having a thickness less than about 1 mm. on a distillation surface heated at or above the boiling temperature of said amide at the operating pressure of said distillation, for a short residence time of between about 1 and about 10 seconds, while distilling said amide from said surface at a reduced pressure between about 0.005 and about 5 mm. mercury, condensing and collecting the vaporized amide on a condenser, the neutralized fatty acid impurities not being distilled; and

c. recovering the purified fatty acid amide.

2. The method of claim **1** which the neutralizing alkali is selected from the group consisting of an alkali metal hydroxide, an alkaline earth metal hydroxide, and an organic quaternary ammonium hydroxide.

3. The method of claim **1** in which the neutralizing alkali is an alcohol solution of an alkali metal hydroxide.

4. The method of claim **1** in which the neutralizing alkali is a solution of sodium hydroxide in methanol.

5. The method of claim **1** in which the neutralizing alkali is employed in a quantity from about 6 to about 20% in excess of that required to neutralize the free fatty acid present.

6. The method of claim **1** in which the amide is oleamide.

7. The method of claim **1** in which the amide is stearamide.

8. The method of claim **1** in which the amide is erucamide.

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