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2,787,633

ACCELERATION OF FATTY AMINE ADDITION REACTIONS

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The present invention relates to the acceleration of the addition reaction between primary fatty amines and alpha beta unsaturated acid derivatives of the acrylate type such as the lower aliphatic esters and nitriles of acrylic acid, methacrylic acid, crotonic acid.

Condensations of this type have previously been disclosed as shown in Isbell Patent 2,468,012. It has now been discovered that it is possible to materially accelerate the reaction rate in this type of addition by carrying out the reaction in the presence of a lower aliphatic alcohol or 1,4 dioxane. The quantity of the alcohol or dioxane employed may be relatively small, much less than is customarily considered as a solvent quantity.

It is, therefore, an object of the present invention to provide a process of condensing fatty amines with acrylate type compounds in the presence of lower aliphatic alcohols or dioxane in order to accelerate the addition rate.

The reaction is applicable to the long chain primary fatty amines of the type RNH_2 in which R is an aliphatic hydrocarbon group containing from 8 to 22 carbon atoms. These primary amines are conventionally produced from fatty acids by way of the nitrile. Accordingly, the amines which may be used in the present invention are those which may be derived from the whole fatty acids of a fat or oil, from any selected fraction thereof, or from any individual fatty acid. Since the starting fatty acids may be either saturated or unsaturated, the resulting amines may likewise be either saturated or unsaturated.

The acrylate derivatives to which the present invention is applicable are the nitriles and lower aliphatic esters of acrylic acid, crotonic acid and methacrylic acid. The alcohol portion of the ester may be an alkyl group containing from 1 to 4 carbon atoms. Since these compounds are readily available in form of their methyl esters these are preferred.

The alcohols which may be employed are the lower aliphatic alcohols, methanol, ethanol, propanol, isopropanol, n-butanol, secondary butanols and tertiary butanols. In addition it has been observed that 1,4 dioxane likewise serves to accelerate this reaction.

The quantity of the additive need be relatively small. Thus even when such a low proportion as 2% based on the total weight of the reactants is employed, the reaction speeds up materially. Generally quantities of from 5 to 15% are preferred although it is possible to use up to 25%. No particular advantage is obtained using quantities of additive over 25% and actually the use of larger quantities usually requires some recovery technique.

The amine and the additive material are mixed and heated to the desired reaction temperature and maintained at this temperature during and after the addition of the acrylate. At room temperature the reaction requires a

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somewhat extended period of time. Accordingly, it is preferred to carry out the reaction at temperatures of from 60 to 120° C. At these temperatures with the additive present the reaction may be essentially complete in from 1 to 35 minutes.

These addition compounds are frequently hydrolyzed to the salts to form surfactants. Accordingly, the small quantity of alcohol or dioxane which may be present may be allowed to remain in the reaction mixture during the saponification. If desired, of course, the additive may be vaporized from the reaction mixture prior to saponification but usually this is not necessary.

In addition to speeding up the rate of reaction, the invention also has other advantages. Inasmuch as these adducts are frequently used as intermediates for the preparation of surfactants, it is desirable that the quantity of free primary amine in the product be reduced to a minimum inasmuch as the free primary amines may produce undesirable skin reactions. Heretofore, in order to attain this end it has been customary to use a large excess of methyl acrylate. The recovery of the excess methyl acrylate has involved an additional processing step.

The use of the excess methyl acrylate has also presented an additional problem. The reaction of primary fatty amines with methyl acrylate may involve the addition of a single acrylate unit to the primary amine or it may involve the addition of two acrylate units inasmuch as there are two available hydrogens on the primary amine. For many purposes it is preferred to obtain the mono-adduct. This has been difficult to accomplish when it is also desired to obtain a product with low primary amine content. The use of the excess acrylate which serves to reduce the free primary amine content also serves to increase the quantity of diadduct. By means of the present invention it is possible to carry on this reaction using only a very slight excess of the acrylate and to obtain a product which is very low in free primary amine and also very low in the diadduct. At the same time the reaction is completed in a period of a few minutes as compared with several hours as previously required.

The use of an alcohol or dioxane also is advantageous during the step of saponifying the adduct. As was pointed out above, these ester adducts are usually saponified with alkali to obtain the salt. In order to obtain a saponified product which is easy to dry, it is necessary to have a high solids content. The saponification of sizeable quantities of the adduct may be carried out in an autoclave using concentrated alkali such as a 50% aqueous solution of sodium hydroxide. Some alcohol is, of course, liberated due to the saponification of the ester. If this is the only alcohol present, however, the saponified product is a heavy paste which is difficult to handle. If sufficient alcohol is present so that the total solids content of the saponified product is 70 to 75%, a slurry is obtained which can readily be pumped. If water is present in the saponified mixture so that the saponified product contains 70 to 75% solids, the product is a stiff paste which cannot be pumped. By having sufficient alcohol present during the addition reaction, to obtain the advantages previously presented for this addition reaction, it is possible to saponify the adduct with 50% aqueous sodium hydroxide and obtain a saponified product having 70 to 75% solids which is convenient to handle. There is no need to have more alcohol present during the saponification than that necessary to give a solids content of 70 to 75% and actually

excess alcohol may be undesirable in this stage because of undesirable side reactions.

The following examples will serve to illustrate the invention.

The results of the various examples are indicated in the following tables. The products not specifically referred to in the examples were prepared under similar conditions with the variations indicated in the table.

Table I

Product Number	Amine	Moles of Amine	Moles of Methyl Acrylate	Additive	Percent Additive Based on Reactants	Reaction Temp., degrees	Reaction Time	Product Analyses, Percentage of Amines		
								Primary	Secondary	Tertiary
1.....	Dodecyl...	1	1.1	None.....		60	30 Min....	23.1	69.1	2.0
2.....	do.....	1	1.1	do.....		60	1 Hr.....	18.6	70.1	7.6
3.....	do.....	1	1.1	do.....		60	4 Hrs.....	10.5	73.8	11.8
4.....	do.....	1	1.1	do.....		90	30 Min....	18.9	74.9	2.3
5.....	do.....	1	1.1	do.....		90	1 Hr.....	13.6	78.4	4.1
6.....	do.....	1	1.1	do.....		90	4 Hrs.....	7.4	80.5	8.2
7.....	Coco.....	1	1.1	Methanol....	7.5	90	1 Min....	4.8	91.1	4.0
8.....	do.....	1	1.1	do.....	7.5	90	5 Min....	5.0	91.2	3.8
9.....	do.....	1	1.1	do.....	7.5	90	15 Min....	3.0	91.7	5.3
10.....	Dodecyl...	1	1.15	do.....	3	95	15 Min....	5.3	87.2	7.3
11.....	do.....	1	1.15	do.....	15	75	15 Min....	0	92.0	7.1
12.....	H26D.....	1	1.15	do.....	7.5	80-100	35 Min....	1.0	83.4	8.8
13.....	Coco.....	1	1.1	Ethanol.....	7.5	90	15 Min....	4	89.0	4.0
14.....	Dodecyl...	1	1.15	1-4 Dioxane...	5.5	90	15 Min....	5.4	81.8	7.9
15.....	Coco.....	1	1.15	Benzene.....	6.75	90	15 Min....	10.1	76.0	3.8

Table II

Product Number	Amine and No. of Moles	Second Reactant	Moles	Percent Methanol Based on Reactants	Reaction Temp., degrees	Reaction Time, Minutes	Product Analyses, Percentage of Amines		
							Primary	Secondary	Tertiary
1.....	Dodecyl, 1 Mole..	Acrylonitrile.....	1.15	0	90	15	33.8	64.7	0
2.....	do.....	do.....	1.15	5	90	15	3.8	94.3	0
3.....	do.....	Ethyl Crotonate...	1.15	0	90	15	60.2	38.0	0
4.....	do.....	do.....	1.15	5	90	15	48.4	50.2	0

EXAMPLE 1

211 g. (1 g. mole) of a special coco amine (stripped of C₈ and C₁₀ amines) were placed in a one liter three necked flask equipped with mechanical stirrer, thermometer, reflux condenser and Mantle heater. Methanol (23 g.) was added and the solution heated to reflux at 90° C. To the refluxing solution 94.6 g. (1.1 g. moles) of methyl acrylate was added over a period of 2 to 3 minutes. Three samples of the reaction mixture were taken and chilled to stop reaction. One was taken immediately after methyl acrylate was added, another four minutes later and a third fifteen minutes after the completion of addition of the acrylate. They were called the one, five and fifteen minute samples. The results of the analyses of these samples are given in Table I, Examples 7, 8 and 9.

EXAMPLE 2

Using a set-up similar to that described in Example 1, .5 g. mole of dodecyl amine containing 22.2 g. of methanol was heated to reflux (79-80° C.) and .575 g. mole of methyl acrylate was rapidly added. The temperature dropped to 75° C. and remained at this temperature. After fifteen minutes the mixture was stripped and analyzed. The results are shown in Table I, Example 11.

EXAMPLE 3

100 g. of dodecyl amine (0.538 mole) containing 7.6 g. of methanol was heated to 90° C. and 32.8 g. (.619 mole) acrylonitrile added. After 15 minutes at this temperature the product was stripped and analyzed. For results see Table II, Example 2.

EXAMPLE 4

100 g. of dodecyl amine (0.538 mole) containing 10.6 g. of methanol was heated to 90° C. and 70.5 g. (0.619 mole) of ethyl crotonate added. After 15 minutes the product was stripped and analyzed. Results are given in Table II, Example 4.

EXAMPLE 5

Thirty-two lbs. of methanol was added to 125 lbs. of distilled hydrogenated tallow amine (100% primary amine). The mixture was stirred and heated to 85° C. in a closed kettle. Fifty-three lbs. of methyl acrylate was pumped in over a period of 18 minutes keeping the temperature below 100° C. The temperature was then brought to 100° C. and held there for one hour. Caustic soda (50% solution) was pumped into the stirred ester during a period of 17 minutes. The temperature was maintained at 95-105° C. by cooling. A free flowing slurry of the soap was obtained which was dried on hot rolls to give a flaked product containing 98% solids.

We hereby claim as our invention:

1. Process which comprises reacting a primary fatty amine in which the fatty group contains from 8 to 22 carbon atoms with a compound selected from the group consisting of the nitriles and lower alkyl esters of acrylic acid, methacrylic acid, and crotonic acid in the presence of an additive selected from the group consisting of methanol, ethanol, propanol, isopropanol, n-butanol, secondary butanols, tertiary butanols and dioxane, said additive being present in the quantity of from 2 to 25% based on the total weight of reactants.

2. Process which comprises reacting a primary fatty amine in which the fatty group contains from 8 to 22 carbon atoms with a lower alkyl acrylate in the presence of an additive selected from the group consisting of methanol, ethanol, propanol, isopropanol, n-butanol, secondary butanols, tertiary butanols and dioxane, said additive being present in a quantity of from 2-25% based on the total weight of reactants.

3. Process which comprises reacting a fatty primary amine in which the fatty group contains from 8 to 22 carbon atoms with a substantially equimolar amount of a lower alkyl acrylate at a temperature of approximately 60 to approximately 90° C. in the presence of an additive selected from the group consisting of methanol, ethanol, propanol, isopropanol, n-butanol, secondary butanols, ter-

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tiary butanols and dioxane, said additive being present in a quantity of from 2-25% based on the total weight of reactants.

4. The process of claim 1 in which said additive is methanol.

5. The process of claim 2 in which said additive is methanol.

6. The process of claim 3 in which said additive is methanol.

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6**References Cited in the file of this patent****UNITED STATES PATENTS**

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