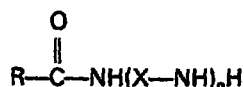


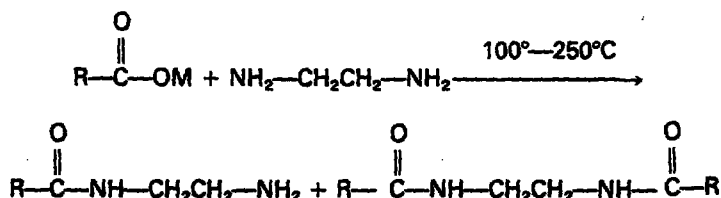
Description

The present invention relates to a process for the preparation of monoacyl polyalkylene polyamines. The monoacyl polyalkylene polyamines which can be prepared by the present process may be represented by the formula



wherein R is straight or branched chain alkyl of from 7 to 21 carbon atoms or mixtures thereof, n is an integer of from 1 to 3 and X is straight or branched chain alkylene or hydroxyalkylene of from 2 to 6 carbon atoms.

The prior art shows many processes for combining amines and fatty acids or esters. Reactions that are satisfactory when amines are involved are often unsatisfactory when diamines are combined with a fatty acid or ester. When diamines are involved, the processes are more complex and more difficult to control as a result of the formation of various side products. See, for example, US—A—1,947,951; US—A—2,387,201; and US—A—2,750,366. In an article entitled "The Aminolysis of Esters. A Preliminary Study", J. Am. Chem. Soc., 72:4149 (1950), Baltzly et al. reported the results of aminolysis of esters utilizing monoamines in the presence of solvents including alcoholic solvents. Monoacyl polyalkylene polyamines can be prepared by reacting a suitable fatty acid or ester with a diamine at elevated temperatures, e.g. 100—250°C for a period of several hours. This reaction can be shown schematically when ethylenediamine is utilized as follows:



Although this process results in the preparation of some of the desired end-product, there is significant contamination of the end-product with undesirable diamide by-products which must be separated out. There may also be off-color and malodor problems as a result of the high temperatures required. Furthermore, due to the temperatures required, the process is energy inefficient and expensive.

GB—A—1 260 883 discloses a process for the production of amides based on polyamines. The process comprises reacting a polyamine with a mono- or di-carboxylic acid, or an ester or lactam thereof, at a temperature above 100°C in the presence of 0.001 to 1% by weight of an alkali metal borohydride. This process requires the presence of the alkali metal borohydride and relatively high temperature to obtain less coloured products.

It is, therefore, an object of this invention to provide a novel process for the preparation of monoacyl polyalkylene polyamines.

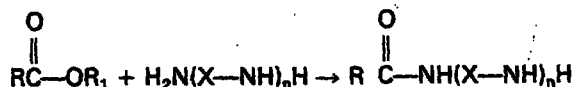
It is a further object of this invention to provide a process for the preparation of monoacyl polyalkylene polyamines which results in good yields and low diamide contamination.

It is a still further object of the present invention to provide a process for the preparation of monoacyl polyalkylene polyamines which can be carried out at relatively low temperatures and is, therefore, energy efficient.

Other objects and advantages of the present invention will be set forth in or apparent from the following description.

The foregoing objects are achieved by reacting a suitable fatty acid ester with a polyalkylene polyamine in the presence of a lower alkanol to yield the desired monoacyl polyalkylene polyamine. The polyalkylene polyamine and fatty acid ester should be present in a ratio of from 25:1 to 5:1, preferably 20:1 to 10:1. The lower alkanols include methanol, ethanol and propanol with the preferred solvent being methanol. The solvent should be present in an amount of from 5 to 40% by weight of the total weight of the reaction mixture. The reaction should be carried out at temperatures of from 20° to 80°C, preferably 40° to 50°C. If the reaction is carried out under pressure, low diamide contamination is observed at higher temperatures and the rate of the reaction remains favorable.

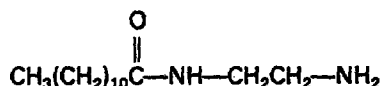
The general reaction of the present invention can be illustrated schematically as follows:



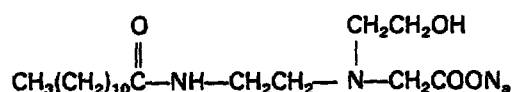
wherein R is alkyl containing from 7 to 21 carbon atoms or mixtures thereof, R₁ is lower alkyl containing from 1 to 3 carbon atoms, n is an integer of from 1 to 3 and X is straight or branched chain alkylene or hydroxyalkylene containing from 2 to 6 carbon atoms.

It has been unexpectedly found that by carrying out this reaction in a lower alkanol solvent and at low temperatures, the quantity of undesirable by-products is greatly reduced and the desired monoacyl polyalkylene polyamine has improved color and odor properties. The process also consumes less energy and utilizes less elaborate equipment when carried out in this manner due to the lower temperatures that may be utilized, if desired. If the reaction is carried out at higher temperatures under pressure, more elaborate equipment is required and more energy will be consumed, but the other advantages of the invention will still be achieved.

The resulting monoacyl polyalkylene polyamines can be utilized as surface active agents in various personal care and industrial applications. These compounds are also useful as intermediates for the production of known useful surface active agents. For example, a monoacyl polyalkylene polyamine of the structure



can be reacted with ethylene chlorohydrin followed by reaction with sodium monochloroacetate in alkaline aqueous medium to yield lauroamphoglycinate of the structure



This compound and related compounds are shown in the CTFA Cosmetic Ingredient Dictionary and are available as surface active agents for use in personal care formulations from a number of commercial sources.

The following examples will illustrate in detail the manner in which the present invention may be practiced.

Example I

Into a reaction flask was placed 51.6 g of ethylene diamine followed by 18.4 g of methylaurate (10:1 molar ratio) and 30.0 g of methanol (30%). The reaction mixture was heated to 75°C for 26 hours at which time the methylaurate was determined by gas chromatography methods to be exhausted. Into a second flask was placed the same reactants under the same reaction conditions except that no methanol was utilized. Analysis of the reaction mixtures was done to determine the amount of 2-aminoethyl dodecanamide and the amount of diamide by-product. The results are shown in Table I below:

TABLE I

Effect of Methanol on Diamide Concentration

% methanol	Mole Ratio Amine/Ester	% Diamide
0	10:1	9.1
30	10:1	5.0

As can readily be seen from the results, there is significantly less diamide formed in the reaction flask containing the methanol solvent.

Example II

Into a reaction flask was placed 300.5 g of ethylene diamine followed by 107.2 g of methylaurate (10:1 molar ratio) and 278.4 g of methanol (40%) and the reaction mixture was heated to 75°C. Into a second flask was placed the same reactants under the same reaction conditions except that no methanol was utilized. The methylaurate concentration was determined by gas chromatography methods to show the rate of consumption of the methylaurate with the results being shown below in Table II.

TABLE II

Effect of Methanol on Reaction Rate

Methanol Conc. (%)	% Methyllaurate Remaining with Time (hours)									
	2	3	4	5	5	10	12	13	15	17
0	96	88	67	63	47	40	21	18	10	5
40	74	63	37	30	20	9	3	--	--	--

The results above clearly demonstrate that the rate of the reaction is significantly enhanced by the presence of the methanol solvent.

Example III

Following the procedure of Example I, various reaction mixtures were prepared at a temperature of 45°C utilizing varying amounts of methanol and various ratios of ethylenediamine to methyllaurate. The reactions were carried out until the methyllaurate was consumed and the amount of diamide was determined. The results are shown below in Table III.

TABLE III

Effect of Methanol on Diamide Concentration

Mole Ratio Ethylenediamine/Methyllaurate

% Methanol

	0	10	20	30	40
25:1	2.9	2.1	2.1	1.9	1.9
20:1	3.7	2.6	2.8	2.8	2.3
15:1	4.9	3.8	3.8	3.2	3.1
10:1	6.1	5.5	4.8	4.4	4.1
5:1	11.5	9.6	10.1	10.4	8.5
2:1	27.4	27.0	25.1	25.4	23.0

Example IV

Following the procedure of Example I, various reaction mixtures were prepared at a temperature of 25°C utilizing varying amounts of methanol and various ratios of ethylenediamine to methyllaurate and the concentrations of methyllaurate and diamide were observed at various time intervals. The results are shown below in Table IV:

TABLE IV
Effect of Methanol on Methylaurate Consumption and Diamide Concentration

MOLE RATIO AMINE/ESTER		TIME (DAYS)					% METHANOL
		1	2	3	4	7	
25:1	% Methylaurate Remaining	27.3	6.2	1.2	1.1	--	40
	% Diamide Formed	1.1	1.7	1.8	2.1	2.6	
15:1	% Methylaurate Remaining	30.0	10.2	2.6	1.3	--	40
	% Diamide Formed	1.6	2.4	3.1	3.4	4.1	
5:1	% Methylaurate Remaining	47.6	26.2	15.5	6.3	1.0	40
	% Diamide Formed	2.3	4.1	7.5	9.4	11.5	
25:1	% Methylaurate Remaining	27.4'	6.4	2.3	0.3	--	30
	% Diamide Formed	1.2	1.8	2.1	2.3	2.3	
15:1	% Methylaurate Remaining	30.4	10.0	2.8	1.1	--	30
	% Diamide Formed	1.5	1.8	2.5	3.3	3.9	
5:1	% Methylaurate Remaining	48.7	26.4	13.8	4.0	--	30
	% Diamide Formed	2.1	5.8	6.6	9.0	10.5	
25:1	% Methylaurate Remaining	35.6	11.0	3.2	--	--	20
	% Diamide Formed	1.0	1.9	2.3	2.4	2.4	

15:1	% Methylaurate Remaining	35.4	17.4	4.2	0.6	--	20
	% Diamide Formed	1.3	2.2	3.5	3.4	3.7	20
5:1	% Methylaurate Remaining	55.9	29.6	16.5	1.8	--	20
	% Diamide Formed	1.5	5.1	5.8	6.9	8.1	20
25:1	% Methylaurate Remaining		26.0	9.3	4.4	--	10
	% Diamide Formed		1.0	2.8	2.8	3.0	10
15:1	% Methylaurate Remaining	51.7	35.3	16.0	6.4	0.7	10
	% Diamide Formed	1.2	1.8	2.6	3.0	4.8	10
5:1	% Methylaurate Remaining	70.4	48.0	25.8	17.3	1.0	10
	% Diamide Formed	1.0	3.2	4.3	4.7	7.8	10
25:1	% Methylaurate Remaining	81.0	66.5	44.9	36.7	19.1	0
	% Diamide Formed	--	0.4	0.9	1.3	2.4	0
15:1	% Methylaurate Remaining	87.5	84.5		48.9	25.9	0
	% Diamide Formed	--	--		1.2	3.3	0
5:1	% Methylaurate Remaining	88.3	84.0		61.2	34.4	0
	% Diamide Formed	0.1	0.3		1.9	5.3	0

Example V

Into a reaction flask was placed 67.9 g ethylene diamine, 12.1 g methylaurate (20:1 molar ratio) and 20.0 g ethanol (20%) and heated to 45°C. The reaction was determined to be complete on the fourth day and 2.7% diamide was found to be present utilizing gas chromatographic methods. When the same reaction was carried out in the absence of a solvent, the diamide level was found to be 4.6%.

Example VI

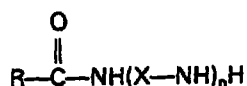
The reaction of Example V was carried out utilizing isopropanol instead of ethanol. The reaction was determined to be complete on the fifth day and 3.3% diamide was found to be present utilizing gas chromatographic methods. When the same reaction was carried out in the absence of a solvent, the diamide level was found to be 4.6%.

Example VII

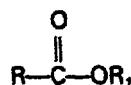
Into a reaction flask was placed 54.2 g ethylenediamine, 25.8 g methyltallowate (10:1 molar ratio) and 20.0 g methanol and heated to 45°C. In a second flask was placed 40.7 g ethylene diamine, 19.3 g of methyltallowate and 40.0 g of methanol and heated to 45°C. Into a third flask was placed 67.7 g of ethylenediamine and 37.3 g of methyltallowate (10:1 molar ratio) and no solvent. The reactions were determined to be completed on the fourth day, third day and seventh day respectively and 2.2%, 1.3% and 2.6% diamide were found to be present, respectively.

Claims

1. A process for the preparation of monoacyl polyalkylene polyamines of the formula



wherein R is straight or branched chain alkyl of from 7 to 21 carbon atoms or mixtures thereof, n is an integer of from 1 to 3 and X is straight or branched chain alkylene or hydroxyalkylene of from 2 to 6 carbon atoms, comprising reacting a fatty acid ester of the formula



wherein R is as above and R₁ is lower alkyl of from 1 to 3 carbon atoms, with a polyalkylene polyamine of the formula



wherein X and n are as above, the polyalkylene polyamine and fatty acid ester being present in a molar ratio of from 25:1 to 5:1, in the presence of from 5 to 40% by weight of the total weight of the reaction mixture of a lower alkanol, the reaction being carried out at a temperature from 20 to 80°C or under pressure.

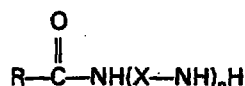
2. The process of claim 1 wherein the lower alkanol is methanol, ethanol or isopropanol.

3. The process of claim 2 wherein the lower alkanol is methanol.

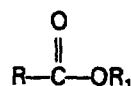
4. The process of any one of claims 1 to 3 wherein the polyalkylene polyamine and fatty acid ester are present in a ratio of from 20:1 to 10:1.

Patentansprüche

1. Verfahren zur Herstellung von Monoacylpolyalkylenpolyaminen mit der Formel



worin R eine gerade oder verzweigte Alkylkette mit 7 bis 21 Kohlenstoffatomen ist oder eine Mischung davon, n eine ganze Zahl von 1 bis 3 und X eine gerade oder verzweigte Alkylen- oder Hydroxyalkylenkette mit 2 bis 6 Kohlenstoffatomen ist, durch Reaktion eines Fettsäureesters der Formel





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Example V

Into a reaction flask was placed 67.9 g ethylene diamine, 12.1 g methylaurate (20:1 molar ratio) and 20.0 g ethanol (20%) and heated to 45°C. The reaction was determined to be complete on the fourth day and 2.7% diamide was found to be present utilizing gas chromatographic methods. When the same reaction was carried out in the absence of a solvent, the diamide level was found to be 4.6%.

Example VI

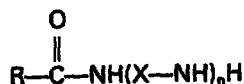
The reaction of Example V was carried out utilizing isopropanol instead of ethanol. The reaction was determined to be complete on the fifth day and 3.3% diamide was found to be present utilizing gas chromatographic methods. When the same reaction was carried out in the absence of a solvent, the diamide level was found to be 4.6%.

Example VII

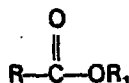
Into a reaction flask was placed 54.2 g ethylenediamine, 25.8 g methyltallowate (10:1 molar ratio) and 20.0 g methanol and heated to 45°C. In a second flask was placed 40.7 g ethylene diamine, 19.3 g of methyltallowate and 40.0 g of methanol and heated to 45°C. Into a third flask was placed 67.7 g of ethylenediamine and 37.3 g of methyltallowate (10:1 molar ratio) and no solvent. The reactions were determined to be completed on the fourth day, third day and seventh day respectively and 2.2%, 1.3% and 2.6% diamide were found to be present, respectively.

Claims

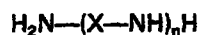
1. A process for the preparation of monoacyl polyalkylene polyamines of the formula



wherein R is straight or branched chain alkyl of from 7 to 21 carbon atoms or mixtures thereof, n is an integer of from 1 to 3 and X is straight or branched chain alkylene or hydroxyalkylene of from 2 to 6 carbon atoms, comprising reacting a fatty acid ester of the formula



wherein R is as above and R₁ is lower alkyl of from 1 to 3 carbon atoms, with a polyalkylene polyamine of the formula



wherein X and n are as above, the polyalkylene polyamine and fatty acid ester being present in a molar ratio of from 25:1 to 5:1, in the presence of from 5 to 40% by weight of the total weight of the reaction mixture of a lower alkanol, the reaction being carried out at a temperature from 20 to 80°C or under pressure.

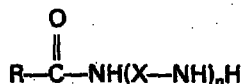
2. The process of claim 1 wherein the lower alkanol is methanol, ethanol or isopropanol.

3. The process of claim 2 wherein the lower alkanol is methanol.

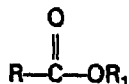
4. The process of any one of claims 1 to 3 wherein the polyalkylene polyamine and fatty acid ester are present in a ratio of from 20:1 to 10:1.

Patentansprüche

1. Verfahren zur Herstellung von Monoacylpolyalkylenpolyaminen mit der Formel



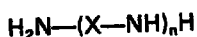
worin R eine gerade oder verzweigte Alkylkette mit 7 bis 21 Kohlenstoffatomen ist oder eine Mischung davon, n eine ganze Zahl von 1 bis 3 und X eine gerade oder verzweigte Alkylen- oder Hydroxyalkylenkette mit 2 bis 6 Kohlenstoffatomen ist, durch Reaktion eines Fettsäureesters der Formel





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worin R wie oben definiert ist und R₁ eine niedere Alkylgruppe mit 1 bis 3 Kohlenstoffatomen ist, mit einem Polyalkylenpolyamin der Formel



5 worin X und n die obige Definition haben, wobei das Polyalkylenpolyamin und der Fettsäureester in einem Molarverhältnis von 25:1 bis 5:1 vorliegen in Gegenwart von 5 bis 40 Gew.-%, bezogen auf das Gesamtgewicht der Reaktionsmischung eines niedrigen Alkohols, wobei die Reaktion bei einer Temperatur von 20 bis 80°C oder unter Druck durchgeführt wird.

- 10 2. Verfahren gemäß Anspruch 1, bei dem der niedere Alkohol Methanol, Ethanol oder Isopropanol ist.
3. Verfahren gemäß Anspruch 2, bei dem der niedere Alkohol Methanol ist.
4. Verfahren gemäß einem der Ansprüche 1 bis 3, bei dem Polyalkylenpolyamine und Fettsäureester in einem Verhältnis von 20:1 bis 10:1 vorliegen.

15 Revendications

1. Procédé de préparation de monoacyl polyalkylène polyamines de formule:



dans laquelle R représente un groupe alkyle à chaîne droite ou ramifiée de 7 à 21 atomes de carbone, ou les mélanges de celui-ci, n est un entier de 1 à 3 et X est un groupe alkylène à chaîne droite ou ramifiée, ou un
25 groupe hydroxyalkylène de 2 à 6 atomes de carbone, dans lequel on fait réagir un ester d'acide gras de formule:



dans laquelle R est tel que défini ci-dessus, et R₁ est un groupe alkyle inférieur de 1 à 3 atomes de carbone, avec une monoacyl polyalkylène polyamine de formule:



dans laquelle X et n sont tels que définis ci-dessus, la polyalkylène polyamine et l'ester d'acide gras étant présents en un rapport molaire de 25:1 à 5:1, en présence de 5 à 40% en poids par rapport au poids total du mélange réactionnel d'un alcanol inférieur, la réaction étant effectuée à une température de 20 à 80°C ou
40 sous pression.

2. Procédé suivant la revendication 1, dans lequel l'alcanol inférieur, est le méthanol, l'éthanol ou l'isopropanol.

3. Procédé suivant la revendication 2, dans lequel l'alcanol inférieur est du méthanol.

4. Procédé suivant l'une quelconques des revendications 1 à 3, dans lequel la polyalkylène polyamine
45 et l'ester d'acide gras, sont présents en un rapport de 20:1 à 10:1.

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