

UNITED STATES PATENT OFFICE

2,355,837

SUBSTITUTED GLYOXALIDINES

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No Drawing. Application March 17, 1942,
Serial No. 435,049

6 Claims. (Cl. 260—309.6)

This invention relates to an improved method for making glyoxalidines (imidazolines) which have aminoalkyl or substituted amino-alkyl side chains in addition to containing higher aliphatic substituent radicals. The basic reaction with which the invention is concerned involves the condensation of higher fatty acid compounds, or mixtures of these, with polyalkylene polyamines having at least three amino groups, at least one of which is a secondary amino group in the 1,2 position to a primary amino group, to produce substituted glyoxalidines. While it is possible by this process to obtain tri-, or even tetrasubstituted glyoxalidines, the production of the 1,2-disubstituted glyoxalidines is the primary object of the invention.

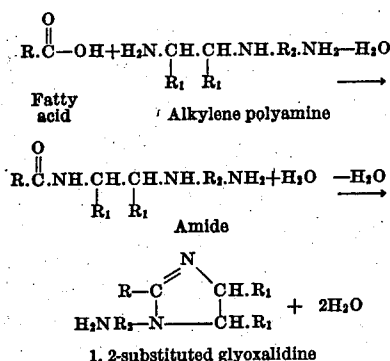
These compounds are characterized as being either high-boiling, viscous liquids, or low-melting, waxy solids. They are highly polar, strongly basic substances, which are soluble in water and in acids, such as dilute hydrochloric acid. 1,2-disubstituted glyoxalidines, when pure, are almost odorless, and they are stable under most conditions.

The glyoxalidine compounds of this invention may be used for various purposes, and it has been found that they are especially valuable as emulsifying agents and detergents, as wetting, softening and scouring agents, and for other uses where their properties of surface activity can be employed. The new substances, and their salts and soaps, when used as emulsifying agents, are particularly efficacious for producing stable dispersions of mineral oils, or other oleaginous substances, and water.

The production of the 1,2-disubstituted glyoxalidines may be accomplished by dehydrating fatty acid amides of various alkylene polyamines and their substitution products, or, more generally stated, by heating these amines with free fatty acids, fatty acid esters or fatty acid amides under such conditions as to effect the splitting out of water in excess of 1.5 mols for each mol of free fatty acid and in excess of 0.5 mol for each mol of combined fatty acid involved. Examples of amines that may be employed in the practice of this invention are: diethylene triamine, dipropylene triamine, triethylene tetramine, tetraethylene pentamine, as well as other polyalkylene polyamines of similar nature. Fatty acid compounds that may be used in the production of the glyoxalidines may include the fatty acids themselves, such as lauric, oleic, linoleic, ricinoleic, stearic and palmitic acids, as well as their amides and esters. Other fatty acids and their esters naturally oc-

curing in such vegetable oils as olive, coconut, linseed and cottonseed oils, which have from 10 to 20 carbon atoms in their molecule, may also be employed.

1,2-disubstituted glyoxalidines may be regarded as dehydration products of substituted ethylene polyamides and fatty acids, or their amides and esters. The formation of the glyoxalidine or imidazoline ring from these substances may be considered as a two-step reaction involving, first, the formation of an amide and a molecule of water, and, second, the dehydration of this amide to yield a substituted glyoxalidine and a second molecule of water. Thus, when a fatty acid, such as oleic acid, is employed, two molecules of water will be formed per molecule of the starting acid. This reaction is illustrated by the following scheme:



wherein R represents an alkyl or alkenyl group containing from 9 to 19 carbon atoms (the residue of a higher fatty acid); R₁ represents hydrogen or a lower alkyl group and R₂ represents an alkylene group, a lower alkyl substituted alkylene group, an alkylene-imino group, or a polyalkylene-polyimino group.

The improvement in this basic reaction with which this invention is concerned involves the procurement of a high yield of the substituted glyoxalidines without resort to high temperatures, that is, to temperatures above 200° C. These high temperatures are undesirable because they promote the formation of side reactions, the decomposition of the alkylene polyamines, and the formation of tarry by-products. These difficulties become more troublesome in large scale operation because many of the substituted glyoxalidines are distillable only on a laboratory scale, which renders burdensome the removal of impurities from glyoxalidines produced at high temperatures of reaction. It has been found that the reaction

was obtained. The product was a clear light-brown liquid which formed clear gels with water. It is useful as an inhibitor of acid corrosion.

If larger quantities of fatty acid are employed than shown in this example, it is possible that at least small amounts of products which contain two glyoxalidine rings may be formed by condensation at both ends of the polyalkylene polyamine.

Example 4

Twenty and seven-tenths (20.7) parts of diethylene triamine and 28.3 parts of oleic acid were placed in a kettle having a distillation column. The charge was slowly heated to 165° C., and sufficient xylene was added to permit moderate boiling in the kettle. An azeotropic mixture of water and xylene was distilled over, the xylene being returned to the kettle after separation from the water, until at the end of 15 hours, 92% of the theoretical amount of water had been removed (1.84 mols per mol of oleic acid). The excess polyamine and xylene were removed by distillation at 184° C. under 1 mm. of mercury absolute pressure, and 33.56 parts of the product 1-aminoethyl-2-heptadecenyl glyoxalidine were obtained at a yield of 95.7% of the theoretical.

Example 5

The reaction vessel consisted of a kettle having a distillation column and receiver so arranged that the system could be placed under a vacuum. One and two-tenths (1.2) mols of diethylene triamine were added to one mol of stearic acid in the kettle at 165° C. and under a reduced absolute pressure of 265 mm. of mercury during a period of 1.33 hours. The temperature in the kettle was then increased to 180° C. for 30 minutes, and the pressure thereafter reduced gradually to 1 mm. of mercury during an additional 4.5 hours. The total reaction time, with allowance for minor adjustments, was 6.5 hours and the amount of water removed was 1.86 mols per mol of fatty acid employed. The product, 1-aminoethyl-2-heptadecyl glyoxalidine was a yellow solid which was soluble in dilute hydrochloric acid. It also formed soluble salts and soaps with mineral and organic acids.

Example 6

The apparatus was the same as that described in the preceding example. Sixty parts by weight of oleic acid and 33 parts by weight of diethylene triamine containing 0.022 part by weight of calcium fluoride as a catalyst were placed in the kettle and agitated for 15 minutes with nitrogen. The kettle was then heated to 165.5° C. in a period of three hours and some water was distilled over. To effect the removal of the remainder of the water, 111.5 parts by weight of xylene were then added to the receiver and kettle. The azeotropic distillation was continued for 3.75 hours, until a maximum kettle temperature of 167° C. and a column temperature of 143° C. were reached, at which time approximately 2 mols of water per mol of the fatty acid had been removed. The xylene and excess polyamine were then removed by distillation at a maximum column temperature of 81° C. under 5 mm. of mercury absolute pressure. The product remaining as a residue, 1-aminoethyl-2-heptadecenyl glyoxalidine, amounted to 68.56 parts by weight. This corresponds to a yield of 92.5%.

This application is a continuation-in-part of

my copending application Serial No. 191,191, filed February 18, 1938.

I claim:

1. Process for making 1,2-substituted glyoxalidines which comprises heating a mixture containing a polyalkylene polyamine having at least three amino groups, at least one of which is a secondary amino group in the 1,2 position relative to a primary amino group, and at least one of the group consisting of free fatty acids containing from 10 to 20 carbon atoms, amides of said acids, and esters of said acids, at least one mol of said polyamine being present for each fatty acid radical of one of said group; carrying out the reaction at temperatures between 140° C. and 200° C., under basic amine conditions in the absence of mineral acid salt groups attached to the polyamine, and in the presence of an inert water-immiscible organic liquid and distilling an azeotropic mixture of the water formed in the reaction and said liquid from said mixture during said heating; the temperature and duration of said heating being so correlated as to cause the splitting out of water in excess of 1.5 mols for each mol of free fatty acid and in excess of 0.5 mol for each mol of combined fatty acid involved.

2. Process for making 1,2-substituted glyoxalidines which comprises heating a mixture containing a polyalkylene polyamine having at least three amino groups, at least one of which is a secondary amino group in the 1,2 position relative to a primary amino group, and at least one of the group consisting of free fatty acids containing from 10 to 20 carbon atoms, amides of said acids, and esters of said acids, at least one mol of said polyamine being present for each fatty acid radical of one of said group; carrying out the reaction at temperatures between 140° C. and 200° C., under basic amine conditions in the absence of mineral acid salt groups attached to the polyamine, and in the presence of xylene; and distilling an azeotropic mixture of the water formed in the reaction and xylene from said mixture during said heating; the temperature and duration of said heating being so correlated as to cause the splitting out of water in excess of 1.5 mols for each mol of free fatty acid and in excess of 0.5 mol for each mol of combined fatty acid involved.

3. Process for making 1,2-substituted glyoxalidines which comprises heating a mixture containing a polyalkylene polyamine having at least three amino groups, at least one of which is a secondary amino group in the 1,2 position relative to a primary amino group, and at least one of the group consisting of free fatty acids containing from 10 to 20 carbon atoms, amides of said acids, and esters of said acids, at least one mol of said polyamine being present for each fatty acid radical of one of said group; carrying out the reaction at temperatures between 140° C. and 200° C., under basic amine conditions in the absence of mineral acid salt groups attached to the polyamine, and in the presence of a catalytic amount of an inorganic fluoride salt and of an inert water-immiscible organic liquid; and distilling an azeotropic mixture of the water formed in the reaction and said liquid from said mixture during said heating; the temperature and duration of said heating being so correlated as to cause the splitting out of water in excess of 1.5 mols for each mol of free fatty acid and in excess of 0.5 mol for each mol of combined fatty acid involved.

4. Process for making 1-aminoethyl-2-heptadecenyl glyoxalidine which comprises heating a mixture containing diethylene triamine and oleic acid, the molar ratio of amine to acid being appreciably greater than one and said amine being substantially free from inorganic salt groups, the heating being carried out at a temperature between 140° and 200° C. and in the presence of a liquid aromatic hydrocarbon, the temperature and duration of said heating being so correlated so as to cause the splitting out of water in excess of 1.5 mols per mol of acid, and distilling at least 0.5 mol of such water from said mixture during such heating as an azeotropic composition with said hydrocarbon.

5. Process for making 1-aminoethyl-2-heptadecyl glyoxalidine which comprises heating a mixture containing diethylene triamine and stearic acid, the molar ratio of amine to acid being appreciably greater than one and said amine being substantially free from inorganic salt groups, the heating being carried out at a temperature between 140° and 200° C. and in the

presence of a liquid aromatic hydrocarbon, the temperature and duration of said heating being so correlated so as to cause the splitting out of water in excess of 1.5 mols per mol of acid, and distilling at least 0.5 mol of such water from said mixture during such heating as an azeotropic composition with said hydrocarbon.

6. Process for making 1-aminoethyl-2-undecyl glyoxalidine which comprises heating a mixture containing diethylene triamine and lauric acid, the molar ratio of amine to acid being appreciably greater than one and said amine being substantially free from inorganic salt groups, the heating being carried out at a temperature between 140° and 200° C. and in the presence of a liquid aromatic hydrocarbon, the temperature and duration of said heating being so correlated so as to cause the splitting out of water in excess of 1.5 mols per mol of acid, and distilling at least 0.5 mol of such water from said mixture during such heating as an azeotropic composition with said hydrocarbon.

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CERTIFICATE OF CORRECTION.

Patent No. 2,355,837.

August 15, 1944.

ALEXANDER L. WILSON.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, second column, line 7, for "polyamides" read --polyamines--; page 2, first column, line 48, for "it it" read --it is--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 3rd day of October, A. D. 1944.

Leslie Frazer

Acting Commissioner of Patents.

(Seal)