Patented Oct. 31, 1950 2,528,380

UNITED STATES PATENT OFFICE

2,528,380

CYCLOIMIDINE DERIVATIVES AND METHODS FOR PREPARING THEM

Hans S. Mannheimer, New York, N. Y., assignor to John J. McCabe, Jr., and Hans S. Mannheimer, as joint venturers

No Drawing. Application October 29, 1948, Serial No. 57,418

4 Claims. (Cl. 260—309.6)

1

This invention relates to novel compositions as well as novel methods for producing and employing them. In one of its more specific aspects this invention is directed to novel compounds finding especial application in the washing of textiles such as cottons and the like as well as in other fields such as dishwashing and other washing in which soaps and synthetic detergents are now used as washing compounds. In another of its more specific aspects the invention is directed to the combination of one or more of my novel compounds with cationic materials and particularly cationic germicides.

Heretofore quaternary ammonium germicides have been combined only with a certain class of synthetic detergents. This class of detergents which were so employed because of their compatibility with the germicides have been those of a non-ionic nature, which as such, have low foaming and foam stability characteristics. Moreover, those detergents cannot be dried in the powdered form because they are not solids in their 100% state. However, it has been proposed to produce powders with those detergents by absorption of them on soda ash. This has not been satisfactory because the compositions so produced contained low concentrations of those detergents and found limited utility because of the high alkalinity. In some cases even that method was of no avail because some of the detergents were not stable at such high alkalinity.

It is also known that cationic products are always poor detergents on cotton, form precipitates with proteins and the like, and under alkaline conditions of pH above 8.5 are usually poor foamers or are partially or completely insoluble.

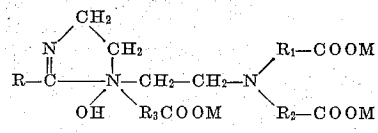
The quaternary ammonium germicides cannot be combined with the usual anionic surface active agents because they precipitate with them and the desirable properties of each are lost.

I have provided novel compounds and was surprised to observe the contra-indications from their chemical formulas of water solubility and detergency characteristics on cottons. The latter was entirely unexpected in view of the cationic groups thereof, their acting like anionic compounds when in alkaline solution. I was still further surprised to observe that these compounds which acted anionically in alkaline solutions were compatible with quaternary ammonium

2

germicides which of course act cationically. Contrary to what one might reasonably expect, these novel surface active agents are compatible and may be combined with water soluble quaternary ammonium germicidal compounds. As a matter of fact, I have provided aqueous solutions at pH's above 8.5 of one or more of my novel compounds together with various water soluble germicidal quaternary ammonium compounds without reducing the germicidal value of the quaternary ammonium compounds or the foam, foam stability and detergency characteristics of my novel compounds. It was also found that these compounds were compatible with soap and other anionic detergents.

The noval compounds of the present invention have the following general Formula I:

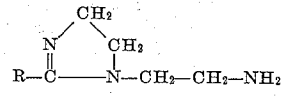


in which R therein and any other formula herein is an organic radical of at least nine carbon atoms and which if connected to a carboxyl group provides a monocarboxylic acid, R_1, R_2 and R_3 may be the same or different and each is a hydrocarbon radical of 1–4 carbon atoms and M is an alkali metal and preferably sodium or potassium.

One of the methods which may be employed for the production of these novel compounds is to first react a compound containing only and not less than three amine groups, namely, a tri-amine such as diethylene triamine

$$(NH_2C_2H_4NH—C_2H_4NH_2)$$

with an organic monocarboxylic acid to provide a reaction product which is a cycloimidine having the following Formula II:



Compounds of Formula II are reacted to provide compounds of Formula I by treating them under controlled conditions with a solution prepared with an alkali metal hydroxide, such as sodium or potassium hydroxide, and one or more monohalo monocarboxylic acids, such as monochloracetic, monochlorpropionic, etc., of the gen-

eral formula R_4XCOOH in which X is a halide and preferably chlorine and R_4 is a hydrocarbon group of 1–4 carbon atoms.

In the production of compounds of Formula II there may be employed any of the organic acids containing a single COOH group or any of the available anhydrides of said acids and by the term monocarboxylic organic acid as used herein, I mean to include both the acid and any of the anhydrides thereof which I regard as the equivalent of the acid. These acids may be: the aliphatic open chain saturated or unsaturated fatty acids as well as said fatty acids containing hydroxy or keto groups and/or other substitutes, such as aryl radicals, as for example, acids of the type of Twitchell fatty acids; cycloaliphatic carboxylic acids preferably containing no more than four condensed nuclei and examples of which are hexahydrobenzoic, resinic, and naphthenic acids; heterocyclic aliphatic carboxylic acids, such as the various pyridine carboxylic acids.

The carboxylic acids employed are those having at least ten carbon atoms. The acids which I employ may be derived from a number of different sources. Among some of them are the acid components chosen from oil of fats of animal, marine or vegetable origin and these include: the acids of cocoanut, palm kernel and palm oil which contain fatty acids having at least eleven carbon atoms and also from soy bean, linseed, olive, rapeseed, cottonseed, peanut and castor oil which contain large proportions of unsaturated hydroxy fatty acids and also the acids derived from tallow, fish and seal oils, whale or shark oils and the hydrogenated acids from these sources. Moreover, the synthetic high molecular weight fatty acids obtained by the oxidation of paraffin wax and similar high molecular weight hydrocarbons by means of gaseous oxidizing agents may be employed. In addition the acid may be one of the resinic acids such as abietic acid or the naphthenic acids and long chain fatty acids having an aromatic hydrocarbon radicle connected directly with the aliphatic chain (Twitchell fatty acids) are obtainable from oleic, ricinoleic, linoleic and similar unsaturated fatty acids. Instead of employing mixture of acids from oil, fats and resins, single acids may be used, for example: pimelic, heptylic, caprylic, sebacic, undecylic, lauric, palmitic, stearic, behenic, arachic, cerotic, oleic, erucic, linoleic, linolenic, ricinoleic and hydroxystearic acids.

The first reaction may be carried out by placing into a reaction vessel one mole of one of said monocarboxylic acids together with 1.06 moles (6% excess) of diethylene triamine. The mixture of said two compounds in the reaction vessel is gradually heated over a six to eight hour period to a temperature of 190–210° C. while being maintained under reduced pressure conditions of 90–120 millimeters of mercury pressure. In the course of the reaction under said conditions a distillate is continuously withdrawn and collected and measures and consists of the excess triamine and 1.72–2 and usually 1.85–1.9 moles of water. The resulting reaction mass contains a compound measuring more than 80% of theoretical and usually 90 to 95% of theoretical yield and is of general Formula II.

Then 3.15 moles (5% excess) of a monohalo monocarboxylic acid is dissolved in three times its weight of water. The temperature of this solution is lowered to 12–18° C. An aqueous solution of an alkali metal hydroxide, preferably sodium or potassium hydroxide because of their availability and cost, is prepared by dissolving six moles of the hydroxide in four times its weight of water. This alkali solution is gradually introduced into the solution of the monohalo monocarboxylic acid over a period sufficient so that the temperature of the mass is continuously maintained in said temperature range of 12–18° C. Subsequently, one mole proportion of the condensate of Formula II is dispersed in about twice its weight of water and is maintained at a temperature no greater than 20° C. This dispersion, while maintained at said reduced temperature, is gradually but rapidly introduced into the aforesaid solution prepared with the monohalo monocarboxylic acid and the alkali hydroxide while the temperature thereof is maintained in said temperature range of 12–18° C. Throughout the addition the mass is continuously vigorously agitated. Then the agitation is continued and the mass is gradually heated over a period of 45 to 60 minutes to a temperature of 95 to 98° C. and is maintained within said temperature range while being continuously agitated for a period of one to two hours and until the pH of the mass, which prior to the heating step measured about eleven, is reduced to 8.3–8.5, and does not change any further upon being maintained in said temperature range for an additional twenty minutes. The resultant mass is an aqueous solution containing an alkali metal salt and an organic reaction product consisting essentially of a compound of Formula I and measuring at least 80 and generally 90 to 95% of theoretical yield. If desired the alkali metal salt may be removed from said solution. However, the solution with or without the alkali metal salt therein may be employed for the purposes herein set forth. In addition, the aqueous solution with or without the alkali metal salt removed may be dehydrated to provide in solid form the novel compounds of Formula I.

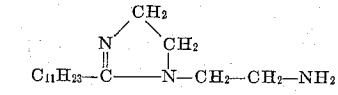
These novel compounds are compatible with and may be combined with germicidal quaternary ammonium compounds under a variety of pH conditions. For most purposes, however, the pH conditions of aqueous solutions thereof adjusted are between 8–9. Various other compounds such as trisodium phosphate, for example, may be combined therewith. The ratio of the quaternary ammonium compound to my novel compound in such combinations may vary over wide limits, but for most purposes I prefer that the ratio of the latter to the former by weight be in the range of 4–1 to 10–1. A particular combination that I have found to be effective comprised nine parts of one of my novel compounds to one part of a quaternary ammonium germicide by weight with or without 1–2 parts by weight of trisodium phosphate. Among some of the quaternary ammonium compounds that I have employed in said combinations are lauryl pyridinium chloride, lauryl dimethyl benzyl chloride, phenylene ethoxy dimethyl ammonium benzyl chloride.

The following examples are given merely to illustrate the invention and are not to be regarded in a limiting sense, all parts being given by weight unless otherwise specified.

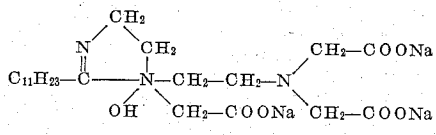
Example I

200 parts of lauric fatty acid (1 mole) and 109 parts of diethylene triamine (1.06 moles, 6% excess) are placed in a reaction vessel and are gradually heated therein to a temperature of

190–210° C. over a period of six to eight hours, while being maintained under reduced pressure conditions of 90–120 mm. of mercury pressure. During the period a distillate is continuously removed and collected. This distillate contains approximately six parts of the triamine and between 30 to 36 parts of water and generally 32–34 parts of water. The resultant organic condensate measured about 268 parts 85 to 90% of which has the following formula:



Then 268 parts of the condensate (approximately 1 mole) is dispersed in 600 parts of water and this dispersion is maintained at a temperature no greater than 20° C. In another container 300 parts of monochloracetic acid (3 moles and 5% excess) are dissolved in 900 parts of water. The temperature of this solution is reduced to 12–18° and while maintained in said temperature range, there is gradually added thereto a solution consisting of 240 parts of sodium hydroxide (6 moles) dissolved in 960 parts of water. It is preferable that the sodium hydroxide solution addition to the solution of the monochloracetic acid be very slow and so slow that the temperature of the resultant mass during the addition does not exceed 18° C. Then said dispersion at a temperature of 20° C. is gradually but rapidly introduced into the resultant mass. The entire mass is then agitated and heated gradually over a period of about three quarters to one hour to a temperature of 95–98° C. and is subsequently maintained in this temperature range for a period of about one to two hours. The end of this period may be ascertained by testing for pH. When the pH has been reduced to the range of 8.3–8.7 and does not change any further after any additional 20 minutes heating in said temperature range the heating step may be terminated. The resultant mass is essentially an aqueous solution containing about 10% of sodium chloride and about 15% of a novel compound having the following formula:



The novel compound was tested for its compatibility with various quaternary ammonium germicides. In cases where a blind test of a given quaternary ammonium germicide indicated a phenol coefficient of five, a combination of this novel compound together with the same quantity of germicide with the ratio of said compound to said germicide being 9–1, showed a phenol coefficient of six. Aqueous combinations of the germicide and the novel compound could be dried and employed as a germicidal detergent. The dried germicidal detergent may be dissolved in water and the solutions may be adjusted to pH's generally between eight to nine. These solutions upon agitation produce voluminous and stable foam; exhibit good cleansing power on cotton without substantivity, very good wetting power and do not precipitate out in the presence of proteins or other anionic active matter. In general the combination exhibited all of the desirable properties of the detergent component without any reduction of the qualities of the germicide.

Example II

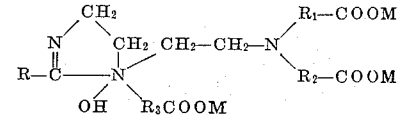
Following the same procedure as that set forth in Example I except that 228 parts of myristic acid were employed in place of the lauric fatty acid and 296 parts of the organic condensate were employed in place of the 268 parts of condensate of Example I. There was produced a condensate consisting essentially of a compound whose formula was the same as that of the end product of Example I except that $C_{13}H_{27}$ occurs in place of the $C_{11}H_{23}$.

The specific Examples I and II have been given merely by way of illustrating a particular method for producing the lauric and myristic derivatives. The various other derivatives may be produced by employing the same procedure as that set forth in Example I and substituting one mole proportion of the desired monocarboxylic acid for the lauric acid of said example.

Since certain changes may be made in the afore-described process for providing the novel compounds of the present invention, it is intended that all matter in the afore-description shall be interpreted as illustrative and not in a limiting sense.

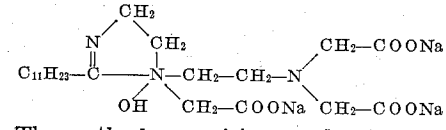
I claim:

1. A novel compound having the following general formula:



in which R is a hydrocarbon radical having at least nine carbon atoms, R_1, R_2 and R_3 are hydrocarbon radicals of 1–4 carbon atoms and M is an alkali metal.

2. A novel compound having the following formula:



3. The method comprising condensing a monocarboxylic fatty acid having at least ten carbon atoms with diethylene triamine, while removing 1.7–2 moles of water and then heating a mixture of approximately one mole of the organic condensate and an aqueous solution prepared with approximately six moles of an alkali metal hydroxide and approximately three moles of a monohalo monocarboxylic acid having a hydrocarbon group of 1–4 carbon atoms.

4. The method comprising reacting (*a*) approximately one mole of a cycloimidine condensate produced by condensing a monocarboxylic fatty acid having at least ten carbon atoms with diethylene triamine with (*b*) an aqueous solution prepared with approximately six moles of an alkali metal hydroxide and approximately three moles of a monohalomonocarboxylic acid having a hydrocarbon group of 1–4 carbon atoms.

HANS S. MANNHEIMER.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,268,273	Wilkes	Dec. 30, 1941
2,355,837	Wilson	Aug. 15, 1944
2,400,394	De Groote	May 14, 1946