Patented July 21, 1942 2,290,412

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2,290,412

METHYLENE DIAMINE ESTER AND METHOD OF MAKING SAME

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10 Claims. (Cl. 260—404)

This invention relates to a new composition of matter, our present application being a division of our parent application, Serial No. 342,730, filed June 27, 1940, which resulted in U. S. Patent No. 2,250,407, dated July 22, 1941.

The main object of our invention is to provide a new material or new composition of matter, that is particularly adapted for use as a demulsifier in the resolution of crude oil emulsions, but which may be employed in some other arts, hereinafter indicated, and may also have additional uses in other arts that we have not as yet investigated.

Another object of our invention is to provide a novel method for making said new material or composition of matter.

The demulsifier or demulsifying agent that forms the subject-matter of our present application consists of a compound or mixture of compounds that comprises the esterification product of a high molecular weight carboxy acid or its equivalent and a hydroxylated tertiary methylene diamine of the kind hereinafter described. Said compound or mixture of compounds is characterized by the presence of an acyl radical derived from a suitable high molecular weight carboxy acid of the kind which will be described in detail subsequently.

In order that our invention may be clearly understood, we will hereinafter give several examples of chemical compounds embodying our invention; and we will explain how said compounds can be produced or obtained.

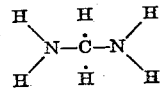
The expression "higher molecular weight carboxy acids" is an expression frequently employed to refer to certain organic acids, particularly monocarboxy acids, having more than six carbon atoms, and generally less than 40 carbon atoms. The commonest examples include the detergent-forming acids, i. e., those acids which combine with alkalis to produce soap or soap-like bodies. The detergent-forming acids, in turn, include naturally-occurring fatty acids, resin acids, such as abietic acid, naturally-occurring petroleum acids, such as naphthenic acids, and carboxy acids produced by the oxidation of petroleum. As will be subsequently indicated, there are other acids which have somewhat similar characteristics and are derived from somewhat different sources and are different in structure, but can be included in the broad generic term previously indicated.

Among sources of such acids may be mentioned straight chain and branched chain, saturated and unsaturated, carboxylic, aliphatic, alicyclic, fatty, aromatic, hydroaromatic, and aralkyl acids, including caprylic acid, butyric acid, heptylic acid, caproic acid, capric acid, pimelic acid, sebacic acid, erucic acid, saturated and unsaturated higher molecular weight aliphatic acids, such as the higher fatty acids containing at least eight carbon atoms, and including, in addition to those mentioned, melissic acid, stearic acid, oleic acid, ricinoleic acid, diricinoleic acid, triricinoleic acid, polyricinoleic acid, ricinostearolic acid, ricinoleyl lactic acid, acetylricinoleic acid, chloracetyl-ricinoleic acid, linoleic acid, linolenic acid, lauric acid, myristic acid, undecylenic acid, palmitic acid, mixtures of any two or more of the above mentioned acids or other acids, mixed higher fatty acids derived from animal or vegetable sources, for example, lard, cocoanut oil, rapeseed oil, sesame oil, palm kernel oil, palm oil, olive oil, corn oil, cottonseed oil, sardine oil, tallow, soyabean oil, peanut oil, castor oil, seal oils, whale oil, shark oil, and other fish oils, teaseed oil, partially or completely hydrogenated animal and vegetable oils, such as those mentioned; hydroxy and alphahydroxy higher carboxylic, aliphatic and fatty acids, such as dihydroxystearic acid, dihydroxy palmitic acid, dihydroxy-behenic acid, alphahydroxy capric acid, alphahydroxystearic acid, alphahydroxy palmitic acid, alphahydroxy lauric acid, alphahydroxy myristic acid, alphahydroxy cocoanut oil mixed fatty acids, alphahydroxy margaric acid, alphahydroxy arachidic acid, and the like; fatty and similar acids derived from various waxes, such as beeswax, spermaceti, montan wax, Japan wax, coccerin, and carnauba wax. Such acids include carnaubic acid, cerotic acid, lacceric acid, montanic acid, psyllastearic acid, etc. As suggested, one may also employ higher molecular weight carboxylic acids derived, by oxidation and other methods, from paraffin wax, petroleum and similar hydrocarbons; resinic and hydroaromatic acids, such as hexahydrobenzoic acid, hydrogenated naphthoic, hydrogenated carboxy diphenyl, naphthenic, and abietic acid; aralkyl and aromatic acids, such as benzoic acid, Twitchell fatty acids, naphthoic acid, carboxydiphenyl, pyridine carboxylic acid, hydroxybenzoic acid, and the like.

Other suitable acids include phenylstearic acid, benzoylnonylic acid, campholic acid, fencholic acid, cetyloxybutyric acid, cetyloxyacetic acid, chlorstearic acid, etc.

It is also well known that diamines, and particularly those having pronounced basic properties, may be derived by various means, provided

that the resultant diamine is characterized by the fact that the two amino nitrogen atoms are not attached to the same carbon atom. Such diamines, generally referred to as alkylene diamines, are well known and may be characterized by ethylene diamine. Derivatives of the diamines herein contemplated are characterized by being a methylene diamine derivative, i. e., a derivative of the hypothetical methylene diamine:



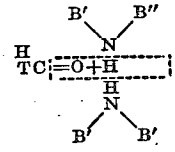
Methylene diamine is almost unknown for practical purposes, since it is very unstable in the form of a free base, but does exist in the form of alkylated or acylated derivatives. In view of this fact, it becomes obvious that the new chemical compound or composition of matter previously referred to must necessarily be obtained indirectly, insofar that the parent diamine is almost non-existent.

It is well known that a large number of secondary amines are available which may be designated by the formula type:

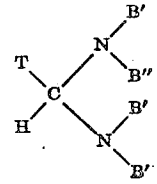
in which B' represents an alkyl, aralkyl, alicyclic, aryl, alkylol, aralkylol, hydroxy alicyclic, heterocyclic, or other equivalent radical; and B'' an alkylol, aralkylol, hydroxy alicyclic, or similar radical. Similarly, the formula

represents a secondary amine, in which a hydroxy hydrocarbon radical may or may not be present as a substituent for an amino hydrogen atom.

It is well known that aldehydes, particularly the aldehydes of relatively low molecular weight, such as formaldehyde, acetaldehyde, aldol, furfural, benzaldehyde, phenylacetaldehyde, hexahydrobenzaldehyde, etc., can combine with two moles of a secondary amine, so as to yield a methylene diamine, characterized by the fact that the two amino nitrogen atoms are attached to the same carbon atom. Such reaction may be indicated in the following manner:

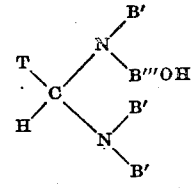


The amine so produced may be indicated by the following formula:

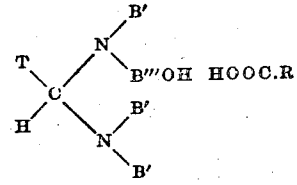


in which, as has been previously pointed out, T may represent a hydrogen atom derived from formaldehyde, or may represent a radical derived from acetaldehyde, propionaldehyde, butyraldehyde, heptaldehyde, lauric aldehyde, palmitic aldehyde, or stearic aldehyde, etc. Naturally, B'' may occur more than once, and B' less than three times. Similarly, instead of aliphatic aldehydes, one may employ heterocyclic aldehydes, such as furfuraldehyde, or aromatic aldehydes, such as benzaldehyde. One may also employ alicyclic aldehydes, such as hexahydrobenzaldehyde. Unsaturated aldehydes, such as acrolein, crotonaldehyde, or tiglic aldehyde, may be employed. As previously indicated, B' may represent radicals, such as methyl, ethyl, propyl, butyl, amyl, hexyl, octyl, decyl, hexadecyl, octadecyl, or similar radicals. Similarly, B' may represent an alkyl radical, such as a benzyl radical, ethyl benzyl radical, dimethyl benzyl radical, an alicyclic radical, such as the cyclohexyl, methyl cyclohexyl, etc.; likewise, B', as well as B'', may represent the radicals hydroxy ethyl, hydroxy propyl, hydroxy butyl, and other similar radicals, including a $C_6H_4C_2H_4OH$ radical, or, a $C_6H_{10}OH$ radical. Other radicals include the furfural radical, or hydroxy derivatives thereof. Piperidine may be considered as a special adaptation, in which one radical replaces two amino hydrogen atoms. As previously indicated, B' may be selected from any of the type of radicals above mentioned; whereas, B'' is limited to those radicals in which there is an alcoholic hydroxy group present, such as an alkylol radical, etc.

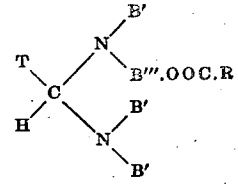
It is to be noted that the methylene diamine, expressed by the above formula, is a tertiary diamine in the sense that neither amino nitrogen atom has attached thereto a replaceable hydrogen atom. For convenience, the above formula may be rewritten as follows, so as to indicate that there is present an alcoholic hydroxyl radical:



in which B'''OH is obviously the monovalent hydroxy hydrocarbon radical, such as an alkylol radical or the like. It is well known that amines, particularly non-aryl, such as triethanolamine or the like, can be acylated by reaction with fatty acids, or a suitable functional derivative thereof, such as the acyl chloride, or the anhydride, or even the ester. If the tertiary hydroxy methylene diamine of the kind just described is reacted with a detergent-forming monobasic carboxy acid, the reaction may be indicated in the following manner:



with the formation of an intermediate ester, which may be indicated in the following manner:

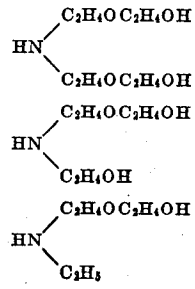


An examination of the previous formulas re-

veals that the hydroxylated tertiary acylated methylene diamine must contain at least one hydroxyl, and might contain as many as nine hydroxyls available for esterification; and as a matter of fact, might contain an even greater number if, instead of using the secondary amine, such as diethanolamine, dipropanolamine, dibutanolamine, etc., one employed ethanolglycerylamine, propyl glycerylamine, or diglycerylamine. Amines derived from diglycerol, instead of glycerol, would furnish radicals containing three hydroxyls, even after attachment to the amino nitrogen atom. If, in all instances, B' and B''' are derived from diglycerylamine, there would be present at least sixteen hydroxyls, and there might be present at least one more if aldol or a higher homologue were employed as a reactant in formation of the intermediate ester.

In addition to aldol, other similar hydroxy aldehydes or aldehyde-alcohols may be employed. As to such aldehydes other than aldol, reference is made to "Richter's Organic Chemistry," (Allott), volume 1, Third English Edition, 1934, pages 389–391.

In view of what has been said previously, it does not appear necessary to enumerate various suitable amines which may be employed for reaction with a selected aldehyde, but it may be well to indicate that among those which may be employed are the following: diethanolamine, dipropanolamine, dibutanolamine, dioctanolamine, dipentanolamine, glycerol hexanolamine, methyl glycerylamine, ethyl glycerylamine, propyl glycerylamine, cyclohexyl glycerylamine, benzyl glycerylamine; dibenzylamine, ethyl benzylamine, methyl benzylamine, propyl benzylamine, phenolmonoethanolamine, naphthylmonoethanolamine, cyclohexyl ethylamine, cyclohexyl propylamine, cyclohexyl hexylamine, diethylamine, dipropylamine, diamylamine, dihexylamine, dioctylamine, diglycerylamine, etc. In all the previous examples each radical indicates a substitute for an amino hydrogen atom. Similarly, amines can be obtained from polyglycerols or polyglycols, as, for instance, the secondary amines, indicated by the following formulas:



Such amines may serve as functional equivalents of the previously described amines, which happen to be free from an ether linkage. Likewise, one may have amines in which there is more than one ether linkage, i. e., in which the hydrocarbon radical which replaces an amino hydrogen atom has been interrupted more than once by an oxygen atom.

In examining the previous formulas, it becomes evident that if two different amines are employed, one of which does not contain a hydroxylated hydrocarbon radical, then the reaction is not limited to two dissimilar amines, but may take place in part in such a manner as to involve two similar amines, i. e., the aldehyde may react with two molecules of the hydroxylated amine; it may react with one mole of the hydroxylated amine and one mole of the non-hydroxylated amine; or it may be united with two moles of the non-hydroxylated amine. In such event, as last mentioned, the resultant compound is without value, unless a hydroxy aldehyde, such as aldol, has been employed. In such event an attempt to esterify with a detergent-monocarboxy acid, or the like, results in the formation of an entirely different type of material, i. e., an acid radical being introduced into the aldehyde radical or residue, as differentiated from the amine radical residue. For practical purposes, then, it is most expedient to manufacture or produce a methylene diamine from a single kind of secondary amine; and in such event, obviously it must be a hydroxylated amine, such as diethanolamine, except if one uses aldol or the like. In subsequent examples, diethanolamine is employed as the secondary amine for reaction with the aldehyde; but in view of what has been said previously, various other secondary amines or mixtures thereof might be employed.

Attention is again directed to the fact that wherever a hydroxyl radical exists, and provided it is not necessary for subsequent reaction, then such hydroxyl radical could be reacted with an acid, such as acetic acid, butyric acid, heptoic acid, etc.; and this statement applies to the hydroxyl radical of an alcohol aldehyde, such as aldol. Furthermore, an alkylol radical might be so combined as has been previously pointed out, or the alcohol radical or its equivalent might be combined with a monohydric alcohol. In essence, such combination simply results in the hydrocarbon chain interrupted at least once by an oxygen atom, as differentiated from an uninterrupted hydrocarbon chain. In the hereto appended claims reference to an alkyl, alkylol, or similar radical is intended specifically to include such examples where there is interruption of the chain or ring by an oxygen atom.

Having obtained the hydroxylated tertiary methylene diamine of the kind described in an anhydrous state or approximately anhydrous state, the next step is to obtain acylation by means of a high molal carboxy acid, and more particularly, a detergent-forming acid. Such procedure is comparable to the type of reaction in which other well known hydroxylated amines are esterified, i. e., made or caused to act like an alcohol. For instance, it is comparable to the reaction by which a fatty acid radical, such as the ricinoleic acid radical is introduced into a hydroxylated tertiary amine. The same procedure is employed, for example, in introducing a high molal carboxy acid radical into a compound, such as tetrahydroxyethyl ethylene diamine or triethanol amine. See U. S. Patents Nos. 2,167,347 and 2,167,348, to De Groote, Keiser and Blair, issued July 25, 1939.

Briefly stated, the method of producing such reactions is as follows: The acid, particularly a fatty acid, or its functional equivalent, is reacted with a tertiary hydroxylated amine under such conditions so as to remove any water which may be formed. The temperature, generally speaking, is above the boiling point of water, i. e., above 120° C. and below the decomposition point of the amine. Since hydroxylated amines are generally high boiling, the reaction can be conducted at a considerably higher temperature, 160–180° C., or even higher, provided that one does not employ a temperature which results in the pyrolysis or decomposition of the amine.

Instead of the acid itself, obvious functional equivalents, such as the anhydride, the acyl chloride, an ester, or an amide may be employed. The entire object is to use a compound which has a labile acyl group, or to state the matter another way, is in essence an acylating or oxy-acylating agent, insofar that the oxy-acyl, or more correctly, the acyloxy group, is introduced. One can, of course, view the alcohol radical as losing either a hydrogen atom or hydroxyl radical. Needless to say, when compounds such as the acyl chloride, ester or amide are employed, some compound other than water is split off, for instance, an alcohol or ammonia or hydrochloric acid. There are certain objections to the use of acyl chloride, in that one obtains the salt of the compound, i. e., the acid chloride, which may not be as desirable as the unneutralized base. The mass may be heated during the reaction period, and the reaction period may vary from 2–8 hours. If desired, an inert gas such as nitrogen may be passed through the mixture while being reacted.

Our preferred reagent is obtained in the following manner:

We react a readily available aldehyde, such as acetaldehyde or heptaldehyde, in the molecular proportions of one mole of aldehyde with two moles of diethanolamine. Such reaction is conducted in the manner previously noted; and after completion of reaction, any water still present which has not been removed previously in the course of reaction, is removed by distillation, preferably under vacuum.

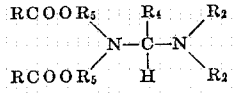
Such hydroxylated diamine is then treated in the proportion of three moles of diamine to two moles of castor oil, which consists essentially of triricinolein. Any suitable quantity of material may be employed, for instance, 500 lbs. of the selected anhydrous diamine and the appropriate amount of castor oil. The two products are mixed together and heated at a reasonable temperature above the boiling point of water and below the point of decomposition, for instance, at some temperature between 135–195° C. for a suitable period of time, i. e., 1 to 5 hours. Constant stirring may be employed, if desired. Also one may pass dried nitrogen gas through the reaction mass. The product so obtained is the acylated diamine mixed with some free glycerol and certain other accompanying cogeneric products.

It is to be noted that the compounds described are basic in character, due to the presence of an unacylated basic amino nitrogen atom, or due to the presence of an esterified group of the kind described. In such instances the compound may be employed as such, or may be employed in basic form, (i. e., after combination with water), or may be employed in salt form by reaction with an acid, such as acetic acid, lactic acid, hydrochloric acid, or any other suitable acid.

It is to be noted that the procedure previously described can be employed to introduce one or more acyl radicals into a hydroxylated tertiary methylene diamine of the kind described. The introduction of more than one acyl radical, of course, obtained from a high molecular weight carboxy acid or the like is predicated on the presence of more than one alcoholic hydroxyl radical. Obviously, the product obtained in the manner described in preparation of the preferred reagent would yield a product containing four hydroxyl radicals. It is our preference to introduce at least one acyl radical, and preferably, not more than two. The most desirable reagents are those which are obtained by the introduction of a single acyl radical derived from a high molecular weight carboxy acid, and more particularly, from the detergent type acid. The fatty acids yield the most desirable compounds, and ricinoleic acid represents the most desirable compounds, and ricinoleic acid represents the most desirable type of fatty acid. It has been previously pointed out that the amino nitrogen atoms present are in basic form, and that either one or both nitrogen atoms may be combined with water or a suitable acid; or the compounds can be employed in uncombined form, i. e., in the form of a free base.

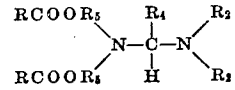
Having thus described our invention, what we claim as new and desire to secure by Letters Patent is:

1. A methylene diamine ester of the formula:



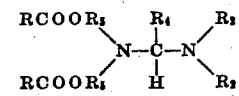
in which R_4 is selected from the class consisting of hydrogen atoms and hydrocarbon radicals having not over 18 carbon atoms; $RCOOR_5$ is a radical in which R_5 is a divalent radical selected from the class of alkylene radicals, alkylene radicals in which the carbon atom chain has been interrupted at least once by an oxygen atom, hydroxyalkylene radicals, and hydroxylated alkylene radicals in which the carbon atom chain has been interrupted at least once by oxygen; RCOO is the acyloxy radical of a high molecular weight carboxy acid having more than 6 and less than 40 carbon atoms; and R_2 is a radical selected from the class consisting of alkyl, aralkyl, alicyclic, aryl, alkylol, aralkylol, hydroxyalicyclic, alkylol-ether, polyhdroxylated alkyl, and polyhydroxylated alkyl-ether, and $RCOOR_5$ radicals and in said last mentioned $RCOOR_5$ radicals, R_5 and RCOO have their prior significance.

2. A methylene diamine ester of the formula:



in which R_4 is selected from the class consisting of hydrogen atoms and hydrocarbon radicals having not over 18 carbon atoms; $RCOOR_5$ is a radical in which R_5 is a divalent radical selected from the class of alkylene radicals, alkylene radicals in which the carbon atom chain has been interrupted at least once by an oxygen atom, hydroxyalkylene radicals, and hydroxylated alkylene radicals in which the carbon atom chain has been interrupted at least once by oxygen; RCOO is the acyloxy radical of a detergent-forming monocarboxy acid having more than 6 and less than 40 carbon atoms; and R_2 is a radical selected from the class consisting of alkyl, aralkyl, alicyclic, aryl, alkylol, aralkylol, hydroxy alicyclic, alkylol-ether, polyhydroxylated alkyl, and polyhydroxylated alkyl-ether, and $RCOOR_5$ radicals and in said last mentioned $RCOOR_5$ radicals, R_5 and RCOO have their prior significance.

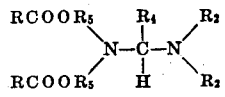
3. A methylene diamine ester of the formula:



in which R_4 is selected from the class consisting of hydrogen atoms and hydrocarbon radicals having not over 18 carbon atoms; $RCOOR_5$ is a radical in which R_5 is a divalent radical selected

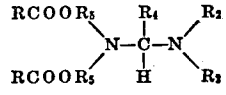
from the class of alkylene radicals, alkylene-radicals in which the carbon atom chain has been interrupted at least once by an oxygen atom, hydroxyalkylene radicals, and hydroxylated alkylene radicals in which the carbon atom chain has been interrupted at least once by oxygen; RCOO is the acyloxy radical of a higher fatty acid; and R_2 is a radical selected from the class consisting of alkyl, aralkyl, alicyclic, aryl, alkylol, aralkylol, hydroxyalicyclic, alkylol-ether, and polyhydroxylated alkyl, and polyhydroxylated alkyl-ether, and $RCOOR_5$ radicals and in said last mentioned $RCOOR_5$ radicals, R_5 and RCOO have their prior significance.

4. A methylene diamine ester of the formula:



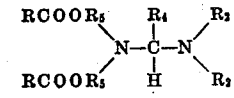
in which R_4 is selected from the class consisting of hydrogen atoms and hydrocarbon radicals having not over 18 carbon atoms; $RCOOR_5$ is a radical in which R_5 is a divalent radical selected from the class of alkylene radicals, alkylene radicals in which the carbon atom chain has been interrupted at least once by an oxygen atom, hydroxyalkylene radicals, and hydroxylated alkylene radicals in which the carbon atom chain has been interrupted at least once by oxygen; RCOO is the acyloxy radical of a higher fatty acid having 18 carbon atoms; and R_2 is a radical selected from the class consisting of alkyl, aralkyl, alicyclic, aryl, alkylol, aralkylol, hydroxyalicyclic, alkylol-ether, polyhydroxylated alkyl, and poyhydroxylated alkyl-ether, and $RCOOR_5$ radicals and in said last mentioned $RCOOR_5$ radicals, R_5 and RCOO have their prior significance.

5. A methylene diamine ester of the formula:



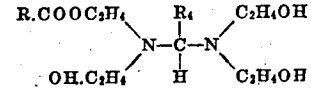
in which R_4 is selected from the class consisting of hydrogen atoms and hydrocarbon radicals, having not over 18 carbon atoms; $RCOOR_5$ is a radical in which R_5 is a divalent radical selected from the class of alkylene radicals, alkylene radicals in which the carbon atom chain has been interrupted at least once by an oxygen atom, hydroxyalkylene radicals, and hydroxylated alkylene radicals in which the carbon atom chain has been interrupted at least once by oxygen; RCOO is the acyloxy radical of a higher unsaturated fatty acid having 18 carbon atoms; and R_2 is a radical selected from the class consisting of alkyl, aralkyl, alicyclic, aryl, alkylol, aralkylol, hydroxyalicyclic, akylol-ether, polyhydroxylated alkyl, and polyhydroxylated alkyl-ether, and $RCOOR_5$ radicals and in said last mentioned $RCOOR_5$ radicals, R_5 and RCOO have their prior significance.

6. A methylene diamine ester of the formula:



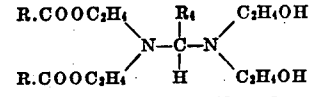
in which R_4 is selected from the class consisting of hydrogen atoms and hydrocarbon radicals having not over 18 carbon atoms; $RCOOR_5$ is a radical in which R_5 is a divalent radical selected from the class of alkylene radicals, alkylene radicals in which the carbon atom chain has been interrupted at least once by an oxygen atom, hydroxyalkylene radicals, and hydroxylated alkylene radicals in which the carbon atom chain has been interrupted at least once by oxygen; RCOO is the ricinoleyloxy radical; and R_2 is a radical selected from the class consisting of alkyl, aralkyl, alicyclic, aryl, alkylol, aralkylol, hydroxyalicyclic, alkylol-ether, polyhydroxylated alkyl, and polyhydroxylated alkyl-ether, and $RCOOR_5$ radicals and in said last mentioned $RCOOR_5$ radicals, R_5 and RCOO have their prior significance.

7. A methylene diamine ester of the formula:



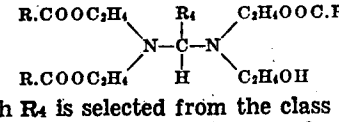
in which R_4 is selected from the class consisting of hydrogen atoms and hydrocarbon radicals having not over 18 carbon atoms, and RCOO is the ricinoleyloxy radical.

8. A methylene diamine ester of the formula:



in which R_4 is selected from the class consisting of hydrogen atoms and hydrocarbon radicals having not over 18 carbon atoms, and RCOO is the ricinoleyloxy radical.

9. A methylene diamine ester of the formula:



in which R_4 is selected from the class consisting of hydrogen atoms and hydrocarbon radicals having not over 18 carbon atoms, and RCOO is the ricinoleyloxy radical.

10. A method for manufacturing the methylene diamine esters defined in claim 1, which consists in reacting a high molecular weight carboxy acid having more than 6 and less than 40 carbon atoms, with a hydroxylated di-tertiary methylene diamine in which at least one amino hydrogen atom has been replaced by a member of the class consisting of alkylol, aralkylol, hydroxyalicyclic, alkylol-ether, polyhydroxylated alkyl, and polyhydroxyl alkyl-ether radicals.

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