

UNITED STATES PATENT OFFICE

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COMPOSITION OF MATTER

Melvin De Groote, University City, Mo., assignor,
by mesne assignments, to Petrolite Corpora-
tion, Ltd., a corporation of Delaware

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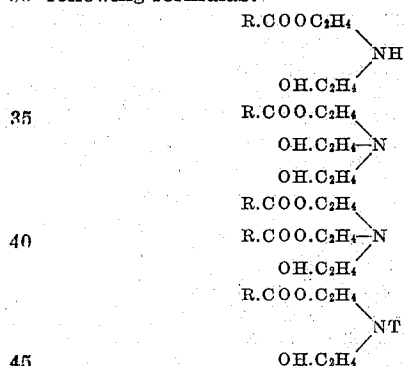
8 Claims. (Cl. 260-404)

This application is a continuation in part of my pending application for patent Serial No. 211,039, filed May 31, 1938, which has subsequently resulted in U. S. Patent No. 2,166,434, dated July 18, 1939.

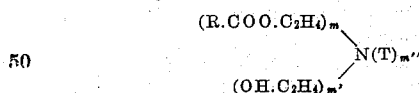
My present invention consists of a new compound or composition of matter, consisting of a certain kind of complex amine derived by reaction between (a) acid esters obtained from phthalated monoricinolein, phthalated diricinolein, phthalated mon-olein, phthalated di-olein, phthalated mononaphthenin, phthalated monobietin, or similar materials, and (b) simpler amines of the kind hereinafter described. I have found that said new compound is particularly adapted for use as a demulsifier in the resolution of crude oil emulsions, either alone, or in admixture with conventional demulsifying agents of a compatible type. It may also have uses in other arts that I have not yet investigated.

In order that the present application may be considered a complete disclosure of my invention, I deem it advisable to describe the raw materials entering into the manufacture of my new compound or composition of matter, as well as the method or procedure employed to produce said compound.

One can obtain or manufacture chemical compounds whose composition is indicated by the following formulas:

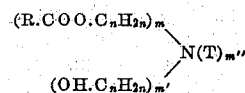


The compounds above described may be summarized by the following formula:



in which m represents the number 1 or 2, m' represents the number 1 or 2, and m'' represents the number 0 or 1, with the proviso that $m+m'+m''=3$.

However, the radical C_2H_4 , which appears in the above formula, may represent any similar radical, such as a C_3H_6 radical, C_4H_8 radical, etc., and therefore, the above formula may be rewritten:



where n represents a small whole number, preferably not over 10.

In the above group, T represents a hydrogen atom or a non-hydroxy aliphatic hydrocarbon radical, such as a methyl, ethyl, propyl, amyl, or similar radical; or T may represent a non-hydroxy alicyclic radical, such as a cyclohexyl radical, or a non-hydroxy aralkyl radical, such as a benzyl radical; or the acylated radical obtained by replacing a hydrogen atom of the hydroxyl group of an alkylol radical by the acyl radical of a monobasic carboxy acid, such as acetic acid, butyric acid, heptic acid, or the like, all of which are characterized by having less than 8 carbon atoms. The alkylol radical, prior to acylation, may be a hydroxy alicyclic or a hydroxy aralkyl radical, provided the hydroxy radical is attached to the aliphatic residue of the aralkyl radical.

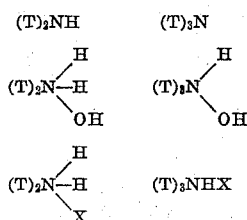
In the above formula R.COO represents the oxy-acyl or acid radical derived from the acid R.COOH . R.COOH represents any monobasic detergent-forming carboxy acid, such as a typical fatty acid or abietic acid or naphthenic acid. Typical fatty acids are those which occur in naturally-occurring oils and fats, and generally have eight or more carbon atoms and not over 32 carbon atoms. Common examples include oleic acid, stearic acid, linoleic acid, linolenic acid, ricinoleic acid, erucic acid, palmitic acid, myristic acid, etc. These acids combine with alkali to produce soap or soap-like materials, and are commonly referred to as being monobasic detergent-forming carboxy acids. Blown oils (oxidized oils) are not included.

The alkylol radical, previously referred to, prior to esterification, may be a hydroxy alicyclic or a hydroxy aralkyl radical, provided the hydroxy radical is attached to the aliphatic residue of the aralkyl radical.

As to the amines above described, which happen to be tertiary amines, it may be well to point out that these may be formed readily by a reaction involving an ester of the selected detergent-forming acid, for instance, a fatty acid ester, such as the glyceride, and a corresponding

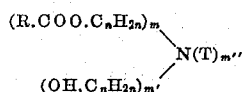
amino nitrogen atom. For this reason, these amine products which are herein contemplated as demulsifying agents and which are necessarily characterized by freedom from any aryl groups, as such, cannot be derived from aryl amines. They are derived solely from alkyl, alicyclic, or aralkyl amines having at least one hydroxyl group present. It is true that in the aralkyl amines there is an aryl group present, but it is not directly attached to the nitrogen atom, as in the case of aryl amines, but, in fact, represents nothing more or less than a substituted alkyl-amine. For instance, I consider benzylamine as being the primary amine, phenmethyl amine.

Finally, it must be recognized that these materials have not lost any basicity in the forms of the esterified amine, and that they exhibit all the properties of a basic amine, that is, they combine with water to form a base, presumably a substituted ammonium compound, but not quaternary ammonium compound insofar that there are always one, two, or three unsubstituted hydrogen atoms of the ammonium radical present. They combine with various acids to form salts. For example, they may be combined with acetic acid, hydrochloric acid, lactic acid, chloracetic acid, nitric acid, butyric acid, phosphoric acid, oxalic acid, or any suitable organic or inorganic acid, to form salts. It is understood that the reference in the specification and appended claims to the amines includes the basic form and the acid salts, as well as the amines themselves. The new compositions of matter herein described have great demulsifying properties which are contributed, in part, by the amine, and it is immaterial whether the amine may be considered as being in any one of the following forms:



in which T represents the substituents for the amino hydrogen atoms of the parent ammonia from which all amines are hypothetically derived, and X simply represents the acid radical of any acid employed. This statement applies with equal force and effect to the final product, or composition of matter, which is also a basic amine of a more complex type.

Reference is again made to the formula which summarizes the various amines used as intermediate raw materials, viz.:

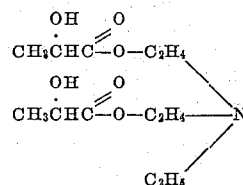


in which the characteristics have their previous significance.

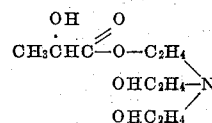
Attention is directed to the fact that where the substituted alkyl radical $OH.R.COO.C_2H_4$ — appears, a suitable non-aryl radical other than an aliphatic residue may serve as the functional equivalent; for instance, an alicyclic radical derived from a cyclohexyl radical, or an aralkyl radical derived from a benzyl radical. In other

words, in the hereto appended claims reference to the C_nH_{2n} radical, as such, or as an alkyl radical or residue, is intended in the broad sense to include the alicyclic radicals or residues, or the aralkyl radicals or residues which are the equivalent thereof. There is no intention to include an aromatic radical where there is a direct linkage between the aromatic nucleus and the amino hydrogen atom, for the reason that such products have little or no basicity and do not have the characteristic properties of the amines previously described.

In indicating the various hydroxylated tertiary amines of the non-aryl type which may be employed to produce the amine herein described, it is desirable to indicate that amines of the type where a hydroxy acyl radical replaces a hydrogen atom of the hydroxyl radical of the hydroxy tertiary amine, are not included within the broad class of hydroxy tertiary amines, unless there is another hydroxyl radical attached to the usual alkyl radical. For instance, if ethyl diethanolamine is treated with two moles of lactic acid so as to form the dilactyl compound of the following formula:

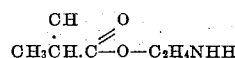


then it is understood that such materials would not represent a hydroxy tertiary amine within the meaning or scope, as herein employed. If, on the other hand, triethanolamine were treated with lactic acid, so as to give monolactyl triethanolamine of the following composition:



then such compound would be included, due to the presence of one or more hydroxyl radicals attached to the alkyl radicals.

Similarly, in indicating the various hydroxylated primary or secondary amines of the non-aryl type which may be employed to produce the amine herein described, it is desirable to indicate that amines of the type where a hydroxy acyl radical replaces a hydrogen atom of the hydroxy radical of a hydroxy primary or secondary amine, are not included within the broad class of hydroxy tertiary amines, unless there is another hydroxyl radical attached to the usual alkyl radical. For instance, if ethanolamine is treated with lactic acid, so as to form the lactyl derivative of the following formula:



then it is understood that such materials would not represent a hydroxy primary amine within the meaning or scope, as herein employed. The same would be true if the corresponding product were derived from diethanolamine, provided both hydroxy radicals had been esterified with lactic acid.

The manufacture of compounds from tertiary amines is relatively simple, because no precau-

tions are necessary to prevent amidification. The selected detergent-forming acid, or ester, as, for example, a fatty oil and the selected hydroxy tertiary amine are mixed in suitable proportions and heated at some point above the boiling point of water, for instance, 110° C., and at a point below the decomposition point of the amine or the fatty oil, for instance, 180° C., for a suitable period of time, such as two to eight hours. Mild agitation is employed. A catalyst such as sodium oleate, sodium carbonate, caustic soda, etc., may be present in amounts of about one-half of 1% or less. It is noted that the fatty acids are employed in this instance in the form of an ester, to wit, the glyceride, although, as previously pointed out, other functional equivalents can be readily employed with equal facility. It is to be noted that the reactions above described do not take place to any appreciable extent if the fatty acid has been converted into the soap or salt. Such salts are not functional equivalents. As previously indicated, an ester of abietic acid might be employed, if desired.

When, however, one is employing a hydroxy secondary amine, precautions must be taken, so that one gets a substantial percentage of products derived by esterification, rather than amidification. Any suitable ester may be employed, but it is often most convenient to employ the glyceride of a fatty acid, for instance, triricinolein.

The selected glyceride and the selected hydroxy secondary amine are mixed in suitable proportions and heated at some point above the boiling point of water, for instance, 110° C., and below the decomposition point of the amine or fatty material, for instance, 180° C., for a suitable period of time, such as 4-24 hours. Mild agitation is employed. A catalyst such as sodium oleate, sodium carbonate, caustic soda, etc., may be present in amounts of about ½% or less. It is to be noted that the fatty acids are present in ester form and not in the form of the free acid, and thus there is no tendency to form the salt to any marked extent, and if conducted at the lower range of reaction temperatures, there is a decided tendency to form the esterification products, rather than the amidification products.

In order to illustrate suitable examples of the amines which may be used as intermediate raw materials, the following examples are given:

Intermediate amine—Example 1

Castor oil is employed. For sake of convenience, its molecular weight is considered as being 925. Commercial triethanolamine and castor oil in the proportion of one mole of castor oil and three moles of triethanolamine are heated to a temperature between 150-180° C. for two hours. Mild agitation is employed. The reaction product so produced may be used as such, or may be converted into the acetate or other suitable form.

Intermediate amine—Example 2

The same procedure is followed as in Intermediate amine Example 1, except that the ratio employed is two moles of the castor oil to three moles of triethanolamine.

Intermediate amine—Example 3

One mole of methyl naphthenate is reacted in the manner previously described with one mole of triethanolamine.

Intermediate amine—Example 4

Diethanolamine is substituted for triethanolamine in Example 3.

Intermediate amine—Example 5

Methyl abietate is substituted for methyl naphthenate in Examples 3 and 4 above.

Intermediate amine—Example 6

Olive oil is substituted for castor oil in Examples 1 and 2 above.

Intermediate amine—Example 7

Ethyl diethanolamine is substituted for triethanolamine in previous examples where triethanolamine has been employed, but ratios are changed, if required, so that there is always one non-esterified ethanol radical present.

Intermediate amine—Example 8

Cyclohexyl diethanolamine is substituted for triethanolamine in previous examples where triethanolamine has been employed, but subject to the same modification as indicated in Example 7 immediately preceding.

Intermediate amine—Example 9

Benzyl diethanolamine is substituted for triethanolamine in previous examples where it has been employed. See modification noted in Examples 7 and 8, immediately above.

Intermediate amine—Example 10

Castor oil (triricinolein) is employed. For convenience its molecular weight is considered as being 925. Commercial diethanolamine and castor oil in the proportion of one mole of castor oil to three moles of diethanolamine are heated to a temperature of 120-140° C. for about twelve hours. Mild agitation is employed. Loss of basicity is an indication of amidification. Time of esterification may be extended or temperature lowered or raised so as to insure maximum esterification, and particularly so as to produce a product characterized by the presence of one unesterified alkylol radical attached to the amino nitrogen. The reaction product, so produced, may be used as such, or may be converted into the acetate or other suitable form.

Having prepared the relatively simpler intermediate amines of the kind previously described, the second step in the preparation of the new composition of matter is to produce acid esters of the kind obtainable by reaction between polybasic carboxy acids or their functional equivalents, such as the anhydrides and esters of detergent-forming acids or the like. Detergent-forming acids are monobasic carboxy acids, such as typical fatty acids, abietic acids, or naphthenic acids. Typical fatty acids are those which occur in naturally-occurring oils and fats and generally have 8 or more carbon atoms and not over 32 carbon atoms. Common examples include oleic acid, stearic acid, linoleic acid, linolenic acid, ricinoleic acid, erucic acid, palmitic acid, myristic acid, etc. These various acids combine with alkali to produce soap or soap-like materials and are commonly referred to as being monobasic detergent-forming acids. Blown oils (oxidized oils) are not included.

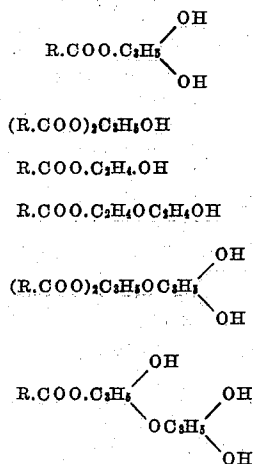
Detergent-forming acids combine with polyhydric alcohols to give esters characterized by the

presence of at least one hydroxyl radical attached to the radical which replaces the carboxylic hydrogen. Polyhydric alcohols include glycerol, ethylene glycol, propylene glycol, and other similar glycols, and also a polyhydroxy ether alcohol type of material such as diethylene glycol, diglycerol, triglycerol, etc. Such materials, whether produced from glycerol or from glycol or from two dissimilar polyhydric alcohols, are characterized by the fact that dehydration produces an oxygen linkage between two organic residues, and thus the material, in addition to having the properties of a polyhydric alcohol, has to some degree at least, the properties of an ether.

As to the manufacture of esters from an alcohol, including polyhydric alcohols, and a carboxy acid, the usual procedure is esterification in presence of dry hydrochloric acid gas. Such method is satisfactory, provided conditions are controlled so that complete esterification does not take place, and thus result in a material containing no free hydroxyl in the polyhydric alcohol residue. For example, if diglycerol is esterified with four molecules of ricinoleic acid, the resultant product will not contain a free hydroxy group in the polyglycerol residue. However, if esterification is continued so that one, two or three ricinoleic acid residues are introduced, and so that three, two, or one free hydroxyl residues remain in the polyglycerol radical, then a suitable compound is produced. Esterifications to produce the desired product may be conducted in the conventional manner, usually employed in such reactions.

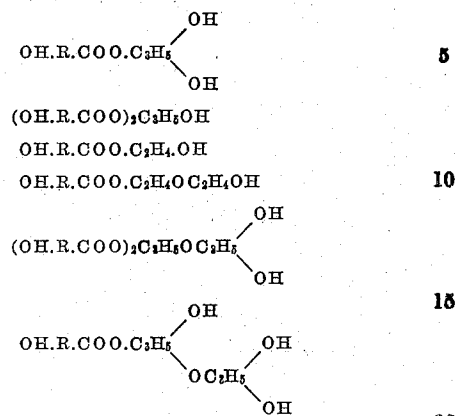
It is, of course, obvious that esters may be produced as readily from naphthenic acid or abietic acid or the like, as from fatty acids. For sake of brevity, reference will be made particularly to fatty acids. A large number of materials derived from fatty acids and characterized by the presence of a free hydroxyl attached to the hydrocarbon radical which replaces the carboxylic hydrogen, is available in the open market and sold under the name of "superglycerinated fats." Such materials are used as emulsifying agents, both in edible and non-edible products. They are derived from a wide variety of acids and a wide variety of polyhydric alcohols of both the ether type and the non-ether type.

The following formulas indicate the types derivable from non-hydroxylated monobasic carboxy acids:

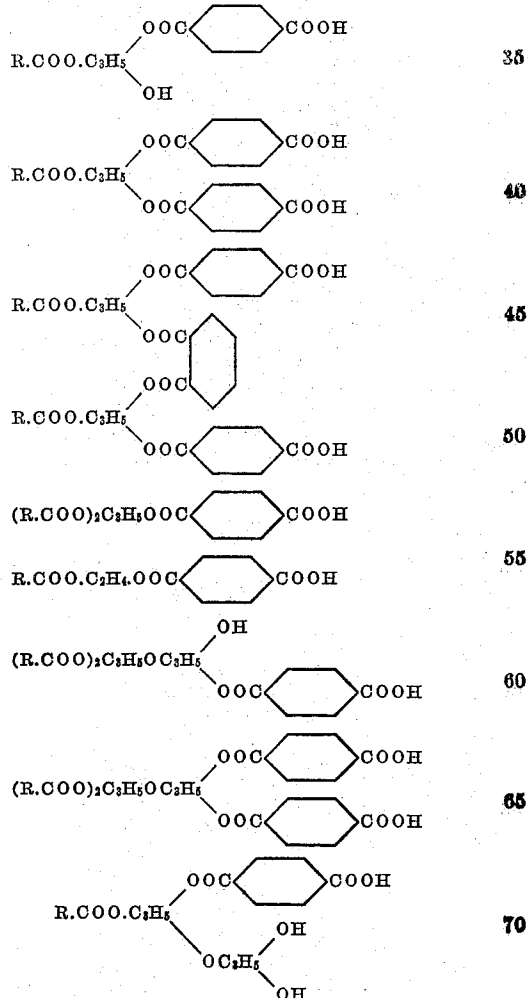


If derived from hydroxylated fatty acids, such as hydroxystearic acid, ricinoleic acid, and the

like, the above formulas would correspond to the following:

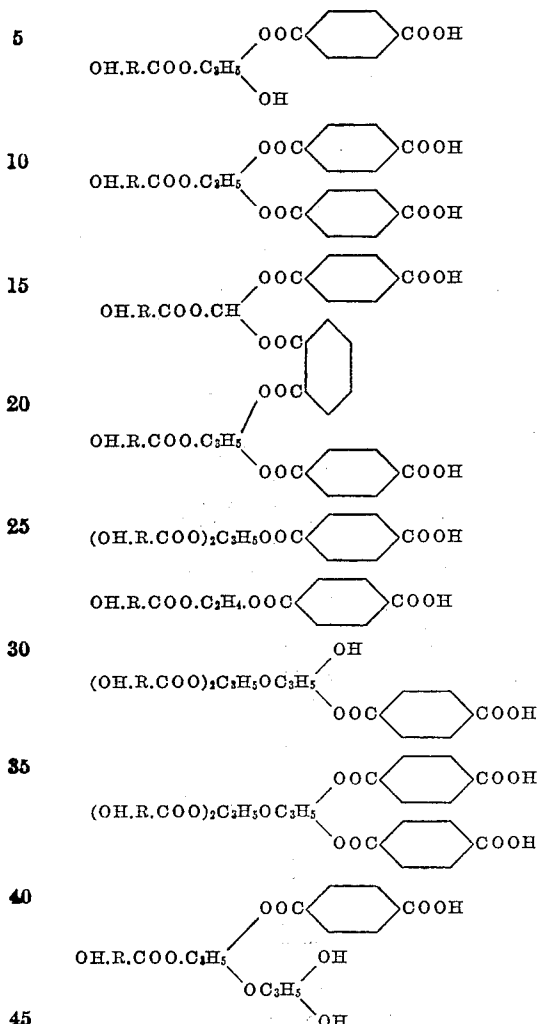


If such products are reacted with the polybasic carboxy acid or the anhydride, as, for example, phthalic acid or phthalic anhydride, one can obtain a large number of esters, which are acidic esters in the sense that there is present a free carboxyl radical. In the following formulas, no attempt is made to show phthalic anhydride as the usual ortho compound, but it is shown as a para compound, purely for the sake of convenience. The selection of phthalic acid is purely for purposes of illustration. Any one of a number of other acids may be employed.

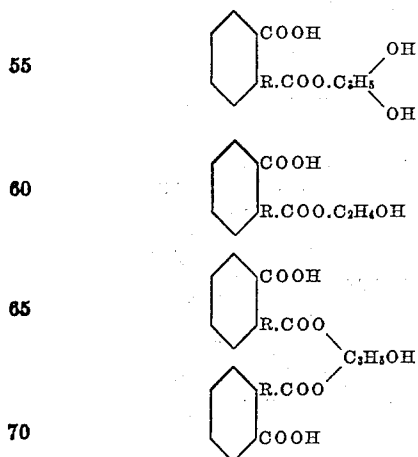


If, however, such materials were derived from hydroxylated fatty acids, without involving the

alcoholiform hydroxyl attached to the fatty acid radical, then the above formula would appear as follows:

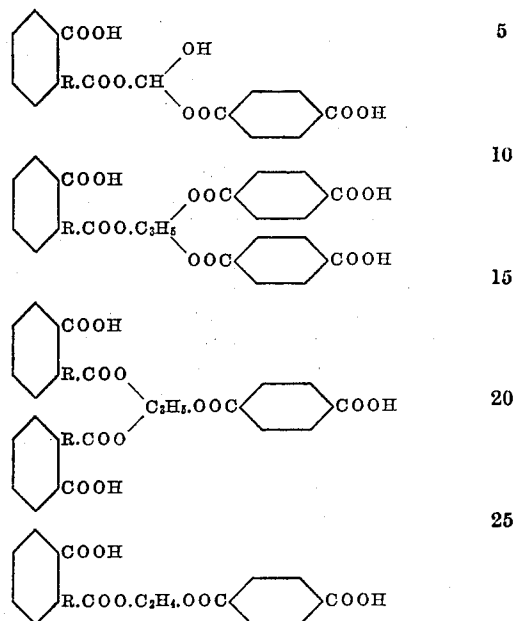


However, if one considers the reactions in which only the alcoholiform hydroxyl of the fatty acid radical, for example, ricinoleic acid, is involved in formation of the reaction products obtained, then they may be indicated by the following formulas:



Similarly, one may have products in which both the alcoholic hydroxyl attached to the fatty acid radical and also the hydroxyl attached to the glycerol or glycol radical are reacted with

phthalic anhydride or its equivalent, so as to produce reagents indicated by the following formulas:



In the examples shown above, where the ester is polybasic, one might remove the acidity of one of the carboxylic hydrogen atoms, or two of the carboxylic hydrogen atoms in any feasible manner, that is, by neutralization with an alkali or by conversion into an ester involving a reaction with any suitable alcohol, i. e., a monohydric, trihydric, etc. In any event, however, the material derived by reaction between a polybasic acid or its functional equivalent and the hydroxylated ester type of fatty material of the kind described, is always characterized by the presence of at least one free carboxyl radical.

Where reference is made to ricinoleic acid, hydroxy-stearic acid, abietic acid, and the like, it is evident that certain simple derivatives, such as the halogenated compounds, are the obvious functional equivalents; for instance, chlorinated ricinoleic acid, may be employed instead of ricinoleic acid; brominated oleic acid might be employed instead of oleic acid; hydrogenated abietic acid might be employed instead of abietic acid. In these instances, the monobasic detergent-forming carboxy material, notwithstanding modifications of the kind indicated, still has the same functional properties as the unmodified material; and thus acts in the same manner, as far as chemical reactions noted are concerned, and also as far as producing an effective demulsifying agent is concerned.

In the hereto appended claims, reference to monobasic detergent-forming carboxy acids includes such obvious functional equivalents.

As to the manufacture of reagents from polybasic carboxy acids and superglycerinated fats or the like, it need simply be stated that these reagents have been produced and used in the arts as plasticizers, demulsifying agents, etc.; and that the method of producing the same is well known. Briefly stated, esterification takes place readily on the application of heat, and the reaction may be hastened by employing a higher temperature, provided the decomposition does not take place; or the reaction may be conducted in presence of an inert solvent, such as xylene, which may be removed after completion of reaction.

The reaction can be hastened also by passing through the mixture a dried inert gas; or the reaction may be conducted under a reflux condenser using material such as xylene and a water trap, so as to remove water as quickly as formed. Generally speaking, however, the reactions take place rapidly, quickly, and completely by simply heating the products together in stoichiometric proportions at a temperature somewhere above the boiling point of water, and particularly at a temperature of about 110–160° C., provided there is no decomposition. Phthalic acid is particularly suitable, because it does not decompose readily, whereas, some other acid, such as oxalic acid, may be readily desirable, but the temperature of esterification must be lower, of course, to prevent decomposition.

The polybasic acids which may be employed, including some having at least three carboxyl radicals, are phthalic, succinic, malic, fumaric, citric, maleic, adipic, tartaric, glutaric, diphenic, naphthalic, oxalic, etc.

It is to be noted that the manufacture of the composition of matter in reality involves three different esterification reactions. For example, a fatty acid may be reacted with a tertiary hydroxylamine to give products of the kind indicated. Naturally, if the tertiary amine, such as triethanolamine, is reacted with a glyceride, the reaction may, in essence, be a rearrangement reaction, rather than an esterification reaction, although for purposes of classification, it may be considered as an esterification reaction. The second esterification reaction involved is the one between the hydroxy fatty body of the kind described, such as super-glycerinated fats and phthalic anhydride, or the like. Monocabetin or mononaphthenin, of course, may be considered broadly as a superglycerinated fat.

The third esterification reaction is between the two types of materials above described, the simpler amine always being characterized by the presence of an alcoholic hydroxyl radical, and the ester being characterized by the presence of the carboxyl group. The last mentioned esterification reaction goes readily and is nothing more or less than a conventional esterification reaction and requires no further elaboration.

Composition of matter—Example 1

One employs an intermediate amine of the kind described under "Intermediate amine Example 1" above. Commercial diricinolein is treated with two moles of phthalic anhydride, so as to yield an ester having two free carboxyl radicals. One molecular weight of this acidic ester is reacted with one mole of material exemplified by Intermediate amine Example 1, so as to yield a product characterized by the presence of both free carboxyl radicals and free alcoholic hydroxyl radicals. This is a conventional esterification reaction, and the materials are intermittently mixed and heated at approximately 120–160° C., with constant agitation, until samples taken from the batch and analyzed show substantially complete reaction. A suitable solvent may be present, and water formed may be distilled off continuously during the esterification process. The solvent may remain behind in the final product or be removed, if desired.

Composition of matter—Example 2

Diphthalated mono-olein is substituted for diphthalated diricinolein in Composition of matter Example 1, immediately above.

Composition of matter—Example 3

Dimaleated monostearin is substituted for diphthalated diricinolein in Composition of matter Example 1 above.

Composition of matter—Example 4

Dioxalated mono-abietin is substituted for diphthalated diricinolein in Composition of matter Example 1 above.

Composition of matter—Example 5

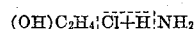
Dicitrated mononaphthenin is substituted for diphthalated diricinolein in Composition of matter Example 1 above.

Composition of matter—Example 6

An amine of the kind characterized by the product described under "Intermediate amine Example 10" is substituted in the above Composition of matter Examples 1–5 for the intermediate amine therein employed.

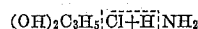
It should be noted, however, that this particular product contains only two hydroxyl radicals available for esterification per atom of nitrogen. Insofar that some amidification may take place in following the directions in preparing the amine from diethanolamine in Intermediate amine Example 10 above, it is probably the safest procedure to determine the acetyl or hydroxyl value before reacting in molecular proportions.

Attention is directed to the fact that the alkylolamines are obtained in such a manner that they may be looked upon as being derivatives of dihydric alcohols, for instance, the chlorhydrin of the dihydric alcohol, as indicated in the following manner:



As previously stated, the C_2H_4 radical may be any one of a number of hydrocarbon radicals which are aliphatic, alicyclic, or aralkyl in nature.

It is at once manifest that similar derivatives are available from glycerols, polyglycerols, and the like, as indicated by the following reaction:



It is not necessary to point out that the same types of reactions will produce secondary or tertiary amines and that the reaction is not limited to a combination with ammonia, but may take place with a combination of other primary or secondary amines, such as amylamine, diamylamine, cyclohexylamine, dicyclohexylamine, benzylamine, dibenzylamine, amylcyclohexylamine, etc.

This means that in the type of material previously described, there is a wide variety of material, such as monoglycerylamine, diglycerylamine, monoglyceryl diethanolamine, monoglyceryl dipropylamine, diglyceryl propylamine, triglycerylamine, etc., which are functional equivalents of the various amines previously described for reaction with triricinolein and the like. When such amines are employed, instead of the radical $-\text{C}_n\text{H}_{2n}-$ appearing in a compound, one would have in place thereof the radical $-\text{OHC}_3\text{H}_5-$; or, in case the hydroxyl radical of these $-\text{OH.C}_3\text{H}_5-$ radical had been removed by esterification with any available carboxyl, then the substituent which replaces the $-\text{C}_n\text{H}_{2n}-$ radical might be indicated by the formula $-\text{D.C}_3\text{H}_5-$. All that has been said here in regard to functional equivalents will be perfectly obvious without further explanation to those skilled

in the art. See U. S. Patent No. 2,091,704, dated August 31, 1937, to Duncan and McAllister, and also U. S. Patent No. 2,042,621, dated June 2, 1936, to Olin.

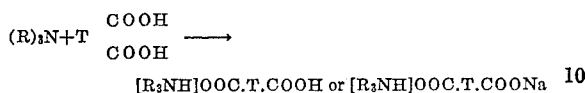
- 5 Similarly, it is evident that where reference is made to phthalic acid, some simple derivative, such as chlorinated phthalic acid, brominated phthalic acid, methylated phthalic acid, or the like, would simply act as a functional equivalent.
- 10 This applies not only to phthalic acid, but all the dibasic acids enumerated.

- Similarly, it is evident that there is no intention to differentiate between isomeric forms. One isomeric form may serve as well as another. Attention is particularly called to the last two examples above, which are characterized especially by the presence of a free carboxyl radical other than the carboxyl radical derived from dibasic acid. Needless to state, in the reaction between the ester derived by reaction between a polybasic carboxy acid material and a selected fatty material of the kind described, if there be a carboxyl radical attached to a fatty chain available for esterification, as well as a carboxyl attached to the dibasic acid, then in such event, if there is sufficient available hydroxyl radicals attached to the amine of the kind previously described, both types of carboxyl radicals, i. e., (a) a carboxyl radical attached to a polybasic carboxy acid residue; and (b) a carboxyl radical attached to a fatty acid residue may enter into the reaction. However, my experience is that the carboxyl radical attached to the polybasic carboxy acid residue is generally more reactive and enters into reaction in preference to the other type of carboxyl radical, although both reactions may take place simultaneously to at least a limited degree.

- I desire to emphasize that any of the products obtained in the above examples, when employed as a demulsifier in the resolution of crude oil emulsions, may be used in the form of the amine by direct contact with an emulsion, without contact with water. It may be contacted with water, i. e., in the form of a solution, so as to produce in a greater or lesser degree the amine base. Furthermore, any of the products above described may be combined with a suitable acid. Acetic acid may be employed. Hydrochloric acid is particularly desirable. In some instances acids, such as oleic acid or naphthenic acid, may be employed to give a suitable salt. As previously pointed out, any carboxylic hydrogen atom may be replaced by a suitable metallic atom, or an organic radical derived from an alcohol or from an amine. All such ionizable hydrogen atom equivalents are considered as the functional equivalent of the ionizable hydrogen atoms themselves, and such neutralized forms are included in the scope of the appended claims as the equivalents of the acidic form. The expression "fatty acid compound" is employed to include the acid itself, as well as salts and esters thereof. It is realized that where a free carboxyl and a basic amine residue exists in the same molecule, there may be a tendency towards the formation of inner salts comparable to sulfanilic acid; but due to the size of the molecule involved, and perhaps for reasons of steric hindrance, I am not aware that such inner salts are formed.

- Briefly, then, the preparation of the composition of matter herein contemplated depends on a reaction involving a polybasic carboxy acid body, or its functional equivalent, as described, and the complex amine of the kind described, in

such a manner as to involve reactions other than salt formation. In other words, the complex amines are basic in nature, and therefore, could react with a polybasic acid to form a salt in a manner which, for sake of convenience, will be indicated by a somewhat simpler reaction, thus:



Such reactions are purely salt formation. The materials of the kind herein contemplated, regardless of their nature, are of the kind obtained by reactions other than salt formation, and also other than amidification.

I desire to emphasize that the expression "polybasic carboxy acid," as it appears in the claims, refers not only to the acid itself, but to any functional equivalent, such as the anhydride, the acyl chloride, a salt form having at least two free carboxyls, such as mono-sodium citrate, etc. It is also understood that in the hereto appended claims the nature of the final product is not limited to the form having a free carboxylic hydrogen, but that such free carboxylic hydrogen may actually be replaced by any functional equivalent of the kind previously described, for instance, a metallic atom, an ammonium radical, an amine radical, such as an amylamine radical, benzylamine radical, ethanolamine radical, diethanolamine radical, triethanolamine radical, a hydrocarbon radical, such as an ethyl, methyl, propyl, or amyl radical, a radical derived from ethylene glycol, glycerol, or the like; a cyclohexyl radical, benzyl radical, etc. All such forms in which such ionizable hydrogen atom equivalent replaces an ionizable hydrogen atom, are obvious functional equivalents.

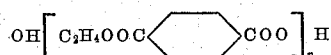
Attention is directed to the fact that the word "amidification" has been applied to the reaction involving the replacement of an amino hydrogen atom by an acyl radical, without conventional limitation to a reaction involving ammonia. The replacement of the amino hydrogen atom of a primary amine, or a secondary amine by an acyl radical has been considered as being amidification, rather than the formation of a substituted amide, or the formation of an imide or substituted imide. Such obvious departure from conventional nomenclature has been for purposes of simplicity and to show the similarity between certain reactions.

It is desirable to emphasize again that in the hereto appended claims reference to a polybasic carboxy acid includes not only the acid itself, but also various salts and esters thereof, and also other functional equivalents, such as the anhydrides, acyl chlorides, etc. Furthermore, in the hereto appended claims, reference to the product derived by reaction between an acid ester of the kind previously described and an amine of the kind previously described, is meant to refer to such products in all its various modifications previously referred to, to wit, such instances where carboxylic hydrogen atoms appear as such, or have been replaced by metallic atoms, organic radicals derived from various alcohols, amine radicals, or residues, etc.; and as to the presence of any basic amine nitrogen atom, it may be in the amine form, or in a salt form, or in a base form, as, for example, obtainable by contact with water. The functional equivalents of all these variations have been pointed out previously and were readily comprehended; and the

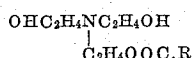
scope of the claims, in the light of such obvious equivalents, requires no further discussion.

As to blown oils, blown fatty acids, polymerized oils, polymerized fatty acids, and other similar materials obtained by oxidation, it is not intended that they should be reacted with amines to produce the intermediate amine, which, in turn, is reacted with the acidic ester derived, in part, from a polybasic carboxy acid.

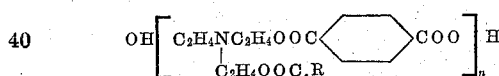
In considering the compositions of matter herein disclosed, at least to the extent that they are derived from basic diols, it is necessary to appreciate that such substances are not resins in the sense that such term is used to indicate materials which are obtained from the same raw materials combined in different proportions and under different conditions of reaction. The simplest resin formation may be exemplified by the reaction between ethylene glycol and phthalic acid. The product of such reaction may be indicated by the following formula:



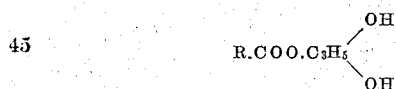
In such resins n represents a fairly large whole number. It is obvious that if one hydroxyl of triethanolamine has been esterified with a monobasic carboxy acid, that the resultant product indicated, as previously stated, by the following formula may conveniently be considered as a "diol".



Similarly, such a product can form a resin comparable to one obtained from the commonest diol, to wit: ethylene glycol and would be indicated thus:



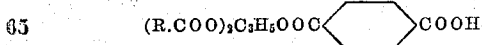
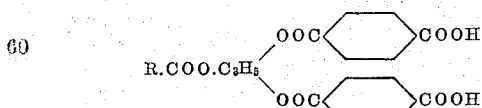
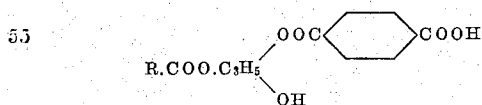
If a monoglyceride be denoted, thus:



and a diglyceride be denoted in the following manner:



it becomes obvious that phthalated derivatives thereof may be indicated thus:



In a dibasic acid such as phthalic acid and the like, where the two carboxyl groups are either attached to adjacent carbon atoms or carbon atoms which are relatively close together, and where the distances from the carboxyl radicals to the common carbon atom chain are substantially uniform, resinification takes place readily. In other words, in the product as exemplified by the diol derived by esterifying a mole of tri-

ethanolamine with a mole of a fatty acid, the product reacts readily with phthalic anhydride under proper conditions to produce a resinous material, as previously indicated. Such resinous material may be modified by introduction of a fatty acid, so as to stop further growth by reacting with the available hydroxyl. Such material as a resin would be comparable to a modified special alkyd resin.

If, however, phthalic anhydride, as such, is not used in the free state, but instead, is used in a state where one carboxyl has been united with a hydroxylated fatty body, such as a monoglyceride, or a diglyceride, or the like, as previously described, then such materials are apt to be monobasic, and hence, not resin-forming. However, even where they are dibasic, they do not react to produce resins, and do not build up molecules of a resinous nature in conjunction with basic diols, for various reasons, some of which are apparent and some of which are not. In the first place, steric hindrances possibly prevent random contact. In the second place, the basicity of the nitrogen atom tends to form inner salts. The space distances between carboxyl radicals becomes large in terms of the intervening atoms or radicals. The alcoholic hydroxyls of the partially esterified glyceryl radical, or similar radicals, is characterized by the fact that there is also attached thereto another long chain monobasic carboxy acid radical which may have an interfering effect to a marked degree. Finally, the molecular reactions really involve three-dimensional components, and the final product is of three dimensions. Chemical formulae, as above employed, are at best limited to two dimensions. It is difficult to contemplate such complex reaction of actual three-dimensional combinations based on structural formulae of two dimensions only. However, enough has been said in this discussion to enable one to realize that the compounds herein contemplated, particularly when derived from basic diols, should not be confused with resinous materials.

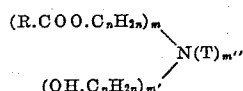
For convenience, in the present instance the expression "diol" has been used in reference to the material derived by an esterification of one hydroxyl triethanolamine, or the like. Similarly, the expression "trihydric" will be conveniently used to indicate combinations that have at least three alcoholic hydroxyl radicals, and thus would include materials which actually have more than three; for instance, materials which have four or more hydroxyl radicals obtained, for instance, by derivatives of dihydroxy stearic acid, or from glycerylamines, or both. Obviously, a polybasic carboxy acid having more than two carboxyl radicals still acts as if it only had two carboxy radicals in such instances where one of such radicals has been rendered inactive by esterification or salt formation, as in the instance of monosodium salt of citric acid, to which previous reference has been made.

The method of using the herein described compound or composition of matter to resolve a petroleum emulsion of the water-in-oil type is clearly disclosed in my parent application Serial No. 211,039, filed May 31, 1938, which has subsequently resulted in U. S. Patent No. 2,166,434, dated July 18, 1939, of which the present application is a continuation in part.

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

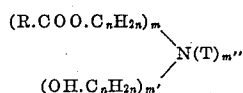
1. The product resulting from an esterification

reaction between (A) an amine of the formula type:



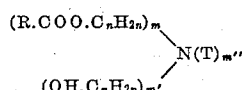
in which R.COO represents the oxy-acyl radical derived from a monobasic detergent-forming carboxy acid; T represents a member of the class consisting of hydrogen atoms, hydrocarbon radicals and non-hydroxy acylated radicals obtained by replacing a hydrogen atom of the hydroxyl group of an alkylol radical by the acyl radical of a monobasic carboxy acid having less than 8 carbon atoms; n represents a small whole number which is less than 10; m represents the numeral 1 or 2; m' represents the numeral 1 or 2, and m'' represents the numeral 0 or 1; with the proviso that $m+m'+m''=3$; and (B) an acidic ester derived by reaction between a polybasic carboxy acid and a hydroxylated ester of a monobasic detergent-forming carboxy acid; said hydroxylated ester containing at least one hydroxyl radical attached to the alcohol residue; and said acidic ester being characterized by the presence of at least one carboxyl radical.

2. The product resulting from an esterification reaction between (A) an amine of the formula type:



in which R.COO represents the oxy-acyl radical derived from a monobasic detergent-forming carboxy acid; T represents a member of the class consisting of hydrogen atoms, hydrocarbon radicals and non-hydroxy acylated radicals obtained by replacing a hydrogen atom of the hydroxyl group of an alkylol radical by the acyl radical of a monobasic carboxy acid having less than 8 carbon atoms; n represents a small whole number which is less than 10; m represents the numeral 1 or 2; m' represents the numeral 1 or 2; and m'' represents the numeral 0 or 1; with the proviso that $m+m'+m''=3$; and (B) an acidic ester derived by reaction between a dibasic carboxy acid and a hydroxylated ester of a monobasic detergent-forming carboxy acid; said hydroxylated ester containing at least one hydroxyl radical attached to the alcohol residue; and said acidic ester being characterized by the presence of at least one carboxyl radical.

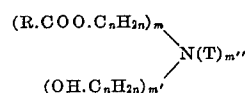
3. The product resulting from an esterification reaction between (A) an amine of the formula type:



in which R.COO represents the oxy-acyl radical derived from a monobasic detergent-forming carboxy acid; T represents a member of the class consisting of hydrogen atoms, hydrocarbon radicals and non-hydroxy acylated radicals obtained by replacing a hydrogen atom of the hydroxyl group of an alkylol radical by the acyl radical of a monobasic carboxy acid having less than 8 carbon atoms; C_nH_{2n} is an aliphatic radical; n represents a small whole number which is less than 10; m represents the numeral 1 or 2; m' represents the numeral 1 or 2, and m'' represents the numeral 0 or 1; with the proviso that $m+m'+m''=3$; and (B) an acidic ester de-

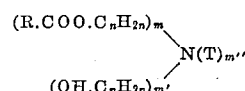
rived by reaction between a dibasic carboxy acid and a hydroxylated ester of a monobasic detergent-forming carboxy acid; said hydroxylated ester containing at least one hydroxyl radical attached to the alcohol residue; and said acidic ester being characterized by the presence of at least one carboxyl radical.

4. The product resulting from an esterification reaction between (A) an amine of the formula type:



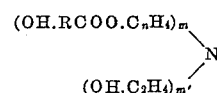
in which R.COO represents the oxy-acyl radical derived from a fatty acid; T represents a member of the class consisting of hydrogen atoms, hydrocarbon radicals and non-hydroxy acylated radicals obtained by replacing a hydrogen atom of the hydroxyl group of an alkylol radical by the acyl radical of a monobasic carboxy acid having less than 8 carbon atoms; C_nH_{2n} is an aliphatic radical; n represents a small whole number which is less than 10; m represents the numeral 1 or 2; m' represents the numeral 1 or 2, and m'' represents the numeral 0 or 1; with the proviso that $m+m'+m''=3$; and (B) an acidic ester derived by reaction between a dibasic carboxy acid and a hydroxylated ester of a monobasic detergent-forming carboxy acid; said hydroxylated ester containing at least one hydroxyl radical attached to the alcohol residue; and said acidic ester being characterized by the presence of at least one carboxyl radical.

5. The product resulting from an esterification reaction between (A) an amine of the formula type:



in which R.COO represents the oxy-acyl radical derived from a hydroxylated fatty acid; T represents a member of the class consisting of hydrogen atoms, hydrocarbon radicals and non-hydroxy acylated radicals obtained by replacing a hydrogen atom of the hydroxyl group of an alkylol radical by the acyl radical of a monobasic carboxy acid having less than 8 carbon atoms; C_nH_{2n} is an aliphatic radical; n represents a small whole number which is less than 10; m represents the numeral 1 or 2, m' represents the numeral 1 or 2; and m'' represents the numeral 0 or 1; with the proviso that $m+m'+m''=3$; and (B) an acidic ester derived by reaction between a dibasic carboxy acid and a hydroxylated ester of a monobasic detergent-forming carboxy acid; said hydroxylated ester containing at least one hydroxyl radical attached to the alcohol residue; and said acidic ester being characterized by the presence of at least one carboxyl radical.

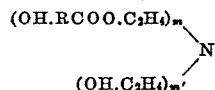
6. The product resulting from an esterification reaction between (A) an amine of the formula type:



in which OH.RCOO represents the oxy-acyl radical derived from a hydroxylated fatty acid; m represents the numeral 1 or 2; m' represents the numeral 1 or 2; with the proviso that $m+m'=3$; and (B) an acidic ester derived by reaction between a dibasic carboxy acid and a hydroxylated

ester of a monobasic detergent-forming carboxy acid; said hydroxylated ester containing at least one hydroxyl radical attached to the alcohol residue; and said acidic ester being characterized by the presence of at least one carboxyl radical.

7. The product resulting from an esterification reaction between (A) an amine of the formula type:



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in which OH.RCOO represents the oxy-acyl radical derived from ricinoleic acid; m represents the numeral 1 or 2; m' represents the numeral 1 or 2; with the proviso that $m+m'=3$; and (B) an acidic ester derived by reaction between a dibasic carboxy acid and a hydroxylated ester of a monobasic detergent-forming carboxy acid; said hydroxylated ester containing at least one hydroxyl radical attached to the alcohol residue; and said

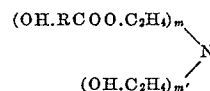
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acidic ester being characterized by the presence of at least one carboxyl radical.

8. The product resulting from an esterification reaction between (A) an amine of the formula type:

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in which OH.RCOO represents the oxy-acyl radical derived from ricinoleic acid; m represents the numeral 1 or 2; m' represents the numeral 1 or 2; with the proviso that $m+m'=3$; and (B) an acidic ester derived by reaction between phthalic anhydride and a hydroxylated ester of a monobasic detergent-forming carboxy acid; said hydroxylated ester containing at least one hydroxyl radical attached to the alcohol residue; said acidic ester being characterized by the presence of at least one carboxyl radical.

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MELVIN DE GROOTE.

CERTIFICATE OF CORRECTION.

Patent No. 2,194,646.

March 26, 1940.

MELVIN DE GROOTE.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, first column, lines 29 and 30, strike out the comma and words ", which subsequently resulted in U. S. Patent No. 2,167,349, dated July 25, 1939" and insert the same after "Blair" and before the period in line 37; lines 61 to 64, in the formula, for



page 5, first column, line 24, for "molecul̄tes" read --molecules--; 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 30th day of July, A. D. 1940.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.