Patented Mar. 28, 1944 2,344,977

UNITED STATES PATENT OFFICE

2,344,977

PROCESS FOR BREAKING PETROLEUM EMULSIONS

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10 Claims. (Cl. 252—341)

This invention relates to the treatment of emulsions of mineral oil and water, such as petroleum emulsions, for the purpose of separating the oil from the water.

The main object of our invention is to provide a novel process for resolving petroleum emulsions of the water-in-oil type that are commonly referred to as "cut oil," "roily oil," "emulsified oil," etc., and which comprise fine droplets of naturally-occurring waters or brines dispersed in a more or less permanent state throughout the oil which constitutes the continuous phase of the emulsion.

Another object of our invention is to provide an economical and rapid process for separating emulsions which have been prepared under controlled conditions from mineral oil, such as crude oil and relatively soft waters or weak brines. Controlled emulsification and subsequent demulsification under the conditions just mentioned is of significant value in removing impurities, particularly inorganic salts from pipeline oil.

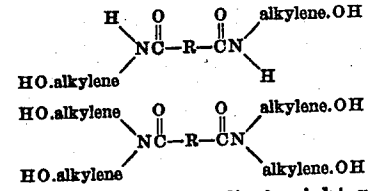
The demulsifier or demulsifying agent employed in the present process consists of a sub-resinous or semi-resinous product obtained by reaction between a polybasic acid or its equivalent, such as the anhydride, and a hydroxylated ester diamide of the kind in which the amido acyl radical is characterized by being derived from a polybasic carboxy acid having not over 10 carbon atoms, and preferably 8 carbon atoms, or less. The acyloxy radical or radicals are characterized by being derived from a monocarboxy detergent-forming acid having at least 8 and not more than 32 carbon atoms.

It is well known that certain monocarboxy organic acids containing eight carbon atoms or more, and not more than 32 carbon atoms, are characterized by the fact that they combine with alkalies to produce soap or soap-like materials. These detergent-forming acids include fatty acids, resin acids, petroleum acids, etc. For the sake of convenience, these acids will be indicated by the formula R'COOH. Certain derivatives of detergent-forming acids react with alkali to produce soap or soap-like materials, and are the obvious equivalent of the unchanged or unmodified detergent-forming acids; for instance, instead of fatty acids, one might employ the chlorinated fatty acids. Instead of the resin acids, one might employ the hydrogenated resin acids. Instead of naphthenic acids, one might employ brominated naphthenic acids, etc.

The fatty acids are of the type commonly referred to as higher fatty acids; and of course, this is also true in regard to derivatives of the kind indicated, insofar that such derivatives are obtained from higher fatty acids. The petroleum acids include not only naturally-occurring naphthenic acids, but also acids obtained by the oxidation of wax, paraffin, etc. Such acids may have as many as 32 carbon atoms. For instance, see U. S. Patent No. 2,242,837, dated May 20, 1941, to Shields.

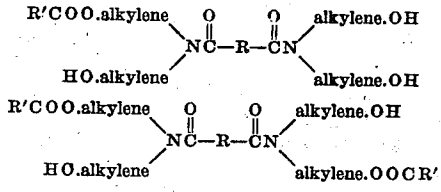
Although any of the high molal monocarboxy acids can be converted by conventional procedure, into new hydroxylated ester diamides of the kind described, it is our preference to employ hydroxylated ester diamides derived from higher fatty acids, rather than petroleum acids, rosin acids, and the like. We have found that by far the most effective demulsifying agents are obtained from unsaturated fatty acids having 18 carbon atoms. Such unsaturated fatty acids include the higher fatty acids, such as oleic acid, ricinoleic acid, linoleic acid, linolenic acid, etc. One may employ mixed fatty acids, as, for example, the fatty acids obtained by the hydrolysis of cottonseed oil, soya-bean oil, corn oil, etc. Our preferred demulsifier is obtained from unsaturated fatty acids, and more especially, unsaturated fatty acids having a hydroxyl radical, or unsaturated fatty acids which have been subjected to oxidation or oxyalkylation, such as oxyethylation.

The hydroxylated ester diamides of the kind herein described, may be obtained in any conventional manner. They are usually obtained from the acids themselves, or preferably, the anhydrides. If desired, however, functional equivalents, such as the acyl chlorides, esters, or other derivatives, may be employed. In many instances the esters prove to be the most suitable raw material, due to their ease of reaction. The diamide of a low molal polycarboxy acid, particularly a dibasic acid, may be treated with an oxyalkylating agent, such as ethylene oxide, propylene oxide, butylene oxide, or the like, so as to produce a compound of the following types:



Actually the alkylene radical might represent an equivalent divalent radical in which the carbon atom chain is interrupted at least once by oxygen, as in $—C_2H_4OC_2H_4—$.

Having obtained a bis(hydroxyalkyl) diamide of the kind described, or, for that matter, a compound having more than two hydroxyalkyl groups, one can react such compound in a conventional manner with a high molal acid or its equivalent, to give a hydroxylated ester diamide. Such a compound may be exemplified by the following formulas:

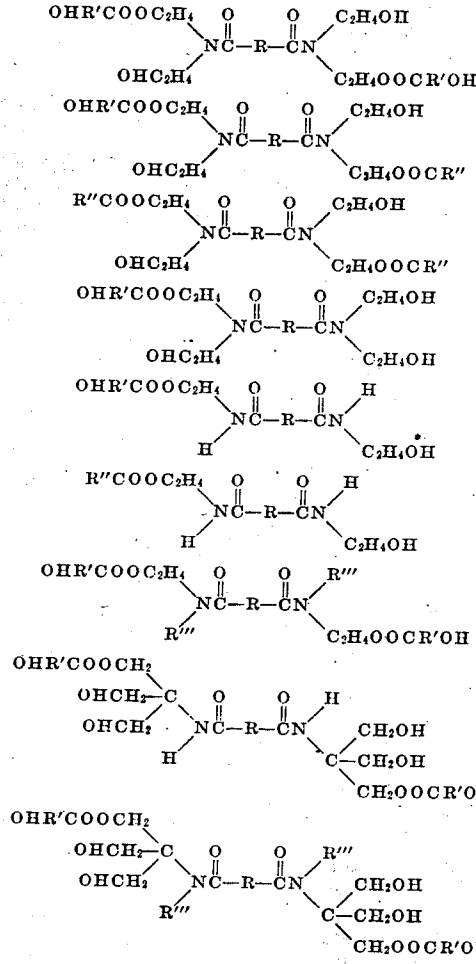


A procedure that is frequently more readily adaptable is simply the reaction between a low molal acid, such as oxalic acid, phthalic acid, maleic acid, or the low molal esters thereof, for instance, the dimethyl ester, diethyl ester, or the like, and diethanolamine, dipropanolamine, or the like. For the sake of brevity, reference hereafter will be made to maleic acid esters and phthalic acid esters of monoethanolamine, diethanolamine, or the like, although other suitable reactants have already been described. The method of manufacturing such ester diamides is simply a variant of the general method of manufacturing esteramides, and is so well known that no further description is required. For convenience, reference is made to U. S. Patent No. 2,238,902, dated April 22, 1941, to Katzman and Harris. Note specifically that this patent teaches a procedure involving conventional steps, such as reaction of monoethanolamine with a diethyl ester of oxalic acid, with subsequent acylation of the diamide with lauric acid. Similar derivatives derived from dimethyl phthalate and the like, are described.

Actually, in the manufacture of demulsifiers we have followed substantially the same procedure as described in the above mentioned Katzman and Harris patent, as far as producing an intermediate is concerned; but we have found that the most desirable compounds are obtained from unsaturated fatty acids, as previously described. Thus, we have substituted oleic acid, ricinoleic acid, various mixed fatty acids derived from unsaturated oils, such as teaseed oil, sunflower seed oil, or the like, and lauric acid, in various examples appearing in the aforementioned patent to Katzman and Harris, No. 2,238,902.

In view of what has been said, it is obvious that numerous hydroxylated ester diamides are available, or can be prepared readily. If primary amines are reacted with dibasic acids or esters, one may obtain diamides in which at least one amino hydrogen atom is replaced by a hydrocarbon radical containing, for example, 4–12 carbon atoms. Such diamides are additionally characterized by the presence of one or more amido hydrogen atoms. Such diamides are additionally characterized by the presence of one or more amido hydrogen atoms. Such diamides can be treated with ethylene oxide or the like to give hydroxylated derivatives. Similarly, one may react diethyl oxalate, diethyl phthalate, diethyl maleate, or the like, with ethyl ethanolamine, propyl ethanolamine, ethyl propanolamine, ethyl glycerylamine, or the like. Wherever the use of an oxyalkylating agent is suggested, it is understood that glycid may be employed, as well as ethylene oxide, propylene oxide, or similar reactants.

As illustrating such hydroxylated ester diamides, reference is made to the following formulas:



In the above formulas, OC—R—CO represents the acyl radical derived from a dibasic acid having 10 carbon atoms or less. OH.R'CO represents the acyl radical of a hydroxylated acid, such as ricinoleic acid, hydroxystearic acid, or similar acids obtained by oxidation, such as blown oleic acid, or acids obtained by the hydrolysis of blown olein. Such acyl radicals all contain at least 8 and not more than 32 carbon atoms, and are apt to contain 18 carbon atoms. R''CO is the acyl radical derived from a non-hydroxylated monocarboxy detergent-forming acid, particularly an unsaturated acid, such as oleic acid, linoleic acid, etc. It is understood, of course, that a mixture of fatty acids may be employed instead of a single fatty acid. R''' is a hydrocarbon radical having 4–12 carbon atoms.

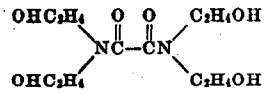
In examining the above formulas, it is to be noted that the ester diamides may be obtained from monobutanolamine, dibutanolamine, monopropanolamine, dipropanolamine, monoglycerylamine, diglycerylamine, or the like, instead of being derived from monoethanolamine or diethanolamine. Similarly, the products shown in some of the formulas are derived from tris(hydroxymethyl) aminomethane. Similarly, derivatives may be derived from 2-amino-2-ethyl-1,3-propane diol and 2-amino-2-methyl-1,3-propane diol.

It has been pointed out that the hydroxylated ester diamides may be derived in any suitable way, such as reaction with ammonia, followed by oxyethylation, or some other suitable procedure. Not only may the dibasic acids or their functional equivalents be reacted with ammonia, but, as has been briefly suggested previously, such acids may be reacted with a primary amine, such as any suitable alkylamine, or an alicyclic amine, or an arylamine, or an aralkylamine, to give the amide or substituted amide, provided, of course, that such compound contains at least one amino hydrogen atom. More specifically, suitable amines which may be employed as reactants include butylamine, amylamine, octylamine, decylamine, cyclohexylamine, benzylamine, phenylamine, etc. Generally speaking, when an amine is employed instead of ammonia for reaction with the low molal dibasic acid, one preferably employs a hydroxylated detergent-forming acid, such as ricinoleic acid, in order to insure a plurality of available alcoholic hydroxyl groups, for subsequent reaction with the polybasic carboxy acid or its equivalent. This is understandable by considering reactions involving, for instance, one mole of diethyl oxalate and one mole of dibutylamine and one mole of butylamine. The compound so obtained would consist of a proportion of diamides having no amino hydrogen atoms, a fraction containing one amino hydrogen atom, and a fraction containing two amino hydrogen atoms. Intermediate reactants so derived having one amino hydrogen atom, would be substantially inert for reactions involving phthalic anhydride, unless one employed an hydroxylated polybasic acid, such as malic acid, tartaric acid, or citric acid. In such an event, if the intermediate reactant was subsequently reacted as an alcohol, a resinification would be possible, especially provided that such intermediate ester had been treated with glycid or the like, prior to reaction with phthalic acid. It will be noted in the previous formulas, however, that where ricinoleic acid is employed as the reactant to supply the high molal acyloxy radical, then the hydroxyl radical, which is part of the ricinoleyl radical, would serve as a reactive function for combination with phthalic anhydride or the like by esterification. Other higher fatty acids, such as hydroxystearic acid, aleuritic acid, etc., may be employed. The fact that glycid or the like may be employed to replace a labile atom or a hydroxyl radical by the equivalent of two hydroxyl radicals, is well known.

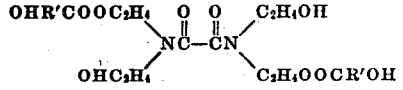
In any event, the reaction of the hydroxylated ester diamide of the kind described with a polybasic carboxy acid or its functional equivalent, such as the anhydride, is a well-known reaction and is nothing more or less than an esterification reaction of the kind employed to produce phthalated castor oil, phthalated ricinoleoamide, etc. For instance, common comparable reactions are described in U. S. Patent No. 1,976,602, dated October 9, 1934, to De Groote, Keiser and Adams, and U. S. Patent No. 2,078,652, to De Groote and Keiser, dated April 27, 1937. Briefly stated, the molar combinations of the reactions selected depends upon the available number of hydroxyl groups and may be illustrated by the following examples:

Example 1

One pound mole of diethyl oxalate is reacted with 2 pound moles of diethanolamine to give a diamide of the following formula:



One pound mole of such diamide is reacted with two pound moles of ricinoleic acid to give an ester diamide of the following formula:



One pound mole of such ester diamide is heated with two pound moles of phthalic anhydride at approximately 125–130° C. until esterification is complete, as indicated by the substantial elimination of two alcoholic hydroxyl radicals. The product so obtained has two free hydroxyl radicals and two free carboxyl radicals.

Example 2

A product is prepared in the same manner as described in the previous example, except that the diamide is derived from diethyl phthalate.

Example 3

A product is prepared in the same manner as described in Example 1, except that the diamide is derived from diethyl maleate.

Example 4

A product is prepared in the same manner as described in the previous examples, except that one pound mole of ricinoleic acid is employed instead of two pound moles of ricinoleic acid; and one pound mole of phthalic anhydride is employed instead of two pound moles of phthalic anhydride. Such compounds may be prepared from diethyl oxalate, diethyl maleate, or diethyl phthalate. Esterification is so controlled, that the final product has one free carboxyl radical.

Example 5

The same procedure is followed as in Example 4, preceding, except that the ester diamide is derived from monoethanolamine instead of diethanolamine.

Example 6

The same procedure is followed as in Example 5, except that monoglycerylamine is substituted for monoethanolamine.

Example 7

The same procedure is followed as in Example 1, 2, 3, or 4, except that dibutanolamine or dipropanolamine is substituted for diethanolamine.

Example 8

Tris(hydroxymethyl)aminomethane is substituted for diethanolamine in Examples 1, 2, 3, and 4, preceding.

Example 9

The same procedure is followed as in the preceding examples, except that a non-hydroxy acid, such as oleic acid, is substituted for ricinoleic acid in the various examples in which there is a residual hydroxyalkyl radical, as differentiated from the hydroxyacyl radical present in ricinoleic acid.

Example 10

Esterification of the hydroxylated ester diamide is accomplished by means of maleic anhydride instead of phthalic anhydride.

Example 11

Esterification is accomplished by means of succinic acid, instead of phthalic anhydride.

Example 12

Esterification is accomplished by means of oxalic acid instead of phthalic anhydride.

In such instances where oxalic acid is employed, it is desirable to use a lower temperature, in view of the fact that oxalic acid or most of its functional equivalents, decompose at a temperature as high as 150°, or thereabouts; and instead a temperature of 105–112° C. should be employed. Such lower temperature requires a longer time for esterification to take place.

Esterification can be conducted in the usual manner, by simply employing heat to drive off the water formed. In some instances where an anhydride is employed, water may not be formed. If desired, one may pass a dried, inert gas, such as dried nitrogen gas, through the mass to hasten esterification. Esterification is also hastened at times by the presence of a mere trace of a suitable acid, such as benzene sulfonic acid. In other instances the reaction is most suitably conducted in the presence of an inert high boiling solvent, such as xylene. The xylene is continuously distilled under a reflux condenser, condensed by such condenser, and returned to the reaction chamber through a trap. The xylene vapors carry off the water, which is removed after being condensed by the trap. This is a conventional procedure, commonly employed in this type or similar types of reaction.

Although we prefer to use phthalic anhydride as the most desirable source of the polybasic carboxy acid, one may use other polybasic carboxy acids or their anhydrides, such as succinic, malic, fumaric, citric, maleic, adipic, tartaric, glutaric, diphenic, naphthalic, oxalic, pimelic, suberic, azelaic, sebacic, etc. Naturally, a simple derivative of a polybasic acid, such as chlorophthalic acid, can be used as advantageously as phthalic acid itself, although there is no added advantage in the use of the more costly chemical compounds.

In view of the large number of reactants and types of materials described, it may be well to note those which we particularly prefer. It has been pointed out that we prefer to use unsaturated fatty acids as the source of the high molal oxyacyl radical, and particularly, the hydroxylated fatty acid commonly available, to wit, recinoleic acid. We prefer to use phthalic acid, maleic acid, or their anhydrides, or oxalic acid as the source of the polybasic carboxy acid, either when employed to furnish the acyl radical, i. e., the radical in which the carbonyl carbon atom is directly linked to an amino nitrogen atom; or, when employed for esterification, where the acyloxy radical indicated thus:

OOC—R—COO

is present. We prefer to use monoethanolamine or diethanolamine as the reactant for the formation of the substituted diamide employed for subsequent reaction to produce the ester diamide.

In view of what has been said, it is apparent that hydroxylated ester diamides of the kind described previously may be considered for the sake of simplicity, as being in the class of an alcohol, i. e., a monohydric or polyhydric alcohol. If an alcohol is indicated by the formula $Y'(OH)_n$, where n indicates the number 1 or more, and if a polybasic acid body be indicated by the formula $X'(COOH)_n$, where n indicates the number 2 or more, then the reaction between a monohydric alcohol and a polybasic acid will result in a compound which may be indicated by the following formula:

$$YX(COOH)_{n'}$$

wherein n' indicates the number 1 or more, and which is in reality a contraction of a more elaborate structural formula, in which X' and Y' are joined by a carboxyl radical or residue. Assuming, however, as would be true in the majority of cases, that the alcohol actually would be a polyhydric alcohol, and that the acid body would be polybasic in nature, for instance, if one employed a diphthalate of a polyhydroxylated ester diamide of the kind previously described, then examination reveals that the formula might result in a combination, in which there were neither residual carboxyl radicals, nor residual hydroxyl radicals, or might result in compounds in which there were residual hydroxyl radicals, and no residual carboxyl radicals, or compounds where there might be residual carboxyl radicals and no residual hydroxyl radicals; or there might be both. This is indicated by the following:

$$(Y.X)_q(OH)_{n'}$$
$$(Y.X)_q(COOH)_{m'}$$
$$(OH)_{n''}(YX)_q(COOH)_{m''}$$

in which q indicates a small whole number (one in the case of a monomer, and probably not over 20 and usually less than 10), and m' and n' indicate the number 1 or more, and m'' and n'' indicate zero or a small or moderately-sized whole number, such as zero, one or more, but in any event, probably a number not in excess of 10–15. Naturally, each residual hydroxyl could combine with a phthalic acid body or its equivalent, or with a similar compound derived from a tribasic acid, such as citric acid; and in such event, there would be a large number of free or uncombined carboxyl radicals present, possibly 20 or more. Actually, the preferable type of reagent would be more apt to include less than 20, and in fact, less than 10 free hydroxyl radicals. It is not necessary to remark that the residual carboxyl radicals can be permitted to remain as such, or can be neutralized in any suitable manner, such as conversion into salts, esters, amides, amino esters, or any other suitable form. Usually, such conversion into salt form would be by means of sodium hydroxide, potassium hydroxide, calcium hydroxide, magnesium hydroxide, ammonium hydroxide, amylamine, butanolamine, ethanolamine, diethanolamine, triethanolamine, cyclohexanolamine, benzylamine, aniline, toluidine, etc. Conversion into the ester would be by means of a monohydric alcohol, such as methyl alcohol, ethyl alcohol, propyl alcohol, butyl alcohol, hexyl alcohol, octyl alcohol, decyl alcohol, ethylene glycol, diethylene glycol, glycerol, diglycerol, triethylene glycol, or the like. One could employ an amino alcohol so as to produce an ester.

We have found, however, as suggested, that the most suitable products are sub-resinous, semi-resinous, or balsam-like products, and are preferably derived from polyhydroxylated reactants, i. e., polyhydroxylated ester diamides. We have found that such products are soluble to a fairly definite extent; for instance, at least 5%

in some solvent, such as water, alcohol, benzene, dichlorethyl ether, acetone, cresylic acid, or the like. This is simply another way of stating that it is preferable, if the product be one of the sub-resins, which are commonly referred to as an A resin, or B resin, as distinguished from a C resin, which is a highly infusible, insoluble resin (see Ellis, "Chemistry of Synthetic Resins," 1935, page 862 et seq.).

In recapitulating what has been said previously, the sub-resinous, semi-resinous, or balsam-like product herein contemplated may be indicated by the following formula:

$$(OH)_{n''}(Y_{y'}X_{x'})\begin{matrix}(COOH)_{m''}\\(COO.Z)_{m''}\end{matrix}$$

in which the characters have their previous significance, and y' represents a small whole number not greater than 5, and x' represents a small whole number not greater than 5; Z represents a hydrogen ion equivalent, such as a metallic atom, organic radical, etc.

It may be well to emphasize that the intermediate products employed for esterification with phthalic anhydride or the like have also been employed as intermediates in the production of other compounds, for instance, typical wetting agents, especially by reactions which involve the introduction of sulfo groups, so as to produce surface-active, water-soluble sulfonic acids or salts thereof. Such salts are entirely different from the sub-resinous materials herein contemplated, and which are apt to be water-insoluble, and in fact, their preferred form, is invariably water-insoluble; but even if water-soluble, they are not wetting agents and do not possess the characteristic property of wetting agents, but only the property of a soluble resin. It is also to be noted that the molecular size of the compounds herein contemplated is entirely different from the simpler monomeric sulfo salts that serve as wetting agents. The preferred form of the present compounds, particularly for use as demulsifiers, are the water-insoluble form, i. e., the form which shows solubility in water to the extent of one part per thousand, or less, thus clearly differentiating from ordinary water-soluble compounds, and yet not excluding water solubility within the ratio that demulsifiers may be used in the oil fields, for instance, one part per 10,000, or one part per 20,000, or one part per 30,000, or in such range.

It will be noted that compounds of the type just described having at least one hydrophobe nucleus are designated as being "polar" when there is present either an unesterified hydroxyl radical, or an unesterified carboxyl radical, or both. We have found that the polar type of material is by far the most effective for demulsification, and it is our preference to use such type. Indeed, this particular type is so much more effective for demulsification than the non-polar type, that it may be considered in essence an invention within an invention.

Conventional demulsifying agents employed in the treatment of oil field emulsions are used as such, or after dilution with any suitable solvent, such as water; petroleum hydrocarbons, such as gasoline, kerosene, stove oil; a coal tar product, such as benzene, toluene, xylene, tar acid oil, cresol, anthracene oil, etc. Alcohols, particularly aliphatic alcohols, such as methyl alcohol, ethyl alcohol, denatured alcohol, propyl alcohol, butyl alcohol, hexyl alcohol, octyl alcohol, etc., may be employed as diluents. Miscellaneous solvents, such as pine oil, carbon tetrachloride, sulfur dioxide extract obtained in the refining of petroleum, etc., may be employed as diluents. Similarly, the material or materials employed as the demulsifying agent of our process may be admixed with one or more of the solvents customarily used in connection with conventional demulsifying agents. Moreover, said material or materials may be used alone, or in admixture with other suitable well known classes of demulsifying agents.

It is well known that conventional demulsifying agents may be used in a water-soluble form, or in an oil-soluble form, or in a form exhibiting both oil and water solubility. Sometimes they may be used in a form which exhibits relatively limited oil solubility. However, since such reagents are sometimes used in a ratio of 1 to 10,000, or 1 to 20,000, or even 1 to 30,000, such an apparent insolubility in oil and water is not significant, because said reagents undoubtedly have solubility within the concentration employed. This same fact is true in regard to the material or materials employed as the demulsifying agent of our process.

We desire to point out that the superiority of the reagent or demulsifying agent contemplated in our process is based upon its ability to treat certain emulsions more advantageously and at a somewhat lower cost than is possible with other available demulsifiers, or conventional mixtures thereof. It is believed that the particular demulsifying agent or treating agent herein described will find comparatively limited application, so far as the majority of oil field emulsions are concerned; but we have found that such a demulsifying agent has commercial value, as it will economically break or resolve oil field emulsions in a number of cases which cannot be treated as easily or at so low a cost with the demulsifying agents heretofore available.

In practising our process for resolving petroleum emulsions of the water-in-oil type, a treating agent or demulsifying agent of the kind above described is brought into contact with or caused to act upon the emulsion to be treated, in any of the various ways, or by any of the various apparatus now generally used to resolve or break petroleum emulsions with a chemical reagent, the above procedure being used either alone, or in combination with other demulsifying procedure, such as the electrical dehydration process.

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

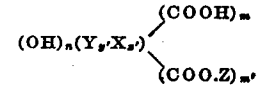
1. A process for breaking petroleum emulsions of the water-in-oil type, which consists in subjecting the emulsion to the action of a demulsifier, comprising a sub-resinous esterification product of the following formula type:

$$(OH)_n(Y_{y'}X_{x'})\begin{matrix}(COOH)_m\\(COO.Z)_{m'}\end{matrix}$$

in which x' and y' are small whole numbers not greater than 10 and m, n, and m' are small whole numbers not over 10, and including zero; Z is an acidic hydrogen atom equivalent; and X is a residue derived from a polybasic carboxy acid; and Y is a residue derived from a hydroxylated ester diamide, containing (a) an acyl radical derived from a polybasic carboxy acid having not over 10 carbon atoms and amido-linked to

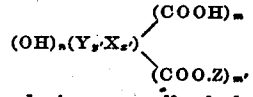
both amino nitrogen atoms; and (*b*) at least one acyloxy radical derived from a monocarboxy detergent-forming acid having at least 8 and not more than 32 carbon atoms, and linked by a divalent aliphatic radical to an amino nitrogen atom.

2. A process for breaking petroleum emulsions of the water-in-oil type, which consists in subjecting the emulsion to the action of a demulsifier, comprising a substantially water-insoluble, sub-resinous esterification product of the following formula type:



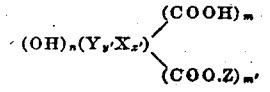
in which x' and y' are small whole numbers not greater than 10 and m, n, and m' are small whole numbers not over 10, and including zero; Z is an acidic hydrogen atom equivalent; and X is a residue derived from a polybasic carboxy acid; and Y is a resdue derived from a hydroxylated ester diamide, containing (*a*) an acyl radical derived from a polybasic carboxy acid having not over 10 carbon atoms and amido-linked to both amino nitrogen atoms; and (*b*) at least one acyloxy radical derived from a monocarboxy detergent-forming acid having at least 8 and not more than 32 carbon atoms, and linked by a divalent aliphatic radical to an amino nitrogen atom.

3. A process for breaking petroleum emulsions of the water-in-oil type, which consists in subjecting the emulsion to the action of a demulsifier, comprising a substantially water-insoluble, sub-resinous, polar esterification product of the following formula type:



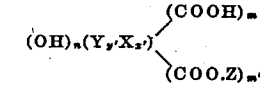
in which x' and y' are small whole numbers not greater than 10 and m, n, and m' are small whole numbers not over 10, and including zero; Z is an acidic hydrogen atom equivalent; and X is a residue derived from a polybasic carboxy acid; and Y is a residue derived from a hydroxylated ester diamide, containing (*a*) an acyl radical derived from a polybasic carboxy acid having not over 10 carbon atoms and amido-linked to both amino nitrogen atoms; and (*b*) at least one acyloxy radical derived from a monocarboxy detergent-forming acid having at least 8 and not more than 32 carbon atoms, and linked by a divalent aliphatic radical to an amino nitrogen atom.

4. A process for breaking petroleum emulsions of the water-in-oil type, which consists in subjecting the emulsion to the action of a demulsifier, comprising a substantially water-insoluble, sub-resinous, polar esterification product of the following formula type:



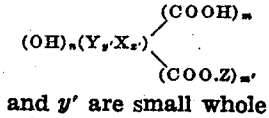
in which x' and y' are small whole numbers not greater than 10 and m, n, and m' are small whole numbers not over 10, and including zero; Z is an acidic hydrogen atom equivalent; and X is a residue derived from a dibasic carboxy acid; and Y is a residue derived from a hydroxylated ester diamide, containing (*a*) an acyl radical derived from a dibasic carboxy acid having not over 10 carbon atoms and amido-linked to both amino nitrogen atoms; and (*b*) at least one acyloxy radical derived from a monocarboxy detergent-forming acid having at least 8 and not more than 32 carbon atoms, and linked by a divalent aliphatic radical to an amino nitrogen.

5. A process for breaking petroleum emulsions of the water-in-oil type, which consists in subjecting the emulsion to the action of a demulsifier, comprising a substantially water-insoluble, sub-resinous, polar esterification product of the following formula type:



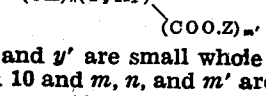
in which x' and y' are small whole numbers not greater than 10 and m, n, and m' are small whole numbers not over 10, and including zero; Z is an acidic hydrogen atom equivalent; and X is a residue derived from a dibasic carboxy acid; and Y is a residue derived from a hydroxylated ester diamide, containing (*a*) an acyl radical derived from a dibasic carboxy acid having not over 10 carbon atoms and amide-linked to both amino nitrogen atoms; and (*b*) at least one acyloxy radical derived from a fatty acid having at least 8 and not more than 32 carbon atoms, and linked by a divalent aliphatic radical to an amino nitrogen atom.

6. A process for breaking petroleum emulsions of the water-in-oil type, which consists in subjecting the emulsion to the action of a demulsifier, comprising a substantially water-insoluble, sub-resinous, polar esterification product of the following formula type:



in which x' and y' are small whole numbers not greater than 10 and m, n, and m' are small whole numbers not over 10, and including zero; Z is an acidic hydrogen atom equivalent; and X is a residue derived from a dibasic carboxy acid; and Y is a residue derived from a hydroxylated ester diamide, containing (*a*) an acyl radical derived from a dibasic carboxy acid having not over 10 carbon atoms and amido-linked to both amino nitrogen atoms; and (*b*) at least one acyloxy radical derived from an unsaturated fatty acid having at least 8 and not more than 32 carbon atoms, and linked by a divalent aliphatic radical to an amino nitrogen atom.

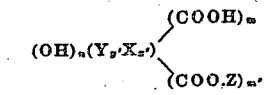
7. A process for breaking petroleum emulsions of the water-in-oil type, which consists in subjecting the emulsion to the action of a demulsifier, comprising a substantially water-insoluble, sub-resinous, polar esterification product of the following formula type:



in which x' and y' are small whole numbers not greater than 10 and m, n, and m' are small whole numbers not over 10, and including zero; Z is an acidic hydrogen atom equivalent; and X is a residue derived from a dibasic carboxy acid; and Y is a residue derived from a hydroxylated ester diamide, containing (*a*) an acyl radical derived from a dibasic carboxy acid having not over 10 carbon atoms and amido-linked to both amino nitrogen atoms; and (*b*) at least one ricinoleyl

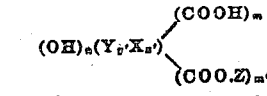
oxy radical, linked by a divalent aliphatic radical to an amino nitrogen atom.

8. A process for breaking petroleum emulsions of the water-in-oil type, which consists in subjecting the emulsion to the action of a demulsifier, comprising a substantially water-insoluble, subresinous, polar esterification product of the following formula type:



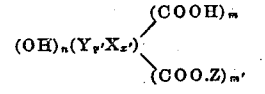
in which x' and y' are small whole numbers not greater than 10, and m, n, and m' are small whole numbers not over 10, and including zero; Z is an acidic hydrogen atom equivalent; and X is a residue derived from a dibasic carboxy acid; and Y is a residue derived from a hydroxylated ester diamide, containing (*a*) an acyl radical derived from phthalic acid and amido-link to both amino nitrogen atoms; and (*b*) at least one ricinoleyl oxy radical, linked by a divalent aliphatic radical to an amino nitrogen atom.

9. A process for breaking petroleum emulsions of the water-in-oil type, which consists in subjecting the emulsion to the action of a demulsifier, comprising a substantially water-insoluble, subresinous, polar esterification product of the following formula type:



in which x' and y' are small whole numbers not greater than 10 and m, n, and m' are small whole numbers not over 10, and including zero; Z is an acidic hydrogen atom equivalent; and X is a residue derived from a dibasic carboxy acid; and Y is a residue derived from a hydroxylated ester diamide, containing (*a*) an acyl radical derived from oxalic acid and amido-linked to both amino nitrogen atoms; and (*b*) at least one ricinoleyl oxy radical, linked by a divalent aliphatic radical to an amino nitrogen atom.

10. A process for breaking petroleum emulsions of the water-in-oil type, which consists in subjecting the emulsion to the action of a demulsifier, comprising a substantially water-insoluble, subresinous, polar esterification product of the following formula type:



in which x' and y' are small whole numbers not greater than 10 and m, n, and m' are small whole numbers not over 10, and including zero; Z is an acidic hydrogen atom equivalent; and X is a residue derived from a dibasic carboxy acid; and Y is a residue derived from a hydroxylated ester diamide, containing (*a*) an acyl radical derived from maleic acid and amido-linked to both amino nitrogen atoms; and (*b*) at least one ricinoleyl oxy radical, linked by a divalent aliphatic radical to an amino nitrogen atom.

MELVIN DE GROOTE.
BERNHARD KEISER.