

2,828,323

REACTION PRODUCT OF EPOXIDIZED MONOHYDRIC ALCOHOL ESTERS AND HYDROXYLATED TERTIARY MONOAMINES

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No Drawing. Application April 13, 1956
Serial No. 577,957

10 Claims. (Cl. 260—404)

The present invention is concerned with the reaction products of certain epoxidized monohydric alcohol esters of fatty acids and particularly the low molal alcohol esters of naturally-occurring fatty acids and modified naturally-occurring fatty acids on the one hand and a hydroxylated tertiary monoamine, and preferably a basic tertiary monoamine, on the other hand.

The products herein described may be employed for a large variety of purposes, either as such or after conversion into salts.

The products also may be used as intermediates for further reaction.

For purpose of convenience what is said hereinafter will be divided into six parts:

Part 1 is concerned with the derivatives obtained by the epoxidation of fatty acid esters of monohydric alcohols and generally characterized by the presence of at least one oxirane ring per fatty acid molecule;

Part 2 is concerned with hydroxylated tertiary monoamines and particularly basic tertiary monoamines which are suitable for reaction with the type of reactant described in Part 1, preceding;

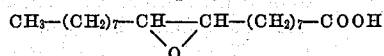
Part 3 is concerned with reactions involving the two classes of reactants above, i. e., those described in Part 1 and those described in Part 2;

Part 4 is concerned with conversion of the reactants into salts by combination with carboxy acids, sulfonic acids, and the like;

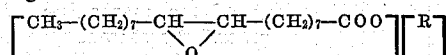
Part 5 is concerned with various uses for the products described in Part 3 or their salts described in Part 4; and

Part 6 is concerned with derivatives which can be prepared by further reaction with the products described in Part 3 by the use of some additional reactant, such as an alkylene oxide or the like. Furthermore, in many instances the products obtained in the manner described in Part 3, preceding, can be heated without the addition of any other reactant so that ring formation or other reactions take place, thus yielding a completely different series of products.

The formula for 9,10-epoxystearic acid is as follows:



If instead of a fatty acid one employed an ester, particularly an ester of a monohydric alcohol, the corresponding formula would be as follows:



in which R is the alcohol radical.

In actual practice commercially available epoxidized esters of a monohydric alcohol represent a product which may vary from a 70% or 75% yield up to 80% or even 85% or 90%, based on the presence of a single oxirane ring per fatty acid radical as representing 100% yield.

In our co-pending application, Serial No. 532,121, filed September 1, 1955, we have described a broad genus of compounds obtained by the process of reacting (A) an

oxirane ring-containing compound obtained by epoxidation of an epoxidation-susceptible fatty acid, fatty acid ester, fatty acid amide or fatty alcohol with (B) an oxyalkylation-susceptible compound having at least one labile hydrogen atom.

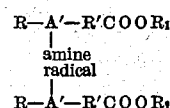
The present invention is concerned with a sub-genus or specie related to the aforementioned generic invention described in our co-pending application, Serial No. 532,121, filed September 1, 1955. The present invention is limited to reactions involving epoxidized monohydric alcohol esters having at least one and not over 2 oxirane rings per fatty acid molecule and hydroxylated tertiary monoamines such as triethanolamine, ethyl diethanolamine, etc.

Such epoxidized ester and preferably one showing approximately one oxirane ring per acyl radical is reacted with a mole of a hydroxylated monoamine as described. Theoretically at least one mole of a hydroxylated monoamine can be caused to react with at least the same number of oxirane rings as appears in the ester, i. e., from one to 2 moles of the amine for each mole of the monohydric alcohol ester.

Bearing in mind the ester can also react to form a simple amide in the same way that the unepoxidized ester can so react it is obvious that each mole of epoxidized ester can be reacted with at least 2 moles of a hydroxylated monoamine to give an amine ester. Also, it is obvious one can react one mole of such amine with 2 or more moles of the epoxidized monohydric alcohol ester.

Although the reactions herein involved invariably and inevitably include a reaction involving a monoamine and an oxirane ring, the complexity of reaction goes further than has been previously indicated. One aspect is the fact that the oxirane ring may be ruptured to produce isomers.

Also, if for convenience one indicated the epoxidized acid as $\text{R}-\text{A}-\text{R}'\text{COOH}$ and the monohydric alcohol derivative as $\text{R}-\text{A}-\text{R}'\text{COOR}_1$ it is obvious that one amine, as previously indicated, may unite 2 such esters as indicated by the following, provided a monoamine has at least 2 hydroxyl groups as in the case of ethyldiethanolamine:

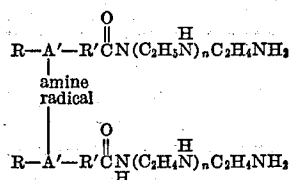


In the preceding formula A has been changed to A' to indicate the ring has been opened and the amine radical is, of course, the divalent radical obtained from amines of the kind described. Needless to say, if there were 2 oxirane rings in the ester such radical could combine with at least 2 other molecules having at least a single reactive hydrogen atom.

Since the ester, like any other fatty acid equivalent, could act as an acylating agent it is obvious that hydroxyamine esters could be formed. For that matter a product of the kind previously described could be reacted with a large number of polyamino compounds, such as ethylenediamine, triethylenetetramine, tetraethylene pentamine, etc., with particular reference to the polyamines described not only in our aforementioned co-pending application, Serial No. 532,121, but also in our two subsequently filed applications, Serial Nos. 548,748, and 548,749, both filed November 23, 1955.

However, having obtained a reaction product in the manner described above by using ethyldiethanolamine, methyl diethanolamine, triethanolamine, or the like with or without oxyalkylation particularly using ethylene

oxide, propylene oxide, or butylene oxide, one can obtain an ester in a manner similar to the formation of an amide by reaction with a polyamine. One can show the amide formation thus:



As a matter of fact, the compounds obtained in the above manner, i. e., using a polyamine which can or cannot be subjected to further reaction such as the formation of the cyclic amidine ring represents an important sub-genus of the present invention.

It is well known, of course, that the amides of polyamines which are characterized by a primary amino radical and a secondary amino radical separated by 2 or 3 carbon atoms on heating yield cyclic amidines and in the case of polyethylene amines yield imidazolines. Various derivatives, of course, also are obtainable such as amido imidazolines, etc. Without going further into the complexity of the invention as herein stated it is obvious it includes a variety of materials resulting from an initial reaction of an oxirane ring as specified and may result in amidification with the formation of cyclic amidines at a point above the initial reaction temperature and a point below pyrolysis. The formation of amides or cyclic amidines may be varied by the addition of more monocarboxy acids; in fact, different carboxy acids may be added. Or if desired one can add dicarboxy acids. For this reason the present invention is limited merely to the reaction involving the rupture of the oxirane ring, subject to certain qualifications.

Although esters of various monohydric alcohols can be employed for any one of a number of reasons, our preference is to use low molal aliphatic alcohols and particularly butyl alcohol, i. e., the butyl ester. If such ester is derived from a polyethylenic acid in which a number of oxirane rings can be introduced one could, of course, have as many as 2 oxirane rings per acyl radical. This would also be the case if butyl ricinoleate, for example, were esterified with oleic acid or soybean fatty acid. Here, again, an oxirane ring could be introduced in the ricinoleyl radical and also in the unsaturated radical which had been linked by virtue of the ricinoleyl hydroxyl radical. Similarly, soybean fatty acid can be esterified with high molal unsaturated alcohols such as those derived from soybean oil and the like. In such instances an oxirane ring could be introduced in both the acyl radical position and the alcohol residue position. Going a step further, one might esterify ricinoleic acid with oleyl alcohol and then acylate with oleic acid and thus produce an ester of a monohydric alcohol in which 3 oxirane rings could be introduced. However, as previously noted, for various reasons and particularly for economy and simplicity of reaction our preference is to use esters such as the butyl ester of soybean fatty acid, the amyl ester of soybean fatty acid, etc.

PART 1

The epoxidation of ethylenic compounds and particularly esters of unsaturated fatty acids, unsaturated aliphatic alcohols, and the unsaturated fatty acids themselves, is well known. For instance, it has been described in the following patents:

U. S. Patent Nos. 2,443,280; 2,445,892; 2,457,328; 2,458,484; 2,485,160; 2,487,829; 2,510,905; 2,556,145; 2,567,237; 2,567,930; 2,569,502; 2,661,367; 2,686,805; 2,692,271.

Additionally epoxidation procedures have been described in the trade literature of organizations which

supply one or more reactants employed in the procedure. For instance, see Bulletin P63-355 entitled "Hydrogen Peroxide-Resin Technique for the Preparation of Peracetic Acid," E. I. du Pont de Nemours & Company; Bulletin P61-454 entitled "Hydrogen Peroxide-Resin Technique for Epoxidation of Unsaturated Fats, Oils, and Derivatives," E. I. du Pont de Nemours & Company; and booklet entitled "Hydrogen Peroxide," issued by Buffalo Electro-Chemical Company, Inc. See also Chemical Week, August 21, 1945, page 100; and Chemical Week, December 25, 1954, page 32.

An excellent brief description is found in aforementioned U. S. Patent No. 2,692,271, dated October 19, 1954, to Greenspan et al. What is said immediately following is substantially as it appears in said patent.

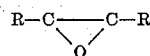
In broad aspect, epoxidation comprises a reaction at a point of unsaturation of the ethylene type in a carbon compound whereby the unsaturated linkage is by the addition of oxygen changed to an oxirane compound.

Many methods of epoxidation have been suggested. For instance, the ethylene linkage has been reacted upon by the employment of perbenzoic acid in a non-aqueous solvent such as chloroform and peracetic acid used in aqueous solution. Many other peracids have been found effective as epoxidizing agents, perphthalic and percamphoric, among others.

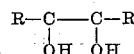
In general, epoxidation of the olefinic compound has been found to proceed best by the employment of peracetic acid and other similar per-compounds. Swern, in U. S. Patent 2,411,762, recommends that epoxidation be performed in special organic solvents, while Terry and Wheeler in 2,458,484 perform epoxidation under vigorous agitation of an aqueous solution of peracetic acid and an insoluble long chain olefinic material. See also Findley et al. J. A. C. S. 67, 412-414 (1945). All of these investigators recognize the necessity of maintaining relatively low temperatures in order to favor the formation of the epoxy compound and to lessen the production, at the olefinic linkage, ultimately of a dihydroxy compound or glycol, by reason of the formation of an hydroxy-acetoxy compound.

However, from a practical operating and commercial point of view, aqueous peracetic acid will be preferred as the epoxidizing agent by reason of its ready formation from acetic acid, glacial or aqueous, or from acetic anhydride by mere reaction with aqueous hydrogen peroxide and, as the latter is now available in high weight concentrations, corresponding high peracid concentrations are available for use.

When the olefinic linkage is reacted with a peracid, it is possible to obtain either or both of two end products; the one being the oxirane compound which may be illustrated broadly as



that is the epoxy compound, the other being the glycol, or derivative thereof, the former being represented by



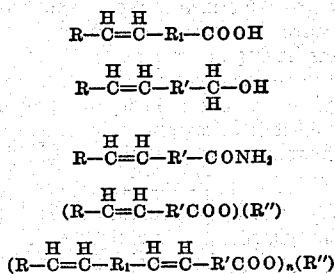
These are the possible end products, irrespective of any theoretical considerations of the mechanism of their formation, although in general the oxirane ring may be considered to be opened up with the production of a glycol by reaction with water, or the production of the hydroxy-acetoxy compound by reaction with acetic acid.

In an epoxidation reaction, several factors are important in determining the efficiency of reaction. One is the amount of the olefinic compound that has been changed in the reaction; another is the quantity of resultant product which exists in the oxirane condition, that is, the epoxy field; and a third is the amount of peracid used.

Fatty acids and fatty acid derivatives which may be

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subjected to epoxidation by conventional procedures are illustrated by the following:



In the above formulas R and R' represent monovalent and divalent hydrocarbon radicals having at least 3 carbon atoms. R₁ is a divalent radical.

Stated another way, it is preferable that the ethylene linkage which is subjected to epoxidation is at least 2 carbon atoms removed from the terminal carbon atom or the carboxyl carbon atom, or what was initially the carboxyl carbon atom. For example, in the second formula, i. e., the formula of the alcohol, it will be noted of course that the carboxyl group has been converted into the terminal alcoholic radical.

In the last two formulas R'' represents the ester radical which may be monohydric, dihydric, trihydric, tetrahydric, etc.

In the last formula n is a small whole number varying from 2 to 6 for example, which corresponds to the valency of the multivalent radical R''.

One can purchase a large number of suitable epoxidation products in the open market or can prepare the same if desired. In a general way, of course, the most economical products are those derived from naturally-occurring glycerides as, for example, soyabean oil. Usually an effort is made to obtain the lowest iodine value consistent with commercial standards. If one started with soap makers' grade olive oil theoretically one might obtain a product having substantially no iodine number and 3 oxirane rings per glyceride radical. Actually, this is not the case for the reason it is difficult by most procedures to obtain an iodine value from a monoethylenic acid glyceride which is less than 10 to 20, and unusual care is required to obtain an iodine value below 10. An iodine value of 10 under such circumstances would appear to be the ultimate goal as far as present commercial procedure is concerned.

If one employs soyabean oil which contains an approximate 50% linoleic acid as a glyceride and about 35% oleic acid, one may readily obtain a product which has on the average 1.5 oxirane rings per fatty acid radical. If one starts with a more highly unsaturated oil, such as linseed oil, one can approximate 2 oxirane rings per fatty acid molecule.

All that has been said previously is a matter of common knowledge and is stated in brief form in aforementioned U. S. Patent No. 2,556,145, dated June 5, 1951, to Niederhauser. For instance, this patent states in substantially verbatim form as follows:

The vegetable oils which when epoxidized may be used in practicing the present invention are those glycerides of saturated and unsaturated acids which have a degree of unsaturation represented by an iodine value of from 90 to 205 and in which the fatty acids neither are hydroxylated nor possess conjugated unsaturation. The semi-drying vegetable oils, which are primarily glycerides of oleic and linoleic acids, are preferred. Among those oils which may be used are epoxidized peanut, rapeseed, cottonseed, corn, tobacco seed, cucurbit, sunflower, safflower, poppyseed, linseed, perilla, and soybean oils. Of these epoxidized oils, soybean oil is particularly efficient. The effectiveness of the epoxidized oils in stabilizing chlorinated rubber is dependent upon both the concentration

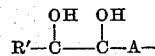
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in which they are used and the degree to which they have been epoxidized; i. e., the number of epoxy groups that have been introduced. Theoretically, each carbon to carbon double bond of the original vegetable oil can be converted to an epoxy group. In practical operation this will seldom, if ever, be attained but it is desirable that highly epoxidized oils be used so that maximum stability be effected. It is recommended that there be used epoxidized oils containing an average of from 2.5 to 6 epoxy groups per molecule.

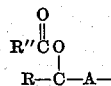
If the fatty acid group has some other functional group present, difficulty may be involved in obtaining optimum yields for some reason that is not entirely clear. This would apply, for example, to castor oil, and ricinoleic acid esters. On the other hand, if castor oil is reacted with a low molal acid such as acetic acid, propionic acid, or the like, then these difficulties appear to be eliminated. There also appears to be difficulty in obtaining suitable yields in the case of conjugated unsaturation. In some instances where the unsaturation is not conjugated there is indication that there may be a shift during reaction to produce conjugation. In other words, in the epoxidation of the fatty acid or fatty acid ester or the like, if the fatty acid is polyethylenic it is very important that the ethylenic radicals be non-conjugated. The fatty acids themselves may contain 8 to 22 carbon atoms. The best example of the monoethylenic acid is, of course, oleic acid and perhaps erucic acid. Both are readily available as glycerides. As to the polyethylenic acids, particular attention is directed to linoleic. As to an example of an acid having 3 ethylenic linkages attention is directed to linolenic. These acids, of course, are available in the form of glycerides, particularly mixed glycerides. Other polyethenoic acids are obtained from oils of aquatic origin.

The alcohols derived from the fatty acids are susceptible to epoxidation but present added difficulties by resulting in somewhat lower yields, perhaps due to the presence of the hydroxyl group. However, alcohols which are suitable for epoxidation include, among others, oleyl alcohol, linoleyl alcohol, linolenyl alcohol, mixed arachidonylclupanodonyl, erucyl alcohol, and ricinoleyl alcohol.

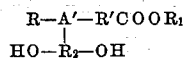
When monohydric alcohol esters of polyethylenic acids are subjected to epoxidation the oxirane ring may be formed and may be opened so as to form a hydroxyl group, or a dihydroxyl group with one ring being left intact. For instance, if one refers to the formulas that have been shown previously it becomes obvious that a radical indicated as R—A— may become



If one starts with a monohydric alcohol ester of a hydroxylated unsaturated acid, for instance, the ethyl, methyl, or butyl ester of ricinoleic acid, it is possible to introduce a group like an acetyl group or an oleyl group and have a radical comparable to the following:



Reference is made to a formula which indicates the combination of the ester with a tertiary hydroxylated monoamine in a mole-for-mole ratio, thus:



in which R₂ is the divalent radical of a hydroxylated monoamine as, for example, the reaction product of one mole of triethanolamine and one mole of glycidic.

Although the effort, as far as this invention goes, is simply to react an epoxidized monohydric alcohol ester of the kind described with an amine or other reactant

of the kind described, so as to open the oxirane ring and not necessarily go any further, yet it follows that as one tries to get a high yield in such reaction invariably and inevitably some other reaction, i. e., some sort of side reaction, may take place. Thus, although the products are described as reaction products involving an oxirane ring of the monohydric alcohol ester yet these side reactions may introduce and yield an appreciable amount in some instances of some of the products herein mentioned, as for example the esters.

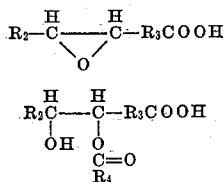
Again, it has been pointed out that the acyl radical carrying the oxirane ring also may contain a single hydroxyl or two hydroxyls as the result of the opening of an oxirane ring by reaction with water. Furthermore, when the amine reacts with the oxirane ring there is a hydroxyl formed on the adjacent carbon atom. Thus, various reactions may take place involving one or more of these hydroxyl groups as, for instance, dehydration with the formation of an unsaturated bond, esterification or perhaps even in some instances the reforming of an oxirane ring from two adjacent hydroxyl groups with possible further reaction. All of which emphasizes the complexity of the reaction involved, or rather the complexity of possible side reactions when one is attempting to produce mainly and substantially the initial resultant of the amine herein described and the epoxidized reactant. The same would apply in reactions involving other reactants.

It is obvious if an unsaturated alcohol were esterified with soyabean acid or the like, one could obtain a monohydric alcohol ester which in reality would be a wax and could be epoxidized to introduce 1, 2, 3 and even 4 oxirane rings provided that both the alcohol radical and the fatty acid radical had at least 2 oxirane rings.

A somewhat similar situation is involved, of course, if one esterified methyl ricinoleate or the like with unsaturated acid such as soyabean fatty acid. Under such circumstances one could readily introduce at least 2 and possibly 3 oxirane rings per ricinoleic acid ester.

The products obtained in the manner described herein, whether single resultants of reaction or a cogeneric mixture, are essentially products in which there has been no decomposition or degradation, and which are solvent soluble, either as such or in the form of salts, particularly salts of a monocarboxy acid such as acetic acid, propionic acid, lactic acid, diglycolic acid, gluconic acid, etc. Solubility means solubility in either water or a hydrocarbon solvent, or an oxygenated organic solvent, or a mixture of the same. The intention is to differentiate from insoluble resins, or resin like materials which could be obtained perhaps from the same reactants.

In the use of epoxidized fatty acids or their equivalents as herein described, we have limited the scope of the invention to reactions involving the formation of a hydrolysis resistant linkage, i. e., a non-ester linkage. One such reason for such limitation is that one can readily conduct epoxidation and hydrolysis or at least cause ring opening so as to produce a dihydroxy fatty acid. Such dihydroxylated compound can easily be esterified. Obviously a reaction involving an epoxidized fatty acid and another acid may be indicated by the following:



In preparing the esters of monohydric alcohols it is to be noted one can use alcohols having fairly high molecular weights, i. e., the alcohols from fatty acids having 16, 18, 20 or even 22 carbon atoms. The oleyl alcohol esters of linoleic acid have been prepared and, similarly, the linoleyl esters. Furthermore, one can pur-

chase mixed oleyl-linoleyl alcohols. These have been esterified with various acids, both monocarboxy and dicarboxy, such as dimerized linolenic acid. Such unsaturated esters have been subjected to epoxidation so as to yield products having at least one oxirane ring per ester unit and in some instances two oxirane rings per ester unit. The yield based on theory is comparatively low but still is sufficient to supply at least one oxirane ring in various compounds of the kind herein described.

PART 2

As previously noted, the present part is concerned with suitable hydroxylated tertiary amines which may be employed for preparing the herein described compounds. Such tertiary monoamines must have at least one hydroxyl radical and may have two or three or even more. For instance, if the primary amine, such as ethylamine, propylamine, butylamine, or the like, is reacted with 2 moles of glycidol to form a tertiary amine one obtains a compound having 4 hydroxyl radicals. Similarly, if a mole of triethanolamine, tripropanolamine or tributanolamine is reacted with 3 moles of glycidol one obtains the monoamine having as many as 6 hydroxyl radicals.

One need not prepare suitable amines but can purchase any one of a number of suitable tertiary monoamines which can be employed as reactants for combination with the epoxidized derivatives. The most common examples are triethanolamine, tripropanolamine and tributanolamine. Other examples include diethylethanolamine, dimethylethanolamine, dimethylisopropanolamine, dimethylbutanolamine, N-methyldiethanolamine, N-hydroxyethylmorpholine, etc. Comparable products can be obtained from high molal amines such as the higher fatty amines which are available in the open market. One is not limited to merely adding sufficient alkylene oxide to convert the product into a tertiary amine but there may be sufficient oxide added to form a repetitious ether radical as in the instance where triethanolamine is reacted with 3, 6, 9, 12 or more moles of ethylene oxide.

In the following list of amines those which are tertiary have at least one hydroxyalkyl radical. Those which are not tertiary, i. e., primary or secondary amines in the list, can be treated with appropriate amounts of alkylene oxides as noted to yield tertiary amines. Ethylene oxide, propylene oxide, butylene oxide, glycidol and other comparable oxides may be used. In this instance again the amounts of the oxide used can be substantial. For instance, 2 to 15 moles instead of merely enough to convert the amine into a tertiary amine.

Other suitable monoamines which may be employed as such, or after treatment with 1, 2 or more moles of alkylene oxide of the kind described, include the following:

n-Butyl amine
 Dibutyl amine
 2-ethylhexylamine
 Di(2-ethylhexyl)amine
 Diethyl ethanolamine
 N-butyl diethanolamine
 Di(2-ethylhexyl)ethanolamine
 Monoisopropanolamine
 Diisopropanolamine
 Triisopropanolamine
 Dimethyl isopropanolamine
 Dibutyl isopropanolamine
 Hexylamine
 Dihexylamine
 Monoethanolamine
 Diethanolamine
 Triethanolamine
 N-methyl ethanolamine
 Dimethyl ethanolamine
 N-ethyl ethanolamine
 N-ethyl diethanolamine
 N-methyl diethanolamine
 n-Amylamine

Di-n-amylamine
 Sec-amylamine
 1,3-bis-ethylaminobutane
 N-ethylbutylamine
 Heptylamine
 Octylamine
 Dioctylamine
 Decylamine
 Dodecylamine
 2-amino-4-methylpentane
 4-amino-2-butanol
 5-isopropylamino-1-pentanol
 N-butylaniline

Similarly, secondary high molecular weight aliphatic amines known as Armeen 2C and Armeen 2HY, as described in circular entitled "Secondary Armeens," as issued by Armour Chemical Division, Chicago, Illinois.

Also, high molecular weight aliphatic amines known as Armeen 10, Armeen 16D, Armeen HTD, Armeen 18D, and Armeen CD, as described in a pamphlet entitled "Armeens," issued by Armour Chemical Division, Armour and Company, Chicago, Illinois.

Suitable amines having an aromatic ring include alpha-methylbenzylamine, alpha-methylbenzylmonoethanolamine and alpha-methylbenzyl diethanolamine.

One may use tertiary alkyl primary amines such as tertiary-octylamine, alkylamine 81-R, alkylamine 81-T, alkylamine JM-R, and alkylamine JM-T. As to a description of these amines see Rohm & Haas Company, Philadelphia, Pa., pamphlet entitled "Tertiary-Alkyl Primary Amines."

Other amines include:

2-amino-2-methyl-1-propanol
 2-amino-2-methyl-1,3-propanediol
 2-amino-2-ethyl-1,3-propanediol
 3-amino-2-methyl-1-propanol
 2-amino-1-butanol
 3-amino-1,2-butanediol
 4-amino-1,2-butanediol
 2-amino-1,3-butanediol
 4-amino-1,3-butanediol
 3-amino-2,2-dimethyl-1-propanol
 2-amino-2,3-dimethyl-1-propanol
 2,2-diethyl-2-amino ethanol
 2,2-dimethyl-2-amino ethanol
 2-amino-1,4-butanediol
 3-amino-1,4-butanediol
 1-amino-2,3-butanediol
 Tris-(hydroxy methyl) amino methane

An additional desirable group of amines are dialiphatic-aminoalkylcardanols, and particularly those having 10 to 40 carbon atoms in the dialiphatic grouping; examples include di-2-ethylhexylaminomethylcardanol, diamylaminomethyl cardanol, dilaurylaminomethyl cardanol, and di-n-butylaminomethyl cardanol. See U. S. Patent No. 2,489,672, dated November 29, 1949, to Revukas.

Further examples of this same type of material, which has available both a phenolic hydroxyl and an alkanol hydroxyl, are the condensation products derived from a phenol, either monofunctional or difunctional, such as para-tertiary butylphenol, para-tertiary amylphenol, octylphenol nonylphenol, and similar phenols having a substituent such as two butyl groups or two nonyl groups in both an ortho and the para position. Such phenols are reacted with an aldehyde, such as formaldehyde, acetaldehyde, etc., and an alkanol amine, such as diethanolamine, ethylethanolamine, dipropanolamine, and other amyl amines having only one amino hydrogen atom. See, for example, U. S. Patent No. 2,457,634, dated December 28, 1948, to Bond et al.

Amines having ring structures of course include aniline, diphenylamine, cyclohexylamine, dicyclohexylamine, and various comparable amines with alkyl substituents in the ring.

Other suitable amines are those obtained from sugars or comparable derivatives, such as glucamine and maltosamine. A product such as glucose can be reacted with a primary amine such as hexylamine, octylamine, decylamine, dodecylamine, or the like, and then subjected to reduction so as to give other suitable primary amines which in turn can be subjected to oxyalkylation. Methylglucamine can be reacted with an alkylene oxide so as to replace the amino hydrogen atom by the hydroxyethyl, hydroxypropyl, or similar radical, to yield a very valuable type of monoamine.

A monoamine compound may be combined with an alkylene oxide so the resultant product may have a molecular weight as high as 3600 or thereabouts, or even higher. Note, for example, the oxyalkylated amine described in U. S. Patent 2,679,510, dated May 25, 1954, to De Groote. The selected compounds may be cyclic or non-cyclic. Those which are cyclic may be heterocyclic as in the case of morpholine derivatives or oxazolines which may be regarded as derivatives of N-acyl-2-aminoethanols. This would apply where instead of being a derivative of monoethanolamine the oxazoline was a derivative of a low molal acid or a high molal acid and 2-amino-2-methyl-1,3-propanediol.

Another particularly valuable reactant is obtained by reacting tris(hydroxymethyl)aminoethane with 5, 10, or 15 moles of ethylene oxide.

Note, again, where primary or secondary amines are herein included, the actual reactants are such amines in combination with at least sufficient alkylene oxides, preferably having not over 8 carbon atoms to convert them into tertiary amines, having of course at least one reactive hydrogen atom.

The olefin oxides most readily available are, of course, ethylene, propylene, and butylene. However, one may also use styrene oxide and recently there has become available olefine oxides having 5 carbon atoms, i. e., pentene oxide and also a product which is commonly referred to as diisobutylene oxide. It is, in fact, a mixture of 1,2-epoxy-2,4,4-trimethylpentane and 2,3-epoxy-2,4,4-trimethylpentane. Glycide can be employed and, of course, is a means of producing tertiary alkyl amines having more than 3 hydroxyl radicals. One also can produce suitable tertiary amines in which more than one olefin is employed, for instance, propylene oxide and ethylene oxide, or butylene oxide and ethylene oxide, or any other combination with or without the use of glycide.

Attention is again directed to the fact that monoamines of the kind herein described can be reacted with 1, 2, or 3 oxirane rings and the product so obtained may greatly increase the hydrophobe character of the acyl radical to which it is attached or it may offset the hydrophobe character by introducing a highly hydrophilic group.

Examples of tertiary amines in which the nitrogen atom is not basic or at least not basic in comparison with triethanolamine, or compounds such as phenyl diethanolamine, phenyl dipropanolamine, phenyl dibutanolamine, or derivatives thereof, obtained by reaction with the olefine oxides previously mentioned.

PART 3

Part Three is concerned with the reaction between the two classes of reactants described in the foregoing, i. e., those described in Parts 1 and 2. For purpose of brevity we are going to limit the examples to products which are available commercially or can be obtained from suppliers of epoxidized products. These products are epoxybutyl stearate, isobutylepoxyacetoxystearate and methylepoxy soyate. These products can be reacted with tertiary monoamines having a reactive hydrogen atom such as triethanolamine, and other comparable monoamines. Our preference is to react such epoxidized compound with basic hydroxylated monoamino compounds as previously

noted. Therefore, the bulk of this part will be concerned with examples illustrating this type.

As previously pointed out the reaction involving the reactant containing the oxirane ring and the selected compound having a labile hydrogen atom is essentially a variety of oxyalkylation. For this reason the reactions are so conducted. The procedure is simpler than is the case when ethylene oxide or propylene oxide is used for the reason that the reactants are non-volatile as a rule and thus one does not have to use an autoclave or similar equipment. Furthermore, many of the reactants employed are basic in character and thus to the extent re-

quired act as their own catalyst. As has been pointed out elsewhere catalysts can be added, particularly alkaline catalysts such as sodium methylate, caustic soda, caustic potash, etc. In a general way, the procedure employed in preparing the reactants is the same and the only precaution taken as a rule is to avoid temperatures above that required to rupture the oxirane ring for the reason that side reactions or secondary reactions may take place. The procedure is illustrated by examples 1a and 15a, and then by Tables I, II and III which present the data covering the preparation of a wide variety of products from the reactants described previously.

TABLE I

Ex. No.	Oxirane ring containing ester	Amt., gms.	Hydroxylated Tertiary monoamine	Amt., gms.	Catalyst sodium methoxide, gms.	Temp., ° C.	Time, hrs.	Product of reaction
1a	Epoxybutyl stearate.	258	Ethyldiethanolamine	93	1.8	165	3.5	Amber visc. liq. xyl. and alc. sol.
2a	do.	246	Dibutyl isopropanolamine	124	1.8	180	3	Brn. visc. liq. xyl. and alc. sol.
3a	do.	258	Triethanolamine	105	1.8	155	3	Dk. brn. visc. liq. xyl. and alc. sol.
4a	do.	258	do.	52	1.5	160	3	Lt. brn. visc. liq. xyl. and alc. sol.
5a	do.	184	Octylamine+4 ethylene oxide	152	1.7	165	4	Dk. red visc. liq. xyl. and alc. sol.
6a	do.	147	Tris(hydroxymethyl)amino methane+10 ethylene oxide	232	1.9	160	4	Dk. yel. visc. liq. xyl. and alc. sol.
7a	do.	246	Morpholine+5 ethylene oxide	204	2.2	170	3	Brn. visc. liq. xyl. and alc. sol.
8a	do.	246	Octylamine+2 glycide	186	2.1	160	4	Dk. yel. visc. liq. xyl. and alc. sol.
9a	do.	184	Triethanolamine+2 glycide	148.5	1.7	160	4	Dk. brn. glassy paste, sol. in isopropanol, sltly. sol. in xyl.
10a	do.	184	Dibutylamine+1 glycide	101.5	1.4	155	3	Dk. red visc. liq. xyl. and alc. sol.
11a	do.	147	Ethomeen S/15	195	1.7	160	4	Yel. visc. liq. xyl. and alc. sol.
12a	do.	184	Abietyl amine+2 ethylene oxide	202	1.9	165	4	Yel. soft solid, xyl. and alc. sol.
13a	do.	184	Diphenylamine+4 ethylene oxide	172	1.8	165	3	Lt. brn. visc. liq. xyl. and alc. sol.
14a	do.	184	Armeen 18D+2 glycide	199	1.9	160	4	Yel. visc. liq. xyl. and alc. sol.

TABLE II

Ex. No.	Oxirane ring containing ester	Amt., gms.	Hydroxylated Tertiary monoamine	Amt., gms.	Catalyst sodium methoxide, gms.	Temp., ° C.	Time, hrs.	Product of reaction
15a	Isobutylepoxy acetoxy stearate.	287	Tri-isopropanolamine	95.5	1.9	160	3	Lt. brn. visc. liq.
16a	do.	287	N,N-dibutyl ethanolamine	86.7	1.9	175	3	Amber color visc. liq. xylene and alc. sol.
17a	do.	287	N,N-di(hydroxyethyl) hexylamine.	85.5	1.9	165	3.5	Dk. brn. visc. liq. xyl. and alc. sol.
18a	do.	198	N,N-di(hydroxy isopropyl) lauryl amine.	101	1.5	170	3	Dk. red visc. liq. xyl. and alc. sol.
19a	do.	287	N,N-dihydroxyethylamino butanol.	89	1.9	160	3	Dk. yel. visc. liq. xyl. and alc. sol.
20a	do.	287	N-phenyldiethanolamine	90	1.9	165	3	Dk. red visc. liq. xyl. and alc. sol.
21a	do.	287	N-cyclohexyldiethanolamine	101.5	2.0	165	3	Amber color visc. liq. xyl. and alc. sol.
22a	do.	287	N-butyl diethanolamine	80.5	1.9	160	3.5	Do.
23a	do.	198	Laurylamine+2 glycide	111	1.6	160	3	Dk. brn. visc. liq. alc. and xyl. sol.
24a	do.	198	Abietylamine+2 glycide	155	1.8	165	4	Lt. yel. visc. liq. xyl. and alc. sol.
25a	do.	118.6	Ethomeen C/25	182.6	1.5	165	4	Do.
26a	do.	198	Cyclohexylamine+2 ethylene oxide	82	1.4	160	3.5	Brown visc. liq. xyl. and alc. sol.
27a	do.	198	Morpholine+5 ethylene oxide	102	1.5	170	3	Dk. amber visc. liq. xyl. and alc. sol.
28a	do.	198	Diisopropanolamine+10 ethylene oxide.	191	2	165	4	Dk. yel. visc. liq. alc. sol. Sltly. benzene sol.

TABLE III

Ex. No.	Compound used	Amt., gms.	Amino compound	Amt., gms.	Molal ratio	Temp., ° C.	Time, hrs.	Product of reaction
1b	1a	167	Hydroxyethyl ethylene diamine.	34.7	1:1	200 200-240 240-310	2 1 1	Blk. soft solid, sol. in alc. sltly. sol. in wtr.
2b	3a	173	Diethylene triamine	34.5	1:1	200 200-240 240-315	2 1 1	Dk. brn. soft solid. Sol. in alc. sltly. sol. in wtr.
3b	4a	221.5	do.	51.6	1:2	200 200-240 240-310	2 1 1	Greenish blk. pasty solid. Sltly. sol. in water.
4b	5a	225.5	Octylamine	43	1:1	200 200-230	1 2.5	Dk. amber visc. liq. sol. in xyl. and alc.
5b	7a	337.5	Sodium hydroxide water	20 339.5	1:1	95-98	3	50% soln. clear yel. gel.
6b	8a	323.5				200 230	1 4	Dk. brn. visc. liq. xyl. and alc. sol.
7b	9a	221.5	Triethanolamine	49.7	1:1	200 220	1 3	Blk. soft solid, xyl. and alc. sol.
8b	10a	190	Hydroxyethyl ethanolamine.	34.7	1:1	200 200-240 240-305	2 1 1	Dk. brn. soft solid, alc. sol. and sltly. xyl. sol.
9b	5b	139	10% BaCl ₂	210	1:1	90-95	2	Yellowish gray solid, sol. in hot alc. and alc. xyl. mix. Insol. in wtr.
10b	13a	181	Tetraethylene pentamine	47.2	1:1	200 200-240 240-315	2 1 1	Blk. soft solid, xyl. and alc. sol.

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Example 1a

A 500 ml. 3-necked flask was fitted with a reflux condenser, a thermometer and an efficient sealed stirrer. In the flask was placed 258 grams of epoxybutyl stearate, 93 grams of ethyl diethanolamine and 1.8 grams of sodium methoxide. The epoxy butyl stearate contained 4.35% oxirane oxygen or approximately one oxirane ring per one theoretical molecule. The mixture was first stirred for 20 minutes to insure thorough mixing, then heat was gradually applied to bring its temperature to 165° C. within half an hour. The heating was allowed to continue for 3.5 hours at 165° C. to complete the reaction. The product was an amber colored viscous liquid, soluble in xylene and alcohol and was surface active.

Example 15a

In the same equipment, set up as used in Example 1a, 287 grams of isobutylepoxyacetoxystearate and 95.5 grams of triisopropanolamine were reacted at 160° C. in the presence of 1.9 grams of sodium methoxide. The epoxy ester contained 2.7% oxirane oxygen or one oxirane ring per 593 grams. At the end of 3 hours heating the reaction was completed. The product was a light brown viscous liquid, soluble in xylene and alcohol. It was surface active and more oil soluble than the product from Example 1a.

Example 1b

In a 300 ml. 3-necked flask, equipped with a Barrett type distillation receiver, a condenser, a thermometer and a sealed stirrer, 34.7 grams of hydroxyethyl ethylenediamine was reacted with 167 grams of the reaction product obtained from Example 1a. The reaction temperature was first maintained at 200° C. for 2 hours, then raised to 240° C. in another hour. During this heating, butyl alcohol was distilled over. When the temperature reached 240° C. the distillation of butyl alcohol ceased but gradually water began to collect in the distillation receiver forming a bottom layer. The heating was continued while a slow stream of nitrogen was introduced into the flask through a side tube. When the temperature reached 310° C. no more distillate was collected. The reaction was considered complete. The distillate consisted of 25.5 grams of yellow colored alcohol layer and 5.8 grams of water layer. The product was a black color glassy solid. It was soluble in alcohol and xylene alcohol mixture, and slightly soluble in xylene or water.

Example 5b

246 grams of epoxybutyl stearate and 204 grams of oxyethylated morpholine (5:1) were reacted at 170° C. for 3 hours in the presence of 2.2 grams of sodium methoxide. (See Example 7a.) To 337.5 grams of this reaction product, 259.5 grams of 7.7% sodium hydroxide was added. This heterogeneous mixture was first reacted at 95-98° C. under slight reflux until a clear homogeneous solution was obtained. Then it was heated for another hour more to insure complete reaction. The total time of heating was 3 hours. The product, 50% in concentration, was a clear yellow gel. It was soluble in alcohol and formed a semi-permanent emulsion of water in xylene.

PART 4

The herein described amines are almost invariably and inevitably basic but some exceptions are amines of a type such as phenyl diethanolamine, phenyl dipropanolamine, etc. Our preference is to use the cheaper and more readily available amines, such as ethyl diethanolamine, methyl diethanolamine, triethanolamine, tripropanolamine, etc. The final products show little basicity and, generally speaking, the addition of a mole of acid such as acetic acid or the like per nitrogen atom, even when a basic amine is employed, such as triethanolamine, is

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apt to yield a salt plus some free acid. Thus, it is possible to add a high molal acid or low molal acid so as to form a salt with the residual basicity. In a number of instances salt formation changes or alters the solubility of the free base in either oil or water and for a number of purposes makes the salt form more attractive. Where the base has a plurality of basic nitrogen atoms one can neutralize one or more as desired. Thus, the basic products of reaction can be reacted with low molal acids such as acetic acid, lactic acid, glycolic acid, propionic acid, diglycolic acid, and the like. On the other hand, one can use naphthenic acid, higher fatty acids, tall oil sulfonic acids, and particularly oil soluble petroleum sulfonic acids such as mahogany acids, to form salts.

Table IV following shows combinations of products which appeared in prior tables combined with various acids illustrating what has been said in this part of the text.

TABLE IV

Compound No.	Amt., gms.	Acid used	Amt., gms.	Isopropanol used, gms.	Solution concentration, per cent
1a-----	50	Acetic acid-----	6.27	56.27	50
2a-----	50	do-----	5.67	55.67	50
3a-----	50	Glycolic acid 70%-----	12.1	54.90	50
4a-----	50	do-----	6.63	52.0	50
8a-----	50	Lactic acid-----	7.37	57.37	50
10a-----	50	do-----	8.30	58.30	50
16a-----	50	Diglycolic acid-----	4.80	54.80	50
17a-----	50	do-----	4.82	54.82	50
21a-----	50	Dinonyl naphthalene sulfonic acid-----	31.7	81.70	50
22a-----	50	do-----	33.4	83.40	50

PART 5

The products herein described fall into two classes; those which are basic by virtue of the presence of one or more basic nitrogen atoms and those which either are not basic or the amino radical does not have significant basicity. Thus, what is said herein applies not only to compounds as such but also to those which are basic enough to form salts and also applies to the salts as described in Part 4, preceding. Such products and others herein described may all be used for the resolution of petroleum emulsions of the water-in-oil type. The products without further reaction are particularly valuable as additives for lubricating oils which are derived from sources other than petroleum.

As to specific uses for the herein described compounds including the various salts it is to be noted such compounds are valuable as a fuel oil additive in the manner described in U. S. Patent 2,553,183, dated May 15, 1951, to Caron et al. It can be used in substantially the same proportions or lower proportions and this is particularly true when used in conjunction with glyoxalidine or amido glyoxalidine.

An analogous use in which these products are equally satisfactory is than described in U. S. Patent No. 2,665,978, dated January 12, 1954, to Stayner et al. The amount employed is in the same proportion or lesser amounts than referred to in said aforementioned Caron et al. patent.

The second use is for the purpose of inhibiting fogs in hydrocarbon products as described in U. S. Patents Nos. 2,550,981 and 2,550,982, both dated May 1, 1951, and both to Eberz. Here again it can be used in the same proportions as herein indicated or even small proportions.

A third use is to replace oil soluble petroleum sulfonates, so-called mahogany soaps, in the preparation of certain emulsions, or soluble oils or emulsifiable lubricants where such mahogany soaps are employed. The cogeneric mix-

tures having this peculiar property serve to replace all or a substantial part of the mahogany soap.

Another use is where the product does not serve as an emulsifying agent alone but serves as an adjunct.

Briefly stated, the fourth use is concerned with use as a coupling agent to be employed with an emulsifying agent. See "The Composition and Structure of Technical Emulsions," J. H. Goodey, Roy. Australian Chem. Inst., J. and Proc., vol. 16, 1949, pp. 47-75. As stated in the summary of this article, it reads:

"The technical oil-in-water emulsion is regarded as a system of four components: the dispersion medium, consisting of the highly polar substance water; the disperse phase composed of hydrocarbons or other substances of comparatively weak polarity; the coupling agent, being an oil-soluble substance involving an hydroxyl, carboxyl or similar polar group; and the emulsifying agent, which is a water-soluble substance involving an hydrocarbon radical attached to an ionizable group."

Such compounds or derivatives also are effective for other purposes such as an anti-fogging agent in motor fuels, a coagulation preventive in burner oils, and as an additive for the prevention of corrosion of ferrous metals. Such invention, however, is not part of what is herein claimed.

The herein described products and the derivatives thereof are particularly valuable in flooding processes for recovery of oil from subterranean oil-bearing strata when employed in the manner described in U. S. Patent No. 2,233,381, dated February 25, 1951, to De Groote and Keiser.

Furthermore, the herein described products may be employed to increase operating efficiency by increasing the oil-to-brine ratio or by increasing the total oil recovery in primary recovery operations as differentiated from secondary recovery operations. The procedures employed are essentially those as described in either U. S. Patent No. 2,331,594, dated October 12, 1943, to Blair, or U. S. Patent No. 2,465,237, dated March 22, 1949, to Larsen.

When the products of the kind herein described are used for water flooding and particularly in the form of salts, they have unusual value in a fresh water or brine system for the inhibition of the growth of both anaerobic and aerobic bacteria but are particularly applicable in controlling the sulfate reducing organisms which cause difficulty in secondary recovery operations. Thus, one may use some other agent or agents in water flood systems and use compounds as herein described primarily for reducing bacterial growth. The use of such industrial bactericide is well known and the procedure is conventional; for instance, one can use the methods described in an article entitled "The Role of Microorganisms," by R. C. Allred, which appeared in Producers Monthly, vol. 18, No. 4, pages 18-22.

In the use of the herein described products as industrial bactericides and particularly in connection with water flood operations we prefer to use the salts obtained by partial or total neutralization with carboxy acids, particularly monocarboxy acids having not over 6 carbon atoms and preferably a hydroxylated acid such as hydroxyacetic acid.

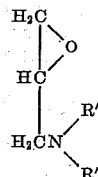
Specific attention is directed to the article entitled "Preparation of Water for Injection Into Water Reservoirs," which appeared in the Journal of Petroleum Technology, volume 7, No. 4, page 9 (April 1955). The author is Torrey.

PART 6

The products obtained in the manner herein described are valuable for various purposes as indicated in Part 5, preceding. Where salts can be formed, i. e., where the products are basic in character this applies to the salts as well as to the unneutralized material. However, one of the most important uses for the herein described products is as an intermediate for further reaction. It is

obvious that reactions of the kind described previously invariably and inevitably yield oxyalkylation susceptible compounds, products or co-generic mixtures. The reason is that when the oxirane ring is open there is produced a hydroxyl group. This hydroxyl group is susceptible to oxyalkylation and there may be present other groups which likewise are susceptible to oxyalkylation as, for example, when an epoxidized butyl soyate is reacted with a mole of triethanolamine and then with a mole of a polyamine such as triethylene tetramine. Thus, the products previously described may be combined with a variety of reactants as chemical intermediates, for instance, with various diepoxides or polyepoxides. They may be combined with a number of other monoepoxides such as epichlorohydrin, styrene oxide, glycidic and methylglycidic. They may be reacted with alkyl glycidyl ether, glycidyl isopropyl ether, and glycidyl phenyl ether.

Furthermore, such products may be reacted with alkylene imines such as ethylene imine or propylene imine, to produce cation-active materials. Instead of an imine, one may employ what is a somewhat equivalent material, to wit, a dialkylaminoepoxypropane of the structure



wherein R' and R'' are alkyl groups.

Likewise, since the products have a hydroxyl group they may be combined by esterification with carboxy acids such as higher fatty acids, so as to change their characteristics or with polycarboxy acids, such as diglycolic, maleic acid, phthalic acid, succinic acid, and the like, to give resins, soft polymers or fractional esters which are essentially monomeric.

A variety of compounds can be formed by merely heating the reaction mass provided there are free hydroxyls present to a point where etherization takes place. This would apply, for example, to the product obtained by reacting one mole of butyl soyate with a mole of triethanolamine. Furthermore, the fatty acid radical may act as an acylating agent and form an ester comparable to the oleic acid ester of triethanolamine. Such reaction can become complex depending on whether it is an intra- or inter-molecular reaction.

As has been pointed out previously, the reaction product, for example, of one mole of triethanolamine and one mole of epoxidized butyl soyate, can be reacted with a polyamine such as triethylene tetramine, so as to form an amide which in turn may be heated so as to form an imidazoline.

Any one of the products above described can be subjected to oxyalkylation with the various epoxides previously noted. The derivatives thus obtained in the manner previously described may be used for various processes where surface-active materials in either an aqueous phase or a hydrophobe phase are indicated for the various industrial uses noted for the products per se in Part 5, preceding.

As is obvious, if products of the kind herein described, i. e., derivatives obtained, for example, from epoxidized butyl soyate and triethanolamine or tripropanolamine, are saponified and acidified under appropriate conditions it is possible to obtain an inner salt involving a basic amino radical and the residual carboxyl radical. However, if such product, or a suitable intermediate, or the initial product itself, is saponified with a strong base, such as caustic soda, or caustic potash, or the like, the resultant product is characterized by the presence of the metallic ion, for instance, sodium or potassium, in the carboxyl

position, and the amino group is merely part of the acyl radical. Both types of products can be obtained by conventional means from the herein described resultants, i. e., either the so-called free acid which in essence is really an inner salt, or the salt involving the use of sodium hydroxide, potassium hydroxide, or the like. The products so obtained, whether metallic salts or inner salts, are effective for prevention of corrosion not only in an aerobic system but also in aerobic systems.

Also, it is to be noted that one need not use sodium hydroxide or potassium hydroxide in the above described compounds but one may also use a quaternary ammonium base, particularly a base whose basicity is greater than the terminal amino group in the acyl radical.

Also, it is to be noted that if one prepares the salts of metal, such as magnesium, aluminum, barium, or the like, the products so obtained are effective for the same purpose and particularly in a hydrophobe system, and also are valuable as additives to lubricating oils, fuel oils, and the like.

What has been said previously in regard to the formation of alkali metal salts (sodium, potassium, and lithium) and in regard to the formation of inner salts is an oversimplification insofar that we are aware that in some instances steric hindrance prevents the formation of an inner salt but does not prevent the formation of intramolecular salts. Thus, in some instances such intramolecular salts have unusual properties including uses for the purpose above indicated for the alkali metal salts or the inner salts.

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

1. Products obtained by reacting under oxyalkylation conditions (A) an epoxidized ester of a lower alkanol and an acid selected from the class consisting of fatty acids and acylated fatty acids in which the epoxidized ester contains on the average approximately one oxirane ring per fatty acid radical, with (B) a hydroxylated tertiary monoamine; said reaction between (A) and (B) involving rupture of the oxirane ring and being limited to the linkage —C—O—C— , which linkage is being characterized by freedom from a carbonyl carbon atom; said product of reaction being hydroxylated and solvent soluble.

2. Products obtained by reacting under oxyalkylation conditions (A) an epoxidized ester of a lower alkanol and a higher fatty acid derived from a naturally occurring glyceride in which the epoxidized ester contains on the average approximately one oxirane ring per fatty acid radical and in which the acyl radical of the ester is free from any residual hydroxy radical, with (B) a hydroxylated tertiary monoamine; said reaction between (A) and (B) involving rupture of the oxirane ring and being limited to the linkage —C—O—C— , which linkage is being characterized by freedom from a carbonyl carbon atom; said product of reaction being hydroxylated and solvent soluble.

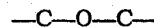
3. Products obtained by reacting under oxyalkylation conditions (A) an epoxidized ester of a lower alkanol and a higher fatty acid derived from a naturally occurring glyceride in which the epoxidized ester contains on the average approximately one oxirane ring per fatty acid radical and in which the acyl radical of the ester is free from any residual hydroxy radical, with (B) a basic hydroxylated tertiary monoamine; said reaction between (A) and (B) involving rupture of the oxirane ring and being limited to the linkage —C—O—C— , which linkage is being characterized by freedom from a carbonyl carbon atom; said product of reaction being hydroxylated and solvent soluble.

4. Products obtained by reacting under oxyalkylation conditions (A) an epoxidized ester of a lower alkanol and a higher fatty acid derived from a naturally occurring glyceride in which the epoxidized ester contains on the average approximately one oxirane ring per fatty

acid radical and in which the acyl radical of the ester is free from any residual hydroxy radical, with (B) a basic hydroxylated tertiary monoamine having at least 2 hydroxyl radicals; said reaction between (A) and (B) involving rupture of the oxirane ring and being limited to the linkage —C—O—C— , which linkage is being characterized by freedom from a carbonyl carbon atom; said product of reaction being hydroxylated and solvent soluble.

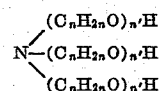
5. Products obtained by reacting under oxyalkylation conditions (A) an epoxidized ester of a lower alkanol and a higher fatty acid derived from a naturally occurring glyceride in which the epoxidized ester contains on the average approximately one oxirane ring per fatty acid radical and in which the acyl radical of the ester is free from any residual hydroxy radical, with (B) a basic hydroxylated tertiary monoamine having at least 3 hydroxyl radicals; said reaction between (A) and (B) involving rupture of the oxirane ring and being limited to the linkage —C—O—C— , which linkage is being characterized by freedom from a carbonyl carbon atom; said product of reaction being hydroxylated and solvent soluble.

6. Products obtained by reacting under oxyalkylation conditions (A) an epoxidized ester of a lower alkanol and a higher fatty acid derived from a naturally occurring glyceride in which the epoxidized ester contains on the average approximately one oxirane ring per fatty acid radical and in which the acyl radical of the ester is free from any residual hydroxy radical, with (B) a tertiary alkanol amine having at least 3 hydroxyl radicals; said reaction between (A) and (B) involving rupture of the oxirane ring and being limited to the linkage



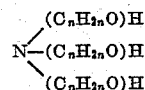
which linkage is being characterized by freedom from a carbonyl carbon atom; said product of reaction being hydroxylated and solvent soluble.

7. Products obtained by reacting under oxyalkylation conditions (A) an epoxidized ester of a lower alkanol and a higher fatty acid derived from a naturally occurring glyceride in which the epoxidized ester contains on the average approximately one oxirane ring per fatty acid radical and in which the acyl radical of the ester is free from any residual hydroxy radical, with (B) a monoamine of the structure



in which n is a small whole number not over 8 and n' is a whole number varying from one to 50; said reaction between (A) and (B) involving rupture of the oxirane ring and being limited to the linkage —C—O—C— , which linkage is being characterized by freedom from a carbonyl carbon atom; said product of reaction being hydroxylated and solvent soluble.

8. Products obtained by reacting under oxyalkylation conditions (A) an epoxidized ester of a lower alkanol and a higher fatty acid derived from a naturally occurring glyceride in which the epoxidized ester contains on the average approximately one oxirane ring per fatty acid radical and in which the acyl radical of the ester is free from any residual hydroxy radical, with (B) a monoamine of the structure



in which n is a small whole number not over 8; said reaction between (A) and (B) involving rupture of the oxirane ring and being limited to the linkage



which linkage is being characterized by freedom from

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a carbonyl carbon atom; said product of reaction being hydroxylated and solvent soluble.

9. The product of claim 8 with the proviso that *n* is 2.

10. The product of claim 8 with the proviso that *n* is 3.

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