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## REACTION PRODUCT OF EPOXIDIZED GLYCERIDES AND HYDROXYLATED TERTIARY MONOAMINES

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The present invention is concerned with the reaction products of certain epoxidized naturally-occurring and modified naturally-occurring fatty acid glycerides and hydroxylated tertiary monoamines, and preferably basic tertiary monoamines.

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 glycerides and generally characterized by the presence of at least two oxirane rings per glyceride 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;

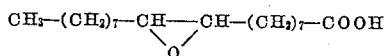
Part 3 is concerned with reactions involving the two classes of reactants above, i. e., those described in Part 1 and those described in Part 2;

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

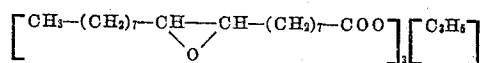
Part 5 is concerned with various uses for the products described in Part 3 of their salts described in Part 4; and

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. For purpose of simplification and particularly for brevity of explanation frequent reference will be made in the introductory part of the specification, and elsewhere for that matter, to the fatty acids and the esters of fatty acids derived from monohydric alcohols.

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



If instead of a fatty acid one employed a glyceride, particularly a naturally-occurring glyceride, the corresponding formula would be as follows:



In actual practice commercially available epoxidized glycerides represent a product which may vary from a 70% or 75% yield up to 80% or even 85% or 90%,

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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. The present invention is limited to reactions involving epoxidized glycerides having at least 2 and not over 6 oxirane rings per glyceride molecule and hydroxylated tertiary monoamines such as triethanolamine, ethyl diethanolamine, etc.

Such epoxidized glyceride and preferably one showing approximately one oxirane ring per acyl radical is reacted with a mole of an amine as described. Theoretically at least one mole of an amine can be caused to react with at least the same number of oxirane rings as appears in the glyceride, i. e., from 2 to 6 moles of the amine for each mole of the glyceride.

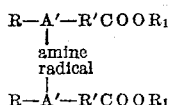
Bearing in mind the acyl radical of the glyceride can also react to form a simple amide in the same way that the unepoxidized acyl radical of the glyceride can so react, it is obvious that each epoxidized acyl radical of the glyceride can be reacted with at least 2 moles of polyethylene amine to give an amino amide. In the case of hydroxylated tertiary monoamine one obtains an ester instead of an amide. This is illustrated by such well known products as the stearic acid ester, or oleic acid ester of triethanolamine. Thus, it is obvious one can react at least two moles of a hydroxylated tertiary monoamine with each epoxidized acyl radical of the glyceride.

As has been suggested previously, the reactions involving epoxidized glycerides are more complicated than those involving an epoxidized fatty acid or, for that matter, the epoxidized ester of a low molal monohydric alcohol instead of a fatty acid as, for example, methyl or butyl soyate. Such simpler reactants may have one or two oxirane rings as a rule whereas the corresponding glyceride would have from 3 to 6 in many instances. Over and above this the reaction involving a fatty acid or a methyl or butyl ester involves in many cases the evolution of water or a volatile low molal alcohol. This is not true with a glyceride and subsequent reactions may convert the glycerine into some product for instance an aldehyde which, in turn, reacts with an amino compound, although this is less likely in the case of a tertiary monoamine as compared with the likelihood in the instance of a primary or secondary amine. For this reason, as far as the underlying mechanism is concerned, and as has been stated previously for purpose of brevity and convenience it is preferable to consider momentarily what would happen if one were employing either an epoxidized fatty acid or an epoxidized fatty acid ester derived from a low molal monohydric alcohol such as methyl alcohol or butyl alcohol.

Although the reactions herein involved invariably and inevitably include a reaction involving a hydroxylated tertiary 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

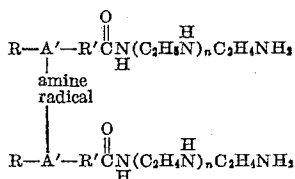
at least 2 hydroxyl groups as in the case of ethyldiethanolamine:



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 radicals having only a single oxirane ring.

Since the monohydric alcohol ester and a glyceride also, like any other fatty acid equivalent, could act as an acylating agent it is obvious that esters of the hydroxylated tertiary monoamine 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 amide by reaction with a polyamine. One can show the amide formation from the precursory product derived in turn from a polyhydroxylated tertiary monoamine, 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 of 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.

Naturally-occurring glycerides include such products as ricinoleic acid which contains an alcohol radical by virtue of the hydroxyl group present in the acyl radical. For this reason the term "glycerides" is intended to include such variants of naturally occurring glycerides, such as the type obtained when castor oil is heated with ricinoleic acid or with oleic acid to give the corresponding glyceride characterized by the presence of 6 moles of a

fatty acid, particularly an unsaturated fatty acid, per glycerol radical. For this reason and considering what has been said in regard to the complicated reactions which may take place it may be well to examine certain limited aspects of monohydroxy alcohol esters of polyethylene acids as described in greater detail in our co-pending application, Serial No. 548,748, filed November 23, 1955. The analogy to glycerides is obvious and reference is made to said co-pending application for such a description.

Although the effort as far as this invention goes is simply to react an epoxidized glyceride of the kind described with a hydroxylated monoamine 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 and the tertiary hydroxylated monoamine yet these side reactions may introduce and yield an appreciable amount in some instances of some of the products herein mentioned.

Again, it has been pointed out that the acyl radical carrying the oxirane ring also may contain a single hydroxyl or 2 hydroxyls as the result of the opening of an oxirane ring by reaction with water. Furthermore, when the tertiary hydroxylated monoamine 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 re-forming of an oxirane ring from 2 adjacent hydroxy groups with ultimate reaction. All of which emphasizes the complexity of the reactions involved, or rather the complexity of possible side reactions when one is attempting to produce mainly and substantially the initial resultant of the monoamine herein described and the epoxidized reactant.

Referring now specifically to the naturally-occurring glycerides or the modified glycerides formed by the introduction of an acyl radical, such as the acetyl radical, ricinoleyl radical, oleyl radical, or the like, into castor oil it is to be noted the simpler products such as epoxidized soyabean oil or the like are available in the open market or one 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

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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 primary 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 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 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 product 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 polyethylenic acids are obtained from oils of aquatic origin.

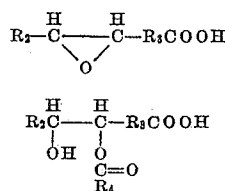
Previous reference has been made to an esterified castor oil although not a naturally-occurring glyceride, still it is included within the present invention. For instance, one could esterify castor oil with soyabean fatty acid. Under such circumstances one could readily introduce at least two and possibly three oxirane rings per castor oil derivative. In other words, one might even introduce as many as 9 oxirane rings per glyceride, all of which simply points to the complexity of the various reactants employed in the present invention and all of which have been described in detail in our co-pending application, Serial No. 432,121.

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 the fatty acid compounds, i. e., the glycerides 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. This can be illustrated in a simple manner by reference to

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an epoxidized fatty acid without the complications involved in the case of a glyceride. 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:



As pointed out in the text it is simpler to examine the epoxidized glycerides from a standpoint of a structure in which there is only one acyl group as, for example, an epoxidized fatty acid or an epoxidized monohydric alcohol ester of an epoxidized glyceride.

However, an epoxidized glyceride having only one oxide ring per acyl radical is polyfunctional. Furthermore, some of the complications which distinguish the reaction product of an epoxidized glyceride and a tertiary hydroxylated monoamine from the comparable product derived from the epoxidized fatty acid ester of a monohydric alcohol are best illustrated by reaction products such as the amide, or ester formed therefrom for this reason it is believed sufficient has been said at this particular point but the matter will again receive consideration from a standpoint of the products obtained by further reaction of, for example, a polyamine with the products obtained initially by reaction involving the amine of the kind herein specified and the epoxidized glyceride of the kind herein specified. For this reason this data is presented in greater detail in Part 6 which appears subsequently.

## 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. Patents 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.

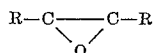
Many methods of epoxidation have been suggested. For instance, the ethylene linkage has been reacted upon by the employment of perbenzoic acid in a non-aqueous solvent such as chloroform and peracetic acid used in aqueous solution. Many other peracids have been found

effective as epoxidizing agents, perphthalic and percamphoric, among others.

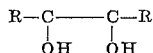
In general, epoxidation of the olefinic compound has been found to proceed best by the employment of peracetic acid and other similar per-compounds. Swern, in U. S. Patent 2,411,762, recommends that epoxidation be performed in special organic solvents, while Terry and Wheeler in 2,458,484 perform epoxidation 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 yield, and a third is the amount of peracid used.

## 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 glycidide 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 glycidide one obtains the monamine 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, glycidide 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:

20 n-Butyl amine	Dodecylamine
Dibutyl amine	Monoethanolamine
2-ethylhexyl amine	Diethanolamine
Di(2-ethylhexyl) amine	Triethanolamine
Diethyl ethanolamine	N-methyl ethanolamine
25 N-butyl diethanolamine	Dimethyl ethanolamine
Di(2-ethylhexyl)ethanolamine	N-ethyl ethanolamine
Monoisopropanolamine	N-ethyl diethanolamine
Diisopropanolamine	N-methyl diethanolamine
30 Triisopropanolamine	n-Amylamine
Dimethyl isopropanolamine	Di-n-amylamine
Dibutyl isopropanolamine	Sec-amylamine
Hexylamine	1,3-bis-ethylaminobutane
Diethylamine	N-ethylbutylamine
35 Heptylamine	2-amino-4-methylpentane
Octylamine	4-amino-2-butanol
Dioctylamine	5-isopropylamino - 1 - pentanol
Decylamine	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 & Hass Company, Philadelphia, Pa., pamphlet entitled "Tertiary-Alkyl Primary Amines."

Other amines include:

2-amino-2-methyl - 1 - propanol	2,2-diethyl-2-amino ethanol
2 - amino-2-methyl-1,3-propanediol	2,2-dimethyl - 2 - amino ethanol
2 - amino-2-ethyl-1,3-propanediol	3-amino-1,2-butanediol
3 - amino-2-methyl-1-propanol	4-amino-1,2-butanediol
2-amino-1-butanol	2-amino-1,3-butanediol
3 - amino - 2,2-dimethyl-1-propanol	4-amino-1,3-butanediol
2 - amino - 2,3-dimethyl-1-propanol	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, diamylamino-

methyl 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 anylphenol, 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. Methyl-glucamine 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 hydrophile 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 3 is concerned with reactions 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 the following:

- (1) Epoxidized soyabean oil
- (2) Epoxidized triacetylated castor oil

These products can be reacted with hydroxylated tertiary monoamines having the reactive hydrogen atom such as triethanolamine, tripropanolamine, tributanolamine, etc. Our preference is to react such compound with basic amino products as differentiated from those having lesser basicity, for example, we prefer ethyl diethanolamine to phenyldiethanolamine.

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 required can act as their own catalyst. As has been pointed out elsewhere catalysts can be added, particularly alkaline catalyst such as sodium methylate, caustic soda, caustic potash, etc. In a general way, the procedure employed in preparing the reaction 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.

It should be noted that an epoxidized glyceride as, for example, epoxidized soyabean oil or the like, may have 2, 3 or more oxirane rings. Assuming the glyceride has 3 oxirane rings it is obvious that the product of reaction is a polyamino compound, at least as long as the glyceride structure is unchanged. Not only is this true, but, as a matter of fact if the monoamine has 2 or more hydroxyl radicals as in the case of ethyl diethanolamine, propyldiethanolamine, or the like, the monoamine may act so as to produce a more complex structure. For instance, if epoxidized soyabean oil containing perhaps just 2 oxirane rings on the outside acyl radicals is reacted mole-for-mole with ethyldiethanolamine one may obtain a sub-resinous or resinous structure in which the size of the molecule is substantially larger than the size of either reactant alone or in mole-for-mole combination. In any event, it is to be noted that polyamino products of reaction are obtainable from monoamino compounds.

The procedure is illustrated by Examples 1a and 15a and by Tables I and II, which present data covering a variety of products from the reactants previously described.

### 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 292 grams of epoxidized soybean oil, 119 grams of triethanolamine and 2 grams of sodium methoxide. The soybean oil contained 4.4% oxirane oxygen, or approximately 3 oxirane rings per one glyceride. The mixture was first stirred for 20 minutes to insure thorough mixing; then heat was gradually applied to bring

its temperature to 155° C. within half an hour. The heating was allowed to continue for 3 hours at 155° C. to complete the reaction. The product was a brown viscous liquid, soluble in xylene and alcohol and was surface active.

#### Example 15a

In the same equipment, set up as used in Example 1a, 270 grams of epoxidized triacetylated castor oil and 80.5 grams of N-butyl diethanolamine were reacted at 160° C. for 3.5 hours in the presence of 1.3 grams of sodium methoxide. The epoxidized oil contained 2.99% oxirane oxygen, or approximately 2 oxirane rings per one triacetylated glyceride. At the end of the reaction the product was an amber colored thick oil. It was soluble in xylene and alcohol.

#### Example 1b

In a 300 ml. 3-necked flask, equipped with a Barrett type distillation receiver, a condenser, a thermometer, and a sealed stirrer, 34.3 grams of diethylene triamine was reacted with 171 grams of the reaction product obtained from Example 1a. The reaction temperature was first maintained at 200° C. for 2 hours, then raised gradually to 240° C. in another hour. When the temperature reached 240° C. water began to collect in the distillation receiver. 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 water was collected. The reaction was considered complete. The distillate consisted of 2.5 mls. of dark yellow oil and 6.7 mls. of water. The product was a soft solid, very dark brown in color. It was soluble in alcohol and

xylene alcohol mixture (1:1), slightly soluble in xylene and water.

#### Example 3b

364 grams of epoxidized soybean oil and 133 grams of ethyl diethanolamine were reacted at 170° C. for 3.5 hours (Example 3a). To 240 grams of this reaction product, 250 grams of 8% sodium hydroxide was added. This heterogeneous mixture was reacted at 98° C. under slight reflux until a clear homogeneous solution was formed. Then it was heated for another hour to insure complete reaction. The total time of reaction was 2.5 hours. The product, 50% in concentration, was a clear yellow gel. It was soluble in alcohol, insoluble in xylene and formed semi-permanent emulsion of water in xylene.

#### Example 10b

In a one-liter beaker, 184 grams of the reaction product obtained from Example 3b, was added with vigorous stirring to 210 grams of 10% barium chloride solution. As soon as the addition was started, a white dense precipitate was formed. The mixture was first stirred at 90-95° C. for 2 hours. Then it was warmed at 50° C. for an hour to allow the precipitate to settle. After settling, the precipitate was washed by decantation, filtered in a fluted filter and dried under vacuum. The dried product was a yellowish white solid, slightly soluble in xylene and alcohol, soluble in hot alcohol or 1:1 xylene alcohol mixture.

As to other examples identified by the suffix "a," see Tables I and II.

As to other examples identified by the suffix "b," see Table III. Note the examples identified by 1b through 10b were obtained from products of the kind described in the two previous tables.

TABLE I

Ex. No.	Oxirane ring containing glyceride	Amt., gms.	Hydroxylated tertiary monoamine	Amt., gms.	Catalyst, NaOCH <sub>3</sub> , gms.	Temp. (max.), ° C.	Time, hrs.	Product of reaction
1a	Epoxidized soybean oil	292	Triethanolamine	110	2	155	3	Brn. visc. liq. sol in xyl. and alcohol.
2a	do.	121	Triisopropanolamine	64	0.93	160	3	Lt. brn. visc. liq. sol. in xyl. and alc.
3a	do.	364	Ethyl diethanolamine	133	2.6	170	3.5	Dk. red visc. liq. xyl. and alc. sol.
4a	do.	121	Dibutyl isopropanolamine	62	0.9	180	3	Amber color visc. liq. xyl. and alcohol sol.
5a	do.	242	Triisopropanolamine	64	1.5	160	3	Brn. very visc. liq. xyl. and alc. sol.
6a	do.	91	Octylamine+4 ethylene oxide	76	0.8	165	4	Dk. red visc. liq. xyl. and alc. sol.
7a	do.	182	N,N'-dihydroxyethylaminebutanol	89	1.3	160	3	Yel. visc. liq. xyl. and alc. sol.
8a	do.	121	N-phenyldiethanolamine	60	0.9	165	3	Amber visc. liq. xyl. and alc. sol.
9a	do.	182	Tris-(hydroxymethyl) aminomethane+10 ethylene oxide	145	1.6	160	4	Lt. yel. visc. liq. xyl. and alc. sol.
10a	do.	182	Tris-(hydroxymethyl) aminomethane+10 ethylene oxide	291	2.4	165	4	Dk. yel. visc. liq. xyl. and alc. sol.
11a	do.	121	Morpholine+5 ethylene oxide	102	1.1	170	3	Brn. visc. liq. xyl. and alc. sol.
12a	do.	182	N-cyclohexyl diethanolamine	101.5	1.4	165	3	Lt. amber visc. liq. xyl. and alc. sol.
13a	do.	121	Triethanolamine+2 glycidide	99	1.1	160	4	Dk. brn. very visc. liq. sol. in alc. slightly sol. in xylene.
14a	do.	121	Dibutylamine+1 glycidide	68	1.0	155	3	Dk. red visc. liq. xyl. and alc. sol.

TABLE II

Ex. No.	Oxirane ring containing glyceride	Amt., gms.	Hydroxylated tertiary monoamine	Amt., gms.	Catalyst, NaOCH <sub>3</sub> , gms.	Temp. (max.), ° C.	Time, hrs.	Product of reaction
15a	Epoxidized triacetylated castor oil	270	N-butyl diethanolamine	80.5	1.3	160	3.5	Amber color thk. oil, xyl. and alc. sol.
16a	do.	270	N,N-dimethylisopropanolamine	51.5	1.2	175	3	Dk. brn. visc. liq. benzene and alc. sol.
17a	do.	270	Triethanolamine	74.5	1.3	155	3	Brn. visc. liq. benzene and alc. sol.
18a	do.	180	N,N-di (hydroxyisopropyl) laurylamine	101	1.1	165	3.5	Dk. red visc. liq. xyl. and alc. sol.
19a	do.	180	Laurylamine+2 glycidide	111	1.2	160	3	Amber visc. liq. xyl. and alc. sol.
20a	do.	135	Abietyl amine+2 ethylene oxide	101	1.0	165	4	Yel. soft solid xyl. and alc. sol.
21a	do.	105	Abietyl amine+2 propylene oxide +12 ethylene oxide	191	1.3	170	4	Dk. yel. visc. liq. xyl. and alc. sol.
22a	do.	135	Ethomeen S/15	125	1.1	160	4	Yel. visc. liq. xyl. and alc. sol.
23a	do.	108	Ethomeen C/25	174	1.2	165	4	Lt. yel. visc. liq. xyl. and alc. sol.
24a	do.	180	Cyclohexylamine + 2 glycidide	82	1.0	160	3.5	Brn. visc. liq. xyl. and alc. sol.
25a	do.	180	Diphenylamine + 4 ethylene oxide	115	1.2	165	3	Lt. brn. visc. liq. alc. and xyl. sol.
26a	do.	180	Alpha-methylbenzyl diethanolamine	64	0.93	165	3	Amber visc. liq. xyl. and alc. sol.
27a	do.	270	N-hydroxyethyl morpholine	66	1.2	160	3.5	Dk. amber visc. liq. xyl. and alc. sol.



TABLE III

Ex. No.	Compd. No.	Amt., gms.	Polyamine or alkali	Amt., gms.	Temp., ° C.	Time, hrs.	Product of reaction
1b.	1a.	171	Diethylene triamine.	34.3	200 200-240 240-310	2 1 1	Very ck. brn. soft sol. Sol. in alc. and xyl. alc. mix. Sltly. sol. in xyl.
2b.	2a.	139	Tetraethylenepentamine.	47.3	200 200-240	2 1	Dk. greenish brn. soft solid sol. in alc. Sltly. sol. in xyl. and water.
3b.	3a.	240	Sodium hydroxide.	20	98	2.5	50% soln. yellow colored gel. Also sol. in alc. Insol. in xyl.
4b.	5a.	115	Tetraethylenepentamine.	47.3	200 200-240 240-310	2 1 1	Blk. pasty solid, sol. in alc. Sltly. sol. in xylene.
5b.	7a.	271	Potassium hydroxide.	28	95	2.5	50% soln. deep yel. gel. Also sol. in alc.
6b.	9a.	327	Sod. hydroxide.	20	95	2.5	50% soln. lt. yel. gel. also sol. in alc.
7b.	11a.	168	Hydroxyethylethylene diamine.	26	200 200-240 240-300	2 1 1	Very dk. amber semisolid, sol. in alc. Sltly. sol. in xylene and water.
8b.	13a.	165	Triethylenetetramine.	36.5	200 200-240 240-300	2 1 1	Very dk. brn. pasty solid. Sol. in alc. Sltly. sol. in xyl.
9b.	1a.	171	Diethylenetriamine+1 formalde- hyde.	38	200 240	2 1	Brn. soft solid, alc. and xyl. sol.
10b.	3b (50% soln.)	184	Barium chloride (10% soln.)	210	90-95	2	Yellowish white solid. Sol. in alc. and xyl. mix. and hot alc. Sltly. sol. in xyl., insol. in wtr.

## PART 4

As previously pointed out, a large proportion of the products described in Part 3 have one or more basic nitrogen atoms. 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 immediately 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

Compd. No.	Amt., gms.	Acid used	Amt., gms.	Isopropanol used, gms.	Water used	Solution concentration, percent
1b.	50	Acetic acid.	5.28	30	25.3	50
2b.	50	do.	8.64	35	23.6	50
2b.	50	Glycolic acid (70%)	15.6	40	25.6	50
7b.	50	do.	3.8	30	23.8	50
7b.	50	Lactic acid.	3.15	30	23.2	50
4b.	50	do.	15	40	25	50
4b.	50	Diglycolic acid.	11.2	35	26.2	50
9b.	50	do.	4.03	30	24	50
9b.	50	p-Toluene sulfonic acid.	10.3	35	25.3	50
8b.	50	do.	19.3	40	29.3	50
8b.	50	Dinonylnaphthalene sulfonic acid.	51.5	101.5		50
1b.	50	do.	40.5	90.5		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 a glyoxalidine or amido glyoxalidine.

An analogous use in which these products are equally satisfactory, is that 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 No. 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 mixtures 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 states:

"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, 1941, 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 afresh 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 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.

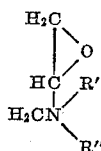
In the use of the herein described products as industrial bactericides and particularly in connection with water flood operations we prefer to use the salts obtained by partial or total neutralization with carboxy acids, particularly monocarboxy acids having not over 6 carbon atoms and preferably a hydroxylated 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 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 3 moles of triethanolamine and then with 3 moles 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, glycidide and methylglycidide. 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 epoxidized soybean oil with 3 moles 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.

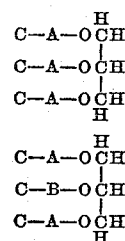
As has been pointed out previously, the reaction product, for example, of 3 moles of triethanolamine and one mole of epoxidized soybean oil can be reacted with a polyamine, such as triethylene tetramine, so as to form an amide which in turn may be heated so as to form an imidazoline.

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 Five, preceding.

Bearing in mind that the ester can also react to form at least a simple amide in the same way that soyabean oil for example could be reacted with 3 moles of polyethyleneamine to give an amino amide, it is obvious the total number of moles of amine that could be reacted with the glyceride is not only the total number of oxirane rings present in the glyceride but also an additional mole for each acyl radical, i. e., 3 moles more.

Restating what has been said previously, one aspect of the present invention is concerned with epoxidized glycerides having at least 2 and not over 3 oxirane rings per glyceride radical and at least one, two or three moles of a tertiary hydroxylated monoamine but, as previously noted, such product can be reacted to form a variety of other compounds by reaction with polyamines or amino amides. Thus, it was stated in the introductory part of the text that the more complicated nature of the reactions involving an epoxidized glyceride instead of an epoxidized ester of a monohydric alcohol are emphasized and of greater importance when one considers preparation of derivatives by further reaction involving some third reactant. Thus, part of which is said hereinafter is analogous to what has been said previously but is concerned from the standpoint of such derivatives by use of an additional reactant such as a polyamine.

For purpose of simplicity what is said hereinafter will be concerned with derivatives of the two predominant types of commercially available epoxidized unsaturated oils, particularly epoxidized soyabean oil and which may be indicated by the following two formulas:



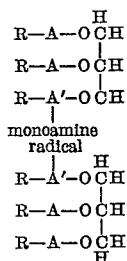
In the first of the formulas it is assumed an oxirane ring appears in all three acyl radicals of the glyceride



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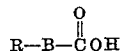
whereas in the second formula it appears in only 2 of the acyl radicals.

It is obvious that one polyhydroxylated tertiary monoamine may unite 2 or more glyceride molecules by supplying a divalent radical. This may be indicated as follows:

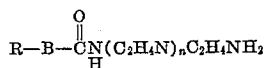


In the above formula A has been changed to A' to indicate that the ring has been opened and the monoamine radical is, of course, the divalent radical obtained from amines of the kind herein described. Needless to say, such cross-linking could involve not only 2 moles of glyceride but 3 or 4 moles.

Since the glyceride, like any other fatty acid equivalent, could act as an acylating agent it is obvious that amides could be formed with some additional reactant such as a polyamine and perhaps the simplest illustration is concerned with the non-saturated acid, or at least an acid which contains no oxirane ring as above depicted and may be indicated thus:



The amide formation from a polyethylene amine would be indicated thus:



in which  $n$  is a small whole number such as 1, 2, 3 or 4.

If one reconsiders the structure of a glyceride wherein the oxirane ring is opened to combine with a hydroxylated tertiary amine perhaps having one or more residual hydroxyl radicals it is obvious a similar amide could be obtained and in fact it would be immaterial whether it were obtained from a monoamine or polyamine. Likewise, an ester could be formed from another mole of a hydroxylated tertiary amine as in the instance of the previous example referred to, i. e., the oleic acid ester of triethanolamine.

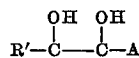
Then, again, of course two moles of an epoxidized glyceride could combine with one mole of ethyl diethanolamine or triethanolamine to give a cross-linked structure. What has been said immediately preceding in regard to the simpler structure showing only one acyl radical would, of course, apply with equal force and effect to a glyceride and it does not require further explanation to indicate the more complicated structure thus obtainable.

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 where the formation of cyclic amidines at a point above the initial reaction temperature and a point below the pyrolysis. The formation of amides of 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 to merely

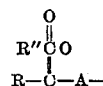
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the reaction involving the rupture of the oxirane ring, subject to certain qualifications.

Actually, the complexities of epoxidized products go further in that when polyethylenic glycerides 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 the radical indicated as R—A may become



Then again if one starts with an unsaturated hydroxylated acid or glyceride, such as castor oil, it is possible to introduce a group like an acetyl group or an oleyl group and have a radical comparable to the following:



Stated another way, although the effort as far as various examples go is simply to react an epoxidized glyceride of the kind described with a hydroxylated tertiary monoamine of the kind described so as to open the oxirane ring and not necessarily go any further, yet it follows that if one tries to get a high yield in such reactions invariably and inevitably some other reaction, i. e., some sort of side reaction such as esterification, may take place. Thus, although the products are described as reaction products involving an oxirane ring and the epoxidized glyceride yet these side reactions may introduce and yield an appreciable amount in some instances of some of the products herein mentioned.

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 monoamine reacted 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 re-forming of an oxirane ring from 2 adjacent hydroxyl groups with ultimate reaction. All of which emphasizes the complexity of the reactions involved, or rather the complexity of possible side reactions when one is attempting to produce mainly and substantially the initial resultant of the polyamine herein described and the epoxidized reactant.

As is obvious, if products of the kind herein described, i. e., derivatives obtained for example from epoxidized soybean oil 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 anaerobic 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 glyceride of 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  $\text{—C—O—C—}$ , 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 naturally-occurring glyceride of a higher fatty acid containing on the average approximately one oxirane ring per fatty acid radical, in which the acyl radical of the glyceride prior to epoxidation 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  $\text{—C—O—C—}$ , 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 naturally-occurring glyceride of a higher fatty acid containing on the average approximately one oxirane ring per fatty acid radical, in which the acyl radical of the glyceride prior to epoxidation 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  $\text{—C—O—C—}$ , which linkage is being characterized by freedom from a carbonyl carbon atom; said product of reaction being hydroxylated and solvent soluble.

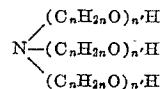
4. Products obtained by reacting under oxyalkylation conditions (A) an epoxidized naturally-occurring glyceride of a higher fatty acid containing on the average approximately one oxirane ring per fatty acid radical, in which the acyl radical of the glyceride prior to epoxidation is free from any residual 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  $\text{—C—O—C—}$ , 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 naturally-occurring glyceride of a higher fatty acid containing on the average approximately one oxirane ring per fatty acid radical, in which the acyl radical of the glyceride prior to epoxidation 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  $\text{—C—O—C—}$ , which linkage is being characterized by freedom from a carbonyl carbon atom; said product of reaction being hydroxylated and solvent soluble.

eride of a higher fatty acid containing on the average approximately one oxirane ring per fatty acid radical, in which the acyl radical of the glyceride prior to epoxidation 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  $\text{—C—O—C—}$ , which linkage is being characterized by freedom from a carbonyl carbon atom; said product of reaction being hydroxylated and solvent soluble.

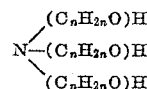
6. Products obtained by reacting under oxyalkylation conditions (A) an epoxidized naturally-occurring glyceride of a higher fatty acid containing on the average approximately one oxirane ring per fatty acid radical, in which the acyl radical of the glyceride prior to epoxidation is free from any residual 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  $\text{—C—O—C—}$ , 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 naturally-occurring glyceride of a higher fatty acid containing on the average approximately one oxirane ring per fatty acid radical, in which the acyl radical of the glyceride prior to epoxidation 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  $\text{—C—O—C—}$ , 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 naturally-occurring glyceride of a higher fatty acid containing on the average approximately one oxirane ring per fatty acid radical, in which the acyl radical of the glyceride prior to epoxidation 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  $\text{—C—O—C—}$ , which linkage is being characterized by freedom from 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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