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REACTION PRODUCTS OF FATTY ACIDS,
DIALKANOLAMINES, AND ALKENYL SUC-
CINIC ACID ANHYDRIDES

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This invention relates, broadly, to organic nitrogen compounds and to corrosion-inhibiting compositions containing them. It is more specifically concerned with the reaction products obtained by reacting fatty acids, dialkanolamines, and alkenyl succinic acid anhydrides; and with corrosion-inhibiting compositions comprising suitable vehicles containing these reaction products.

As is well known to those familiar with the art, whenever machines and devices have been constructed in whole or in part of metals, particularly of ferrous metals, the occurrence of surface corrosion has presented serious problems. For example, farming implements are frequently stored under conditions where they are subject to rusting. Rusting also presents problems in the storage of infrequently used machinery, in the shipment of machined metal parts, such as sewing machine parts and gun barrels, and in the use of structural steel members, such as bridge trusses. These difficulties have been overcome in part by coating the exposed surfaces with paints, greases, oils, and the like. In many cases, however, it has been disadvantageous to use these expedients since it is often necessary to remove such coatings completely before the object is used. Accordingly, recourse has been had to corrosion-inhibiting compositions which can be applied to metal surfaces and which can be removed easily and cheaply.

In the field of lubrication, the rusting of ferrous metal surfaces has been a common occurrence. This has been a serious problem in steam turbines, particularly during the initial operation of new installations. The rusting is most pronounced at points where the clearance between bearing surfaces is very small, such as in the governor mechanism. This is usually caused by water entering the oil supply, as by condensation, and becoming entrained in the oil throughout the circulating system, thereby coming into contact with the ferrous metal surfaces. Manifestly, this constitutes a menace to the operational life of the turbine.

Many materials have been proposed as coating compositions or as addition agents for lubricating oils to inhibit rusting. In United States Letters Patents Nos. 2,124,628; 2,133,734; and 2,279,688, there were disclosed alkenyl succinic acids, and halogenated and/or sulfurized derivatives thereof, as compounds useful in the prevention of corrosion. In these patents, the patentees stipulate that the acids must have at least 16 carbon atoms, and, preferably, 20 carbon atoms per molecule.

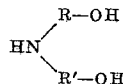
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It has now been found that a new type of corrosion inhibitor can be produced from alkenyl succinic acid anhydrides having any number of carbon atoms in the alkenyl radical thereof. It has now been discovered that useful corrosion inhibitors can be produced by first reacting a fatty acid with a dialkanolamine to produce an intermediate product, and then reacting this intermediate product with an alkenyl succinic acid anhydride.

Accordingly, it is a broad object of this invention to provide novel corrosion inhibitors. Another object is to provide corrosion inhibitors produced from alkenyl succinic acids having any number of carbon atoms in the alkenyl radical. A specific object is to provide corrosion inhibitors by reacting a fatty acid with a dialkanolamine to produce an intermediate product, and then reacting this intermediate product with an alkenyl succinic acid anhydride. A more specific object is to provide substantially neutral vehicles containing such corrosion inhibitors. An important object is to provide mineral lubricating oils containing minor amounts of corrosion inhibitors of the type described hereinbefore. Other objects and advantages of the present invention will become apparent to those skilled in the art from the following detailed description.

Broadly stated, the present invention provides new compositions of matter obtained by reacting a fatty acid containing at least about five carbon atoms per molecule with a dialkanolamine, in a molar proportion of about 1:1, respectively, to produce an intermediate product, and reacting an alkenyl succinic acid anhydride with the intermediate product, in a molar proportion varying between about 1:1, respectively, and about 2:1 respectively. The present invention also provides a substantially neutral vehicle containing between about 0.01 per cent and about 50 per cent, by weight, of these compositions of matter.

In general, the dialkanolamine reactants utilized herein are those compounds having the structural formula,



wherein R and R' are alkylene radicals or hydrocarbon-substituted alkylene radicals, having between about two and about seven carbon atoms per radical. These radicals can be similar or dissimilar radicals. Ordinarily, they will be the same in any given molecule. Since it is more difficult to esterify secondary and tertiary alcohol groups, it is preferable that the alkylene radicals do not

contain secondary or tertiary carbon atoms attached to the hydroxyl group, so as to form secondary and tertiary alcohol groups, respectively. However, because of their greater commercial availability, it is preferred to use diethanolamine and hydrocarbon-substituted diethanolamines. These compounds have the structural formula, $\text{HN}(\text{CH}_2\text{CHROH})_2$, wherein R is a hydrogen atom or a hydrocarbon radical, preferably an alkyl radical. Non-limiting examples of the dialkanolamine reactant are diethanolamine; dipropanolamine; di-iso-propanolamine; 2,2'-iminodibutanol-1; 3,3'-iminodibutanol-1; 4,4'-iminodibutanol-1; di-tert-butanolamine; 3,3'-iminodipentanol-2; 6,6'-iminodihexanol-1; and 7,7'-iminodiheptanol-1.

The dialkanolamines can be prepared by several methods well known to those skilled in the art. One method is by the direct addition reaction between ammonia and an epoxy compound, such as ethylene oxide and propylene oxide. Another, less direct, process comprises the reaction between ammonia and a halogenated alcohol, such as 2-chlorobutanol-1. The halogenated alcohols, in turn, are produced by several methods, for example, by careful halogenation of a dihydric alcohol.

Any fatty acid, or its anhydride or acid halide, can be reacted with the dialkanolamine reactant to produce the intermediate products used in preparing the reaction products of the present invention. Fatty acids containing substituent groups, such as halogen atoms, nitro groups, amino groups, etc., are also applicable herein. The fatty acid reactants can be branched-chain or straight-chain, and saturated or unsaturated aliphatic monocarboxylic acids, and the acid halides and acid anhydrides thereof. Accordingly, when the term "fatty acid" is used herein, it must be clearly understood that the term embraces fatty acids, fatty acid anhydrides, and fatty acid halides, and derivatives thereof. Particularly preferred are the fatty acids having relatively long carbon chain lengths, such as a carbon chain length of between about 8 carbon atoms and about 30 carbon atoms. Non-limiting examples of the fatty acid reactant are valeric acid; α -bromoisovaleric acid; hexanoic acid; hexanoyl chloride; caproic acid anhydride; sorbic acid; aminovaleric acid; amino hexanoic acid; heptanoic acid; heptanoic acid anhydride; 2-ethylhexanoic acid; α -bromo-octanoic acid; decanoic acid; dodecanoic acid; undecylenic acid; tetradecanoic acid; myristoyl bromide; hexadecanoic acid; palmitic acid; oleic acid, heptadecanoic acid; stearic acid; linoleic acid; phenylstearic acid; xylilstearic acid; α -dodecyltetradecanoic acid; arachidic acid; behenic acid; behenolic acid; erucic acid; erucic acid anhydride; erotic acid; selacholeic acid; heptacosanoic acid anhydride; montanic acid; melissic acid; ketotriacontic acid; naphthenic acids; and acids obtained from the oxidation of petroleum fractions.

The fatty acid reactant is reacted with the dialkanolamine reactant in a molar proportion of about 1:1. A molar excess of dialkanolamine reactant, as much as 25 mole per cent or more, can be used advantageously to ensure complete reaction. After the reaction is complete, the excess, unreacted dialkanolamine reactant will be removed by usual means, such as by water washing or by distillation. However, a small excess of dialkanolamine reactant in the intermediate has not been found deleterious to the purpose of producing an effective antirust agent therefrom. In any event, the net result will be an intermediate

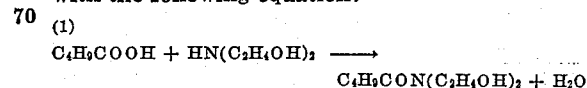
product produced by reacting the reactants in a 1:1 molar proportion.

The temperature at which the reaction between the fatty acid reactant and the dialkanolamine reactant is effected is not too critical a factor. Since the reaction involved appears to be an amide-formation reaction, the general temperature conditions for that reaction, which are well known to those skilled in the art, are applicable. Nevertheless, it is usually preferred to operate at temperatures varying between about 130° C. and about 160° C. It must be strictly understood, however, that the reaction between the fatty acid reactant and the dialkanolamine reactant can be effected at temperatures substantially lower than 130° C. and substantially higher than 160° C., and that this invention is not to be limited to the preferred temperature range.

Water is formed as a by-product of the reaction between the fatty acid reactant and the dialkanolamine reactant. In order to facilitate the removal of this water, to effect a more complete reaction in accordance with the principle of le Chatelier, a hydrocarbon solvent which forms an azeotropic mixture with water can be added to the reaction mixture. Heating is continued with the liquid reaction mixture at the preferred reaction temperature, until the removal of water by azeotropic distillation has substantially ceased. In general, any hydrocarbon solvent which forms an azeotropic mixture with water can be used. It is preferred, however, to use an aromatic hydrocarbon solvent of the benzene series. Non-limiting examples of the preferred solvent are benzene, toluene, and xylene. The amount of solvent used is a variable and non-critical factor. It is dependent on the size of the reaction vessel and the reaction temperature selected. Accordingly, a sufficient amount of solvent must be used to support the azeotropic distillation, but a large excess must be avoided since the reaction temperature will be lowered thereby. Water produced by the reaction can also be removed by operating under reduced pressure. When operating with a reaction vessel equipped with a reflux condenser provided with a water takeoff trap, sufficient reduced pressure can be achieved by applying a slight vacuum to the upper end of the condenser. The pressure is usually reduced to between about 50 millimeters and about 300 millimeters. If desired, the water can be removed also by distillation, while operating under relatively high temperature conditions.

The time of reaction between the fatty acid reactant and the dialkanolamine reactant is dependent on the weight of the charge, the reaction temperature selected, and the means employed for removing the water from the reaction mixture. In practice, the reaction is continued until the formation of water has substantially ceased. In general, the time of reaction will vary between about six hours and about ten hours.

Without any intent of limiting the scope of the present invention, it is postulated that the reaction between the fatty acid reactant and the dialkanolamine reactant results in the formation of a dialkanolamide of the fatty acid. Thus, the reaction between valeric acid and the diethanolamine could proceed, theoretically, in accordance with the following equation:

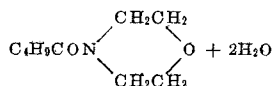
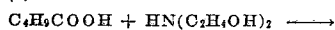


On the other hand, a secondary reaction could take place between the hydroxyl groups of the

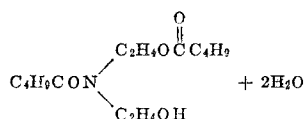
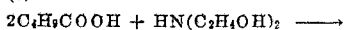
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diethanolamine to form morpholine, or reactions could occur simultaneously between two molecules of the fatty acid and both the amino hydrogen and a hydroxyl group of the diethanolamine, as set forth in the following equations:

(2)

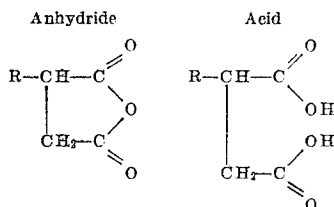


(3)



The reaction of Equation 3 would produce some unreacted diethanolamine in the reaction mixture, but this reaction probably does not occur to an appreciable extent. It will be apparent, however, that, in view of the foregoing, any designation assigned to these intermediate products, other than a definition comprising a recitation of the process of producing them, is not accurately descriptive of them.

Any alkenyl succinic acid anhydride or the corresponding acid is utilizable for the production of the reaction products of the present invention. The general structural formulae of these compounds are:



wherein R is an alkenyl radical. The alkenyl radical can be straight-chain or branched-chain; and it can be saturated at the point of unsaturation by the addition of a substance which adds to olefinic double bonds, such as hydrogen, sulfur, bromine, chlorine, or iodine. It is obvious, of course, that there must be at least two carbon atoms in the alkenyl radical, but there is no real upper limit to the number of carbon atoms therein. In order to produce the reaction products of this invention, however, an alkenyl succinic acid anhydride or the corresponding acid must be used. Succinic acid anhydride and succinic acid are not utilizable herein. For example, the reaction product produced by reacting an intermediate product with succinic acid anhydride is not an effective rust inhibitor. Although their use is less desirable, the alkenyl succinic acids also react, in accordance with this invention, to produce satisfactory reaction products. It has been found, however, that their use necessitates the removal of water formed during the reaction, and also, often causes undesirable side reactions to occur to some extent. Nevertheless, the alkenyl succinic acid anhydrides and the alkenyl succinic acids are interchangeable for the purposes of the present invention. Accordingly, when the term "alkenyl succinic acid anhydride," is used herein, it must be clearly understood that it embraces the alkenyl succinic acids as well as their anhydrides, and the derivatives thereof in which the olefinic double bond has been saturated as set forth hereinbefore. Non-limiting examples of

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the alkenyl succinic acid anhydride reactant are ethenyl succinic acid anhydride; ethenyl succinic acid, ethyl succinic acid anhydride; propenyl succinic acid hydride; sulfurized propenyl succinic acid anhydride; butenyl succinic acid; 2-methylbutenyl succinic acid anhydride; 1,2-dichloropentenyl succinic acid anhydride; hexenyl succinic acid anhydride; hexyl succinic acid; sulfurized 3-methyl pentenyl succinic acid anhydride; 2,3-dimethylbutenyl succinic acid anhydride; 3,3-dimethylbutenyl succinic acid; 1,2-dibromo-2-ethyl-butyl succinic acid; heptenyl succinic acid anhydride; 1,2-diiodooctyl succinic acid; octenyl succinic acid anhydride; octenyl succinic acid 15 2-methylheptenyl succinic acid anhydride; 4-ethylhexenyl succinic acid; diisobutenyl succinic acid anhydride; 2-isopropylpentenyl succinic acid anhydride; nonenyl succinic acid anhydride; 2-propylhexenyl succinic acid anhydride; decenyl succinic acid; decenyl succinic acid anhydride; 20 5-methyl-2-isopropylhexenyl succinic acid anhydride; 1,2-dibromo-2-ethyl-octenyl succinic acid anhydride; decyl succinic acid anhydride; undecenyl succinic acid anhydride; 1,2-dichloroundecenyl succinic acid; 3-ethyl-2-t-butylpentenyl succinic acid anhydride; triisobutenyl succinic acid anhydride; dodecenyl succinic acid anhydride; dodecenyl succinic acid; 2-propynoneyl succinic acid anhydride; 3-butyl-octenyl succinic acid anhydride; tridecenyl succinic acid anhydride; tetradecenyl succinic acid anhydride; hexadecenyl succinic acid anhydride; sulfurized octadecenyl succinic acid; octadecyl succinic acid anhydride; 1,2-dibromo-2-methylpentadecenyl succinic acid anhydride; 8-propylpentadecyl succinic acid anhydride; eicosenyl succinic acid anhydride; 1,2-dichloro-2-methylnonadecenyl succinic acid anhydride; 2-octyldodecenyl succinic acid; 1,2-diiodotetracosenyl succinic acid anhydride; hexacosenyl succinic acid; hexacosenyl succinic acid anhydride; and hentriacontenyl succinic acid anhydride.

The methods of preparing the alkenyl succinic acid anhydrides are well known to those familiar with the art. The most feasible method is by the reaction of an olefin with maleic acid anhydride. Since relatively pure olefins are difficult to obtain, and when thus obtainable, are often too expensive for commercial use, alkenyl succinic acid anhydrides are usually prepared as mixtures by reacting mixtures of olefins with maleic acid anhydride. Such mixtures, as well as relatively pure anhydrides, are utilizable herein.

The alkenyl succinic acid anhydride reactant is reacted with the intermediate product in a proportion varying between about one mole and about two moles of alkenyl succinic acid anhydride reactant for each mole of dialkanolamine reactant used in the preparation of the intermediate product.

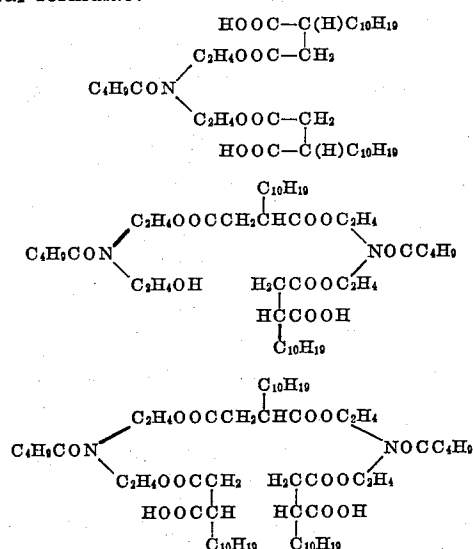
The reaction between the alkenyl succinic acid anhydride reactant and the intermediate product takes place at any temperature ranging from ambient temperatures and upwards. This reaction is apparently a monoester formation reaction effected by the well known addition of the anhydride group to an alcohol group. This addition proceeds at any temperature, but temperatures of about 115-130° C. are preferred. When an alkenyl succinic acid is used, water is formed. Therefore, in this case, the reaction temperature, preferably, should be somewhat higher.

The reaction between the alkenyl succinic acid anhydride reactant and the intermediate product proceeds smoothly in the absence of solvents, at

atmospheric pressure. However, the occurrence of undesirable side reactions is minimized when a solvent is employed. Since a small amount of water is usually formed also when an alkenyl succinic acid anhydride is used in the reaction, the solvent employed is preferably one which will form an azeotropic mixture with water. These solvents have been discussed fully, heretofore, in conjunction with the reaction between the fatty acid reactant and the dialkanolamine reactant. The same solvents and the same methods of using them are applicable to the reaction between the intermediate product and the alkenyl succinic acid anhydride reactant. For example, products of this invention have been prepared at temperatures varying between about 115° C. and about 130° C., using an aromatic hydrocarbon solvent of the benzene series.

The time of reaction is dependent on the size of the charge, the reaction temperature selected, and the means employed for removing any water from the reaction mixture. Ordinarily, the addition reaction of the anhydride reactant is substantially complete within a few minutes. In order to ensure complete reaction, however, it is preferred to continue heating for several hours. When water is formed during the reaction, as when an alkenyl succinic acid is used, the completion of the reaction is indicated by a substantial decrease in the formation of water. In general, the reaction time will vary between several minutes and about ten hours.

Without any intent of limiting the scope of the present invention, it is postulated that the reaction products contemplated herein are ester-amide products of the dialkanolamine reactant having at least one free carboxylic acid group. For example, when the theoretical intermediate product of Equation 1 is reacted with two moles of decenyl succinic acid anhydride the reaction product can contain any, or several, products, such as those set forth in the following structural formulae:



or isomers thereof. The reaction products probably contain other substances. Accordingly, these reaction products are most accurately defined by a definition comprising a recitation of the process by which they are produced. In the interests of brevity, they are defined by reciting the reactants and the number of moles of each which are used. For example the reaction product produced by reacting one mole of valeric acid with

one mole of diethanolamine to produce an intermediate product, which is then reacted with two moles of decenyl succinic acid anhydride may be defined as valeric acid+diethanolamine+decenyl succinic acid anhydride (1:1:2).

In addition to the products described in the illustrative examples, set forth hereinafter, non-limiting examples of the reaction products contemplated herein are those produced by reacting the following combinations of reactants: valeric acid+diethanolamine+ethenyl succinic acid anhydride (1:1:2); α -bromoisovaleric acid+di-propanolamine+ethyl succinic acid (1:1:1.8); hexanoic acid+di-iso-propanolamine+propenyl succinic acid anhydride (1:1:1); hexanoyl chloride+2,2'-iminobutanol-1+sulfurized propenyl succinic acid anhydride (1:1:2); caproic acid anhydride+3,3'-iminodibutanol-1+butenyl succinic acid (1:2:4); sorbic acid+4,4'-iminodibutanol-1+1,2-dichloropentyl succinic acid anhydride (1:1:1.5); aminovaleric acid+di-tert-butanolamine+hexenyl succinic acid (1:1:2); amino-hexanoic acid+3,3'-iminodipentanol-2+sulfurized 3-methylpentenyl succinic acid anhydride (1:1:1.2); heptanoic acid+6,6'-iminodihexanol-1+2,3-dimethylbutenyl succinic acid anhydride (1:1:2); heptanoic acid anhydride+7,7'-iminodihexanol-1+1,2-dibromo-2-ethylbutyl succinic acid (1:2:2); 2-ethylhexanoic acid+diethanolamine+heptenylsuccinic acid anhydride (1:1:1.7); α -bromooctanoic acid+dipropanolamine+1,2-diiodooctyl succinic acid (1:1:1); decanoic acid+di-iso-propanolamine+octenyl succinic acid anhydride (1:1:2); dodecanoic acid+2,2'-iminodibutanol-1+2-methylheptenyl succinic acid anhydride (1:1:1); undecylenic acid+3,3'-iminodibutanol-1+4-ethylhexenyl succinic acid (1:1:2); tetradecanoic acid+4,4'-iminodibutanol-1+diisobutenyl succinic acid anhydride (1:1:2); myristoyl bromide+di-tert-butanolamine+2-propylhexenyl succinic acid anhydride (1:1:1); hexadecanoic acid+3,3'-iminodipentanol-2+decenyl succinic acid (1:1:1.6); palmitic acid+6,6'-iminohexanol-1+decenyl succinic acid anhydride (1:1:2); oleic acid+7,7'-iminodihexanol-1+undecenyl succinic acid anhydride (1:1:1.4); heptadecanoic acid+diethanolamine+1,2-dichloroundecyl succinic acid (1:1:2); stearic acid+dipropanolamine+dodecenyl succinic acid (1:1:1.8); linoleic acid+di-iso-propanolamine+2-propylnonenyl succinic acid anhydride (1:1:1); xyllyl-stearic acid+2,2'-iminodibutanol-1+triisobutenyl succinic acid anhydride (1:1:2); α -dodecyl tetradecanoic acid+3,3'-iminodibutanol-1+hentriacontenyl succinic acid anhydride (1:1:1); arachidic acid+4,4'-iminodibutanol-1+hexacosenyl succinic acid anhydride (1:1:2); behenic acid+di-tert-butanolamine+hexacosenyl succinic acid (1:1:1.2); behenolic acid+3,3'-iminodipentanol-2+1,2-diiodotetracosenyl succinic acid anhydride (1:1:2); erucic acid+6,6'-iminodihexanol-1+2-octyldodecenyl succinic acid anhydride (1:1:1.4); erucic acid anhydride+7,7'-iminodihexanol-1(1:2:2.8); cerotic acid+diethanolamine+eicosenyl succinic acid anhydride (1:1:2); selacholeic acid+dipropanolamine+1,2-dibromo-2-methylpentadecenyl succinic acid anhydride (1:1:1); heptacosanoic acid anhydride+di-iso-propanolamine+octadecyl succinic acid anhydride (1:2:4); montanic acid+2,2'-iminodibutanol-1 (1:1:1); melissic acid+di-tert-butanolamine+sulfurized octadecenyl succinic acid anhydride (1:1:2); and ketotriacontic acid+7,7'-iminodihexanol-1+hexadecenyl succinic acid anhydride (1:1:2).

The following specific examples are for the purpose of illustrating the present invention, and of demonstrating the advantages thereof. It must be strictly understood that this invention is not to be limited to the particular reactants and molar proportions employed, or to the operations and manipulations described therein. A wide variety of other reactants and molar proportions, as set forth hereinbefore, may be used, as those skilled in the art will readily understand.

The alkenyl succinic acid anhydrides used in the following specific examples are commercial mixtures of alkenyl succinic acid anhydrides in which the number of carbon atoms in the alkenyl radical varies between specified limits. The C₆₋₈ASAA is a mixture of hexenyl, heptenyl, and octenyl succinic acid anhydrides; C₈₋₁₀ASAA is a mixture of octenyl, nonenyl, and decenyl succinic acid anhydrides; and C₁₀₋₁₂ASAA is a mixture of decenyl, undecenyl, and dodecenyl succinic acid anhydrides.

PREPARATION OF INTERMEDIATE PRODUCTS

Example 1

Stearic acid (1 mole) (284 grams) and diethanolamine (1 mole) (105 grams) were weighed into a reaction vessel provided with a mechanical stirrer, a thermometer, and a condenser device (reflux take-off) for removing water from the reaction mixture as it is evolved in an azeotropic mixture of water and xylene. The reactants were heated to 150° C. Then, the reflux take-off was filled with xylene, and 100 milliliters of xylene were gradually added to the reaction mixture. The initial xylene refluxing occurred at a 155° C. pot temperature. After 3.25 hours, the pot temperature which sustained a xylene reflux was 168° C. The amount of water collected from the reaction was 23-24 milliliters (theory is 18 milliliters for amide formation). Xylene was removed under reduced pressure, with the reactants at 100° C. The residue thus obtained, was a wax-like, tan-colored solid having a neutralization number of 0.15.

Example 2

Oleic acid (1 mole) (282 grams) and diethanolamine (1.2 moles) (126 grams) were weighed into a reaction vessel provided with a mechanical stirrer, a thermometer, and a reflux take-off. The reflux take-off was filled with xylene, and xylene (200 milliliters) was added to the reaction vessel. The reaction mixture was heated to 145° C., whereupon refluxing commenced. Refluxing was continued at 145-150° C. for seven hours. A total of 25.5 milliliters of water was collected (theory for amide formation is 18 milliliters). The reaction mixture was cooled to 95° C. Then 75 milliliters of distilled water and 10 milliliters of t-butyl alcohol were added. The entire mixture was stirred for one minute. After separation of layers had occurred, the lower water layer was drawn off through a capillary tube which was connected to a source of light vacuum. The xylene solution of intermediate (i.e., the reaction mixture) was washed four more times in the manner described hereinabove, using the following wash mixtures:

- (1) 75 ml. water+20 ml. t-butyl alcohol
- (2) 75 ml. water+50 ml. t-butyl alcohol
- (3) 75 ml. water+20 ml. t-butyl alcohol
- (4) 100 ml. water+no ml. t-butyl alcohol

The t-butyl alcohol was used to provide a more

efficient separation of the aqueous and the organic layers. The diethanolamine-free xylene solution of intermediate product was filtered and the xylene was removed at a pot temperature of 95° C., under reduced pressure. The liquid intermediate product had a neutralization number of 1.3.

Example 3

Stearic acid (0.344 mole) (95 grams) and diethanolamine (0.419 mole) (44 grams) were weighed into a reaction vessel equipped with a mechanical stirrer, a thermometer, and a reflux take-off. The reactants were heated to 120° C. Then, the reflux take-off was filled with xylene, and xylene (100 milliliters) was added to the reaction mixture. Refluxing was maintained, for 4.75 hours, at a pot temperature of 140-151° C. A total of 8.7 milliliters of water was collected. The reaction mixture was cooled to 95° C. and washed four times with the following distilled water mixtures:

- (1) 50 ml. water+20 ml. t-butyl alcohol
- (2) 75 ml. water
- (3) 50 ml. water
- (4) 50 ml. water

The diethanolamine-free xylene solution of intermediate product was filtered, and topped free of xylene under reduced pressure, at a pot temperature of 100° C. The wax-like, tan-colored, solid product has a neutralization number of 0.9.

Example 4

An intermediate reaction product was produced, in the manner described in Example 1, using valeric acid and diethanolamine in a molar proportion of 1:1, respectively.

Example 5

An intermediate reaction product was produced, in the manner described in Example 2, using caprylic acid and diethanolamine, in a molar proportion of 1:1.2, respectively.

Example 6

An intermediate product was prepared, in the manner described in Example 1, using dodecanoic acid and diethanolamine, in a molar proportion of 1:1, respectively.

Example 7

An intermediate reaction product was prepared in the manner described in Example 1, using oleic acid and di-iso-propanolamine, in a molar proportion of 1:1, respectively.

PREPARATION OF THE FINAL REACTION PRODUCT

Example 8

A portion, 37.1 grams (0.1 mole) of the intermediate product described in Example 1, and 59 grams (0.2 mole) of C₁₀₋₁₂ASAA were placed in a reaction vessel provided with a mechanical stirrer, a thermometer, and a reflux take-off. The reaction mixture was heated at 115-120° C. for 0.5 hour. Then, the reflux take-off was filled with benzene, and benzene (30 milliliters) was added to the reaction mixture. Refluxing was maintained for one hour, with the flask contents at 115° C. No water was collected. The flask contents were diluted with an additional 70 milliliters of benzene. The resultant solution was filtered and benzene was removed by evaporation

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on the steam bath. The liquid reaction product had a neutralization number of 129.

Example 9

A portion, 36.9 grams (0.1 mole), of the intermediate product described in Example 2 and 29.5 grams (0.1 mole) of C₁₀₋₁₂ASAA were placed in a reaction vessel equipped with a mechanical stirrer, a thermometer, and a reflux take-off. The reaction mixture was heated at 115–125° C. for two hours. Some water evolved. Benzene was added so that refluxing occurred at a pot temperature of 128–129° C. After 1.5 hours, 0.8 milliliter of water had been collected. The reaction was stopped and the benzene was removed under reduced pressure. The liquid reaction product had a neutralization number of 48.

Example 10

A portion, 36.9 grams (0.1 mole) of the intermediate product described in Example 2 and 44.4 grams (0.15 mole) of C₁₀₋₁₂ASAA were placed in a reaction vessel and heated at 115–125° C., for two hours. No solvent was used. The liquid reaction product had a neutralization number of 109.

Example 11

A portion, 37.1 grams (0.1 mole) of the intermediate product described in Example 3 and 41.9 grams (0.2 mole) of C₆₋₈ASAA were heated together at 120–125° C. for 2.75 hours. The liquid reaction product had a neutralization number of 158.

Example 12

C₈₋₁₀ASAA and the intermediate product described in Example 3 were reacted in a molar proportion of 2:1, respectively, at 125–130° C. for 1.5 hours, using the procedure of Example 10. The reaction product had a neutralization number of 145.

Example 13

C₁₀₋₁₂ASAA and the intermediate product described in Example 3 were reacted in a molar proportion of 1.4:1, respectively, at 115–118° C. for 2.5 hours, using the procedure of Example 10. The reaction product had a neutralization number of 95.

Example 14

C₁₀₋₁₂ASAA and the intermediate product described in Example 3 were reacted in a molar proportion of 1.6:1, respectively, at 115–118° C., for 2.5 hours, using the procedure of Example 10. The reaction product had a neutralization number of 112.

Example 15

C₁₀₋₁₂ASAA and the intermediate product described in Example 3 were reacted in a molar proportion of 1.8:1, respectively, at 110–120° C., for 2.5 hours, using the procedure of Example 10. The reaction product had a neutralization number of 123.

Example 16

C₁₀₋₁₂ASAA and the intermediate product described in Example 3 were reacted in a molar proportion of 1.9:1, respectively, at 110–120° C., for 2.5 hours, using the procedure of Example 10. The reaction product had a neutralization number of 127.

Example 17

C₁₀₋₁₂ASAA and the intermediate product described in Example 2 were reacted, in a molar

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proportion of 2:1, respectively, at 124° C., for two hours, using the procedure of Example 10. The reaction product had a neutralization number of 131.

Example 18

C₁₀₋₁₂ASAA and the intermediate product described in Example 2 were reacted in a molar proportion of 1.9:1, respectively, at 120–132° C., for 2.25 hours, using the procedure of Example 10. The reaction product had a neutralization number of 123.

Example 19

C₁₀₋₁₂ASAA and the intermediate product described in Example 4 were reacted in a molar proportion of 2:1, respectively, at 123–125° C., for 1.75 hours, using the procedure of Example 10. The reaction product had a neutralization number of 159.

Example 20

C₁₀₋₁₂ASAA and the intermediate product described in Example 5 were reacted in a molar proportion of 2:1, respectively, at 120–130° C., for 1.5 hours, using the procedure of Example 10. The reaction product had a neutralization number of 166.

Example 21

C₁₀₋₁₂ASAA and the intermediate product described in Example 6 were reacted in a molar proportion of 2:1, respectively, at 122° C., for two hours, using the procedure of Example 10. The reaction product had a neutralization number of 141.

Example 22

C₁₀₋₁₂ASAA and the intermediate product described in Example 7 were reacted in a molar proportion of 2:1, respectively, at 120–125° C., for 1.5 hours, using the procedure of Example 10. The reaction product had a neutralization number of 130.

Example 23

A reaction product was prepared by reacting succinic acid anhydride and the intermediate product described in Example 2, in a molar proportion of 2:1, respectively, at 115–119° C., for two hours, using a toluene reflux in the manner described in Example 8. The reaction product had a neutralization number of 152.

In order to demonstrate the outstanding properties of the reaction products of this invention, typical rust test data and emulsion test data were obtained for mineral lubricating oil blends containing the reaction products described in the examples. Pertinent test data are set forth in Table I.

The mineral oil used in these tests was a blend of solvent-refined, Midcontinent residual stock with a solvent-refined, Midcontinent (Rodessa) distillate stock. It had a specific gravity of 0.872, a flash point of 445° F., and a Saybolt Universal viscosity of 407.7 seconds at 100° F. This mineral lubricating oil is suitable for use in steam turbines. Unless otherwise indicated in the tables, the test oils contained 0.2 per cent by weight of 2,6-di-*t*-butyl-4-methyl phenol and 0.1 per cent by weight of phenyl- α -naphthylamine, both well known anti-oxidants.

The test method used to distinguish the rusting characteristics of lubricating oil blends was the ASTM test D665-44T for determining "Rust Preventing Characteristics of Steam Turbine Oils in Presence of Water," in which synthetic sea water was used as well as distilled water. The

synthetic sea water contained 25 grams of sodium chloride, 11 grams of magnesium chloride hexahydrate, 4 grams of sodium sulfate, and 1.2 grams of calcium chloride per liter. In this test a cylindrical polished steel specimen is suspended and soaked in 300 cubic centimeters of the oil under test at 140° F. for thirty minutes. Thirty cubic centimeters of synthetic sea water (or distilled water) are added and the mixture is stirred at 1000 R. P. M. After 48 hours, the steel specimen is removed and examined for evidence of rust on the portion of the specimen which hangs in the oil. In the tables, rust test results are given in terms of per cent of exposed metal surface which has rusted. The complete rusting which is evident when uninhibited base oils are tested is taken as 100 per cent.

The emulsion test used is the emulsion test for lubricating oils, Federal Stock Catalog, section IV, part 5, Federal Specifications VV-L-791b, February 19, 1942. In test method 320.13, 40 cubic centimeters of oil and 40 cubic centimeters of emulsant in a 100-cubic centimeter graduated cylinder are stirred with a paddle at 1500 R. P. M., for 5 minutes, at 130° F. Separation of the emulsion is observed while the cylinder is kept at 130° F. The figures in the tables show the number of minutes at which there is no continuous layer of emulsion between the oil and the emulsant, or the number of cubic centimeters of emulsion persisting at the end of thirty minutes.

sirable emulsion characteristics to the oil. Some of these reaction products have poorer emulsion characteristics than others. Accordingly, at some concentration the emulsion characteristics of the blend may not be desirable. In such an event, however, a demulsifying agent, of which several are well known to the art, can be incorporated in the blend to improve the emulsion characteristics thereof. It must be noted that the intermediate product of Example 2 was entirely ineffective in preventing rusting in the presence of sea water and that it was very unsatisfactory in the presence of distilled water. Likewise, the reaction product made with succinic acid anhydride (Example 23) was not satisfactory, demonstrating the necessity of the alkenyl group in the succinic acid anhydride molecule.

Example 24

The rusting characteristics of a mineral lubricating oil containing the product of Example 8 were further tested, along with the oxidation characteristics thereof, by means of the ASTM Test Method D943-47T. In accordance with this test, the oil and distilled water are placed in a large test tube, which is maintained at 203° F. A polished copper-iron catalyst coil is inserted into the oil, but it does not extend into the water layer. Oxygen gas is passed through the water and oil at the rate of three liters per hour throughout the 1000-hour test period. The test

TABLE

Prod. of Example	Reactants			Proportion ASAA/Intermediate	Percent Conc. in Oil	Rust Test, Percent Metal Rusted		Emulsion Test Break, Min.	
	Fatty Acid	Amine	ASAA ¹			Sea Water	Dist. Water	Dist. Water	1% NaCl
9.....	(Uninhibited Oil)								
10.....	Oleic	Diethanolamine	C ₁₀₋₁₂	1:1	0.2	100	100	2	1
18.....	do.	do.	C ₁₀₋₁₂	1.5:1	0.1	0	0	8	25
17.....	do.	do.	C ₁₀₋₁₂	1.9:1	0.05	0	0	29	23
8.....	Stearic	do.	C ₁₀₋₁₂	2:1	0.03	0	0	25	23
11.....	do.	do.	C ₁₀₋₁₂	2:1	0.02	0	0	25	15
12.....	do.	do.	C ₁₀₋₁₂	2:1	0.05	0	0	25	15
13.....	do.	do.	C ₁₀₋₁₂	2:1	0.03	0	0	25	15
14.....	do.	do.	C ₁₀₋₁₂	2:1	0.02	0	0	25	15
15.....	do.	do.	C ₁₀₋₁₂	2:1	0.01	0	0	25	15
16.....	do.	do.	C ₁₀₋₁₂	2:1	0.05	0	0	25	15
19.....	Valeric	do.	C ₁₀₋₁₂	1.4:1	0.05	0	0	24	24
20.....	Caprylic	do.	C ₁₀₋₁₂	1.5:1	0.03	0	0	29	25
21.....	Dodecanoic	do.	C ₁₀₋₁₂	1.8:1	0.05	0	0	25	20
22.....	Oleic	Diisopropanolamine	C ₁₀₋₁₂	1.9:1	0.05	0	0	25	19
23.....	do.	Diethanolamine	C ₁₀₋₁₂	2:1	0.05	100	100	22	20
24.....	do.	do.	C ₁₀₋₁₂	2:1	0.01	0	0	23	16
25.....	do.	do.	C ₁₀₋₁₂	2:1	0.08	0	0	25	18
26.....	do.	do.	C ₁₀₋₁₂	2:1	0.01	0	0	25	18
27.....	do.	do.	C ₁₀₋₁₂	2:1	0.075	0	0	25	18
28.....	do.	do.	C ₁₀₋₁₂	2:1	0.25	100	15	8	9
29.....	do.	do.	C ₁₀₋₁₂	2:1	0.05	100	15	8	9

¹ ASAA is alkenyl succinic acid anhydride.

From the data set forth in the tables, it will be apparent that good antirust characteristics are imparted to lubricating oils which contain the reaction products of the present invention. To be completely acceptable for use in a turbine oil, an additive, preferably, should not impart undesirable emulsion characteristics thereto. It will be apparent from the emulsion test data given in the table that, as a class, the reaction products of this invention do not impart unde-

oil defined hereinbefore containing by weight 0.05 per cent of the product of Example 8, 0.2 per cent 2,6-di-t-butyl-4-methylphenol, and 0.1 per cent phenyl- α -naphthylamine was not oxidized in this test as evidenced by an N. N. of 0.04. The catalyst coil showed only a few spots of rust at the top thereof. When the oil is tested without the antirust additive the catalyst coil rusts within as short a period of time as twenty-four hours.

PREVENTION OF ATMOSPHERIC CORROSION

In order to evaluate the new reaction products as coating compounds for the prevention of atmospheric corrosion, a test was run as follows: Two polished steel specimens were coated with the reaction product of Example 11 by dipping them in a two per cent by weight solution of the product in benzene. Likewise, two additional specimens were coated with the reaction product of Example 19, and two more were coated with the reaction product of Example 18. Two other specimens were left uncoated, as the controls. These specimens were suspended in the chemical laboratory, exposed to the various vapors and fumes ordinarily found therein. After 24 hours of such exposure, none of the specimens showed visible signs of corrosion. Then, each specimen was immersed in distilled water for about 30 seconds, by raising a separate beaker of distilled water under each one. After one hour this procedure was repeated. The control specimens showed a light surface rusting about five minutes after this treatment. The coated specimens remained free of corrosion. The immersion process was repeated (considering initial immersion time as zero) at 20, 22, 24, 26, 42, 44, 46, 48, and 50 hours. Considerable more rusting was noted on the control specimens after each immersion, but, the coated specimens were still free of any trace of corrosion.

In the foregoing specific illustrative examples, the effectiveness of the reaction products for the prevention of rust in lubricated systems and for the prevention of atmospheric corrosion has been demonstrated. In addition to the use in turbine oils or as coating agents, these reaction products are utilizable for numerous purposes. They can be added to a wide variety of vehicles to produce improved compositions. They can be dissolved in the vehicle or they can be dispersed therein, in the form of suspension or emulsions.

The vehicles can be liquids or plastics, the basic requirement being that they must be spreadable over metal surfaces. Spreading may be accomplished by immersion, flooding, spraying, brushing, trowelling, etc. Additionally, the vehicle should be substantially neutral. It can be oleaginous, i. e., substantially insoluble in water, or it can be aqueous. Aqueous vehicles include aqueous solutions of liquids, such as alcohol-water mixtures and the like. Oleaginous vehicles can be hydrocarbon materials, such as mineral oils and hydrocarbon solvents, or non-hydrocarbon materials, such as fatty oils and fats.

Non-limiting examples of suitable vehicles for the additives of this invention are mineral lubricating oils of all grades; gasolines and other light petroleum products, such as fuel oil; water, alcohols, such as ethanol isopropanol, butanol, cyclohexanol, methylcyclohexanol, octanol, decanol, dodecanol, hexadecanol, octadecanol, oleyl alcohol, benzyl alcohol, etc.; phenols; glycols, such as ethylene glycol, propylene glycol, butylene glycol, glycerol, etc.; ketones, such as acetone, methyl ethyl ketone, dipropyl ketone, cyclohexanone, etc.; keto alcohols, such as benzoin; ethers, such as diethyl ether, dipropyl ether, diethylene dioxide, dichloro diethyl ether, diphenyl oxide, diethylene glycol, triethylene glycol, ethylene glycol monobutyl ether, etc.;

neutral esters, such as ethyl acetate, butyl propionate, cresyl acetate, dodecyl acetate, ethyl maleate, butyl stearate, tridecyl phosphate, tributyl trihiophosphate, triamyl phosphite, etc.; petroleum waxes, such as slack wax and paraffin wax; natural waxes, such as carnauba wax, Japan wax, beeswax, etc.; natural fats and oils, such as sperm oil, tallow, cottonseed oil, castor oil, linseed oil, tung oil, soybean oil, oiticica oil, tar oil, oleo oil, etc.; hydrocarbons and halogenated hydrocarbons, such as butanes, chlorinated hexanes, octanes, brominated decanes, dodecanes, Freon, eicosane, benzene, toluene, xylenes, cumene, indene, alkyl naphthalenes, etc.; greases; asphalts; chlorinated petroleum fractions, such as chlorowax; and paints, varnishes and the like.

As those skilled in the art will readily appreciate, the applications of the compositions of the present invention are many. Lubricating oils of all types usually permit corrosion of metal surfaces. This poses a problem in the lubrication of all types of engines, particularly steam turbines. Lubricating oils containing the reaction products of this invention are effectively inhibited against such corrosion. Diesel fuels containing these additives will have less tendency to corrode injection nozzles. Steam cylinder oils and cutting oils can be inhibited against corrosive tendencies by the addition thereto of these new additives, particularly the more emulsive types. Greases can be inhibited likewise. Additionally, the more emulsive products of this invention can be substituted in whole or in part, for the emulsifying agents commonly used in compounding greases, cutting oils, steam cylinder oils, etc. Hydraulic systems can be protected against corrosion by using hydraulic fluids containing the additives of the present invention.

The storage of infrequently used machinery, and the shipment and storage of metal shapes and metal parts, such as machined sewing machine parts or gun parts, present corrosion problems. Such corrosion can be prevented by treating them with slushing oils containing the additives of this invention, by coating them with organic solvent solutions or dispersions of these additives, such as the benzene solutions described hereinbefore, or by treating the surfaces thereof with dispersions of these additives in water. Corrosive tendencies of coolants and antifreeze solutions or mixtures, such as those used as coolants in internal combustion engines, can be reduced by addition thereto of the reaction products of this invention. Such antifreezes include water, alcohol-water, glycols, glycol-water, etc. When gasoline and other fuels are stored in drums or tanks, water often enters the storage space, as by "breathing," and corrodes the inner surfaces thereof. This can be prevented through the use of the additives contemplated herein.

Relatively more permanent corrosion-preventive coatings can be produced by the application to metal surfaces of paints, and the like, containing the additives of this invention. Vehicles utilizable for this purpose are paints, varnishes, lacquers, drying oils, asphalt roofing compositions, and the like.

The amount of the reaction products which are added to a vehicle to produce a composition in accordance with this invention varies between about 0.01 per cent and about 50 per cent by weight, depending on the specific use contemplated and on the specific reaction product selected. Generally, it is sufficient to use an

amount varying between about 0.01 per cent and about 10 per cent. However, smaller amounts, as low as about 0.005 per cent will be effective in some cases. Likewise, amounts up to as much as about 50 per cent are required when the vehicle contains resinous bodies, or when the reaction product is also used as an emulsifier, such as in a steam cylinder oil.

Other substances in addition to the reaction products of this invention can be added to the compositions contemplated herein to impart other desirable properties thereto. For example, there may be added antioxidants, pour point depressants, V. I. improvers, antidetonants, cetane number improvers, emulsifiers, thinners, driers, etc.

Although the present invention has been described with preferred embodiments, it is to be understood that modifications may be resorted to without departing from the spirit and scope thereof, as those skilled in the art will readily understand. Such variations and modifications are considered to be within the purview and scope of the appended claims.

What is claimed is:

1. A corrosion-inhibiting composition which comprises a substantially neutral vehicle containing between about 0.01 per cent and about 50 per cent, by weight, of the final reaction product obtained by initially reacting a fatty acid containing at least about five carbon atoms per molecule with a dialkanolamine having between two and seven carbon atoms per alkanol radical, in a molar proportion of about 1:1, respectively, at a temperature of between about 130° C. and about 160° C. to produce an intermediate product, and then reacting an alkenyl succinic acid anhydride with said intermediate product, in a molar proportion varying between about 1:1, respectively, and about 2:1, respectively, at a temperature of between about 110° C. and about 130° C.

2. The composition of claim 1, wherein said vehicle is an oleaginous vehicle.

3. The composition of claim 1, wherein said vehicle is an aqueous vehicle.

4. The composition of claim 1, wherein said vehicle is a non-hydrocarbon vehicle.

5. The composition of claim 1, wherein said vehicle is a fatty oil vehicle.

6. The composition of claim 1, wherein said vehicle is a hydrocarbon vehicle.

7. The composition of claim 1, wherein said fatty acid contains between about 8 and about 30 carbon atoms per molecule.

8. The composition of claim 7, wherein said dialkanolamine is a compound having the formula, $\text{HN}(\text{CH}_2\text{CHROH})_2$, wherein R is selected from the group consisting of hydrogen atoms and alkyl radicals.

9. The composition of claim 8, wherein said vehicle is a mineral lubricating oil.

10. A mineral lubricating oil containing between about 0.01 per cent and about 50 per cent, by weight, of the final reaction product obtained by initially reacting stearic acid with diethanolamine, in a molar proportion of about 1:1, respectively, at a temperature of between about 130° C. and about 160° C. to produce an intermediate product, and then reacting an alkenyl succinic acid anhydride, having between about ten and about twelve carbon atoms per alkenyl radical, with said intermediate product, in a molar proportion of about 2:1, respectively, at a temperature of between about 110° C. and about 130° C.

11. A mineral lubricating oil containing be-

tween about 0.01 per cent and about 50 per cent, by weight, of the final reaction product obtained by initially reacting stearic acid with diethanolamine, in a molar proportion of about 1:1, respectively, at a temperature of between about 130° C. and about 160° C. to produce an intermediate product, and then reacting an alkenyl succinic acid anhydride, having between about eight and about ten carbon atoms per alkenyl radical, with said intermediate product, in a molar proportion of about 2:1, respectively, at a temperature of between about 110° C. and about 130° C.

12. A mineral lubricating oil containing between about 0.01 per cent and about 50 per cent, by weight, of the final reaction product obtained by initially reacting oleic acid with diethanolamine, in a molar proportion of about 1:1, respectively, at a temperature of between about 130° C. and about 160° C. to produce an intermediate product, and then reacting an alkenyl succinic acid anhydride, having between about ten and about twelve carbon atoms per alkenyl radical, with said intermediate product, in a molar proportion of about 2:1, respectively, at a temperature of between about 110° C. and about 130° C.

13. The final reaction product obtained by initially reacting a fatty acid containing at least about five carbon atoms per molecule with a dialkanolamine having between two and seven carbon atoms per alkanol radical, in a molar proportion of about 1:1, respectively, at a temperature of between about 130° C. and about 160° C. to produce an intermediate product, and then reacting an alkenyl succinic acid anhydride with said intermediate product, in a molar proportion of between about 1:1, respectively, and about 2:1, respectively, at a temperature of between about 110° C. and about 130° C.

14. The reaction product of claim 13, wherein said fatty acid contains between about 8 and about 30 carbon atoms per molecule.

15. The reaction product of claim 14, wherein said dialkanolamine is a compound having the formula, $\text{HN}(\text{CH}_2\text{CHROH})_2$, wherein R is selected from the group consisting of hydrogen atoms and alkyl radicals.

16. The reaction product of claim 15, wherein said fatty acid is stearic acid.

17. The reaction product of claim 15, wherein said fatty acid is oleic acid.

18. The final reaction product obtained by initially reacting stearic acid with diethanolamine, in a molar proportion of about 1:1, respectively, at a temperature of between about 130° C. and about 160° C. to produce a reaction product, and then reacting an alkenyl succinic acid anhydride, having between about ten and about twelve carbon atoms per alkenyl radical, with said intermediate product, in a molar proportion of about 2:1, respectively, at a temperature of between about 110° C. and about 130° C.

19. The final reaction product obtained by initially reacting stearic acid with diethanolamine, in a molar proportion of about 1:1, respectively, at a temperature of between about 130° C. and about 160° C. to produce an intermediate product, and then reacting an alkenyl succinic acid anhydride, having between about eight and about ten carbon atoms per alkenyl radical, with said intermediate product, in a molar proportion of about 2:1, respectively, at a temperature of between about 110° C. and about 130° C.

20. The final reaction product obtained by in-

initially reacting oleic acid with diethanolamine, in a molar proportion of about 1:1, respectively, at a temperature of between about 130° C. and about 160° C. to produce an intermediate product, and then reacting an alkenyl succinic acid anhydride, having between about ten and about twelve carbon atoms per alkenyl radical, with said intermediate product, in a molar proportion of about 2:1, respectively, at a temperature of between about 110° C. and about 130° C.

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References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
5 2,225,189	Wayne	Dec. 17, 1940
2,345,632	Robinson et al.	Apr. 4, 1944
2,412,708	Blair	Dec. 17, 1946
2,484,146	Barber et al.	Oct. 11, 1949
2,490,744	Trigg et al.	Dec. 6, 1949

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