United States Patent Office 3,288,774 Patented Nov. 29, 1966

3,288,774

REACTION PRODUCT OF SUBSTITUTED-AMINOALKYL ALKANOLAMINE AND POLYCARBOXYLIC ACID OR THE LIKE

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No Drawing. Filed Dec. 3, 1963, Ser. No. 327,815
11 Claims. (Cl. 260—97)

This application is a continuation-in-part of my copending and now abandoned application Serial No. 49,157, filed August 12, 1960, which is a continuation-in-part of application Serial No. 756,521, filed August 22, 1958, now abandoned, which is a continuation-in-part of application Serial No. 655,199, filed April 26, 1957, now Patent Number 3,018,173, issued January 23, 1962, and relates to a novel composition of matter which is particularly useful as an additive for the stabilization of organic compounds and, more particularly, for use in preventing deterioration of organic compounds in storage, during transportation or in use.

The novel additives of the present invention are particularly advantageous for use in the stabilization of hydrocarbon distillates and serves to improve the hydrocarbon distillate in a number of different ways. For example, in fuel oils, burner oils, range oils, diesel oils, marine oils, turbine oils, cutting oils, rolling oils, soluble oils, drawing oils, slushing oils, slushing greases, lubricating oils, lubricating greases, fingerprint removers, etc., the distillate or grease is removed in one or more ways including retarding and/or preventing sediment formation, dispersion of sediment when formed, preventing and/or retarding discoloration, oxidation inhiibtor, rust or corrosion inhibitor, detergent, etc. In lubricating type oils, in addition to all or some of the properties hereinbefore set forth, the additive may function as a pour point depressant, viscosity index improver, anti-foaming agent, etc. In liquefied petroleum gases, gasoline, naphtha, aromatic solvents, kerosene, jet fuels, etc., the additive serves as a corrosion inhibitor along with one or more of the other functions mentioned above. In other organic compounds, including alcohols, ethers, chlorinated hydrocarbons, etc., and compositions containing them, glyceridic oils and fats, waxes, other oils and fats of animal or vegetable origin, etc., the additive functions as a beneficent in one or more of the manners herein set forth or otherwise.

The invention is particularly applicable to the stabilization of hydrocarbon distillates heavier than gasoline. The hydrocarbon distillate may be cracked, straight run or mixtures thereof. Many fuel oils and particularly blends of straight run and cracked fuel oils undergo deterioration in storage, resulting in the formation of sediment, discoloration, etc. The formation of sediment is objectionable because the sediment tends to plug burner tips, injectors, etc. In jet fuels, oil-fuel heat exchangers and burner nozzles are plugged, particularly in view of the high temperatures encountered in such service. In diesel fuel, the deterioration tends to form varnish and sludge in the diesel engine. Discoloration of fuel oils is objectionable for various reasons, including customer's preference for light colored oils.

In handling of hydrocarbon distillates and other organic liquids, it is often necessary to transport and/or store such materials in metal containers, as in steel or other metal pipe lines, drums, tanks, etc. Since these materials often contain varying amounts of water in solution or in suspension which may separate, due to temperature changes, internal corrosion of the container by separating water almost invariably occurs to a greater or lesser degree. The water thus separated forms as a film or in

minute droplets in the pipe line or on the container walls or even in small pools at the bottom of the container. This brings about ideal conditions for corrosion and consequent damage to the metal surfaces of the container, as well as the serious contamination of the hydrocarbon oil or other materials contained therein by the corrosion products.

Corrosion problems also occur, for example, in the lubrication of internal combustion engines or steam engines, including turbines and other similar machinery, in which a quantity of water often is observed as a separate phase within the lubricating system as a result of the condensation of water from the atmosphere or, in the case of internal combustion engines, as the result of dispersion or absorption in lubricating oil of water formed as a product of fuel combustion. Water in such instances corrodes the various metal parts of the machinery with which it comes into contact, the corrosion products causing further mechanical damage to bearing surfaces and the like due to their abrasive nature and catalytically promoting the chemical degradation of the lubricant. Corrosion problems also arise in the preparation, transportation and use of various coating compositions such as greases, household oils, paints, lacquers, etc., which often are applied to metal surfaces for protective purposes.

In addition to the particular utility as additives to organic compounds, the products of the present invention and particularly the reaction product of the reductive alkylation product with dibasic acid or anhydride will have utility as cross-linking agents for resins, plastics and elastomers, and as intermediates for the preparation of polyurethanes. Polyfunctional chain-extending or network-extending agents are generally employed to create structures of high molecular weight in the preparation of resins, plastics and elastomers. Accordingly, polyethers, polyamides, polyurethanes and epoxy resins, which contain functional groups including, for example, hydroxyl, carboxyl, isocyanate or epoxy groups, which are free to react with functional groups of the reaction products of the present invention, are converted into polymeric structures.

In one embodiment the present invention relates to a novel composition of matter formed by reacting (1) a substituted-aminoalkyl alkanolamine of the following formula

$$RC\overset{HH}{\underset{R'}{N}}(CHR'')_nN\overset{H}{}(CHR'')_nOH$$

where n is from 2 to 4, R and R' are hydrocarbon radicals and the total number of carbon atoms in R and R' is from 2 to about 50, and R'' is selected from the group consisting of hydrogen and a hydrocarbon group, with (2) a compound selected from the group consisting of polycarboxylic acid, anhydride thereof, ester thereof and the reaction product of a terpene and a compound selected from the group consisting of alpha,beta-unsaturated polycarboxylic acid, anhydride thereof and ester thereof.

The substituted-aminoalkyl alkanolamine generally is prepared by the reductive alkylation of a ketone and an aminoalkyl alkanolamine. In one embodiment the ketone may contain from 3 to about 50 carbon atoms and, in another embodiment, the ketone contains at least 8 and more preferably at least 12 carbon atoms, and usually will contain from about 8 and preferably from about 12 to about 40 carbon atoms, although ketones containing up to 50 carbon atoms may be employed.

Any suitable ketone is used in accordance with the present invention. A preferred ketone comprises an aliphatic ketone. Preferred illustrative ketones include methyl decyl ketone, methyl undecyl ketone, methyl dodecyl ketone, methyl tridecyl ketone, methyl tetradecyl

ketone, methyl pentadecyl ketone, methyl hexadecyl ketone, methyl heptadecyl ketone, methyl octadecyl ketone, methyl nonadecyl ketone, methyl eicosyl ketone, methyl heneicosyl ketone, methyl docosyl ketone, methyl tricosyl ketone, methyl tetracosyl ketone, methyl pentacosyl ketone, methyl hexacosyl ketone, methyl heptacosyl ketone, methyl octacosyl ketone, methyl nonacosyl ketone, methyl triacontyl ketone, methyl hentriacontyl ketone, methyl dotriacontyl ketone, methyl tritriacontyl ketone, methyl tetratriacontyl ketone, methyl pentatriacontyl ketone, methyl hexatriacontyl ketone, methyl octatriacontyl ketone, etc., ethyl nonyl ketone, ethyl decyl ketone, ethyl undecyl ketone, ethyl dodecyl ketone, ethyl tridecyl ketone, ethyl tetradecyl ketone, ethyl pentadecyl ketone, ethyl hexadecyl ketone, ethyl heptadecyl ketone, ethyl octadecyl ketone, ethyl nonadecyl ketone, ethyl eicosyl ketone, ethyl heneiscosyl ketone, ethyl docosyl ketone, ethyl tricosyl ketone, ethyl tetracosyl ketone, ethyl pentacosyl ketone, ethyl hexacosyl ketone, ethyl heptacosyl ketone, ethyl octacosyl ketone, ethyl nonacosyl ketone, ethyl triacontyl ketone, ethyl hentriacontyl ketone, ethyl dotriacontyl ketone, ethyl tritriacontyl ketone, ethyl tetratriacontyl ketone, ethyl pentatriacontyl ketone, ethyl hexatriacontyl ketone, ethyl heptatriacontyl ketone, etc., propyl octyl ketone, propyl nonyl ketone, propyl decyl ketone, propyl undecyl ketone, propyl dodecyl ketone, propyl tridecyl ketone, propyl tetradecyl ketone, propyl pentadecyl ketone, propyl hexadecyl ketone, propyl heptadecyl ketone, propyl octadecyl ketone, propyl nonadecyl ketone, propyl eicosyl ketone, propyl heneicosyl ketone, propyl docosyl ketone, propyl tricosyl ketone, propyl tetracosyl ketone, propyl pentacosyl ketone, propyl hexacosyl ketone, propyl heptacosyl ketone, propyl octacosyl ketone, propyl nonacosyl ketone, propyl triacontyl ketone, propyl hentriacontyl ketone, propyl dotriacontyl ketone, propyl tritriacontyl ketone, propyl tetratriacontyl ketone, propyl pentatriacontyl ketone, propyl hexatriacontyl ketone, etc., butyl heptyl ketone, butyl octyl ketone, butyl nonyl ketone, butyl decyl ketone, butyl undecyl ketone, butyl dodecyl ketone, butyl tridecyl ketone, butyl tetradecyl ketone, butyl pentadecyl ketone, butyl hexadecyl ketone, butyl heptadecyl ketone, butyl octadecyl ketone, butyl nonadecyl ketone, butyl eicosyl ketone, butyl heneicosyl ketone, butyl docosyl ketone, butyl tricosyl ketone, butyl tetracosyl ketone, butyl pentacosyl ketone, butyl hexacosyl ketone, butyl heptacosyl ketone, butyl octacosyl ketone, butyl nonacosyl ketone, butyl triacontyl ketone, butyl hentriacontyl ketone, butyl dotriacontyl ketone, butyl tritriacontyl ketone, butyl tetratriacontyl ketone, butyl pentatriacontyl ketone, etc.

The specific ketones listed above comprise those containing from 12 to 40 carbon atoms each. Additional aliphatic ketones containing a lesser number of carbon atoms include acetone, methyl ethyl ketone, methyl propyl ketone, methyl butyl ketone, methyl amyl ketone, methyl hexyl ketone, methyl heptyl ketone, methyl octyl ketone, methyl nonyl ketone, diethyl ketone, ethyl propyl ketone, ethyl butyl ketone, ethyl amyl ketone, ethyl hexyl ketone, ethyl heptyl ketone, ethyl octyl ketone, dipropyl ketone, propyl butyl ketone, propyl amyl ketone, propyl hexyl ketone, propyl heptyl ketone, dibutyl ketone, butyl amyl ketone, butyl hexyl ketone, diamyl ketone, etc. Still additional aliphatic ketones include dihexyl ketone, diheptyl ketone, dioctyl ketone, dinonyl ketone, didecyl ketone, diundecyl ketone, didodecyl ketone, ditridecyl ketone, ditetradecyl ketone, dipentadecyl ketone, dihexadecyl ketone, diheptadecyl ketone, dioctadecyl ketone, dinonadecyl ketone, dieicosyl ketone, etc., as well as ketones containing one more carbon atoms in one group attached to the keto carbon atom than in the other group as, for example, heptyl octyl ketone, decyl undecyl ketone, heptadecyl octadecyl ketone, etc.

A number of ketones containing at least 12 carbon atoms are available as mixtures which are either products or byproducts of commercial operations. These mixtures generally are available at comparatively low cost and, as another advantage of the present invention, the mixtures may be used without the added time and expense of separating specific compounds in pure state. One such mixture available commercially as a primary product of the process is Stearone which is diheptadecyl ketone.

While the alkyl ketones are preferred, in some cases, ketones containing unsaturation in the aliphatic group may be employed. Also, aromatic ketones, aromatic aliphatic ketones, cycloaliphatic ketones, cycloaliphatic aliphatic ketones and cycloaliphatic aromatic ketones may be utilized. Furthermore, while it generally is preferred to utilize the same ketone in forming the reductive alkylation product, it is understood that a mixture of ketones may be employed. In another embodiment the ketone may contain a non-hydrocarbon substituent in the chain, this substitutent containing oxygen, nitrogen, sulfur, etc.

From the above, it will be noted that a number of different ketones meeting the requirements hereinbefore set forth may be employed. However, it is understood that the different ketones are not necessarily equivalent for use in preparing the reductive alkylation product and that the particular ketone will be selected with regard to the particular aminoalkyl alkanolamine with which it is to be reacted, the particular substrate in which the additive is to be used, availability, cost, etc.

Referring to the above formula, in a particularly preferred embodiment the total number of carbon atoms in R and R′ is from about 7 to about 39, these being obtained by utilizing a ketone containing from about 8 to about 40 carbon atoms and still more preferably R and R′ are alkyl radicals.

The aminoalkyl alkanolamine to be utilized for reductive alkylation with the hereinbefore described ketone is illustrated by the following general formula:

$$H_2N(CHR'')_nNH(CHR'')_nOH$$

where n is from 2 to 4 and R″ is selected from the group consisting of hydrogen and a hydrocarbon group.

Where R″ in the above general formula is hydrogen, illustrative preferred compounds include aminoethyl ethanolamine, aminopropyl propanolamine, aminobutyl butanolamine, aminopropyl ethanolamine, aminobutyl ethanolamine, aminoethyl propanolamine, aminobutyl propanolamine, aminoethyl butanolamine and aminopropyl butanolamine. In general, it is preferred that both R″ substituents are the same. A particularly preferred compound for use in the present invention comprises aminoethyl ethanolamine.

Where R″ in the above general formula is a hydrocarbon group, the hydrocarbon group is selected from alkyl, alkaryl, aryl, aralkyl, cyclohexylalkyl, cyclohexyl, alkylcyclohexyl, etc. In another embodiment, the hydrocarbon group is seected from alkenyl, alkenyl, aryl, aryl alkenyl, alkenyl cyclohexyl, cyclohexyl, alkenyl, cyclopentenyl, etc. In al cases, it wil be noted that there are from 2 to 4 carbon atoms between the nitrogen atom and the hydroxy group. Where R″ is selected from a mixture of hydrogen and alkyl groups, illustrative compounds include

1-aminoethylamino-propanol-2,
1-aminoethylamino-butanol-2,
1-aminoethylamino-pentanol-2,
1-aminoethylamino-hexanol-2,
1-aminoethylamino-heptanol-2,
1-aminoethylamino-octanol-2, etc.,
1-aminoethylamino-butanol-3,
1-aminoethylamino-pentanol-3,
1-aminoethylamino-hexanol-3,
1-aminoethylamino-heptanol-3,
1-aminoethylamino-octanol-3, etc.,
1-aminoethylamino-pentanol-4,
1-aminoethylamino-hexanol-4,
1-aminoethylamino-heptanol-4,
1-aminoethylamino-octanol-4, etc.,

1-aminopropylamino-propanol-2,
1-aminopropylamino-butanol-2,
1-aminopropylamino-pentanol-2,
1-aminopropylamino-hexanol-2,
1-aminopropylamino-heptanol-2,
1-aminopropylamino-octanol-2, etc.,
1-aminopropylamino-butanol-3,
1-aminopropylamino-pentanol-3,
1-aminonpropylamino-hexanol-3,
1-aminopropylamino-heptanol-3,
1-aminopropylamino-octanol-3,etc.,
1-aminoethylamino-pentanol-4,
1-aminopropylamino-hexanol-4,
1-aminopropylamino-heptanol-4,
1-aminopropylamino-octanol-4, etc.,
1-aminobutylamino-propanol-2,
1-aminobutylamino-butanol-2,
1-aminobutylamino-pentanol-2,
1-aminobutylamino-hexanol-2,
1-aminobutylamino-heptanol-2,
1-aminobutylamino-octanol-2, etc.,
1-aminobutylamino-butanol-3,
1-aminobutylamino-pentanol-3,
1-aminobutylamino-hexanol-3,
1-aminobutylamino-heptanol-3,
1-aminobutylamino-octanol-3, etc.,
1-aminobutylamino-pentanol-4,
1-aminobutylamino-hexanol-4,
1-aminobutylamino-heptanol-4,
1-aminoethylamino-octanol-4, etc.

Where R'' is an aryl group, illustrative compounds include

1-aminoethylamino-2-phenyl-ethanol-2,
1-aminoethylamino-2-tolyl-propanol-3,
1-aminoethylamino-2-phenyl-butanol-4,
1-aminoethylamino-2-tolyl-hexanol-2,
1-aminoethylamino-2-phenyl-heptanol-3,
1-aminoethylamino-2-tolyl-octanol-4,
1-aminopropylamino-2-phenyl-ethanol-2,
1-aminopropylamino-2-tolyl-propanol-3, etc.

It will be noted that a number of different aminoalkyl alkanolamines may be utilized in preparing the reductive alkylation products. It is understood that the different compounds which may be used are not necessarily equivalent and that the particular compound will be selected with regard to the ketone with which it is to be reacted, as well as the particular substrate in which the additive is to be used, availability, cost, etc.

The reductive alkylation of the ketone and aminoalkyl alkanolamine may be effected in any suitable manner. In general, the reaction is effected using an equimolar proportion of ketone and aminolkyl alkanolamine, although an excess of one or the other may be employed in order to insure complete reaction.

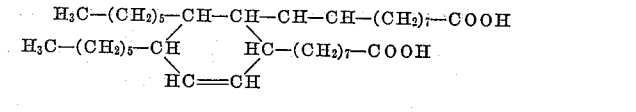
In a preferred embodiment, the reductive alkylation is effected in two steps. In the first step, a Schiff's base of the ketone and aminoalkyl alkanolamine is prepared, and the Schiff's base then is reduced to the desired product. In the first step, the ketone and aminoalkyl alkanolamine are reacted by heating at refluxing conditions. For ease in handling and operation, a solvent preferably is employed. Any suitable solvent may be used and preferably comprises a hydrocarbon including benzene, toluene, xylene, ethylbenzene, cumene, decalin, naphtha, etc. The temperature of reaction will depend upon whether a solvent is employed and, when employed, upon the particular solvent. In general, the temperature of reaction will be within the range of from about 80° to about 200° C. Water formed during the reaction may be removed in any suitable manner including, for example, by separating under reduced pressure, by removing an azeotrope of water-solvent, by distilling the reaction product at elevated temperature, etc.

The Schiff's base formed in the first step is subjected to reduction in any suitable manner. Preferably this is effected in the presence of hydrogen and a hydrognation catalyst. Any suitable catalyst may be employed including nickel, platinum, palladium, etc., preferably composited with a suitable support. A particularly preferred catalyst comprises a composite of platinum and alumina which may or may not contain combined halogen. The platinum generally is present in the catalyst in a concentration of from about 0.1 to about 2% by weight of the final catalyst and the halogen, when present, is in a concentration of total halogen of from about 0.01% to about 1% by weight of the final catalyst, the halogen preferably comprising fluorine and/or chlorine. A preferred nickel catalyst is a composite of nickel and kieselguhr containing from about 30 to about 60% by weight of nickel. It is understood that the platinum or nickel may be present as the free metal and/or compounds thereof. These catalysts are well-known in the art and need not be described in detail in the present application because no novelty is being claimed herein for the catalyst per se. While these are the preferred catalysts, it is understood that any other suitable hydrogenation catalyst may be employed. The temperature of the hydrogenation will depend upon the particular catalyst and method employed, and in general will be within the range of from about 100° to about 300° C., although higher or lower temperatures may be employed in some cases. Generally the hydrogenation is effected using a hydrogen pressure within the range of from about 50 to about 3000 pounds per square inch or more.

In another embodiment, the reductive alkylation is effected in a single step. In this embodiment, the reaction is conducted in the presence of a suitable reductive alkylation catalyst and hydrogen. A preferred catalyst comprises the platinum-containing catalyst hereinbefore described. Other catalysts include a composite of copper oxide, chromium oxide and barium oxide, as well as catalysts containing nickel, palladium, etc. The temperature employed will be between about 80° and about 300° C. and preferably between about 100° and about 250° C., and the hydrogen pressure is from about 100 to about 3000 p.s.i.

The substituted-aminoalkyl alkanolamine, prepared in the manner described above, is reacted with a polycarboxylic acid or the like. The polycarboxylic acid preferably comprises an aliphatic dicarboxylic acid and accordingly is selected from the alkyl and alkenyl dicarboxylic acids. Illustrative dicarboxylic acids include oxalic, malonic, succinic, glutaric, adipic, alkyl-adipic, pimelic, suberic, azelaic, sebacic, isosebacic, dodecanedioic, maleic, fumaric, citraconic, mesaconic, etc. While the dicarboxylic acids are preferred, it is understood that polycarboxylic acids containing 3, 4 or more carboxylic acid groups may be employed. Furthermore, it is understood that a mixture of polycarboxylic acids and particularly of dicarboxylic acids may be used. A number of relatively inexpensive dicarboxylic acids comprising a mixture of these acids are marketed commercially under various trade names, including "VR-1 Acid," "Dimer Acid," etc., and these acids may be used in accordance with the present invention. For example, "VR-1 Acid" is a mixture of dicarboxylic acids and has an average molecular weight of about 700, is a liquid at 77° F., has an acid number of about 150 and an iodine number of about 36. It contains 36 carbon atoms per molecule.

Another preferred dicarboxylic acid comprises a mixed acid being marketed commercially under the trade name of "Empol 1022." This dimer acid is a dilinoleic acid and is represented by the following general formula:



This acid is a viscous liquid, having an apparent molecular weight of approximately 600. It has an acid value of 180–192, an iodine value of 80–95, a saponification value of 185–195, a neutralization equivalent of 290–310, a refractive index at 25° C. of 1.4919, a specific gravity at 15.5° C./15.5° C. of 0.95, a flash point of 530° F., a fire point of 600° F., and a viscosity at 100° C. of 100 centistokes.

While the polycarboxylic acid may be employed, advantages appear to be obtained in some cases when using anhydrides thereof and particularly alkenyl-acid anhydrides. A preferred alkenyl-acid anhydride is dodecenyl-succinic anhydride. Other alkenyl-acid anhydrides include butenyl-succinic anhydride, pentenyl-succinic anhydride, hexenyl-succinic anhydride, heptentyl-succinic anhydride, octenyl-succinic anhydride, nonenyl-succinic anhydride, decenyl-succinic anhydride, undecenyl-succinic anhydride, tridecenyl-succinic anhydride, tetradecenyl-succinic anhydride, pentadecenyl-succinic anhydride, hexadecenyl-succinic anhydride, heptadecenyl-succinic anhydride, octadecenyl-succinic anhydride, nonadecenyl-succinic anhydride, eicosenyl-succinic anhydride, etc. While the alkenyl-succinic anhydrides are preferred, it is understood that the alkyl-succinic anhydrides may be employed, the alkyl groups preferably corresponding to the alkenyl groups hereinbefore specifically set forth. Similarly, while the aliphatic-succinic anhydrides are preferred, it is understood that the anhydrides and particularly aliphatic-substituted anhydrides of other acids may be employed, including, for example, adipic anhydride and particularly aliphatic adipic anhydrdes, glutaric anhydride and partcularly aliphatic glutaric anhydrides, etc.

In another embodiment of the present invention, the substituted-aminoalkyl alkanolamine is reacted further with an alpha,beta-unsaturated polycarboxylic acid, anhydride or ester formed by the reaction of a terpene with an alpha,beta-unsaturated polycarboxylic acid, anhydride or ester. The reaction product will comprise primarily the anhydride but the acid and/or ester also will be present. Any suitable terpenic compound may be reacted with any suitable alpha,beta-unsaturated polycarboxylic acid, anhydride or ester to form the reaction product for subsequent condensation with the substituted-alkylamino alkanolamine. In one embodiment, a terpene hydrocarbon having the formula $C_{10}H_{16}$ is employed, including alpha-pinene, beta-pinene, dipentene, di-limonene, 1-limonene and terpinoline. These terpene hydrocarbons have boiling points ranging from about 150° to about 185° C. In another embodiment the terpene may contain three double bonds in monomeric form, including terpenes as allo-o-cymene, o-cymene, myrcene, etc. Other terpenic compounds include alpha-terpinene, p-cymene, etc. Also included as terpenic compounds are rosins comprising the terpenic hydrocarbons and/or terpenic acids. These rosins and acids generally are tricyclic compounds. However, they are obtained from pine trees and therefore may be included in the broad classification as terpene or terpenic compounds.

In a particularly preferred embodiment, the terpene contains from 1 to 2 double bonds. As hereinbefore set forth, the terpene is reacted with an alpha,beta-unsaturated polycarboxylic acid, anhydride or ester thereof. Any unsaturated polycarboxylic acid having a point of unsaturation between the alpha and beta carbon atoms may be employed. Illustrative unsaturated dicarboxylic acids include maleic acid, fumaric acid, citraconic acid, mesaconic acid, aconitic acid, itaconic acid. While the dicarboxylic acids are preferred, it is understood that alpha, beta-unsaturated polycarboxylic acids containing 3, 4 or more carboxylic acid groups may be employed. Furthermore, it is understood that a mixture of alpha,beta-unsaturated polycarboxylic acids and particularly of alpha, beta-unsaturated dicarboxylic acids may be used.

While the alpha,beta-unsaturated polycarboxylic acid may be employed for reaction with the terpene, advantages appear to be obtained in some cases when using the anhydrides thereof. Illustrative anhydrides include maleic anhydride, citraconic anhydride, aconitic anhydride, itaconic anhydride, etc. It is understood that a mixture of anhydrides may be employed and also that the anhydride may contain substituents and particularly hydrocarbon groups attached thereto. Furthermore, it is understood that the various anhydrides are not necessarily equivalent but all of them will serve to produce useful products. Also, it is understood that esters of the alpha,beta-unsaturated polycarboxylic acids may be employed, the ester group being selected from alkyl, alkaryl, aralkyl, aryl and cycloalkyl substituents replacing one or more of the hydrogen atoms of the carboxylic acid groups. The alkyl esters are particularly preferred for use in the present invention and preferably are prepared from alkanols containing from 1 to 3 carbon atoms although, when desired, alkanols containing from 4 to 20 carbon atoms may be used. The advantages of using the alcohols prepared from methanol, ethanol and propanol are that transesterification occurs and apparently results in the preparation of reaction products of higher molecular weight than are obtained when using the polycarboxylic acids. This reaction may be effected by heating the reactants in the absence of a catalyst or in the presence of a transesterification catalyst including, for example, titanium alkyls, tin alkyls, etc., methanol, ethanol, or propanol are liberated during the reaction and preferably continuously removed from the reaction zone. Accordingly, the heating is effected at a temperature sufficient to effect the transesterification and liberation of the alcohol. Completion of the reaction is determined when the liberation of alcohol ceases.

The reaction of terpene and alpha,beta-unsaturated acid, anhydride or ester generally is effected at a temperature of from about 150° to about 300° C., and preferably of from about 160° to about 200° C. The time of heating will depend upon the particular reactants and may range from 2 hours to 24 hours or more. When desired, a suitable solvent may be utilized. Following the reaction, impurities or unreacted materials may be removed by vacuum distillation or otherwise, to leave a resinous product which may be a viscous liquid or a solid.

A terpene-maleic anhydride reaction product is available commercially under the trade name of "Petrex Acid." This acid is a stringy, yellow-amber colored mass and is mostly dibasic. It has an acid number of approximately 530, a molecular weight of approximately 215 and a softening point of 40°–50° C.

Another reaction product is available commercially under the trade name of "Lewisol 40 Acid." This is a triboxylic acid and is formed by the reaction of fumaric acid and rosin. It is a hard, brittle solid having a softening point of 150°–160° C. and a specific gravity of 25/25° C. of 1.178.

The reaction of the substituted-aminoalkyl alkanolamine with the dicarboxylic acid, anhydride or the terpene reaction product is effected in any suitable manner. In general, the reaction is effected using one or two moles of substituted-aminoalkyl alkanolamine per one mole of acid, anhydride or terpene reaction product, although an excess of one of the reactants may be employed in order to insure complete reaction. The reaction generally is effected at a temperature above about 80° C. and preferably at a higher temperature which usually will not exceed about 200° C., although higher or lower temperatures may be employed in some cases. The exact temperature will depend upon whether a solvent is used and, when employed, on the particular solvent. For example, with benzene as the solvent, the temperature will be in the order of 80° C., with toluene the temperature will be in the order of 120° C. and with xylene in the order of 150°–155° C. Other preferred solvents include cumene, naphtha, decalin, etc. Any suitable amount of the solvent may be employed but preferably should not

comprise a large excess because this will tend to lower the reaction temperature and slow the reaction. Water formed during the reaction may be removed in any suitable manner including, for example, by operating under reduced pressure, by removing an azeotrope of water-solvent, by distilling the reaction product at an elevated temperature, etc. A higher temperature may be utilized in effecting the reaction in order to remove the water as it is being formed. However, for many uses, the reaction need not go to completion, but in any event at least a substantial portion of the reaction product will comprise that formed by the condensation of the reductive alkylation product with the terpene-acid, anhydride or ester reaction product.

Here again, it is understood that a number of different compounds may be prepared and used in accordance with the present invention and will depend upon the specific substituted-aminoalkyl akanolamine and dicarboxylic acid, anhydride or terpene reaction product employed. It is understood that the different compositions are not necessarily equivalent in the same or different substrates or for the same or different uses, but the different compositions will be utility in one or more substrates.

The reaction product, prepared as hereinbefore described, is recovered as a final product ranging from a clear liquid to a viscous liquid or solid. In some cases the product will be marketed and utilized as a solution in a solvent. Conveniently, this solvent comprises the same solvent used in preparing the reaction product and is recovered in admixture with at least a portion of the solvent, thereby avoiding the necessity of removing all of the solvent and subsequently adding it back. When a more dilute solution is desired than is recovered in the manner hereinbefore set forth, it is understood that the same or different solvent may be commingled with the mixture to form a solution of the desired concentration.

The concentration of additive to be used in the organic substrate will depend upon the particular substrate and the particular benefits desired. In general, the additive will be used in a concentration of from about 0.00001% to about 5% by weight or more and more specifically is used in a concentration of from about 0.0001% to about 1% by weight of the substrate. The additive may be used along with other additives which are incorporated in the substrate for specific purposes including, for example, metal deactivators, antioxidants, antiozidants, synergists, dyes, fuel improvers, etc.

The additive may be incorporated in the substrate in any suitable manner. As hereinbefore set forth, the additive conveniently is marketed and utilized as a solution in a suitable solvent, including hydrocarbons and particularly aromatic hydrocarbons as benzene, toluene, xylene, cumene, etc. When the additive is to be incorporated in a liquid substrate, it may be added thereto in the desired amount and the resultant mixture suitably agitated in order to obtain intimate mixing of the additive in the substrate. When the additive is to be utilized as a corrosion inhibitor in plant equipment, it may be introduced into a fractionator, vapor line or at any other suitable point in order to prevent corrosion of the plant equipment. In this embodiment, the additive carries over into the product of the process and also serves therein as a beneficent. It is understood that portion of the additive may be introduced into the plant equipment and an additional portion of the additive incorporated in the effluent product when so desired.

The following examples are introduced to illustrate further the novelty and utility of the present invention but not with the invention of unduly limiting the same.

Example I

The substituted-aminoalkyl alkanolamine of this example is N^1-1-heptadecyloctadecyl-aminoethyl ethanolamine and was prepared by the reductive alkylation of Stearone and aminoethyl ethanolamine. As hereinbefore set forth, Stearone is diheptadecyl ketone. The reductive alkylation was prepared in two steps as follows: 538 g. (1 mole) of Stearone and 109 g. (1 mole+5% excess) of aminoethyl ethanolamine were refluxed in 100 g. of toluene. 18.6 cc. of water was recovered from the reaction. The resultant Schiff's base was reduced in a rocker bomb at 140° C. with 125 atmospheres of hydrogen in the presence of 100 g. of a catalyst comprising alumina, about 0.4% platinum and about 0.3% combined halogen. The hydrogenated product was dissolved in benzene, filtered to remove catalyst, and the benzene and toluene were removed by evaporation in a steam bath under water pump vacuum. The product is a waxy-white solid having a basic mole combining weight of 329. The calculated basic mole combining weight is 312.

Example II

The aminoalkyl alkanolamine of this example is N^1-1-methyloctadecyl-aminoethyl ethanolamine and was prepared by the two-step reductive alkylation of methyl heptadecyl ketone and aminoethyl ethanolamine. 282 g. (1 mole) of methyl heptadecyl ketone and 109 g. (1 mole) of aminoethyl ethanolamine and 100 g. of xylene were refluxed, with the evolution of 22 cc. of water. The resultant Schiff's base with 200 g. of toluene was reduced in the presence of 100 g. of alumina-platinum-combined halogen catalyst referred to in Example I at 120° C. using 125 atmospheres of hydrogen. The product was dissolved in benzene and filtered. The toluene and benzene were removed on a steam bath at water pump vacuum. The resulting product is an amber-greasy solid, having a basic mole combining weight of 201. Calculated combining weight is 185. For additional characterization, the product was distilled at a vacuum of 0.35 mm. Hg. The main fraction (about 80–90% of the total) distilled at 212°–214° C. This distillate had a basic mole combining weight of 187.5 and a molecular weight of 375 (theoretical is 370). It is a soft pale-orange microcrystalline waxy solid. Its specific gravity at 60° F. is 0.8849.

Example III

N^1 - 1 - heptadecyloctadecyl-aminoethyl ethanolamine, prepared as described in Example I, was reacted with Petrex Acid, the latter being described in detail hereinbefore. 131.6 g. (0.4 equivalent) of the reductive alkylation product of Example I and 21 g. (0.2 equivalent) of Petrex Acid were dissolved in 100 g. of xylene and refluxed. 2.3 cc. of water was collected after 24 hours of refluxing. The solvent was removed on a steam bath at water pump vacuum.

The reaction product, prepared in the above manner, was evaluated in a method referred to as the Erdco test. In this method, heated oil is passed through a filter, and the time required to develop a differential pressure across the filter of 25 in. Hg is determined It is apparent that the longer the time, the more effective is the additive. However, with a very effective additive, the time to reach a differential pressure across the filter of 25 in. Hg is lengthened beyond reasonable limits that the test is stopped after about 300 minutes and the differential pressure after that time is reported.

0.001% by weight of the reaction product prepared in the above manner was incorporated in a commercial range oil and evaluated in the Erdco test. After 300 minutes, the differential pressure across the filter was 0.9 in. Hg. In contrast, a control sample (not containing this additive) developed a differential pressure across the filter of 25 in. Hg in about 125 minutes.

From the above data, it will be noted that the additive of the present invention served to considerably retard deterioration of the range oil and thus prevents clogging of burner tips, injectors, etc., during use of the oil as a fuel oil, diesel fuel, jet fuel, etc.

Example IV

The substituted-aminoalkyl alkanolamine of this example is N^1-1-methylheptyl-aminoethyl ethanolamine and was prepared by the two-step reductive alkylation of methylhexyl ketone and aminoethyl ethanolamine. The reductive alkylation was effected in substantially the same manner as hereinbefore set forth. 520 g. (4.06 moles) of methylhexyl ketone was refluxed with 208 g. (2 moles) of aminoethyl ethanolamine. The reduction of the Schiff's base was effected at 160° C. in the presence of 100 atmospheres of hydrogen in a rocker bomb for six hours using 100 g. of the alumina-platinum-combined halogen catalyst previously described. In this case, an exces of ketone was employed, and the excess ketone was removed by distillation. The final product was a water-white liquid, distilling at 172–4° C. and had a basic mole combining weight of 119.2. The calculated mole combining weight is 108. Other physical properties are a specific gravity at 60° F. of 0.8984 and an index of refraction at 20° C. of 1.4630.

Example V

Another method of evaluating the additives is by a test known as Recycle Test in which successive 400 cc. portions of a commercial fuel oil is passed through a 400 mesh screen, and the time in seconds for each successive portion to pass through the screen is measured. It is apparent that the time required for the successive portions to pass through the screen is an indication of deterioration of the oil, the longer time indicating greater deterioration. The following table reports results obtained when using a control sample (not containing the additive) and when using the additive prepared as described in Example III. The additive was used in a concentration of 0.01% by weight of the oil.

Another indication of deterioration is in discoloration and the following table also reports the colors of the different samples of the oil after storage at 100° F. for about 180 days. The colors were determined in a Lumetron, model 402–E, spectrophotometer. Distilled water has a rating of 100 and very dark oil has a rating of 0.

TABLE I.—TIME IN SECONDS FOR SUCCESSIVE 400 CC. PORTIONS TO PASS

Additive	1	2	3	Color
None	37	70	125	32.5
Example III	25	29	34	37.5

From the data in the above table, it will be noted that the sample of oil which did not contain an additive required 125 seconds for the third portion to pass through the screen, whereas the third portion of the example containing the additive passed through the screen in 34 seconds. The color of the oil was improved through the use of the additive as shown by the data in the above table.

Example VI

The substituted-aminoalkyl alkanolamine of this example is N^1-1-methylhexadecyl-aminoethyl ethanolamine and was prepared by the two-step reductive alkylation of methyl pentadecyl ketone and aminoethyl ethanolamine. 508 g. (2 moles) of methyl pentadecyl ketone were refluxed with 218 g. (2 moles + 10 g. excess) of aminoethyl ethanolamine. The Schiff's base was reduced at 160° C. and 100 atmospheres of hydrogen for 6 hours in the presence of 100 g. of the alumina-platinum-combined halogen catalyst previously described. The reduced product was then heated at 155° C. under 0.3 mm. vacuum to remove excess aminoethyl ethanolamine. The product was a yellow-green liquid at room temperature. The mole combining weight was 180, calculated combining weight is 171. The molecular weight was 360. The theoretical molecular weight is 341. For the purpose of further characterization, the product was distilled at a vacuum of 0.3 mm. Hg. The main fraction, about 90% of the total, had a boiling point of 201°–203° C. This is a pale tan, almost white liquid, solidifying or melting at about 22°–24° C. The liquid solidifies in the form of fine soft needles. Titrated with 0.1 normal perchloric acid, it gave a basic mole combining weight of 177.3 or a molecular weight of 354.6. The specific gravity of the product at 60° F. is 0.8855. The index of refraction at 20° C. is 1.5280.

Example VII

Jet fuels in superonic military aircraft under the effect of high temperatures oxidize while being used as cooling mediums in heat exchangers with temperatures ranging to 500° F. or higher. The fuel degradation products formed either in heat exchangers or in burner nozzles foul the operation of the engine. The formation of the deposit is prevented by a reaction product of Petrex Acid and the reductive alkylation product of Stearone and aminoethyl ethanolamine described in Example I. In this condensation, 21 g. of Petrex Acid (0.2 equivalent) were reacted with 65.8 g. (0.2 equivalent) of the reductive alkylation product of Stearone and aminoethyl ethanolamine, described in Example I, in 100 g. of xylene. After 24 hours refluxing, the xylene was removed on a steam bath under vacuum. The resulting product is a polyamine having a basic mole combining weight of 928 and an acidic mole combining weight of 5550 (acid number 10.1).

0.001% of this condensation product was incorporated in another range oil containing 15% of catalytically cracked gasoline, and was evaluated in the Erdco test. After 180 minutes, the differential pressure across the filter was 0.1 in. Hg. The filter temperature was kept at 400° F. and the preheater temperature at 350° F. No visible deposit was formed on the preheater tube after 180 minutes operation. The noninhibited fuel reached a mercury differential of 25 inches after 25 minutes. The absence of any deposit on the preheater tube indicates that the additive is effective as a heat exchanger antifouling agent at high temperature.

Example VIII

65.8 g. of the reductive alkylation product of Stearone and aminoethyl ethanolamine was reacted with 27.5 g. of dodecenyl succinic anhydride in 200 g. of xylene. Two cc. of water was collected in a Dean-Stark water trap. The xylene was removed on a steam bath under vacuum. The product is a polymer having a basic equivalent weight of 749.

Example IX

54 g. (0.15 mole) of the reductive alkylation product of methyl pentadecyl ketone and aminoethyl ethanolamine (Example VI) was refluxed with 31.2 g. of Petrex Acid (0.15 mole equivalents) in 100 g. of xylene. 2.6 cc. H_2O was collected after 9 hours refluxing. The xylene was removed under vacuum. The resulting polymer is a somewhat rubbery soft solid, having an isocyanate equivalent of 203, basic equivalent of 559 and acidic equivalent of 1035.

Example X

54.0 g. of the reductive alkylation product described in Example VI, equivalent of 0.15 mole, was reacted with 41.25 g. of dodecenyl succinic anhydride (equivalent to 0.15 mole) in 200 g. of xylene. After 12 hours of refluxing, 2.6 cc. water was collected. The xylene was removed under vacuum at 160° C. The resulting polymer is a heavy almost solid mass. The average cryoscopic molecular weight is 1859, isocyanate equivalent is 320, basic equivalent is 715 and acidic equivalent is 1930.

Example XI

The additive of this example is prepared first by the reductive alkylation of methyl heptyl ketone and aminopropyl propanolamine, followed by reaction with sebacic

acid. The reductive alkylation is effected in a one step method by reacting methyl heptyl ketone and aminopropyl propanolamine in equal mole proportions in the presence of an alumina-platinum catalyst and 100 atmospheres of hydrogen at 150° C. Equal mole proportions of the reductive alkylation product and sebacic acid then are refluxed in the presence of xylene. Water formed during the reaction is continuously removed. The product is recovered as a viscous oil which is diluted with additional xylene to form a fluid oil.

Example XII

The reductive alkylation product of methyl hexyl ketone and aminoethyl ethanolamine, prepared as described in Example IV, is reacted with methyl adipate in equal mole proportions. The reactants are heated to refluxing temperature, in the absence of solvent and catalyst, and methanol formed during the reaction is continuously removed. The reaction is effected under vacuum. The reaction product is recovered as a viscous oil.

I claim as my invention:

1. The composition of matter formed by reacting at a temperature of from about 80° to about 200° C. (1) a substituted-aminoalkyl alkanolamine of the following formula

$$R\underset{R'}{\overset{H}{C}}N(CHR'')_nN(CHR'')_nOH$$

where n is from 2 to 4, R and R′ are alkyl radicals and the total number of carbon atoms in R and R′ is from 2 to about 50, and R″ is selected from the group consisting of hydrogen and an alkyl group, with (2) a compound selected from the group consisting of polycarboxylic acid, anhydride thereof, ester thereof and the reaction product of a terpene and a compound selected from the group consisting of alpha,beta-unsaturated polycarboxylic acid, anhydride thereof and ester thereof.

2. The composition of claim **1** wherein from 1 to 2 moles of said substituted-aminoalkyl alkanolamine are reacted with 1 mole of said compound.

3. A composition of matter formed by reacting (1) from 1 to 2 mole proportions of an N-sec-alkyl-aminoethyl ethanolamine containing from 2 to about 50 carbon atoms in said alkyl with (2) 1 mole proportion of an aliphatic dicarboxylic acid at a temperature of from about 80° to about 200° C.

4. A composition of matter formed by reacting at a temperature of from about 80° to about 200° C. (1) from 1 to 2 mole proportions of an N-sec-alkyl-aminoethyl ethanolamine containing from 2 to about 50 carbon atoms in said alkyl with (2) 1 mole proportion of the reaction product formed at a temperature of from about 150° to about 300° C. of a terpene having the formula $C_{10}H_{16}$ and a boiling point within the range of from about 150° to about 185° C. and maleic anhydride.

5. A composition of matter formed by reacting at a temperature of from about 80° to about 200° C. (1) from 1 to 2 mole proportions of an N-sec-alkyl-aminoethyl ethanolamine containing from 2 to about 50 carbon atoms in said alkyl with (2) 1 mole proportion of the reaction product formed at a temperature of from about 150° to about 300° C. of rosin and fumaric acid.

6. A composition of matter formed by reacting (1) from 1 to 2 mole proportions of an N-sec-alkyl-aminoethyl ethanolamine containing from 2 to about 50 carbon atoms in said alkyl with (2) 1 mole proportion of an aliphatic dicarboxylic acid at a temperature of from about 80° to about 200° C.

7. A composition of matter formed by reacting (1) from 1 to 2 mole proportions of an N-sec-alkyl-aminoethyl ethanolamine containing from 2 to about 50 carbon atoms in said alkyl with (2) 1 mole proportion of an anhydride of an aliphatic dicarboxylic acid at a temperature of from about 80° to about 200° C.

8. The composition of claim **1** wherein said substituted-aminoalkyl alkanolamine is N^1-1-heptadecyloctadecyl-aminoethyl ethanolamine.

9. The composition of claim **1** wherein said substituted aminoalkyl alkanolamine is N^1-1-methyloctadecyl-aminoethyl ethanolamine.

10. The composition of claim **1** wherein said substituted-aminoalkyl alkanolamine is N^1 - 1 - methylheptyl-aminoethyl ethanolamine.

11. The composition of claim **1** wherein said substituted-aminoalkyl alkanolamine is N^1-1-methylhexadecyl-aminoethyl ethanolamine.

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