

UNITED STATES PATENT OFFICE

2,638,450

REACTION PRODUCTS OF N-ALKYLATED
POLYALKYLENEPOLYAMINES AND AL-
KENYL SUCCINIC ACID ANHYDRIDESRalph V. White, Pitman, and Phillip S. Landis,
Glassboro, N. J., assignors to Socony-Vacuum
Oil Company, Incorporated, a corporation of
New YorkNo Drawing. Application January 17, 1950,
Serial No. 139,124

17 Claims. (Cl. 252—51.5)

1

This invention relates, broadly, to organic nitrogen compounds and to corrosion-inhibiting compositions containing the same. It is more specifically concerned with the reaction products obtained by reacting alkyl halides, polyalkylenepolyamines having one more nitrogen atom per molecule than there are alkylene groups in the molecule, 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 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 2,279,638, 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

2

that the acids must have at least 16 carbon atoms, and preferably, 20 carbon atoms per molecule.

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 an alkyl halide with a polyalkylenepolyamine 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 an alkyl halide with a polyalkylenepolyamine 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 an alkyl halide having at least four carbon atoms per molecule with a polyalkylenepolyamine having one more nitrogen atom per molecule than there are alkylene groups in the molecule, in a molar proportion varying between about one and about $(x-1)$ to one, respectively, wherein x represents the number of nitrogen atoms in the polyalkylenepolyamine molecule, to produce an intermediate product, and reacting an alkenyl succinic acid anhydride with the intermediate product, in a molar proportion varying between about $(x-1)$ to one, respectively; the sum of the number of moles of the alkyl halide and of the alkenyl succinic acid anhydride reacted with each mole of said polyalkylenepolyamine being no greater than x . The present invention provides also a substantially neutral vehicle containing between about 0.003 per cent and about 50 per cent by weight of these compositions of matter.

In general, the polyalkylenepolyamine reactants utilizable herein are those compounds having the structural formula, $H_2N(RNH)_xH$, wherein R is an alkylene radical- or a hydro-

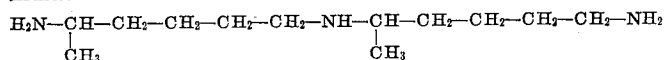
3

carbon radical-substituted alkylene radical, and z is an integer greater than one, there being no upper limit to the number of alkylene groups in the molecule. It is preferred, however, to use the polyethylenepolyamines, because of their greater commercial availability. These compounds have the formula:



wherein z is an integer varying between about two and about six.

In naming the polyalkylenepolyamine reactants, the nitrogen atoms are considered to be attached to the terminal carbon atoms of the main carbon atom chain indicated in each compound name. For example, di-(1-methylamylene)tri-amine has the structural formula:



In numbering the main carbon atom chain, the carbon atom attached to a terminal $-\text{NH}_2$ radical is designated as the carbon atom in the 1-position. Similar alkylene groups recur throughout the molecule. Non-limiting examples of the polyalkylenepolyamine reactants are diethylenetriamine; triethylenetetramine; tetraethylenepentamine; di-(methylethylene)tri-amine; hexapropyleneheptamine; tri(ethylethylene)tetramine; penta-(1-methylpropylene)-hexamine; tetrabutylene-pentamine; hexa-(1,1-dimethylethylene)heptamine; di-(1-methyl-butylene)tri-amine; pentaamylenehexamine; tri-(1,2,2-trimethylethylene)tetramine; di-(1-methylamylene)tri-amine; tetra-(1,3-dimethylpropylene)pentamine; penta-(1,5-dimethylamylene)-hexamine; di-(1-methyl-4-ethylbutylene)-tri-amine; penta-(1,2-dimethyl-1-isopropylethylene)hexamine; tetraoctylene-pentamine; tri-(1,4-diethylbutylene)tetramine; tridecylene-tetramine; tetra-(1,4-dipropylbutylene)pentamine; didodecylene-tri-amine; tetra-tetradecylene-pentamine; penta-(1-methyl-4-nonylbutylene)hexamine; tri-(1,15-dimethylepentadecylene)-tetramine; trioctadecylenetetramine; di-eicosylenetriamine; di-(1,2-dimethyl-14-nonyltetradecylene)tri-amine; di-(1,18-dioctyloctadecylene)tri-amine; penta-(1-methyl-2-benzylethylene)hexamine; tetra-(1-methyl-3-benzylpropylene)pentamine; tri-(1-methyl-1-phenyl-3-propylpropylene)tetramine; and tetra-(1-ethyl-2-benzylethylene)pentamine.

The polyalkylenepolyamines can be prepared by several methods well known to the art. One well accepted method comprises reacting ammonia with an alkyl, or substituted alkyl, dihalide. For example, tetraethylenepentamine has been prepared by reacting ammonia with ethylene bromide.

Any alkyl halide which contains at least four carbon atoms and up to about thirty carbon atoms or more per molecule is utilisable for producing the reaction products of this invention. It is especially preferred to use alkyl halides having between about eight and about eighteen carbon atoms per molecule. Those having between about 14 and about 18 carbon atoms are more particularly preferred for certain products, such as those used to prevent corrosion in the presence of sea water. The halogen portion of the alkyl halide reactant molecule can be any halogen atom, i. e., chlorine, bromine, fluorine, and iodine. In practice, the alkyl bromides and chlorides are used, due to their greater commercial availability. Non-limiting examples

4

of the alkyl halide reactant are n-butyl bromide; n-butyl chloride; sec-butyl iodide; t-butyl fluoride; n-amyl bromide; isoamyl chloride; n-hexyl bromide; n-hexyl iodide; heptyl fluoride; 2-ethyl-hexyl chloride; n-octyl bromide; decyl iodide; dodecyl bromide; 7-ethyl-2-methylundecyl iodide; tetradecyl bromide; hexadecyl bromide; hexadecyl fluoride; heptadecyl chloride; octadecyl bromide; docosyl chloride; tetracosyl iodide; hexacosyl bromide; octacosyl chloride; and triacontyl chloride.

The alkyl halides can be chemically pure compounds or of commercial purity. Mixtures of alkyl halides, having carbon chain lengths falling within the range specified hereinbefore, can also be used. Examples of such mixtures are mono-chlorinated wax and mono-chlorinated kerosene. Complete instructions for the preparation of

mono-chlorowax have been set forth in United States Letters Patent 2,238,790.

The number of moles of alkyl halide reactant which is reacted with each mole of polyalkylenepolyamine reactant varies between about one mole and about $(x-1)$ moles, wherein x is the number of nitrogen atoms in the polyalkylenepolyamine reactant molecule. In order to obtain an intermediate product which can be used to produce the reaction products of this invention, it is essential that at least one nitrogen atom in the polyalkylenepolyamine reactant be left unsubstituted. Accordingly, the maximum number of moles of alkyl halide reactant which is reacted with each mole of polyalkylenepolyamine reactant will be one less than the number of nitrogen atoms in the polyalkylenepolyamine molecule. In accordance with the present invention, a fewer number of moles of alkyl halide reactant can be used. For example, if tetraethylenepentamine is utilized as the polyalkylenepolyamine reactant, one, two, three, or even four moles of an alkyl halide reactant can be reacted with each mole thereof to produce intermediate products suitable for the purposes contemplated herein. When five moles of alkyl halide reactant are used, the intermediate product is not utilisable in the production of the reaction products of the present invention. Tests have indicated that no more than one molecule of alkyl halide reactant can be reacted with each nitrogen atom in the molecule of the polyalkylenepolyamine reactant. Accordingly, the molar proportion of the reactants is varied as set forth hereinbefore.

Since the reaction between the alkyl halide reactant and the polyalkylenepolyamine reactant is a condensation reaction, or an alkylation reaction, characterized by the elimination of hydrogen halide, the general conditions for such reactions are applicable herein. It is preferable to carry out the reaction at temperatures of between about 100°C . and about 250°C ., preferably between about 140°C . and about 200°C ., in the presence of a basic material which is capable of reacting with the hydrogen halide to remove it. Such basic materials are, for example, sodium bicarbonate, sodium carbonate, pyridine, tertiary alkyl amines, alkali- or alkaline-earth metal hydroxides, and the like.

It is preferred to perform the reaction between the alkyl halide reactant and the polyalkylenepolyamine reactant in a hydrocarbon solvent under reflux conditions. The aromatic hydrocarbon solvents of the benzene series are especially

sive 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.

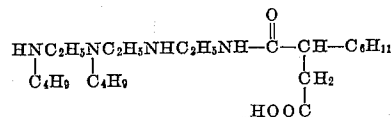
The alkenyl succinic acid anhydride reactant is reacted with the intermediate product in a proportion of between about $(x-1)$ and about one mole of alkenyl succinic acid anhydride reactant for each mole of polyalkylenepolyamine reactant used in the preparation of the intermediate product, x representing the number of nitrogen atoms in the polyalkylenepolyamine reactant molecule. The sum of the number of moles of alkyl halide reactant and of alkenyl succinic acid anhydride reactant reacted with each mole of polyalkylenepolyamine reactant, in accordance with this invention, must not exceed the number of nitrogen atoms in the polyalkylenepolyamine reactant molecule. Accordingly, the maximum number of moles of alkenyl succinic acid anhydride reactant used is the difference between the number of nitrogen atoms in the polyalkylenepolyamine reactant molecule and the number of moles of alkyl halide reactant used per mole of polyalkylenepolyamine reactant. For example, when two moles of butyl bromide are reacted with one mole of triethylenetetramine to produce an intermediate product, one or two moles, but not more than two moles, of an alkenyl succinic acid anhydride is reacted with this 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 an amide formation reaction effected by the well known addition of the anhydride group to an amino or imino group. This addition proceeds at any temperature, but temperatures of about 140° C. or lower are preferred. When an alkenyl succinic acid is used, water is formed. Therefore, in this case, the reaction temperature preferably should be higher than about 100° C., preferably about 150° C. 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. Use of a solvent is preferable when the reaction product is to be used in a steam turbine lubricating oil. 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, hereinbefore, in conjunction with the reaction between the alkyl halide reactant and the polyalkylenepolyamine 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. The preferred products of this invention have been prepared at temperatures varying between about 130° C. and about 140° 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 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. For example, when benzene is used as the solvent at a temperature of 130–140° C., heating is continued for about five 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 acylated products of the polyalkylenepolyamine reactant having at least one free carboxylic acid group. For example, when the intermediate product of Formula 3, is reacted with one mole of hexenyl succinic acid anhydride, a possible structural formula of the product is:



or an isomer thereof. The reaction products probably contain other substances, such as cyclic imides. Accordingly, and in the interest of brevity, the reaction products are best defined by reciting the reactants and the number of moles of each which are used in the reaction. For example, the reaction product produced by reacting one mole of octyl bromide with one mole of triethylenetetramine to produce an intermediate product which is then reacted with two moles of decenyl succinic acid anhydride may be defined as the reaction product of octyl bromide (I)—triethylenetetramine (I)—decenyl succinic acid anhydride (II).

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: n-butyl bromide (II)+tetraethylenepentamine (I)+hexacosenyl succinic acid anhydride (II); n-butyl chloride (II)+hexapropyleneheptamine (I)+octenyl succinic acid anhydride (V); sec-butyl iodide (I)+tri-(1,2,2-trimethylethylene) tetramine (I)+heptenyl succinic acid anhydride (III); t-butyl fluoride (II)+triethylenetetramine (I)+tetradecenyl succinic acid anhydride (II); n-amyl bromide (IV)+tetra-(1-ethyl-2-benzylethylene) pentamine (I)+ethenyl succinic acid anhydride (I); isoamyl chloride (I)+tri-(1-methyl-1-phenyl-3-propylpropylene) tetramine (I)+ethenyl succinic acid (I); n-hexyl bromide (II)+tetra-(1-methyl-3-benzylpropylene) pentamine (I)+ethyl succinic acid anhydride (III); n-hexyl iodide (I)+penta-(1-methyl-2-benzylethylene) hexamine (I)+propenyl succinic acid anhydride (V); heptyl fluoride (I)+di-(1,18-dioctyloctadecylene) triamine (I)+sulfurized propenyl succinic acid anhydride (I); 2-ethylhexyl chloride (II)+di-(1,2-di-methyl-14-nonyltetradecylene) triamine (I)+butenyl succinic acid anhydride (I); n-octyl bromide (I)+dieicosylenetriamine (I)+2-methylbutenyl succinic acid anhydride (II); decyl iodide (III)+trioctadecylene-tetramine (I)+1,2-dichloropentenyl succinic acid anhydride (I); dodecyl bromide (I)+tri-(1,15-dimethylpentadecylene) tetramine (I)+hexenyl succinic acid (I); 7-ethyl-2-methyl undecyl iodide (I)+penta-(1-methyl-4-nonylbutylene) hexamine (I)+hexyl succinic acid anhydride (IV); tetradecyl bromide (II)+

tetradecylenepentamine (I) + sulfurized 3-methylpentenyl succinic acid anhydride (II); hexadecyl bromide (I) + didodecylene-triamine (I) + 2,3-dimethylbutenyl succinic acid anhydride (I); hexadecyl fluoride (III) + tetra-(1,4-dipropylbutylene)pentamine (I) + 3,3-dimethylbutenyl succinic acid (I); heptadecyl chloride (II) + tridecylene-triamine (I) + 1,2-dibromo-2-ethylbutyl succinic acid (I); octadecyl bromide (I) + tri-(1,4-diethylbutylene)tetramine (I) + heptenyl succinic acid anhydride (I); docosyl chloride (IV) + tetraoctylenepentamine (I) + 1,2-diiodooctyl succinic acid (I); tetracosyl iodide (I) + penta-(1,2-dimethyl-1-isopropylethylene)hexamine (I) + octenyl succinic acid anhydride (V); hexacosyl bromide (I) + di-(1-methyl-4-ethylbutylene)triamine (I) + 2-methylheptenyl succinic acid anhydride (II); octacosyl chloride (V) + penta-(1,5-dimethylamylene) hexamine (I) + 4-ethylhexenyl succinic acid (I); triacontyl chloride (II) + tetra-(1,3-dimethyl-propylene)pentamine (I) + 2-isopropylpentenyl succinic acid anhydride (II); chlorinated paraffin wax (I) + di-(1-methylamylene)triamine (I) + nonenyl succinic acid anhydride (II); chlorinated kerosene (II) + tri-(1,2-trimethylethylene)tetramine (I) + 2-propyl-hexenyl succinic acid anhydride (I); n-butyl bromide (II) + pentaamylenehexamine (I) + decenyl succinic acid anhydride (II); sec-butyl iodide (I) + di-(1-methylbutylene)triamine (I) + decenyl succinic acid (II); n-amyl bromide (V) + hexa-(1,1-dimethylethylene)heptamine (I) + 5-methyl-2-isopropylhexenyl succinic acid anhydride (II); n-hexyl bromide (II) + tetrabutylene-pentamine (I) + 1,2-dibromo-2-ethyloctenyl succinic acid anhydride (II); heptyl fluoride (II) + penta-(1-methylpropylene)hexamine (I) + octenyl succinic acid anhydride (II); n-octyl bromide (I) + tri(ethyl-ethylene)tetramine (I) + decyl succinic acid anhydride (III); dodecyl bromide (VI) + hexapropyleneheptamine (I) + undecenyl succinic acid anhydride (I); tetradecyl bromide (I) + di(methylethylene)triamine (I) + 1,2-dichloroundecyl succinic acid (I); hexadecyl fluoride (IV) + tetraethylenepentamine (I) + 3-ethyl-2-t-butylpentenyl succinic acid anhydride (I); octadecyl bromide (I) + hexapropyleneheptamine (I) + dodecenyl succinic acid anhydride (VI); tetracosyl iodide (II) + hexa-(1,1-diethylethylene) heptamine (I) + dodecenyl succinic acid (I); octacosyl chloride (I) + triethylene-tetramine (I) + 2-propylnonyl succinic acid anhydride (III); chlorinated paraffin wax (I) + diethylenetriamine (I) + 3-butyloctenyl succinic acid anhydride (I); n-butyl chloride (II) + di-(methylethylene)triamine (I) + tridecenyl succinic acid anhydride (I); t-butyl fluoride (II) + diethylenetriamine (I) + tetradecenyl succinic acid anhydride (I); isoamyl chloride (II) + tetra-(1,3-dimethylpropylene)pentamine (I) + hexadecyl succinic acid anhydride (III); n-hexyl iodide (III) + tetrabutylene-pentamine (I) + sulfurized octadecenyl succinic acid anhydride (II); 2-ethylhexyl chloride (III) + tetraethylene-pentamine (I) + octadecyl succinic acid anhydride (II); decyl iodide (II) + hexaethyleneheptamine (I) + 1,2-dibromo-2-methylpentadecenyl succinic acid anhydride (V); 7-ethyl-2-methylundecyl iodide (I) + diethylenetriamine (I) + 8-propylpentadecyl succinic acid anhydride (I); hexadecyl bromide (II) + triethylenetetramine (I) + eicosenyl succinic acid anhydride (II); heptadecyl chloride (I) + di-(1-methylbutylene)triamine (I) + 1,2-dichloro-2-methylnonadecyl succinic acid anhydride (II);

docosyl chloride (V) + penta-(1-methylpropylene)hexamine (I) + 2-octyldodecenyl succinic acid (I); hexacosyl bromide (I) + diethylenetriamine (I) + 1,2-diiodotetracosenyl succinic acid anhydride (I); triacontyl chloride (III) + pentaamylenehexamine (I) + hexacosenyl succinic acid (II); decyl bromide (I) + tetraethylenepentamine (I) + hexacosenyl succinic acid anhydride (II); n-octyl chloride (III) + tetraoctylenepentamine (I) + hentriacontenyl succinic acid anhydride (II).

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 ratios employed, or to the operations and manipulations described therein. A wide variety of other reactants and molar ratios, 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. These products are predominantly mixtures of relative pure anhydrides. Sometimes, however, they contain minor amounts of the corresponding alkenyl succinic acids, but these are utilisable, as set forth hereinbefore.

PREPARATION OF INTERMEDIATE PRODUCTS

EXAMPLE 1

Cetyl bromide (0.4 mole) (122 grams), tetraethylenepentamine (0.4 mole) (75.6 grams), and sodium bicarbonate (0.4 mole) (33.6 grams) were placed in a reaction vessel provided with a mechanical stirrer, a thermometer, and a condenser device (reflux take-off) for removal of water from the reaction as it is evolved in an azeotropic mixture of water and a non-polar hydrocarbon solvent. The reflux take-off was filled with benzene. The stirred reactants were heated to about 80° C., whereupon an exothermic reaction caused the temperature to rise to 130° C. The reaction temperature was then increased to 160° C. and held there for two hours. Then, benzene was added to the reaction vessel in an amount sufficient to cause a benzene reflux to take place at a pot temperature of 150-170° C. The reaction was continued for 6 hours and 7.0 milliliters of water were collected. Benzene (200 milliliters) was added to the reaction mixture and the resultant solution was filtered. The filtrate was freed of benzene by evaporation on the steam bath. The product was a yellow oil.

EXAMPLE 2

A mixture of 66.6 grams (0.2 mole) octadecyl bromide, 29.2 grams (0.2 mole) triethylenetetramine, and 18 grams (0.214 mole) sodium bicarbonate was placed in a reaction vessel equipped with a mechanical stirrer, a thermometer, and a reflux take-off. The reactants were heated at 170-180° C. for seven hours, with stirring. Sufficient benzene was added to the system to permit refluxing at a pot temperature of 160-170° C. This reflux was maintained for two hours. Four

11

milliliters of water were collected. Benzene (150 milliliters) was added to the cooled reaction mixture and the resultant solution was filtered. The product was freed of benzene on the steam bath. No halogen was present in this product, as evidenced by a negative Beilstein copper wire test.

EXAMPLE 3

A mixture of 122 grams (0.4 mole) cetyl bromide, 37.8 grams (0.2 mole) tetraethylenepentamine, and 33.6 grams (0.4 mole) sodium bicarbonate were placed in a reaction vessel equipped as hereinbefore described. The reactants were heated at 130° C. for two hours. During this period of time, a visible reaction occurred, evidenced by the formation of a viscous, slushy, yellow liquid which slowly changed to a yellow oil. Benzene was added to the system to permit refluxing at a pot temperature of 160° C. Refluxing was continued until most of the water was removed from the reaction mixture (about two hours). Then heating was continued, without refluxing, for 4.5 hours, at 160° C. Benzene (100 milliliters) was added to the reaction mixture, and the benzene solution was filtered. After benzene was removed on the steam bath, a waxy product was obtained, which gave a negative Beilstein halogen test.

EXAMPLE 4

A mixture of 66.6 grams (0.2 mole) octadecyl bromide, 18.9 grams (0.1 mole) tetraethylenepentamine, and 16.8 grams (0.2 mole) sodium bicarbonate was heated to 170° C. in the reaction vessel described hereinbefore. Then, benzene was added, so as to maintain a benzene reflux for nine hours. Benzene (150 milliliters) was added to the reaction product. The benzene solution thus obtained was filtered and benzene was removed from the filtrate on the steam bath.

EXAMPLE 5

A mixture of 116 grams (0.5 mole) tetradecyl chloride, 51.5 grams (0.5 mole) diethylenetriamine, and 42 grams (0.5 mole) sodium bicarbonate were heated, in the aforescribed reaction vessel, to 140° C. An exothermic reaction occurred with the formation of a slushy, yellow liquid. After heating for two hours at 140° C., the slushy material changed to a clear yellow liquid. Heating was continued at 140° C., for six hours additional, a light vacuum being applied to the system throughout this period, to remove the water formed in the reaction. Benzene (150 milliliters) was added to the reaction product and the solution therein was filtered. Then, the solvent was removed on the steam bath.

EXAMPLE 6

A mixture of 23.2 grams (0.1 mole) tetradecyl chloride, 18.9 grams (0.1 mole) tetraethylenepentamine, and 8.4 grams (0.1 mole) sodium bicarbonate was placed in the reaction vessel aforescribed. The reactants were heated to 140° C., whereupon the reaction mixture deepened in color and changed to a slushy liquid. Heating was continued, at 140–160° C., for seven hours. Then, 100 milliliters of benzene were added to the reaction mixture, the resultant solution was filtered, and the benzene was evaporated off on the steam bath.

EXAMPLE 7

A mixture of 30.5 grams (0.1 mole) hexadecyl bromide and 29.2 grams (0.2 mole) triethylenetetramine were heated in the reaction vessel described hereinbefore, at 160° C., for six hours.

12

Then, the temperature was increased to 205° C., for two hours additional. The reaction mixture was cooled and 100 milliliters of distilled water were added. A yellow layer separated from the aqueous phase. This layer was dissolved in benzene and separation of the layers was effected. The benzene solution was washed with distilled water. Then, the solvent was removed by evaporation on the steam bath, leaving a yellow-white, waxy product.

EXAMPLE 8

An intermediate product was produced, as described in Example 3, with the exception that a temperature of 140–150° C. was maintained for seven hours.

EXAMPLE 9

An intermediate reaction product was prepared, as described in Example 8, using 0.4 mole of cetyl chloride instead of cetyl bromide.

EXAMPLE 10

An intermediate reaction product was prepared, as described in Example 8, with the exception that 0.4 mole of tetradecyl chloride was used in place of 0.4 mole of cetyl bromide.

EXAMPLE 11

An intermediate product was produced, as described in Example 8, using 0.4 mole of dodecyl chloride instead of the cetyl bromide.

EXAMPLE 12

An intermediate product was produced, as described in Example 8, using 0.4 mole of octyl chloride in place of the cetyl bromide.

EXAMPLE 13

An intermediate product was prepared, in the manner set forth in Example 8, using 0.4 mole of butyl chloride instead of cetyl bromide. This reaction was carried out at 84° C. for four hours and then at 170° C. for six hours additional.

EXAMPLE 14

A mixture of 0.3 mole octadecyl bromide, 0.1 mole tetraethylenepentamine, and 0.3 mole of sodium bicarbonate were reacted, in the manner described in Example 4, to produce an intermediate product.

EXAMPLE 15

An intermediate product was produced in a manner similar to that described in Example 6, except that dodecyl chloride was used and a temperature of 170° C. was maintained for six hours.

EXAMPLE 16

Using the general technique described in the preceding examples, a mixture of 0.2 mole octadecyl bromide, 0.2 mole tetraethylenepentamine, and 0.2 mole sodium bicarbonate was reacted at 180° C. for five hours, to produce an intermediate product.

EXAMPLE 17

An intermediate product was produced by reacting 0.1 mole cetyl chloride, 0.1 mole triethylenetetramine, and 0.1 mole sodium bicarbonate, at 140–160° C., for eight hours, using the general technique described hereinbefore.

EXAMPLE 18

Using the general technique described in the preceding examples, an intermediate product was prepared by reacting 0.2 mole cetyl bromide, 0.1 mole triethylenetetramine, and 0.2 mole sodium bicarbonate at 160–180° C. for six hours.

EXAMPLE 19

An intermediate product was produced by reacting 0.5 mole tetradecyl chloride, 0.5 mole triethylenetetramine and 0.5 mole sodium bicarbonate at 140° C. for 9 hours, using the technique described in the preceding examples.

EXAMPLE 20

An intermediate product was prepared, using the general technique described hereinbefore, by reacting 0.2 mole dodecyl chloride, 0.2 mole triethylenetetramine, and 0.2 mole sodium bicarbonate, for seven hours, at 140° C.

EXAMPLE 21

Using the aforesaid technique, 0.2 mole butyl chloride, 0.2 mole triethylenetetramine, and 0.2 mole sodium bicarbonate were reacted at 84–130° C. for two hours, and then at 170° C. for six hours, to produce an intermediate product.

EXAMPLE 22

An intermediate product was produced, using the aforesaid technique, by reacting 0.2 mole butyl chloride, 0.2 mole diethylenetriamine, and 0.2 mole sodium bicarbonate, at 84–130° C. for three hours, and finally at 130–140° C. for six hours.

PREPARATION OF THE FINAL REACTION PRODUCT

EXAMPLE 23

In a reaction vessel provided with a thermometer, a mechanical stirrer, and a reflux take-off, were placed 20.6 grams (0.05 mole) of the reaction product of Example 1 and 44.1 grams (0.15 mole) C_{10–12}ASAA. The reflux take-off was filled with benzene, and additional benzene was added to the reactants until, when the mixture was heated, the benzene refluxed at a pot temperature of 130° C. Refluxing at 130° C. was continued for six hours. Then, the benzene was removed from the product by distillation under reduced pressure, at a pot temperature of 130° C. The reaction product thus obtained had a neutralization number (N. N.) of 148.

EXAMPLE 24

Into a reaction vessel described hereinbefore, were weighed 20.0 grams (0.05 mole) of the product of Example 2 and 29.4 grams (0.1 mole) C_{10–12}ASAA. The reactants were heated, with stirring, to 135° C. and maintained at that temperature for five hours by the addition of sufficient benzene to maintain reflux. Benzene was topped from the product under reduced pressure, at a pot temperature of 140° C. This reaction product had an N. N. of 106.3.

EXAMPLE 25

Into the aforesaid reaction vessel were placed 31.9 grams (0.05 mole) of the reaction product of Example 3 and 29.4 grams (0.1 mole) C_{10–12}ASAA. The reactants were heated to 130° C. and benzene was added to permit refluxing at that temperature. After five hours, 0.1 milliliter of water had been collected and benzene was removed under reduced pressure. The reaction product had an N. N. of 117.6.

EXAMPLE 26

A mixture of 34.6 grams (0.05 mole) of the reaction product of Example 4 and 29.4 grams (0.1 mole) C_{10–12}ASAA was placed in the aforesaid reaction vessel. The reactants were heated at 140–145° C. for six hours, under a benzene

reflux. During the reaction, 0.5 milliliter of water was collected. Benzene was topped under reduced pressure at a pot temperature of 150° C. The reaction product had an N. N. of 92.3.

EXAMPLE 27

Into the reaction vessel described hereinbefore were weighed 29.9 grams (0.1 mole) of the intermediate described in Example 5 and 44.2 grams (0.15 mole) C_{10–12}ASAA. The reactants were heated, with stirring, to 105° C., and maintained at that temperature for six hours under a benzene reflux. During that time, 0.6 milliliter of water was collected. The solvent was topped at 105° C., under reduced pressure. This reaction product had an N. N. of 125.7.

EXAMPLE 28

A mixture of 29.9 grams (0.1 mole) of the intermediate product of Example 5 and 38.7 grams (0.15 mole) C_{8–10}ASAA was placed in the reaction vessel aforesaid. The reactants were heated to 110° C., and benzene was added to allow refluxing at 105–110° C. After five hours, 0.7 milliliter of water was collected. Benzene was removed under reduced pressure at a pot temperature of 110° C. The product had an N. N. of 116.7.

EXAMPLE 29

In the aforesaid reaction vessel, 29.9 grams (0.1 mole) of the intermediate of Example 5 and 33.5 grams (0.15 mole) C_{8–10}ASAA were heated to 110° C. Benzene was added so that refluxing occurred at 104–110° C. After six hours of reaction, 0.5 milliliter of water had been collected. Benzene was removed at 110° C., under reduced pressure. This product had an N. N. of 143.3.

EXAMPLE 30

Into a reaction vessel were placed 11 grams (0.029 mole) of the intermediate product described in Example 6 and 34.1 grams (0.116 mole) C_{10–12}ASAA. The reactants were heated, without solvent, at 105° C. for five hours. The reaction product thus obtained had an N. N. of 169.1.

EXAMPLE 31

Into the reaction vessel equipped as aforesaid were placed 27 grams (0.039 mole) of the intermediate product of Example 4 and 11.7 grams (0.039 mole) C_{10–12}ASAA. The reactants were heated to 140° C. and light vacuum was applied to the system. The reaction was continued under these conditions, at 130–140° C., for five hours. The resultant product had an N. N. of 38.2.

EXAMPLE 32

In a reaction vessel as described hereinbefore, 16 grams (0.043 mole) of the intermediate product described in Example 7 and 25.5 grams (0.086 mole) C_{10–12}ASAA were heated at 140° C., under a benzene reflux. The total amount of water collected during the reaction was 5.2 milliliters. The solvent was topped off at 145° C., under reduced pressure. This reaction product had an N. N. of 159.2.

EXAMPLE 33

A reaction product was produced by reacting 0.0187 mole of the intermediate product of Example 3 and 0.0187 mole C_{10–12}ASAA, in the manner described in Example 25. This product had an N. N. of 62.8.

EXAMPLE 34

A reaction product was produced by reacting 0.023 mole of the intermediate product of Ex-

15

ample 3 and 0.069 mole C₁₀₋₁₂ASAA, in the manner described in Example 25. The reaction product had an N. N. of 142.8.

EXAMPLE 35

A reaction product was produced by reacting 0.023 mole of the intermediate product of Example 8 and 0.069 mole C₁₀₋₁₂ASAA, at 105° C., for 5.5 hours, using a benzene reflux. The reaction product had an N. N. of 131.1.

EXAMPLE 36

In the manner described in Example 28, 0.05 mole of the intermediate product of Example 8 and 0.10 mole C₁₀₋₁₂ASAA were reacted. The reaction product had an N. N. of 107.7.

EXAMPLE 37

In the manner described in Example 26, were reacted 0.028 mole of the intermediate product of Example 9 and 0.084 mole C₁₀₋₁₂ASAA. The reaction product had an N. N. of 104.0.

EXAMPLE 38

Using a benzene reflux, a reaction product was produced by reacting 0.05 mole of the intermediate product of Example 3 and 0.10 mole C₈₋₁₀ASAA, at 110° C., for 5.5 hours. The reaction product had an N. N. of 114.3.

EXAMPLE 39

In the manner described in Example 32, were reacted 0.075 mole of the intermediate product of Example 10 and 0.15 mole C₁₀₋₁₂ASAA. The reaction product had an N. N. of 83.8.

EXAMPLE 40

In the manner described in Example 28, were reacted 0.05 mole of the intermediate product of Example 11 and 0.1 mole C₁₀₋₁₂ASAA. The reaction product had an N. N. of 71.0.

EXAMPLE 41

In the manner described in Example 28, there were reacted 0.025 mole of the intermediate product of Example 11 and 0.075 mole C₁₀₋₁₂ASAA. The reaction product had an N. N. of 118.8.

EXAMPLE 42

In the manner described in Example 28, there were reacted 0.1 mole of the intermediate product of Example 12 and 0.2 mole C₁₀₋₁₂ASAA. The reaction product had an N. N. of 89.7.

EXAMPLE 43

In the manner described in Example 32, there were reacted 0.1 mole of the intermediate product of Example 13 and 0.2 mole C₁₀₋₁₂ASAA. The reaction product had an N. N. of 58.1.

EXAMPLE 44

A reaction product was produced in the general manner aforescribed, by reacting 0.05 mole of the intermediate product of Example 18 and 0.1 mole C₁₀₋₁₂ASAA, at 130° C., for 5.5 hours, under benzene reflux. The reaction product thus obtained had an N. N. of 99.3.

EXAMPLE 45

In the manner described in Example 32, a reaction product was produced from 0.05 mole of the intermediate product of Example 14 and 0.1 mole C₁₀₋₁₂ASAA. This reaction product had an N. N. of 72.9.

EXAMPLE 46

A reaction product was produced in the manner aforescribed by reacting 0.05 mole of the inter-

16

mediate product of Example 16 and 0.1 mole C₁₀₋₁₂ASAA, at 130-135° C., for six hours, under benzene reflux. The reaction product thus obtained had an N. N. of 97.7.

EXAMPLE 47

A reaction product was produced in the manner aforescribed by reacting 0.05 mole of the intermediate product of Example 16 and 0.15 mole C₁₀₋₁₂ASAA, for 5.5 hours, at 130-140° C., under benzene reflux. The reaction product thus obtained had an N. N. of 138.4.

EXAMPLE 48

In the manner aforescribed, a reaction product was produced by reacting 0.1 mole of the intermediate product of Example 1 and 0.1 mole C₁₀₋₁₂ASAA, at 120° C., for five hours, under benzene reflux. The reaction product thus obtained had an N. N. of 38.5.

EXAMPLE 49

In the manner described in Example 25, a reaction product was prepared from 0.05 mole of the intermediate product of Example 1 and 0.1 mole C₁₀₋₁₂ASAA. The reaction product had an N. N. of 112.2.

EXAMPLE 50

In the manner aforescribed, a reaction product was prepared by reacting 0.05 mole of the intermediate product of Example 6 and 0.15 mole C₁₀₋₁₂ASAA, at 145° C., for 6.5 hours, using a benzene reflux. The reaction product thus obtained had an N. N. of 42.4.

EXAMPLE 51

In the aforescribed manner, a reaction product was produced by reacting 0.1 mole of the intermediate product of Example 15 and 0.2 mole C₁₀₋₁₂ASAA, at 120-130° C., for six hours, under a benzene reflux. This reaction product had an N. N. of 41.3.

EXAMPLE 52

In the manner described in Example 25, a reaction product was produced by reacting 0.1 mole of the intermediate product of Example 5 and 0.1 mole C₁₀₋₁₂ASAA. The reaction product so obtained had an N. N. of 63.2.

EXAMPLE 53

In the manner described in Example 26, a reaction product was prepared by reacting 0.1 mole of the intermediate product of Example 22 and 0.15 mole C₁₀₋₁₂ASAA. This reaction product had an N. N. of 67.8.

EXAMPLE 54

In the manner described hereinbefore, a reaction product was produced by reacting 0.1 mole of the intermediate product of Example 17 and 0.2 mole C₁₀₋₁₂ASAA, for six hours, at 145-150° C., using a benzene reflux. The reaction product thus produced had an N. N. of 64.0.

EXAMPLE 55

In the manner described in Example 25, a reaction product was produced by reacting 0.1 mole of the intermediate product of Example 19 and 0.2 mole C₁₀₋₁₂ASAA. This reaction product had an N. N. of 78.0.

EXAMPLE 56

A reaction product was produced by reacting 0.1 mole C₁₀₋₁₂ASAA and 0.1 mole of the intermediate product of Example 19, in the manner

17

described in Example 25. The reaction product thus obtained had an N. N. of 19.0.

EXAMPLE 57

In the manner described in Example 32, a reaction product was produced by reacting 0.05 mole of the intermediate product of Example 19 and 0.15 mole C₁₀₋₁₂ASAA. This reaction product had an N. N. of 124.3.

EXAMPLE 58

In the manner described in Example 28, a re-

18

action product was produced by reacting 0.1 mole of the intermediate product of Example 20 and 0.2 mole C₁₀₋₁₂ASAA. This reaction product had an N. N. of 98.8.

EXAMPLE 59

A reaction product was prepared by reacting 0.1 mole of the intermediate product of Example 21 and 0.2 mole C₁₀₋₁₂ASAA, in the manner described hereinbefore, at 130-135° C., for five hours, using a benzene reflux. The reaction product thus produced had an N. N. of 29.7.

Table I

ALKYL HALIDE (II-III)+POLYETHYLENEPOLYAMINE (I)+ASAA (I-III)

Example	Reactants			Molar Prop., Halide:Amine: ASAA	Percent Concn.	Oil	Rust Test, Per- cent Metal Rusted		Emulsion Test Break, Min.	
	Alkyl Halide	Amine ¹	ASAA				Sea Water	Dist. Water	Dist. Water	1% NaCl
26.....	Octadecyl Bromide.....	TEPA	C ₁₀₋₁₂	2:1:2	0.08	A or B	100	100	25	24
33.....	Hexadecyl Bromide.....	TEPA	C ₁₀₋₁₂	2:1:1	0.10	A	1	0	18	18
25.....	do.....	TEPA	C ₁₀₋₁₂	2:1:2	0.15	A	0	0	25	22
34.....	do.....	TEPA	C ₁₀₋₁₂	2:1:3	0.06	A	0	0	25	23
35.....	do.....	TEPA	C ₁₀₋₁₂	2:1:3	0.05	A	0	0	28	21
36.....	do.....	TEPA	C ₁₀₋₁₂	2:1:2	0.08	A	0	0	28	23
37.....	Hexadecyl Chloride.....	TEPA	C ₁₀₋₁₂	2:1:3	0.08	A	0	0	8	13
38.....	Hexadecyl Bromide.....	TEPA	C ₈₋₁₀	2:1:2	0.05	A	0	0	25	22
39.....	Tetradecyl Chloride.....	TEPA	C ₁₀₋₁₂	2:1:2	0.07	A	0	0	5	7
40.....	Dodecyl Chloride.....	TEPA	C ₁₀₋₁₂	2:1:2	0.10	A	10	0	30	29
41.....	do.....	TEPA	C ₁₀₋₁₂	2:1:3	0.13	A	3	0	28	24
42.....	Octyl Chloride.....	TEPA	C ₁₀₋₁₂	2:1:2	0.75	A	15	0	13	10
43.....	Butyl Chloride.....	TEPA	C ₁₀₋₁₂	2:1:2	0.10	A	5	10	0	0
31.....	Octadecyl Bromide.....	TEPA	C ₁₀₋₁₂	2:1:1	0.25	A	1	0	29	29
44.....	Hexadecyl Bromide.....	TETA	C ₁₀₋₁₂	2:1:2	0.05	B	1	0	23	21
45.....	Octadecyl Bromide.....	TEPA	C ₁₀₋₁₂	3:1:2	0.08	A	0	0	29	29
					0.01	A	1	1	23	21
					0.10	A	1	0	23	21
					0.13	A	0	0	23	21

¹ TEPA is tetraethylenepentamine; TETA is triethylenetetramine.

² Tested without oxidation inhibitors.

Table II

ALKYL HALIDE (I)+TETRAETHYLENEPENTAMINE (I)+ASAA (I-IV)

Example	Reactants			Molar Prop., Halide:Amine: ASAA	Percent Concn.	Oil	Rust Test, Per- cent Metal Rusted		Emulsion Test Break, Min.	
	Alkyl Halide	Amine ¹	ASAA				Sea Water	Dist. Water	Dist. Water	1% NaCl
46.....	Octadecyl Bromide.....	TEPA	C ₁₀₋₁₂	1:1:2	0.10	A	100	100	33	25
47.....	do.....	TEPA	C ₁₀₋₁₂	1:1:3	0.05	A	1	0	30	23
48.....	Hexadecyl Bromide.....	TEPA	C ₁₀₋₁₂	1:1:1	0.08	A	0	0	7	10
49.....	do.....	TEPA	C ₁₀₋₁₂	1:1:2	0.20	A	5	0	25	25
23.....	do.....	TEPA	C ₁₀₋₁₂	1:1:2	0.05	A	0	0	29	25
50.....	Tetradecyl Chloride.....	TEPA	C ₁₀₋₁₂	1:1:3	0.02	A	0	0	15	5
30.....	do.....	TEPA	C ₁₀₋₁₂	1:1:3	0.05	A	10	0	29	29
51.....	Dodecyl Chloride.....	TEPA	C ₁₀₋₁₂	1:1:4	0.20	A	0	0	5	7
				1:1:2	0.10	A	10	0	5	7

¹ TEPA is tetraethylenepentamine.

² Tested without oxidation inhibitors.

Table III

ALKYL HALIDE (I)+DIETHYLENETRIAMINE (I)+ASAA (I-II)

Example	Reactants			Molar Prop., Halide:Amine: ASAA	Percent Concn.	Oil	Rust Test, Per- cent Metal Rusted		Emulsion Test Break, Min.	
	Alkyl Halide	Amine ¹	ASAA				Sea Water	Dist. Water	Dist. Water	1% NaCl
27.....	Tetradecyl Chloride.....	DETA	C ₁₀₋₁₂	1:1:1.5	0.07	A	100	100	25	21
28.....	do.....	DETA	C ₈₋₁₀	1:1:1.5	0.08	A	0	0	22	16
29.....	do.....	DETA	C ₆₋₈	1:1:1.5	0.06	A	3	0	11	11
52.....	do.....	DETA	C ₁₀₋₁₂	1:1:1	0.15	A	10	0	18	18
53.....	Butyl Chloride.....	DETA	C ₁₀₋₁₂	1:1:1.5	0.13	A	10	10	10	10

DETA is diethylenetriamine.

Table IV

ALKYL HALIDE (I)+TRIETHYLENETETRAMINE (I)+ASAA (I-III)

Example	Reactants			Molar Prop., Halide:Amine: ASAA	Percent Concn.	Oil	Rust Test, Per- cent Metal Rusted		Emulsion Test Break, Min.	
	Alkyl Halide	Amine ¹	ASAA				Sea Water	Dist. Water	Dist. Water	1% NaCl
24	Octadecyl Bromide	TETA	C ₁₀₋₁₂	1:1:2	0.08	A or B	100	100	25	24
54	Hexadecyl Chloride	TETA	C ₁₀₋₁₂	1:1:2	0.08	A	0	0	23	10
55	Tetradecyl Chloride	TETA	C ₁₀₋₁₂	1:1:2	0.10	A	10	0	25	23
56	do	TETA	C ₁₀₋₁₂	1:1:1	0.50	A	10	0	30	30
57	do	TETA	C ₁₀₋₁₂	1:1:3	0.05	A	15	0	21	25
58	Dodecyl Chloride	TETA	C ₁₀₋₁₂	1:1:2	0.09	A	0	0		
59	Butyl Chloride	TETA	C ₁₀₋₁₂	1:1:2	0.30	A	0	0		
32	Hexadecyl Bromide	TETA	C ₁₀₋₁₂	1:1:2	0.05	A	0	0		

¹ TETA is triethylenetetramine.

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 data are set forth in Tables I through IV.

Mineral oil A used in these tests was a blend of solvent-refined, Mid-Continent residual stock with a solvent-refined, Mid-Continent (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. Mineral oil B was a furfural-refined, Mid-Continent (Rodessa) distillate stock. It had a specific gravity of 0.860, a flash point of 405° F., and a Saybolt Universal viscosity of 155 seconds at 100° F. Both of these mineral lubricating oils are suitable for use in steam turbines. Unless otherwise indicated in the tables, the test oil 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 antioxidants.

The test method used to distinguish the rusting characteristics of lubricating oil blends was the ASTM test D665-47T for determining "Rust Preventing Characteristics of Steam Turbine Oils in Presence of Water," in which synthetic sea water (Procedure B) was used as well as distilled water (Procedure A). The synthetic sea water contained 24.54 grams of sodium chloride, 11.1 grams of magnesium chloride hexahydrate, 4.09 grams of sodium sulfate, 1.16 grams of calcium chloride, 0.69 gram of potassium chloride, 0.2 gram of sodium bicarbonate, 0.1 gram of potassium bromide, 0.03 gram of boric acid, 0.04 gram of strontium chloride hexahydrate, and 0.003 gram of sodium fluoride per liter. The pH of this solution is adjusted to 7.8-8.2 by adding 1-2 milliliters of 0.1N sodium carbonate solution. 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 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.

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 tables that, as a class, the reaction products of this invention do not impart undesirable emulsion characteristics to the oil. Some products, however, may produce undesirably emulsive oils. Several demulsifying agents are known, however, and incorporation of such agents in such emulsive oils improves the emulsion characteristics thereof.

EXAMPLE 60

The rusting characteristics of a mineral lubricating oil containing the product of Example 44 (Table I) 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. Test oil B containing by weight 0.08 per cent of the product of Example 44, 0.2 per cent 2,6-di-t-butyl-4-methylphenol, and 0.1 per cent phenyl- α -naphthylamine permitted no trace of rust on the catalyst coil in this test. When the oil is tested without the antirust additive the catalyst coil rusts within as short a period of time as five hours.

EXAMPLE 61

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 product of Example 44 (Table I) by dipping them in a two per cent by weight solution of the

product in benzene. Likewise, two additional specimens were coated with the product of Example 49 (Table II). Two 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 every hour, over a period of five hours, each specimen was immersed in distilled water for about 30 seconds, by raising a separate beaker of distilled water under each one. The control specimens showed a green stain and light surface rusting in two hours. Two days thereafter, 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 suspensions 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 liquid, 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.; natural esters, such as ethyl acetate, butyl propionate, cresyl acetate, dodecyl acetate, ethyl maleate, butyl stearate, tridecyl phosphate, tributyl trithiophosphate, 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, soy bean 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 is added to a vehicle to produce a composition in accordance with this invention varies between about 0.003 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 0.003 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, antideionants, 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 modi-

fications 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 0.003 per cent and about 50 per cent by weight of the reaction product obtained by reacting an alkyl monohalide having between eight and eighteen carbon atoms per molecule with a polyalkylenepolyamine having one more nitrogen atom per molecule than there are alkylene groups in the molecule, in a molar proportion varying between about one and about $(x-1)$ to one, respectively, wherein x represents the number of nitrogen atoms in the polyalkylenepolyamine molecule, at a temperature of between about 100° C. and about 250° C., for a period of time varying between about 6 hours and about 10 hours, to produce an intermediate product, and reacting an alkenyl succinic acid anhydride having between two carbon atoms and twelve carbon atoms per alkenyl radical, with said intermediate product, in a molar proportion varying between about $(x-1)$ and about one to one, respectively, at a temperature of between ambient temperatures and about 150° C., for a period of time varying between several minutes and about 10 hours; the sum of the number of moles of said alkyl halide and of said alkenyl succinic acid anhydride reacted with each mole of said polyalkylenepolyamine being no greater than x .

2. The composition of claim 1, wherein said polyalkylenepolyamine is a polyethylenepolyamine having between two and six ethylene groups per molecule.

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

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

5. The reaction product obtained by reacting an alkyl monohalide having between 8 and 18 carbon atoms per molecule with a polyalkylenepolyamine having one more nitrogen atom per molecule than there are alkylene groups in the molecule, in a molar proportion varying between about one and about $(x-1)$ to one, respectively, wherein x represents the number of nitrogen atoms in the polyalkylenepolyamine molecule, at a temperature of between about 100° C. and about 250° C., for a period of time varying between about 6 hours and about 10 hours, to produce an intermediate product, and reacting an alkenyl succinic acid anhydride having between two carbon atoms and twelve carbon atoms per alkenyl radical with said intermediate product, in a molar proportion varying between about $(x-1)$ and about one to one, respectively, at a temperature of between ambient temperatures and about 150° C., for a period of time varying between several minutes and about 10 hours; the sum of the number of moles of said alkyl halide and of said alkenyl succinic acid anhydride reacted with each mole of said polyalkylenepolyamine being no greater than x .

6. The reaction product obtained by reacting an alkyl monohalide having between 8 and 18 carbon atoms per molecule with a polyethylenepolyamine having one more nitrogen atom per molecule than there are ethylene groups in the molecule and having between about two and about six ethylene groups per molecule, in a molar proportion varying between about one and about $(x-1)$ to one, respectively, wherein x represents the number of nitrogen atoms in the

polyethylenepolyamine molecule, at a temperature of between about 100° C. and about 250° C., for a period of time varying between about 6 hours and about 10 hours, to produce an intermediate product, and reacting an alkenyl succinic acid anhydride having between two carbon atoms and twelve carbon atoms per alkenyl radical with said intermediate product, in a molar proportion varying between about $(x-1)$ and about one to one, respectively, at a temperature of between ambient temperatures and about 150° C., for a period of time varying between several minutes and about 10 hours; the sum of the number of moles of said alkyl halide and of said alkenyl succinic acid anhydride reacted with each mole of said polyethylenepolyamine being no greater than x .

7. The reaction product obtained by reacting an alkyl monohalide having between 14 and 18 carbon atoms per molecule with tetraethylenepentamine, in a molar proportion varying between about one and about four to one, respectively, at a temperature of between about 100° C. and about 250° C., for a period of time varying between about 6 hours and about 10 hours, to produce an intermediate product, and reacting an alkenyl succinic acid anhydride having between ten carbon atoms and twelve carbon atoms per alkenyl radical with said intermediate product, in a molar proportion varying between about four and about one to one, respectively, at a temperature of between ambient temperatures and about 150° C., for a period of time varying between several minutes and about 10 hours; the sum of the number of moles of said alkyl halide and of said alkenyl succinic acid anhydride reacted with each mole of said triethylenetetramine being no greater than five.

8. The reaction product obtained by reacting hexadecyl monochloride with tetraethylenepentamine, in a molar proportion of about two to one, respectively, at a temperature of between about 100° C. and about 250° C., for a period of time varying between about 6 hours and about 10 hours, to produce an intermediate product, and reacting an alkenyl succinic acid anhydride having between ten carbon atoms and twelve carbon atoms per alkenyl radical with said intermediate product, in a molar proportion of about three to one, respectively, at a temperature of between ambient temperatures and about 150° C., for a period of time varying between several minutes and about 10 hours.

9. The reaction product obtained by reacting octadecyl bromide with tetraethylenepentamine, in a molar proportion of about one to one, respectively, at a temperature of between about 100° C. and about 250° C., for a period of time varying between about 6 hours and about 10 hours, to produce an intermediate product, and reacting an alkenyl succinic acid anhydride having between about ten carbon atoms and about twelve carbon atoms per alkenyl radical with said intermediate product, in a molar proportion of about three to one, respectively, at a temperature of between ambient temperatures and about 150° C., for a period of time varying between several minutes and about 10 hours.

10. The reaction product obtained by reacting octadecyl monobromide with triethylenetetramine, in a molar proportion of about one to one, respectively, at a temperature of between about 100° C. and about 250° C., for a period of time varying between about 6 hours and about 10 hours, to produce an intermediate

25

product, and reacting an alkenyl succinic acid anhydride having between ten carbon atoms and twelve carbon atoms per alkenyl radical with said intermediate product, in a molar proportion of about two to one, respectively, at a temperature of between ambient temperatures and about 150° C., for a period of time varying between several minutes and about 10 hours.

11. A mineral lubricating oil containing between about 0.01 per cent and about 10 per cent, by weight, of the reaction product obtained by reacting hexadecyl monochloride with tetraethylenepentamine, in a molar proportion of about two to one, respectively, at a temperature of between about 100° C. and about 250° C., for a period of time varying between about 6 hours and about 10 hours, to produce an intermediate product, and reacting an alkenyl succinic acid anhydride having between ten carbon atoms and twelve carbon atoms per alkenyl radical with said intermediate product, in a molar proportion of about three to one, respectively, at a temperature of between ambient temperatures and about 150° C., for a period of time varying between several minutes and about 10 hours.

12. A mineral lubricating oil containing between about 0.01 per cent and about 10 per cent, by weight, of the reaction product obtained by reacting octadecyl monobromide with tetraethylenepentamine, in a molar proportion of about one to one, respectively, at a temperature of between about 100° C. and about 250° C., for a period of time varying between about 6 hours and about 10 hours, to produce an intermediate product, and reacting an alkenyl succinic acid anhydride having between ten carbon atoms and twelve carbon atoms per alkenyl radical with said intermediate product, in a molar proportion of about three to one, respectively, at a temperature of between ambient temperatures and about 150° C., for a period of time varying between several minutes and about 10 hours.

13. A mineral lubricating oil containing between about 0.01 per cent and about 10 per cent, by weight, of the reaction product obtained by reacting octadecyl monobromide with triethylenetetramine, in a molar proportion of about one to one, respectively, at a temperature of between about 100° C. and about 250° C., for a period of time varying between about 6 hours and about 10 hours, to produce an intermediate product, and reacting an alkenyl succinic acid anhydride having between ten carbon atoms and twelve carbon atoms per alkenyl radical with said intermediate product, in a molar proportion of about two to one, respectively, at a temperature of between ambient temperatures and about 150° C., for a period of time varying between several minutes and about 10 hours.

14. A mineral lubricating oil containing between about 0.01 per cent and about 10 per cent, by weight, of the reaction product obtained by reacting tetradecyl monochloride with diethylenetriamine, in a molar proportion of about one to one, respectively, at a temperature of between about 100° C. and about 250° C., for a period of time varying between about 6 hours and about 10 hours, to produce an intermediate product, and reacting an alkenyl succinic acid anhydride having between eight carbon atoms

26

and ten carbon atoms per alkenyl radical with said intermediate product, in a molar proportion of about 1.5 to one, respectively, at a temperature of between ambient temperatures and about 150° C., for a period of time varying between several minutes and about 10 hours.

15. A mineral lubricating oil containing between about 0.01 per cent and about 10 per cent, by weight, of the reaction product obtained by reacting tetradecyl monochloride with tetraethylenepentamine, in a molar proportion of about one to one, respectively, at a temperature of between about 100° C. and about 250° C., for a period of time varying between about 6 hours and about 10 hours, to produce an intermediate product, and reacting an alkenyl succinic acid anhydride having between ten carbon atoms and twelve carbon atoms per alkenyl radical with said intermediate product, in a molar proportion of about four to one, respectively, at a temperature of between ambient temperatures and about 150° C., for a period of time varying between several minutes and about 10 hours.

16. The reaction product obtained by reacting tetradecyl monochloride with diethylenetriamine, in a molar proportion of about one to one, respectively, at a temperature of between about 100° C. and about 250° C., for a period of time varying between about 6 hours and about 10 hours, to produce an intermediate product, and reacting an alkenyl succinic acid anhydride having between eight carbon atoms and ten carbon atoms per alkenyl radical with said intermediate product, in a molar proportion of about 1.5 to one, respectively, at a temperature of between ambient temperatures and about 150° C., for a period of time varying between several minutes and about 10 hours.

17. The reaction product obtained by reacting tetradecyl monochloride with tetraethylenepentamine, in a molar proportion of about one to one, respectively, at a temperature of between about 100° C. and about 250° C., for a period of time varying between about 6 hours and about 10 hours, to produce an intermediate product, and reacting an alkenyl succinic acid anhydride having between ten carbon atoms and twelve carbon atoms per alkenyl radical with said intermediate product, in a molar proportion of about four to one, respectively, at a temperature of between ambient temperatures and about 150° C., for a period of time varying between several minutes and about 10 hours.

RALPH V. WHITE.

PHILLIP S. LANDIS.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
2,176,441	Ulrich et al.	Oct. 17, 1939
2,191,738	Balle	Feb. 27, 1940
2,246,264	Pinkernelle	June 17, 1941
2,279,688	Larsen	Apr. 14, 1942
2,301,969	Pinkernelle	Nov. 17, 1942
2,371,142	Barnum	Mar. 13, 1945
2,402,825	Lovell et al.	June 25, 1946

FOREIGN PATENTS

Number	Country	Date
437,104	Great Britain	Oct. 16, 1935
482,352	Great Britain	Mar. 28, 1938