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[54] **REACTION PRODUCT OF ALKYLENE
 POLYAMINES AND CHLORINATED ALKENYL
 SUCCINIC ACID DERIVATIVES**
13 Claims, No Drawings

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252 51.5 A
 [50] Field of Search..... **260/268,**
326.5 F, 326.3, 326.5 FA

ABSTRACT: Compositions are obtained by halogenating an alkenyl succinic acid or acid derivative in a hydroxylic solvent and treating the resulting product under dehydrating conditions with an amine. The products with relatively long hydrocarbon chains find use as detergents in lubricating oils and as emulsifiers.

REACTION PRODUCT OF ALKYLENE POLYAMINES AND CHLORINATED ALKENYL SUCCINIC ACID DERIVATIVES

BACKGROUND OF THE INVENTION

Field of the Invention

A significant breakthrough in the field of improved lubricating oils was the advent of ashless detergents. These ashless detergents were initially, for the most part, acyl derivatives of amines having a relatively long hydrocarbon chain bonded to the acyl group. Numerous patents have issued describing various ashless-type lubricating oil detergents; see for example U.S. Pat. Nos. 3,219,666, 3,296,128, 3,200,075, 3,373,112, and 3,275,554.

While the above additives provide good sludge dispersancy, in many instances their protection against varnish deposits is not as good. Therefore, there have been continued efforts to find additives which provide not only good sludge dispersancy but also minimize varnish deposits.

Description of the Prior Art

The patents aforesaid are, for the most part, illustrative of the relevant prior art.

SUMMARY OF THE INVENTION

Compositions are prepared by halogenating an oil-soluble alkenyl succinic acid or acid derivative, e.g. anhydride, monoester, diester etc., and then treating the resulting halogenated product with an amine to form an acyl and/or alkyl amine product which has the amine compound in greater than a 1:1 mole ratio of amine to acid compound. These materials are particularly useful as lubricating oil detergents, providing protection from sludge and varnish.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Product

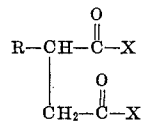
The products which find use as lubricating oil detergents will generally have weight average molecular weights of from about 700 to 10,000, more usually from about 1,000 to 6,000. In the molecule, there will be at least 30 aliphatic carbon atoms and preferably at least 50 aliphatic carbon atoms, usually not exceeding a total of 650 carbon atoms, more usually a total of 400 carbon atoms. There will be at least one aliphatic hydrocarbon group of 14 carbon atoms, preferably of at least 30 carbon atoms and usually not exceeding 300 carbon atoms in length.

The compositions will generally have from 1 to 2 succinyl groups per molecule, usually averaging at least 1 and between 1 and 2 succinyl groups. The succinyl includes lactone derivatives such as paraconic acid.

The amines employed will provide at least 1.5 weight percent nitrogen in the composition and generally not exceed 12 weight percent nitrogen, more usually in the range of about 2 to 8 weight percent nitrogen.

Method of Preparation

In preparing the compositions, an alkenyl succinic acid or acid derivative will initially be halogenated to introduce at least about one atom of halogen per molecule of alkenyl succinic acid compound. The alkenyl succinic acid compound will generally have the following formula:



wherein R is an oil solubilizing alkenyl group of at least about 14 and up to about 300 carbon atoms having alpha or beta aliphatic unsaturation, more usually from about 30 to 250 carbon atoms and, preferably, from about 50 to 200 carbon atoms; the two X's may be hydroxyl or hydrocarbyloxy of from one to 12 carbon atoms, more usually of from one to

three carbon atoms, or may be taken together to form an oxy (-O-) group of an anhydride. Preferably, the composition is a monoester or anhydride.

R, the alkenyl group, will normally be free of heteroatoms, although up to about 5 weight percent of R may be present as heteroatoms forming functional groups which do not interfere with the process of preparation of the compositions of this invention or their performance.

R will have olefinic unsaturation in the alpha or beta position to the succinic moiety and be substantially free of other unsaturation. R may be a straight or branched chain alkenyl group; ordinarily, R will be a branched chain aliphatic group having on the average about one side chain of from one to four carbon atoms for every four carbon atoms along the longest chain; more usually, the side chain will be from one to two carbon atoms and, preferably, methyl. Preferably, R will be polypropylene or polyisobutylene, although other oil-solubilizing alkyl groups may be used.

When the succinic acid compound is a monoester or diester, any hydroxylic hydrocarbon can be used to form the ester group, since the hydrocarbyloxy radical X will normally be lost, for the most part, during the preparation of the subject compositions. Usually, X will conveniently be a lower alkoxy group of from one to three carbon atoms, more usually X will be methoxy. The monoester may be prepared or be prepared in situ.

The halogen employed is either chlorine or bromine, (halogen of atomic number 17 or 35) and preferably chlorine. Halogenating agents may be used which will provide positive halogen under the conditions of e.g., reaction, e.g., tert.-butyl hypochlorite.

The halogenation is carried out neat or in the presence of a solvent. The halogenation is carried out under ionic conditions. These conditions usually result in the addition of halogen across the double bond. However, with the alkenyl succinic derivatives, it is believed that only one halogen is added to the molecule at the double-bond site and a lactone or other derivative is formed.

Various solvents may be used which do not interfere with the halogenation of the alkenyl succinic acid. The solvents may be aromatic hydrocarbons, aliphatic hydroxylic compounds or other polar or nonpolar solvents, as well as mixtures. A preferred method of halogenation is to halogenate the anhydride in the presence of a hydroxylic solvent.

Illustrative hydroxylic solvents include water and alkanols of from one to six carbon atoms, preferably alkanols of from one to two carbon atoms, i.e., methanol and ethanol. In addition to the hydroxylic solvent, an inert hydrocarbon or halohydrocarbon solvent may be used. The preferred inert solvent is an aromatic hydrocarbon such as benzene or tert.-butyl benzene, or an inert halohydrocarbon such as chlorobenzene.

The temperature for the reaction will generally be from about -10° C. to about 100° C., more usually from about 0° C. to about 50° C. The halogenation should be carried out so as to minimize side reactions of the halogen.

The amounts of inert solvent and hydroxylic solvent may be varied widely. Based on the alkenyl succinyl compound, the amount of inert solvent may vary from 0.1 to about 2 parts of solvent per part of succinyl compound. The hydroxylic solvent will usually vary from about 0.01 to about 1 part per part of succinyl compound.

The halogenation will be continued until at least about one atom of halogen is introduced per succinyl molecule and not more than about two atoms, preferably from about one to 1.5 atoms. Of course, less halogen may be introduced, but this will result in reduction of the amount of desired product which is ultimately obtained. However, if mixtures are desired of materials prepared in the prior art and the compositions of this invention, reducing the amount of halogen introduced to below one atom per succinyl molecule would directly provide such mixtures.

When the reaction is complete, the volatile materials are removed and the residue is ready to be used in the subsequent reaction.

Amines which find use are other than tertiary amines i.e. primary and secondary amines, which may be monoamines or polyamines or hydroxyalkyl or polyalkyleneoxy amines. Tertiary amines may be present in combination with primary or secondary amines. The amines may be ammonia or amines of from one to 30 carbon atoms, more usually of from one to 20 carbon atoms having from one to 10 amine nitrogen atoms and from one to 10 oxygen atoms, either hydroxylic or ethereal. The amines will be free of other heteroatoms than those designated. Usually, not more than three of the oxygen atoms will be hydroxylic, more usually not more than two.

The alkylene polyamines will be of from two to 24 carbon atoms having from two to 10 amine nitrogen atoms, preferably two to six amine nitrogen atoms and alkylene groups of from two to six carbon atoms, preferably two to three carbon atoms, there being at least two carbon atoms between the nitrogen atoms. Also included in the category of alkylene polyamines are piperazine derivatives and aminoalkylene piperazine. The piperazine compositions frequently accompany the alkylene polyamines, depending on the method of preparation of the alkylene polyamines.

Commercially, alkylene polyamines are rarely individual compounds. Usually one compound predominates and the composition has an average composition that of the dominant compound. Therefore, when referring to a specific alkylene polyamine, it is intended to include such mixtures as substantially equivalent to the alkylene polyamine named.

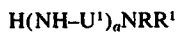
The alkylene polyamines will generally have the following formula:



wherein U is alkylene of from 2 to 6, more usually of from two to three carbon atoms, there being at least two carbon atoms between the nitrogen atoms; and n is an integer of from 2 to 10, more usually of from 2 to 6, generally averaging in the range of 2 to 6 over the entire composition.

Illustrative alkylene polyamines include ethylene diamine, propylene diamine, diethylene triamine, dipropylene triamine, dihexamethylene triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, nonaethylene decamine, etc.

Monoamines and diamines having at least one hydrocarbon group bonded to only one nitrogen atom will have the following formula:

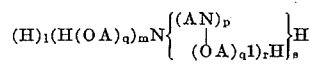


wherein U¹ is alkylene of from two to three carbon atoms, there being at least two carbon atoms between the nitrogen atoms, R is a hydrocarbon group free of aromatic unsaturation, having from 0 to 2 sites of ethylenic unsaturation and is of from one to 20 carbon atoms, R¹ is hydrogen or a hydrocarbon group free of aromatic unsaturation having from 0 to 2 sites of ethylenic unsaturation and of from one to 20 carbon atoms and may be the same or different than R. a is 0 or 1.

The entire molecule will have from one to 24 carbon atoms, more usually from four to 20 carbon atoms.

Illustrative compositions include dimethyl amine, propyl amine, cyclohexylamine, N-hexyl propylene diamine, N-dodecyl propylene diamine, N-hexadecyl propylene diamine, N-octadecenyl ethylene diamine, N-octadecenyl propylene diamine, N,N-dimethyl propylene diamine, etc.

The alkanol amines and polyalkyleneoxy amines have for the most part the following formula:



wherein m is an integer of from 0 to 2; l is an integer of from 0 to 2; the sum of l and m is 2; p is an integer of from 0 to 5; q and q' are the number of AO units in a chain pendant from nitrogen and each are in the range of 0 to 10, the sum of q+q' being in the range of 1 to 10; r is an integer of from 0 to 1; the sum of m and r is equal to or greater than 1; s is an integer of from 0 to 1; and A is alkylene of from two to three carbon atoms, there being at least two carbon atoms between the heteroatoms.

The total number of AO units will be in the range of 1 to 10, more usually in the range of 1 to 6.

Illustrative alkanol amines include ethanol amine, diethanol amine, N-hydroxyalkyl ethylene diamine, N-hydroxyethyl propylene diamine, tetraethyleneoxy ethylene diamine, the reaction product of tetraethylene pentamine and ethylene oxide in 1 to 5 mole ratio, pentaethyleneoxy amine, and diethyleneoxy amine.

The reaction between the amine and the halogen-succinyl product may be carried out neat or in an inert hydrocarbon solvent; or, in two steps, first in solution and then neat. Inert solvents will usually be hydrocarbons or acyl halides, generally having boiling points or ranges in the range of 100° C. to 175° C. Illustrative solvents include xylene, cumene, tert.-butylbenzene, chlorobenzene etc.

The mole ratio of the amine to the halogenated-succinyl reaction product will be at least 1:1, usually, about 1.5 to 10:1, and more usually from about 2 to 7:1.

The concentration of the reactants will generally range from about 0.5 to 20 parts of total reactants per part of solvent, usually from about 1 to 10 parts per part of solvent.

The reaction temperature will ordinarily be in the range of 100° C. to 225° C., more usually 110° C. to 200° C.

The time for the reaction will vary widely depending on the temperature employed, the reactants, the size of the reaction mixture and other variables.

When the reaction has come to completion, the reaction mixture may be allowed to cool, which will usually result in phase separation. The organic layer may be separated from the amine salt layer and worked up in any conventional manner. Usually the organic layer will be freed of residual unreacted amine and purified by extraction, chromatography, etc.

EXAMPLES

The following examples are offered by way of illustration and not by way of limitation.

EXAMPLE 1

Into a reaction vessel was introduced 1,134 g. of polyisobutenyl succinic anhydride (polyisobutenyl having a weight average molecular weight of about 1,000), 500 ml. of benzene and 60 ml. of water; chlorine was bubbled into the reaction mixture for 3 hours (Flow Meter 1044B-Sapphire Ball Reading 5), followed by bubbling nitrogen through the mixture for 1 hour. Benzene and water were then removed in vacuo. Complete removal of the water was aided by the addition of 300 ml. of benzene and azeotroping off the benzene with nitrogen bubbling. An aliquot was taken and further stripped in vacuo to provide a sample for analysis. Analysis: % Cl=4.29.

To the above composition was added 500 g. of diethylene triamine and 250 ml. of xylene. Any residual benzene was stripped and the solution heated to 145° C. Xylene and water were taken overhead during a period of about 1 hour. The temperature was then raised to 170°-175° C., distilling over any volatile materials and the temperature maintained for 6 hours. After allowing the mixture to stand and cool, the reaction mixture separated into 2 layers. After decanting the liquid upper layer, the bottom solid layer was washed with an aliphatic thinner and the 2 organic layers combined.

To the combined organic solutions was added 1 gallon of methanol; the mixture was stirred, allowed to settle, and the supernatant layer decanted. The precipitate was extracted with methanol, followed by extraction with acetone and then redissolved with mixed hexanes and reprecipitated with acetone. The precipitate was dissolved in benzene to permit easy handling in preparing oil solutions. Analysis: % N=2.54, 2.57; % Cl=0.20; molecular weight, (ThermoNAM) 3113.

EXAMPLE 2

Into a reaction vessel was introduced 600 g. of polyisobutenyl succinic anhydride (polyisobutenyl of about 1,000 weight

average molecular weight), 400 ml. of benzene and 50 ml. of methanol. Chlorine was bubbled through the reaction mixture for 1.5 hours (Flow Meter 1044B-Sapphire Ball Reading 5), followed by nitrogen bubbling for one-half hour. Volatile materials were then removed in vacuo, as the temperature was raised to a maximum bath temperature of 95° C. Analysis: % C=5.11.

To the residue was added 120 ml. of xylene and 250 g. of diethylene triamine. The solution was then heated for 6 hours at 145°-160° C., taking off water and xylene overhead. All volatile materials were then removed in vacuo to a final temperature of 150° C. After cooling the mixture, 300 ml. of an aliphatic thinner was added, followed by the addition of 700 ml. of a 50/50 by volume mixture of methanol and water. Upon stirring, the mixture emulsified. To the solution was then added 1 gallon of methanol and 400 ml. of water and the solution allowed to settle. The liquid layer was decanted and the solid layer extracted with aqueous methanol followed by extraction with acetone. An aliquot was taken of the combined liquid layers and extracts and the solvent removed in vacuo. Analysis: % N=3.33; % Cl=1.07, molecular weight (ThermoNAM) 3578.

EXAMPLE 3

Into a reaction vessel was introduced 650 g. of polyisobut-nyl succinic anhydride (polyisobutenyl having about 1,000 weight average molecular weight), 400 ml. of benzene and 50 ml. of methanol. Chlorine was introduced at ambient temperatures for 1.75 hours (Flow Meter 1044B-Sapphire Ball Reading 5), followed by nitrogen bubbling. Volatile materials were removed by slowly reducing the pressure and raising the temperature to a final pressure of 10 mm. Hg and a final bottoms temperature of 100° C.

To the residue was added 200 ml. of xylene and 200 ml. of ethylene diamine, and a mixture refluxed for 64 hours at about 110° C. After allowing the mixture to cool, 550 ml. of aliphatic thinner were added and the solution filtered through Celite. To the filtrate was added 800 ml. of water, 550 ml. of mixed hexanes and 1 gallon of methanol. The solution was allowed to settle, the layers separated and the organic layer washed with aqueous methanol. The organic layer was then filtered through Celite and the product isolated. Analysis: % N=2.76; % Cl=1.06, molecular weight (ThermoNAM) 2558.

EXAMPLE 4

Into a reaction flask was introduced 650 g. of polyisobut-nyl succinic anhydride (polyisobutenyl of about 1,000 weight average molecular weight), 400 cc. benzene and 50 B-Sapphire of methanol. Chlorine was bubbled through the reaction mixture for 4 hours (Flow Meter 1044B-Sapphire Ball Reading at 3.5) followed by nitrogen for one-half hour. The solvent was distilled in vacuo lowering the pressure to 15 mm. Hg and raising the temperature to 115° C. The residue weighed 714 g. Analysis: % Cl, 5-5.5; Mol. wt. (ThermoNAM), 1100.

A portion of the above product (0.59 mole) was combined with 250 g. (2.42 moles) of diethylene triamine and heated at 160° C. for 7 hours in a nitrogen atmosphere. The reaction mixture was then allowed to cool to 100° C., when 850 cc. of an aliphatic thinner was added, the mixture stirred, transferred to a separatory funnel and the resulting two phases separated. The top layer was filtered through Celite, stripped free of solvent and other volatiles by heating to 155° C. at 5 mm. Hg. The residue weighed 680 g. Analysis: % N, 4.05, Mol. wt. (ThermoNAM) 4245.

EXAMPLE 5

Into a reaction vessel was introduced 650 g. of polyisobut-nyl succinic anhydride (polyisobutenyl of about 1,000 weight average molecular weight), 400 cc. of benzene and 50 cc. of methanol and chlorine passed through the mixture for 1.75 hours (Flow Meter 1044B-Sapphire Ball Reading, 5-5.2). At the end of the chlorination, nitrogen was bubbled through the

mixture for 1 hour and solvent distilled off in vacuo, the temperature being raised to about 95° C. The residue weighed 707 g. Analysis: % Cl, 4.74.

The above procedure was repeated, the final product having 4.91 percent chlorine.

Each of the batches was diluted with 120 cc. of xylene and then 250 g. diethylene triamine added to each batch. The two batches were treated in a parallel manner as follows. The solution was azeotroped for 6 hours at 160° C., cooled to room temperature, and decanted from the resulting salt layer. The salt layer was washed with mixed hexanes, the hexanes evaporated and the residue added to the decanted solution. An additional 250 g. diethylene triamine was charged and the mixture stirred at 105° C. for 2 hours. After cooling to room temperature, approximately 2l of an aliphatic thinner was used to dilute the reaction mixture and the resulting mixture filtered through Celite and solvent distilled off from the filtrate. The residue from the first batch weighed 666 g. and the residue from the second batch weighed 630 g.

Analysis: 1st, % N, 4.30, % Cl, 1.39, Mol. wt. (ThermoNAM), 2934; 2nd, % N, 4.20, % Cl 0.71, Mol. wt. (ThermoNAM) 2442.

LUBRICATING OILS

The compositions of this invention may be formulated with various lubricating fluids (hereinafter referred to as oils) which are either derived from natural or synthetic sources. Oils generally have viscosities of from about 35 to 50,000 Saybolt Universal Seconds (SUS) at 100° F. Among natural hydrocarbonaceous oils are paraffin-base, naphthenic-base, asphaltic-base and mixed-base oils.

Illustrative of synthetic oils are: hydrocarbon oils such as polymers of various olefins, generally of from two to eight carbon atoms, and alkylated aromatic hydrocarbons; and non-hydrocarbon oils, such as polyalkylene oxides, aromatic ethers, carboxylate esters, phosphate esters, and silicon esters. The preferred media are the hydrocarbonaceous media, both natural and synthetic.

The above oils may be used individually or together whenever miscible or made so by the use of mutual solvents.

When the detergents of this invention are compounded with lubricating oils for use in an engine, the detergents will be present in at least about 0.1 weight percent and usually not more than 20 weight percent, more usually in the range of about 1 to 10 weight percent. The compounds can be prepared as concentrates due to their excellent compatibility with oils. As concentrates, the compounds of this invention will generally range from about 10 to 70 weight percent, more usually from about 20 to 50 weight percent of the total composition. Therefore, the detergents of this invention will be found in lubricating oil compositions in amounts of from about 0.1 to 70 weight percent.

A preferred aspect in using the compounds of this invention in lubricating oils is to include in the oil from about 1 to 50 mM./kg. of a dihydrocarbyl phosphorodithioate, wherein the hydrocarbyl groups are of from about four to 35 carbon atoms. Usually, the hydrocarbyl groups will be alkyl or alkaryl groups. The remaining valence of the phosphorodithioate will usually be satisfied by zinc, but polyalkyleneoxy or a third hydrocarbyl group may also be used. (Hydrocarbyl is an organic radical composed solely of carbon and hydrogen which may be aliphatic, alicyclic, aromatic or a combination thereof.)

Other additives may also be included in the oil such as pour point depressants, oiliness agents, antioxidants, rust inhibitors, etc. Usually, the total amount of these additives will range from about 0.1 to 10 weight percent, more usually from about 0.5 to 5 weight percent. The individual additives may vary from about 0.01 to 5 weight percent of the composition.

In order to demonstrate the effectiveness of the subject compositions on pistons for their effect on varnish, the exemplary composition of example 2 was tested in what is referred

to as a Ford 6-Cylinder Varnish Engine Test. A highly compounded oil is used, having the following formulation: 1.9 weight percent of example 2, 50 mM./kg. of calcium as a calcium carbonate overbased calcium mahogany sulfonate; and 15 mM./kg. of zinc, 0,0-dialkyl phosphorodithioate (alkyl of from four to six carbon atoms). The oil used is a mixture of SUNRAY DX 250 neutral oil and SUNRAY DX 150 bright stock in a 6.16:1 weight ratio.

The test is carried out with a six-Cylinder Ford engine having a 240 cu. in. displacement. The engine conditions are the same as the cyclic conditions of the ASTM Sequence VB test. The engine conditions are stressed by using a "dirty" fuel which is comprised of 30 volume percent of FCC heavy cut having a boiling range of from 253° to 424° F. with 70 percent of a commercial regular grade gasoline. The fuel has 2 ml. per gallon of lead and approximately 0.1 weight percent sulfur. The crankcase depression is maintained at 1-inch water. The engine test is carried out for 60 hours.

When using the oil composition described above without any of the subject composition, the piston varnish rating is 5.3 (based on 0-10, 10 being clean). With the subject additive, the rating is 7.3, a significant improvement.

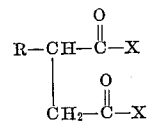
The above test was repeated using 3 weight percent of a 50 weight percent solution in Mid-Continent 100 neutral oil of the combined compositions of example 5. The result for piston varnish was 8.0. The results for total varnish and total sludge (on a basis of 0-50, 50 being clean) were 40.9 and 42.5, respectively.

The subject compositions were also tested for their effectiveness as dispersants in maintaining sludge dispersed in oil and preventing deposits in a 120-hour 1-G Caterpillar Test. The oil used was a Mid-Continent SAE 30 oil, with 2.25 weight percent of the exemplary composition of example 2, and 12 mM./kg. of zinc di(alkylphenyl)phosphorodithioate. (The alkyl groups are polypropylene of from about 12 to 15 carbon atoms.) The groove deposit results are reported on a basis of 0-100, 100 being completely full grooves. The land deposits are reported on the basis of 0-800, 800 being completely black. When the above oil is used without detergent, the groove deposits are 93-15-5-2 and the land deposits are 500-800-330. For the oil composition with the detergent additive, the results are: for the grooves, 64-0.8-0.2-0; for the lands, 60-0-10.

It is evident from the above results that the compositions of this invention are effective not only in preventing varnish deposits, but also in preventing deposits resulting from sludge. Therefore, the subject compositions do not contribute by their own decomposition to deposits, but remain stable for long periods of time, while being capable of dispersing sludge and deposit-forming intermediates in oil.

We claim:

1. A lubricating oil composition having an oil of lubricating viscosity and from 0.1 to 10 weight percent of a detergent composition prepared by reacting (A) an alkenyl succinic acid compound of the formula:



wherein R is an oil-solubilizing alkenyl group of at least about 14 and up to about 300 carbon atoms having alpha or beta ethylenic unsaturation, the X's are the same or different and are hydroxyl or hydrocarbyloxy of from one to 12 carbon atoms, or may be taken together to form the oxy group of an anhydride, with the proviso that when the X's are taken together to form the oxy group, a hydroxylic solvent is employed,

with (B) a halogenating agent, wherein the halogen is of atomic number 17 or 35, introducing at least about one

atom of halogen per succinyl molecule to form the halogenated succinyl compound as a lactone (C), contacting at a temperature in the range of from about 100° to 225° C., said lactone (C) with (D), wherein (D) is ammonia, an aliphatic hydrocarbon amine other than tertiary or alkylene polyamine of from two to 10 amine nitrogen atoms, wherein the mole ratio of (D) to (C) is 1.5-10:1.

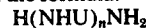
2. A lubricating oil composition according to claim 1 wherein (A) is reacted with (B) at a temperature in the range of -10° to about 100° C.

3. A lubricating oil composition according to claim 2 wherein the halogen of said halogenating agent is chlorine.

4. A lubricating oil composition according to claim 1 wherein said amine (D) is an alkylene polyamine of from two to six amine nitrogen atoms and the alkylene group is from two to three carbon atoms, there being at least two carbon atoms between the nitrogen atoms; and R is polyisobutenyl of from about 50 to 200 carbon atoms.

5. A lubricating oil composition according to claim 4 wherein the mole ratio of amine (D) to halogenated succinyl compound (D) is in the range of 2-7:1.

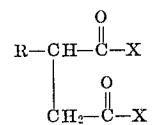
6. A lubricating oil composition according to claim 1 wherein R is polyisobutenyl of from 50 to 200 carbon atoms, the halogen of said halogenating agent is chlorine, the reaction of (A) and (B) is carried out in the presence of an alkanol of from one to six carbon atoms at a temperature in the range of -10° to about 50° C. to introduce from about one to 1.5 atoms of chlorine per succinyl compound (A) and said amine is an alkylene polyamine of the formula:



wherein U is alkylene of from two to three carbon atoms, there being at least two carbon atoms being the nitrogen atoms, and n is an integer of from 2 to 6.

7. A lubricating oil composition according to claim 6 wherein n is 2.

8. A composition useful as a detergent in lubricating oils which is prepared by reacting (A) an alkenyl succinic acid compound of the formula:

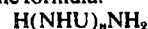


wherein R is an oil solubilizing alkenyl group of at least about 14 and up to about 300 carbon atoms having alpha or beta ethylenic unsaturation, the X's are the same or different and are hydroxyl or hydrocarbyloxy of from one to 12 carbon atoms, or may be taken together to form the oxy group of an anhydride, with the proviso that when the X's are taken together to form the oxy group, a hydroxylic solvent is employed,

with (B) a halogenating agent, wherein the halogen is of atomic number 17 or 35, introducing at least about one atom of halogen per succinyl molecule to form the halogenated succinyl compound as a lactone (C),

contacting at a temperature in the range of from about 100° to 225° C., said lactone (C) with (D), wherein (D) is ammonia, an aliphatic hydrocarbon amine other than tertiary or alkylene polyamine of from two to 10 amine nitrogen atoms, wherein the mole ratio of (D) to (C) is 1.5-10:1.

9. A composition according to claim 8 wherein R is polyisobutenyl of from 50 to 200 carbon atoms, the halogen of said halogenating agent is chlorine, the reaction of (A) and (B) is carried out in the presence of an alkanol of from one to six carbon atoms at a temperature in the range of -10° to about 50° C. to introduce from about one to 1.5 atoms of chlorine per succinyl compound (A) and said amine is an alkylene polyamine of the formula:



wherein U is alkylene of from two to three carbon atoms, there being at least two carbon atoms between the nitrogen atoms, and *n* is an integer of from 2 to 6.

10. A composition according to claim 8, wherein said amine (D) is an alkylene polyamine of from two to six amine nitrogen atoms and the alkylene group is from two to three carbon atoms, there being at least two carbon atoms between the nitrogen atoms; and R is polyisobutenyl of from about 50 to 200 carbon atoms.

11. A lubricating oil composition according to claim 1

wherein said amine (D) has from one to 10 oxygen atoms as ethereal or hydroxylic functional groups.

12. A composition according to claim 8 wherein said amine (D) has from one to 10 oxygen atoms as ethereal or hydroxylic functional groups.

13. A lubricating oil composition having a minor amount of an oil of lubricating viscosity and from 10 to 70 weight percent of a detergent composition according to claim 8.

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