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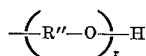
LUBRICATING OILS AND FUELS CONTAINING ACYLATED NITROGEN ADDITIVES

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No Drawing. Continuation-in-part of applications Ser. No. 742,133, July 3, 1968, and Ser. No. 851,736, Aug. 18, 1969. This application Nov. 10, 1969, Ser. No. 875,580
Int. Cl. C10m 1/20, 1/32; C10l 1/22
U.S. Cl. 252—51.5 A

30 Claims

ABSTRACT OF THE DISCLOSURE

Compositions of matter particularly useful as lubricant and fuel additives prepared by reacting various nitrogen-containing reactants with a mono- or polycarboxylic acid acylating agent containing at least about thirty aliphatic carbon atoms. The nitrogen-containing reactants are characterized by the presence of at least one N-substituent corresponding to



where r is 1–10 and R' is hydrocarbylene of up to 10 carbon atoms. An exemplary composition is one prepared by reacting polyisobutenyl succinic anhydride with the reaction product of N-(hydroxyethyl)-ethylene diamine and adipic acid.

This is a continuation-in-part application of applicants copending applications Ser. No. 742,133, filed July 3, 1968, and Ser. No. 851,736, filed Aug. 18, 1969, both now abandoned.

This application relates to novel compositions of matter and to lubricants and fuels containing these compositions. More specifically, the invention relates to novel, oil-soluble, acylated nitrogen compositions, methods for their preparation, and to lubricants and fuels containing the novel acylated nitrogen compositions.

As is well known, high molecular weight acylated nitrogen compositions have achieved widespread use as ashless dispersants in lubricants and fuels during the past decade. Generally, these ashless dispersants are prepared by reacting a high molecular weight mono- or polycarboxylic acid acylating agent with a suitable amine or hydroxy compound. Typical prior-art acylated nitrogen compositions which have utility as sludge-dispersing additives in lubricants and fuels are presented in detail in the following U.S. patents: 3,172,892; 3,219,666; 3,272,746; 3,340,281; 3,341,542; 3,361,673; and 3,381,022.

The commercial success of these acylated nitrogen compositions as ashless dispersants is conclusive evidence of their effectiveness as sludge-dispersants. However, their use has not been entirely free from problems. For example, in certain types of automobile engines, it has been found that a sludge forms on metal surfaces in areas of the engine where water vapor can condense and which also comes into contact with the lubricating oil containing one or more of these ashless dispersants. For example, such sludges have been found in the rocker arm covers and oil-fill caps of certain engines, particularly, smaller car engines. Apparently, the breathing systems of these engines are such that they permit moisture-laden air to come into contact with these metal surfaces which are sufficiently cool to permit the condensation of water. When the lubricating oil containing the ashless dispersant comes into contact with the condensed water, the oil and water apparently form water-in-oil emulsions in the presence of the dispersant. However, it should also be noted at this point that other additives used in lubricating oils

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can also promote the formation of such water-in-oil emulsions, for example, some of the commercially used viscosity index improving agents. It is obviously desirable to eliminate or reduce the amount of emulsion sludge formed in the engine.

It has now been determined that the emulsion-forming tendency of the lubricating oil containing the ashless dispersants can be eliminated or greatly reduced if the ashless dispersant is prepared from a particular class of nitrogen-containing compounds without any substantial adverse effect on the sludge-dispersing capabilities of the acylated nitrogen composition. Not only are the novel acylated nitrogen compositions of this invention themselves characterized by a reduced tendency to form the water-in-oil emulsions, their presence in lubricating oils also serves to retard the emulsion sludge-forming tendencies of other additives in the lubricating oil composition.

In accordance with the foregoing, it is a principal object of this invention to provide novel acylated compositions.

A further object is to provide oil-soluble acylated nitrogen compositions suitable as additives in lubricants and fuels.

An additional object is to provide acylated nitrogen compositions characterized by a reduced tendency to promote water-in-oil emulsions.

Still another object is to provide a process for preparing the oil-soluble acylated nitrogen compositions.

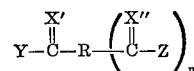
Another object is to provide novel post-treated additives for lubricants and fuels.

A still further object is to provide lubricants and fuels containing the acylated nitrogen compositions of this invention.

These and other objects of this invention are readily achieved by providing oil-soluble acylated nitrogen compositions produced by the process comprising reacting

(I) At least one mono- or polycarboxylic acylating agent characterized by the presence of at least about thirty aliphatic carbon atoms, exclusive of carboxyl carbon atoms, with

(II) At least one nitrogen-containing reactant of the formula



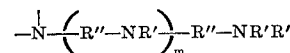
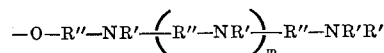
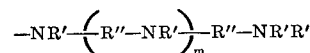
where:

(a) R is a polyvalent organic radical having up to twenty carbon atoms whose valence equals $n+1$ with the proviso that when $n=1$ R can be a direct linkage between the two carbon atoms;

(b) n is a whole number of 1 to 3;

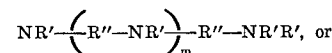
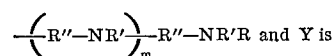
(c) X' and X'' are each independently $\text{O}=\text{}$ or $\text{R}_1-\text{N}=\text{}$;

(d) when x' is $\text{O}=\text{}$, then Y is



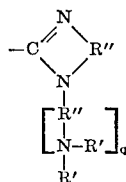
where m is 0 or a whole number of 1 to 8;

(e) when X' is $\text{R}_1\text{N}=\text{}$ then R_1 is



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R_1 together with Y form a cyclic amidine of the formula

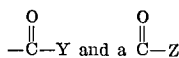


where q is 0 or a whole number of 1 to 8;

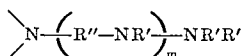
(f) when X'' is O= then Z is O-M⁺, halo, lower alkoxy, or Y as Y is defined when X' is O=, M⁺ being the cation of an amine;

(g) when X'' is $R_1N=$ then Z and R_1 are the same as Y and R_1 as these variables are defined when X' is $R_1N=$;

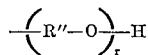
(h) when X' and X'' are both O= and R separates



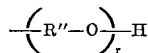
group by two or three carbon atoms, then Y and Z taken together can be



where R' is H, hydrocarbyl of up to ten carbon atoms, or



where r is 1 to 10 but at least one R' is



per nitrogen-containing reactant; R'' is hydrocarbylene of up to ten carbon atoms; (I) and (II) being reacted in amounts such that there is at least one equivalent of (I) to each mole of (II).

Carboxylic acid acylating agents, that is, (I) above, suitable for preparing the products of the invention are well-known in the art and have been described in detail, for example, in U.S. Pats. 3,087,936, 3,163,603; 3,172,892; 3,189,544; 3,219,666; 3,272,746; 3,288,714; 3,306,907; 3,331,776; 3,340,281; 3,341,542; 3,346,354; 3,374,174; and 3,381,022. In the interest of brevity, these patents are incorporated herein for their disclosure of suitable mono- and polycarboxylic acid acylating agents which can be used for the preparation of these products.

As disclosed in the foregoing patents, there are several processes for preparing the acylating agents. Generally, the process involves the reaction of (1) an ethylenically unsaturated carboxylic acid, acid halide, or anhydride with (2) an ethylenically unsaturated hydrocarbon containing at least above fifty aliphatic carbon atoms or a chlorinated hydrocarbon containing at least about fifty aliphatic carbon atoms at a temperature within the range of about 100°–300° C. The chlorinated hydrocarbon or ethylenically unsaturated hydrocarbon reactant can, of course, contain polar substituents, oil-solubilizing pedant groups, and be unsaturated within the general limitations explained hereinbelow. It is these hydrocarbon reactants which provides most of the aliphatic carbon atoms present in the acyl moiety of the final products.

When preparing the carboxylic acid acylating agent according to one of these two processes, the carboxylic acid reactant usually corresponds to the formula



where R_0 is characterized by the presence of at least one ethylenically unsaturated carbon-to-carbon covalent bond and n is an integer from one to six and preferably one to two. The acidic reactant can also be the corresponding carboxylic acid halide, anhydride, ester, or other equivalent acylating agent and mixtures of one or more of these. Ordinarily, the total number of carbon atoms in the acidic

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reactant will not exceed ten and generally will not exceed six. Preferably the acidic reactant will have at least one ethylenic linkage in an α,β -position with respect to at least one carboxyl function. Exemplary acidic reactants are acrylic acid, methacrylic acid, maleic acid, maleic anhydride, fumaric acid, itaconic acid, itaconic anhydride, citraconic acid, citraconic anhydride, mesaconic acid, glutaric acid, chloromaleic acid, aconitic acid, crotonic acid, methylcrotonic acid, sorbic acid, 3-hexenoic acid, 10-decenoic acid, and the like. Due to such considerations as economy, availability, reactivity, and performance of the products, the acid reactants usually employed are the α,β -unsaturated dicarboxylic acid acylating agents, particularly α,β -ethylenically unsaturated dicarboxylic acids and the corresponding anhydrides such as maleic acid, maleic acid anhydride, fumaric acid, etc.

As is apparent from the foregoing discussion, the carboxylic acid acylating agents may contain cyclic and/or aromatic groups. However, the acids are essentially aliphatic in nature and, in most instances, the preferred acid acylating agents are aliphatic polycarboxylic acids, anhydrides, or halides, usually the chlorides in case of the latter.

The substantially saturated aliphatic hydrocarbon-substituted succinic acids and anhydrides are especially preferred as acylating agents. These succinic acid acylating agents are readily prepared by reacting maleic anhydride with a high molecular weight olefin or a chlorinated hydrocarbon such as a chlorinated polyolefin. The reaction involves merely heating the two reactants at a temperature of about 100°–300° C., preferably, 100°–200° C. The product from such a reaction is a substituted succinic anhydride where the substituent is derived from the olefin or chlorinated hydrocarbon as described in the above cited patents. The product may be hydrogenated to remove all or a portion of any ethylenically unsaturated covalent linkages remaining by standard hydrogenation procedures, if desired. The substituted succinic anhydrides may be hydrolyzed by treatment with water or steam to the corresponding acid and either the anhydride or the acid may be converted to the corresponding acid halide or ester by reacting with phosphorus halide or lower alkanols.

The ethylenically unsaturated hydrocarbon reactant and the chlorinated hydrocarbon reactant used in the preparation of the acylating agents are principally the high molecular weight, substantially saturated petroleum fractions and substantially saturated olefin polymers and the corresponding chlorinated products. The polymers and chlorinated polymers derived from mono-olefins having from two to about thirty carbon atoms are preferred. The especially useful polymers are the polymers of 1-mono-olefins such as ethylene, propylene, 1-butene, isobutene, 1-hexene, 1-octene, 2-methyl-1-heptene, 3-cyclohexyl-1-butene, and 2-methyl-5-propyl-1-hexene. Polymers of medial olefins, i.e., olefins in which the olefinic linkage is not at the terminal position, likewise are useful. These are exemplified by 2-butene, 3-pentene, and 4-octene.

The interpolymers of 1-mono-olefins such as illustrated above with each other and with other interpolymerizable olefinic substances such as aromatic olefins, cyclic olefins, and polyolefins, are also useful sources of the ethylenically unsaturated reactant. Such interpolymers include for example, those prepared by polymerizing isobutene with styrene, isobutene with butadiene, propene with isoprene, propene with isobutene, ethylene with piperylene, isobutene with chloroprene, isobutene with p-methylstyrene, 1-hexene with 1,3-hexadiene, 1-octene with 1-hexene, 1-heptene with 1-pentene, 3-methyl-1-butene with 1-octene, 3,3-dimethyl-1-pentene with 1-hexene, isobutene with styrene and piperylene, isobutene with propylene, etc.

For reasons of oil-solubility and stability, the polymers contemplated for use in preparing the acylating agents of this invention should be substantially aliphatic and substantially saturated, that is, they should contain at least about 80% and preferably about 95%, on a

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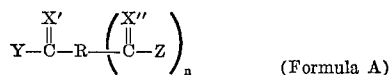
weight basis, of units derived from aliphatic mono-olefins. They usually will contain no more than about 5%, preferably no more than about 2%, olefinic linkages based on the total number of the carbon-to-carbon covalent linkages present therein.

The chlorinated hydrocarbons and ethylenically unsaturated hydrocarbons used in the preparation of the acylating agents can have molecular weights of from about 400 up to about 100,000 or even higher. The above described polyolefins and chlorinated polyolefins having an average molecular weight of about 400 to about 5,000 are preferred for preparing (I). Those having molecular weights of about 700 to about 5000 are especially preferred. Polypropylene, polyisobutylene, copolymers of propylene and isobutylene and their chlorinated derivatives are particularly useful for reacting with the unsaturated acid compound to prepare suitable acylating agents. When the acylating agent has a molecular weight in excess of about 10,000, the acylated nitrogen composition also possess viscosity index improving qualities.

In lieu of the high molecular weight hydrocarbons and chlorinated hydrocarbons discussed above, hydrocarbons containing activating polar substituents which are capable of activating the hydrocarbon molecule in respect to reaction with an ethylenically unsaturated acid reactant may be used in the above-illustrated reactions for preparing the acylating agents. Such polar substituents include sulfide and disulfide linkages, and nitro, mercapto, carbonyl, and formyl radicals. Examples of these polar-substituted hydrocarbons include polypropylene sulfide, dipolyisobutene disulfide, nitrated mineral oil, di-polyethylene sulfide, brominated polyethylene, etc.

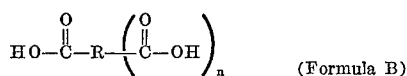
The acylating agents may also be prepared by halogenating a high molecular weight hydrocarbon such as the above described olefin polymers to produce a polyhalogenated product, converting the polyhalogenated product to a polynitrile, and then hydrolyzing the polynitrile. They may be prepared by oxidation of a high molecular weight polyhydric alcohol with potassium permanganate, nitric acid, or a similar oxidizing agent. Another method for preparing such polycarboxylic acids involves the reaction of an olefin or a polar-substituted hydrocarbon such as a chloropolyisobutene with an unsaturated polycarboxylic acid such as 2-pentene-1,3,5-tricarboxylic acid prepared by dehydration of citric acid. Monocarboxylic acid acylating agents may be obtained by oxidizing a monoalcohol with potassium permanganate or by reacting a halogenated high molecular weight olefin polymer with a ketene. Another convenient method for preparing monocarboxylic acid involves the reaction of metallic sodium with an acetoacetic ester or a malonic ester of an alkanol to form a sodium derivative of the ester and the subsequent reaction of the sodium derivative with a halogenated high molecular weight hydrocarbon such as brominated wax or brominated polyisobutene.

The nitrogen-containing reactants, that is,



are available through the reaction of commercially available products using conventional reaction techniques. Organic polycarboxylic acid acylating reagents are reacted with alkylene polyamines characterized by the presence within the structure of the polyamines of at least one hydroxy alkyl group to form these nitrogen-containing reactants.

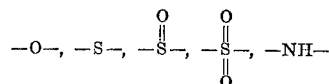
The polycarboxylic acid acylating reagents useful in preparing the nitrogen-containing reactant correspond to the general formula



and include the corresponding acyl halides, lower alkyl esters, and anhydrides. In this formula, R is a polyvalent organic radical whose valence equals $n+1$ and n is 1 to

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3 provided that when $n=1$, R may also be a direct linkage between the carbon atoms. That is Formula B also represents oxalic acid acylating agents. R can be aliphatic, cycloaliphatic, aromatic, or heterocyclic and can be substituted or unsubstituted. Ordinarily, R will not contain more than twenty carbon atoms and preferably not more than ten carbon atoms. Such acids are well-known in the art as shown by Kirk-Othmer, Encyclopedia of Chemical Technology (2nd ed.), vol. 1, pages 222-254 (1963), and other prior art references such as Beilsteins Handbuch der Organischen Chemie, vol. II and IX, and the corresponding supplements. When R is substituted, it can contain one or more substituents selected from the class consisting of halo, lower alkoxy, lower alkyl mercapto, nitro, lower alkyl, and oxo. It also may contain interrupting groups such as

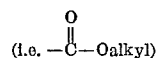


and the like.

Exemplary acylating reagents include phthalic acid, oxalic acid, N-phenylglycine-o-carboxylic acid, quinolinic acid, cinchomeronic acid, diphenic acid, nitrophthalic acid, isophthalic acid, terephthalic acid, mellitic acid, trimellitic acid, citric acid, tartaric acid, keto-succinic acid, bromosuccinic acid, malic acid, succinic acid, diglycolic acid, cyclohexene-4,5-dicarboxylic acid, maleic acid, fumaric acid, muconic acid, traumatic acid, naphthalic acid, 2,3-pyrazine dicarboxylic acid, brassylic acid, itaconic acid, citraconic acid, mesaconic acid, acetone dicarboxylic acid, glutaric acid, aconitic acid, triarballic acid, ethylenediaminetetracetic acid, camphoric acid, homophthalic acid, o-phenylenediacetic acid, hexahydrophthalic acid, carboxymethylthiosuccinic acid, thiodiglycolic acid, dithiodiglycolic acid, methylenebis(thioacetic acid), methylenebis(thiopropionic acid), ethylenebis(thioglycolic acid), thiophenedicarboxylic acid, tetrahydrothiophenedicarboxylic acid, thiodisuccinic acid, iminodiacetic acid, iminodipropionic acid, 2,5-diethoxy-p-benzenediacetic acid, m-benzenediacrylic acid, 7,7'-p-phenyleneheptanoic acid, 2,2-dimethyl-1,3-cyclobutanedicarboxylic acid, 1,2-cyclobutanedicarboxylic acid, 1,3-cyclobutane dicarboxylic acid, and the like.

A preferred group of acids for preparing the nitrogen-containing compounds used as intermediates in the preparation of the products of this invention are the dicarboxylic acids wherein the variable R is a divalent hydrocarbon radical having up to about 10 carbon atoms. The divalent hydrocarbon radical may be aliphatic, cycloaliphatic or aromatic, although it is preferably aliphatic.

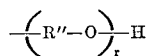
An especially preferred group of dicarboxylic acids are those wherein the variable R is a straight or branched chain alkylene containing up to ten carbon atoms. Preferably, R separates the acid groups by at least 4 carbon atoms. Illustrative of this group of acids are malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, and sebacic acid. As mentioned above, the derivatives of the foregoing acids normally employed as acylating agents can be used in lieu of the acids per se. Thus, the carboxylic acid halides, lower alkyl esters (where the alkyl groups have up to 7 carbon atoms and preferably 1-3 carbon atoms), and anhydrides of the foregoing acids can be used as acylating agents in preparing the nitrogen-containing reactant. It should also be understood that the various carboxyl groups present in the carboxylic acids need not be present in the same form, that is, one may be a carboxyl group per se and another can be a carboalkoxy group



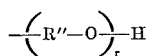
or carboxylic acid halide group. Obviously, mixtures of these various acylating agents can also be employed in

the preparation of the nitrogen-containing reactant. Such mixtures could include two or more of any of the foregoing polycarboxylic acids or their halides, esters, or anhydrides, such as a combination of succinic acid anhydride and adipic acid.

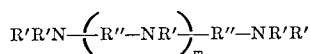
The amines which are reacted with the polycarboxylic acids to form the nitrogen-containing reactant are alkylene polyamines having up to ten amino nitrogens present in their structure and having at least one hydroxy alkyl group, i.e.,



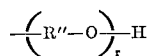
present in the polyamine molecule. The presence of this hydroxy alkyl group is an important characteristic of the amines used to prepare the present additives. The emulsion resistance and emulsion breaking capabilities of the additives seems to depend, in part at least, on the presence of at least one



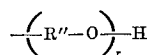
group in the nitrogen-containing reactant. These amines can be represented by the following general formula:



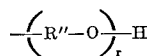
(Formula C) wherein m , R' and R'' are as defined hereinbefore with the further proviso that at least one R' per polyamine molecule is ---H . A preferred class of polyamines are those where the R' variables are either H--- or



where R'' and r are as defined above providing at least one R' is H--- and at least one is

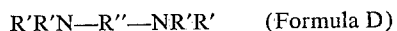


An especially preferred group of amines are those of the type described above where the variable R'' is alkylene of up to six carbon atoms and particularly ethylene or propylene, one R' is

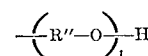


and the remaining R' variables are ---H 's.

The most preferred polyamine reactants are those falling within the class represented by the formula



that is, where m of Formula C is 0. In this most preferred group, those amines where one R' variable is



and the remaining three R' variables are hydrogen are particularly useful. In this most preferred class of alkylene diamines, the variable R'' generally will contain from two to six carbon atoms and desirably will be ethylene or propylene. The R'' variables need not be identical within a given polyamine. The N -(hydroxy-lower alkyl)-alkylene diamines (particularly ethylene diamines) such as N -(β -hydroxyethyl)-ethylene diamine, N -(β -hydroxypropyl)-ethylene diamine, N -(β -hydroxy- β -methylpropyl)-ethylenediamine constitute especially useful amines within this most preferred class.

Other specific exemplary polyamines corresponding to Formula C include N -(3-hydroxypropyl)-trimethylene diamine, N -(4-hydroxybutyl)-tetramethylene diamine, N -(β -hydroxyethyl)-hexamethylene diamine, N -(4-hydroxybutyl)-ethylene diamine, N -(3-hydroxyhexyl)-ethylene diamine, N -(2-tolyl-3-hydroxypropyl)-trimethylene diamine, N -(2-phenyl-3-hydroxyheptyl)-ethylene diamine, mono-hydroxy propyl substituted diethylene triamines, dihydroxypropyl-substituted tetraethylene pentamines,

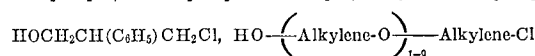
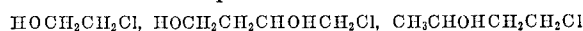
and the like. Other polyamines falling within the class of preferred amines are disclosed in the prior art such as in U.S. Pat. 3,018,173 which is hereby incorporated by reference.

These amines are available commercially or can be synthesized according to known techniques. See for example, U.S. Pats. 3,018,173 and 3,282,836 and M. S. Malinovskii, Okisi Olefinov I Ikh Prizvodnye (1961), translated by L. Balig as Epoxides and Their Derivatives (1965) published by Daniel Davey & Co., Inc. N.Y. particularly pages 222-223 of the translation. Basically, these amines can be prepared by reacting an alkylene polyamine such as ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, propylene diamine, dipropylene triamine, tripropylene tetramine, trimethylene diamine, tetramethylene diamine, pentamethylene diamine, hexamethylene diamine, di(trimethylene)triamine, and the like with at least one epoxide. The term "epoxide" as used herein means alkylene oxides or mono-aryl substituted alkylene oxides having from two to eight carbon atoms such as ethylene oxide, propylene oxide, epichlorohydrin, butylene oxides, styrene oxide or mixtures thereof. The 1,2-alkylene oxides such as ethylene and propylene oxide are preferred. The alkylene polyamine and the alkylene oxide should be reacted in a molar ratio of alkylene polyamine to alkylene oxide of about 1:1 to about 1:10. Normally, however, the number of moles of alkylene oxide reacted with each mole of alkylene polyamine will not exceed that number which is one less than the number of amino groups in the polyamine. For example, the number of moles of alkylene oxide to be reacted with tetraethylene pentamine normally would not exceed four; with dipropylene triamine, two, etc. A mole ratio of about 1:1 results in particularly useful intermediates.

As will be apparent to those skilled in the art, when the epoxide contains an aryl substituent on the alkylene group, the reaction product will also retain this substituent. For example, styrene oxide and ethylene diamine react to produce N -(β -hydroxy- β -phenylethyl)-ethylene. (See Balig, above.) Usually, if present, there will be only one such aryl substituent per alkylene oxide and it will be a phenyl or substituted phenyl substituent such as lower alkyl substituted phenyl, lower alkoxy substituted phenyl, nitro phenyl, and the like. Similarly, the alkylene group of the epoxide may contain other groups such as halo and alkoxy. Again these groups will become substituents on the polyamine-epoxide reaction products.

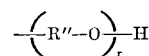
Suitable epoxides include glycidol, epichlorohydrin, epibromohydrin, ethylether of glycidol, amyl ether of glycidol, phenyl glycidol, 1,2-epoxypentane, 1,2-epoxyhexane, 2,3-epoxypentane, 1,2-epoxyoctane, 1,2,5,6-diepoxyhexane, 2,4,4-trimethyl-2,3-epoxypentane, styrene oxide, and the like.

Other methods for preparing hydroxyhydrocarbyl-substituted polyamines are known in the prior art. For example, a hydroxyhydrocarbyl halide can be reacted with a polyamine having reactive $>\text{NH}$ groups to prepare N -(hydroxycarbyl)-substituted polyamines. Thus, the polyamines useful for reacting with epoxides can also be reacted with such compounds as



according to known procedures to prepare suitable amines.

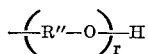
The variable R'' in the amines and the



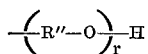
group can be an aliphatic, cycloaliphatic, or aryl hydrocarbylene group. As used herein "hydrocarbylene" is a term generic to divalent hydrocarbon groups free from ethylene or acetylenic unsaturation such as alkylene, phenyl-substituted alkylene, cyclohexyl-substituted alkyl-

ene, phenylene, and the like. The hydrocarbylene groups may contain nonhydrocarbon substituents such as lower alkoxy, lower alkylmercapto, oxo, nitro, amino, etc., and such polar-substituted hydrocarbylene groups are contemplated as equivalent to hydrocarbylene groups per se. However, such substituents do not appear to contribute to any substantial improvement in the final products. Thus, R'' normally will be divalent hydrocarbon and, preferably, alkylene of up to ten carbon atoms.

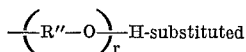
As suggested above, it is contemplated that some of the R' variables on the polyamines and the nitrogen-containing reactants, that is, (II), may be hydrocarbyl of up to ten carbon atoms. This term is intended to describe monovalent aliphatic, cycloaliphatic, araliphatic, aryl, etc. hydrocarbon radicals which are free from ethylenic or acetylenic unsaturation. Again, the corresponding substituted radicals containing such substituents as lower alkoxy, lower alkylmercapto, nitro, lower alkyl, etc., are deemed to be equivalent to the unsubstituted hydrocarbon radical. Such substituted hydrocarbyl groups are contemplated as being within the scope of this invention herein. Generally, when R' is a hydrocarbyl radical, it will be a monovalent hydrocarbon such as cyclohexyl, 3-ethylcyclohexyl, cyclopentyl, phenyl, tolyl, benzyl, phenethyl, propyl, heptyl, etc. Preferably, if a R' variable is other than H or



it will be lower alkyl of up to seven carbon atoms. As stated before, R' is preferably H if not



The polycarboxylic acid acylating reagents (Formula B) are reacted with the



polyamines in amounts such that there is at least about one equivalent of the carboxylic acid acylating agent for each mole of polyamine reactant. Usually, not more than one mole of carboxylic acid acylating reagent will be used for each mole of polyamine reactant. For purposes of this invention, the equivalent weight of the carboxylic acid acylating reagent is its molecular weight divided by the number of carboxylic acid groups or acylating functional derivatives thereof present in the molecule. Thus, ethylenediaminetetracetic acid has four equivalents per mole while succinic acid and adipic acid each have two equivalents per mole. Preferably, the acylating reagent and polyamine will be reacted in a ratio of about one equivalent to one mole.

The carboxylic acid acylating reagents and the polyamines can be reacted at temperatures of about 50° C. up to the decomposition temperature of the reactants or the resulting product. Normally, however, there is no advantage in exceeding temperatures of about 300° C. Preferably, temperatures of at least 100° C. to about 260° C. will be employed.

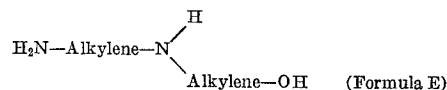
If desired, the reaction can be conducted in the presence of a substantially inert diluent such as the liquid hydrocarbons and halohydrocarbons, ethers, and the like. Specific inert liquid diluents suitable for the use in this process include mineral oils, naphthas, benzenes, toluene, xylenes, chlorobenzenes, heptane, hexane, pentane, cycloheptane, cyclohexane, chlorohexane, butyl ether, isobutyl ether, amyl ether, isoamyl ether, methyl amyl ether, ethyl amyl ether, dimethyl formamide, dimethyl acetamide, dimethyl sulfoxide, and the like, and mixtures thereof. Inert atmosphere (e.g., nitrogen, helium, etc.) and superatmospheric or subatmospheric pressures can be used.

As is apparent to those skilled in the art, both the carboxylic acid acylating reagents and the polyamines have a plurality of reactive functional groups. Accordingly, a

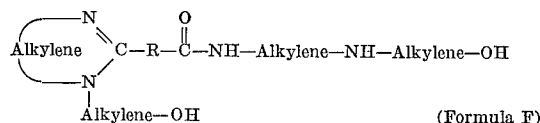
diverse group of reaction products is possible and the specific nature of the product will depend on the particular carboxylic acid and polyamines utilized, the ratio of the reactants, the reaction temperature, and the like. Thus, the carboxylic acid acylating reagents can react with amino hydrogens to form amides, imides, or amidines. On the other hand, the carboxyl groups can react with the hydroxyl hydrogen to form esters. Likewise, the carboxylic acid acylating reagent may retain some unreacted carboxyl functions. The products of the reaction between the carboxylic acid acylating agent and the polyamine are represented by general Formula A above.

While any nitrogen-containing compounds corresponding to Formula A are suitable reactants including mixtures thereof, it is preferred that the polycarboxylic acid acylating agent and the polyamine be reacted under conditions whereby no (or substantially no) unreacted carboxyl groups remains. This is readily accomplished simply by conducting the reaction at a sufficiently high temperature (100° C. or higher) and/or for a sufficient length of time to permit complete reaction. Obviously there will have to be at least about one equivalent of HO— or HN= or combination thereof present in the reaction mixture for each equivalent of acylating agent in order to provide for the reaction of all the carboxyl groups or equivalent acylating function derivatives thereof.

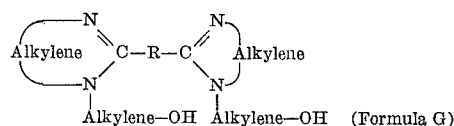
When the polyamine used to prepare the nitrogen-containing reactant is a member of the most preferred class of amines represented by the general formula:



the acylating agent is an aliphatic dicarboxylic acid acylating agent corresponding to Formula B, and the amine and acid are reacted in a molar ratio of about 2:1 then the nitrogen-containing reaction product consists predominantly of compounds of the formula:

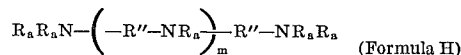


or



or mixtures thereof. For example, when N-(β-hydroxyethyl)-ethylene diamine and adipic acid are reacted as discussed below, the product would consist predominantly of compounds corresponding to Formula F or G or mixtures thereof where the alkylene groups are ethylene and the R variable is —(CH₂)₄—.

An alternative process for preparing suitable nitrogen-containing reactants involves first reacting at least one polycarboxylic acid acylating reagent represented by Formula B with at least one polyamine of the formula:



where R'' and m are as defined above and R_a is hydrogen or hydrocarbyl of up to ten carbon atoms. At least two R_a's are H and, desirably all of them are H. Preferably, R'' will be alkylene having two to six carbon atoms therein, the ethylene polyamines and propylene polyamines corresponding to Formula H being particularly preferred. The acylating reagent and the alkylene polyamine should be reacted at temperatures of from about 50° C. up to about the decomposition temperature of the reactants or reaction products. However, there is usually no advantage in employing temperatures in excess of 300° C. Temperatures of at least about 100° C. are preferred with tem-

peratures of at least about 200° C. being especially preferred. This process is discussed in more detail hereinbelow.

The acylating reagent and the polyamine are reacted in amounts such that there is at least one equivalent of acylating agent for each mole of polyamine but the ratio of acylating reagent to polyamine should be such that there is an average of at least one unreacted =NH group remaining per molecule of the reaction product for subsequent reaction with an epoxide. Accordingly, the maximum amount of the acylating reagent which should be employed in the reactant is that amount such that the ratio of equivalents of acylating reagent to polyamine is not greater than $X-1:X$ where X is the number of equivalents of polyamine present in the reaction mixture. For purposes of this invention, the equivalent weight of a polyamine is its molecular weight divided by the number of =NH groups present therein. Thus, the equivalent weight of ethylene diamine is one-half of its molecular weight, the equivalent weight of tetraethylene pentamine is one-fifth of its molecular weight; and so forth. The preferred ratio of reactant is about one equivalent of acylating reagent for each mole of polyamine. The products of this reaction are amides, imides, amidines, or mixtures thereof. As in the preparation of the nitrogen-containing intermediate according to the other general process discussed above, the process should be conducted under conditions which result in no (or substantially no) unreacted carboxyl groups.

This first reaction product is then further reacted with at least one epoxide of the type described hereinabove. The amount of epoxide employed in this subsequent reaction should be such that there is at least about one mole of epoxide for each mole of alkylene polyamine used in preparing the first reaction product. Up to ten moles of epoxide can be used for each mole of alkylene polyamine.

As with the first method of preparing the nitrogen-containing reactant, the processes can be conducted in the presence of inert diluents such as those enumerated hereinbefore. Likewise, inert atmospheres as well as sub-atmospheric and super-atmospheric pressures can be employed. The epoxides can be reacted with the acylated nitrogen reaction products at temperatures from about 25° C. up to the decomposition temperature of the reactant or the reaction product. There is little advantage in exceeding temperatures of about 300° C. Reaction temperatures of about 40° to about 150° C. are usually very satisfactory.

It is critical to this invention that the nitrogen-containing reactant (II) be first prepared and subsequently reacted with the acylating agent (I). If the polyamines represented by Formula C are first reacted with the acylating agent (I) and thereafter with the acylating reagents represented by Formula B, different reaction products are produced. Similarly, if polyamines corresponding to Formula C wherein all the R' variables are H are first reacted with the acylating reagents, then that reaction product is reacted with (I), and this second reaction product then reacted with an epoxide, the final reaction product is different from the additives of this invention. Moreover, the simultaneous reaction of all these starting materials also results in reaction products which are different from the present additives.

In preparing the additives of this invention, at least one mono- or polycarboxylic acid acylating agent characterized by the presence within its structure of at least about thirty aliphatic carbon atoms exclusive of carboxyl carbon atoms is reacted with at least one nitrogen-containing reactant of the type represented by Formula A above. The acylating agent and the nitrogen-containing reactant are reacted in amounts such that there is at least one equivalent of the acylating agent for each mole of the nitrogen-containing reactant. As with the acylating reagents discussed above, the equivalent weight of the

mono- or polycarboxylic acid acylating agent is its average molecular weight divided by the number of carboxyl functions present. Thus, an alkenyl-substituted methacrylic acid has one equivalent per mole while an alkenyl-substituted succinic acid or anhydride would have two equivalents per mole as mentioned before. As the nitrogen-containing product can be a mixture of various products corresponding to Formula A, it would be difficult to determine with absolute certainty the number of moles of nitrogen-containing product actually present in the reaction mixture. Accordingly, for purposes of this invention, it is assumed that the number of moles of nitrogen-containing product is equivalent to the number of moles of acylating reagent which are reacted in the preparation of the nitrogen-containing product. For example, if the nitrogen-containing reaction product is prepared by reacting one mole of adipic acid with two moles of N -(β -hydroxyethyl)-ethylene diamine, it is assumed that the reaction product contains one mole of nitrogen-containing reactant.

The acylating agent and the nitrogen-containing reactant can be reacted at temperatures ranging from about 75° C. up to the decomposition temperature of the reactants and of the final product. Ordinarily, however, the temperature will not exceed 300° C. Preferably, temperatures of at least 100° C. up to about 260° C. will be used to facilitate the formation of predominantly ester, amide, imide, or amidine groups in lieu of amine salt groups in the additive.

The reaction can be conducted in the presence of inert diluents of the type described hereinbefore if desired. Mineral oils are particularly useful diluents if the resulting products are to be used as additives for lubricating oils including two-cycle engine lubricants. More volatile diluents may be advantageous where the product is to be incorporated in fuel compositions such as gasoline, diesel fuel, furnace fuel oils, and the like. Of course, where the diluent is sufficiently volatile, it can be easily removed by conventional distillation techniques, if desired.

The reaction can be conducted in an inert atmosphere such as nitrogen or helium if desired. Moreover, sub-atmospheric and super-atmospheric pressures can be employed as desired.

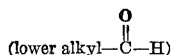
It has also been found that the dispersant-capabilities and/or the emulsion sludge resistant properties as well as other characteristics of the additives of this invention may be enhanced by post-treatment of the reaction products of (I) and (II) with at least one member selected from the group consisting lower aliphatic acids, lower aliphatic aldehydes, and epoxides. Mixtures of one or more of these post-treating materials are also useful. The post-treatment comprises contacting the reaction products of (I) and (II) with one of the above enumerated materials at a temperature of about 25° C. up to about 300° C. and preferably from about 50° C. up to about 200° C. The post-treating materials will be employed in an amount ranging from about 0.01% to about 20% by weight based on the total weight of (I) and (II) used in the preparation of the reaction products. Usually, 0.1% to 10.0% of the post-treating materials will be employed. Any unreacted post-treating material can be removed, if desired, by conventional techniques such as low pressure distillation, etc.

The lower aliphatic acids which can be used in the post-treatment process include principally the lower aliphatic mono- and dicarboxylic acid acylating agents containing from one to seven carbon atoms as well as their acyl halides, lower alkyl esters, and their anhydrides. Such acids are illustrated by formic acid, acetic acid, propionic acid, butanoic acid, pentanoic acid, hexanoic acid, heptanoic acid, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, malic acid, fumaric acid, gluconic acid, acetyl chloride, ethyl propionate, succinic anhydride, glacial acetic acid, and the like. The

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lower alkanolic acids per se are preferred with formic acid being especially preferred.

The aldehydes contemplated for use in the post-treatment process are the aliphatic aldehydes containing up to seven carbon atoms such as formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, valeraldehyde, hexaldehyde, heptaldehyde, acrolein, and the like. The lower alkyl monoaldehydes



are preferred with formaldehyde or its equivalents such as paraldehyde and formalin being especially preferred.

The epoxide suitable for use in the post-treatment process are those described hereinabove with regard to the preparation of the nitrogen-containing intermediate. The 1,2-alkylene oxides, especially ethylene and propylene oxide are preferred for use in the post-treatment process.

The present invention is further illustrated by the following examples. As used in the present specification and claims, "percentages" and "parts" refer to percent by weight and parts by weight unless otherwise indicated.

EXAMPLE 1

To a reaction flask fitted with a reflux condenser there is added 150 parts of ethylene diamine, then 110 parts of ethylene oxide are blown through the ethylene diamine during a 1.75-hour period at a rate of about 1-1.5 standard cubic feet per hour while maintaining the temperature of the reaction mixture at 95°-145° C. To the resulting mixture is then added 146 parts of adipic acid and

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anhydride and 629 parts of mineral oil are mixed and heated at 185-195° C. for five hours while blowing with nitrogen at a rate of about 1-2 standard cubic feet per hour. The reaction mass is then filtered at 125° C., the filtrate being an oil solution of the desired additive of this invention.

EXAMPLE 3

A mixture consisting of 930 parts of N-(hydroxyethyl)-ethylene diamine and 651 parts of adipic acid are heated under reflux conditions to 190° C. with nitrogen blowing over a 1.5 hour period. This mixture is maintained at 185-195° C. until 230 cc. of water are evolved. The resulting reaction mixture is then stripped to 200° C. at 13 mm. (Hg).

Thereafter, 425 parts of the above produced reaction product which consists predominantly of products conforming to the general Formulas F and G, 1540 parts of polyisobutenyl-substituted succinic anhydride having an average molecular weight of 1030, and 1292 parts of mineral oil are charged to a reaction flask fitted with a reflux condenser. This mixture is then heated to 185° C. over a 1-hour period while blowing with nitrogen and is thereafter held at 185-199° C. for 3.25 hours during which time the nitrogen blowing is continued. The reaction mass is then cooled to 130° C. and filtered producing 2975 grams of a 40% oil solution of the desired additive.

Following the general procedure of Example 3, the materials enumerated in Table I below are reacted in the indicated quantities to produce additional additives of the type contemplated by the present invention.

TABLE I

Example No.	Amine reactant (A)	Carboxylic acid acylating reagent (B)	Acylating agent (C)	Molar ratio (A):(B):(C)
4.....	N-(3-hydroxypropyl)-propylene diamine.....	Adipic acid.....	Polypropylene (mol. wt. 800)-substituted succinic anhydride.	2:1:1:1
5.....	N-(2-hydroxypropyl)-ethylene diamine.....	Malonic acid.....	Polyisobutylene (mol. wt. 450)-substituted succinic anhydride.	2:1:0.5
6.....	N-(4-hydroxyoctyl)-ethylene diamine.....	Glutaric acid.....	Polyisobutylene (mol. wt. 1,200)-substituted succinic anhydride.	2.2:1:0.75
7.....	N-(3-hydroxyheptyl)-tetramethylene diamine.....	Sebacic acid.....	Polyisobutylene (mol. wt. 900)-substituted acrylic acid.	2:1:2
8.....	N-(2-hydroxyethyl)-ethylene diamine.....	Terephthalic acid.....	Isobutylene-propylene copolymer (80% by wt. isobutylene units; (mol. wt. 1,500)-substituted succinic anhydride).	2:1:1
9.....	N-(3-hydroxypentyl)-trimethylene diamine (1 mole). N-(2-hydroxyheptyl)-tetramethylene diamine (1 mole).	Adipic acid (0.5 mole)..... Azelaic acid (0.5 mole).....	Polypropylene (mol. wt. 600)-substituted succinic acid.	2:1:1
10.....	N-(2-hydroxy-2-phenylethyl)-ethylene diamine.....	Diglycolic acid.....	Polyisobutylene (mol. wt. 3,000)-substituted succinic anhydride.	2:1:1
11.....	N-(2-tolyl-3-hydroxypropyl)-propylene diamine.....	Iminodiacetic acid.....	Same as Example 5.....	2:1:1
12.....	N-(2-hydroxypropyl)-ethylene diamine.....	1,4-phenylenediacetic acid.	Same as Example 7.....	2:1:0.1

this mixture is then heated at 150-160° C. for 4 hours while blowing with nitrogen. During this time 42 milliliters of water are evolved and trapped. Thereafter, 1057 parts of polyisobutenyl-substituted succinic anhydride having an average molecular weight of about 1057 is introduced into the mixture over a 1.5 hour period while maintaining a temperature of 150-163° C. The mass is then heated to 200° C. with nitrogen blowing over a 1.25 hour period and held for 1.5 hours at 200-210° C. while continuing the nitrogen blowing. This mixture is then cooled to 165° C. and 940 parts of mineral oil are added producing a mineral oil solution of the desired product. This solution is then heated to 150° C. and filtered, the filtrate being an oil solution of the desired additive.

EXAMPLE 2

A mixture of 260 parts of N-(hydroxyethyl)-ethylene diamine and 260 parts of xylene is heated to 80° C. Thereafter 146 parts of adipic acid are added to the mixture over a 5 minute-period while maintaining a temperature of 80-120° C. This mixture is heated under reflux at 140-145° C. for twenty-four hours. Thereafter, the solvent is stripped from the reaction product by heating to 180° C. at 12 millimeters (Hg) pressure. Then, 209 parts of the residue, 755 parts of polyisobutenyl-substituted succinic

Following the general procedure of Example 3, it is possible to prepare other additives of the type contemplated by the present invention simply by replacing all or part of the materials identified in Table I as (A)-(C) with other amines, acylating reagents, and acylating agents of the type discussed more fully hereinabove.

While the foregoing examples are directed to a preferred subgenus of the present invention, that is, additives prepared from N-(hydroxyalkyl)-alkylene diamines, additives can also be readily prepared by using polyamines corresponding to Formula C other than the hydroxyalkylene diamines. The following example illustrates the preparation of other polyamines which are suitable for synthesizing the nitrogen-containing reactants used to prepare the additives of this invention.

EXAMPLE 13

(A) Tetraethylene pentamine (1 mole) is charged to a reaction flask fitted with a Dry Ice reflux condenser and 1.5 moles of ethylene oxide are slowly blown through the amine while maintaining a temperature of 50°-60° C. for 4 hours.

(B) A mixture of ethylene polyamine consisting of two moles of diethylene triamine and 2 moles of triethylene tetramine is reacted with 1.25 moles each of eth-

ylene oxide and propylene oxide following the procedure of (A) above.

(C) Following the procedure of (A) above, 1 mole of tetraethylene pentamine is reacted with 1.75 moles of epichlorohydrin.

(D) Two hundred and thirty-three parts of a commercially available mixture of ethylene polyamine sold under the name Polyamine D by Union Carbide Corporation is reacted with 174 parts of propylene oxide following the general procedure of (A) above.

(E) Following the procedure of (A), 1 mole of diethylene triamine is reacted with 1 mole of styrene oxide.

(F) Following the procedure of (A), 1 mole of triethylene tetramine is reacted with styrene oxide.

By substituting equimolar amounts of the reaction products of the above polyamines and epoxides for all or part of (A) in Examples 1-12 above, additional additives of the type falling within the scope of the present invention are readily prepared.

EXAMPLE 14

(A) To a reaction mixture comprising 240 parts of ethylene diamine and 450 parts of xylene, there is slowly added over a period of one hour 146 parts of adipic acid while maintaining a temperature of about 75° C. Thereafter, the reaction mixture is refluxed for 8 hours at a temperature of about 235-245° C. while nitrogen gas is blown through the mass. Then 200 parts of mineral oil are added with stirring. The oil containing mixture is then stripped at reduced pressure to remove unreacted amine and xylene. Then 90 parts of ethylene oxide are slowly introduced (evenly over a two hour period) into the residue which is in a reaction flask fitted with a Dry Ice-cooled reflux condenser while maintaining a temperature of about 90° C. After all the ethylene oxide has been added, the mass is maintained under reflux conditions for an additional two hours at 140-145° C. Subsequently, 300 parts of mineral oil and 1100 parts of polyisobutylsuccinic anhydride (average N.W. about 1100) are added and this mixture is heated at about 200° C. for four hours while nitrogen is blown through the mass at about 2.0 standard cubic feet per hour. The reaction mixture is filtered, the filtrate being an oil-solution of the desired additive.

(B) The process of (A) is repeated substituting an equimolar amount of diethylene triamine and propylene oxide for the ethylene diamine and ethylene oxide.

(C) The procedure of (A) is repeated substituting an equimolar amount of tetraethylene pentamine and propylene oxide for the ethylene diamine and ethylene oxide, respectively.

(D) Part (A) is repeated using 240 parts of propylene oxide in lieu of the 90 parts of ethylene oxide.

(E) Part (A) is repeated substituting 800 parts of the acylating agent of Example 4 for the polyisobutylsuccinic anhydride.

(F) Part (C) is repeated using 205 parts of sebacic acid in lieu of the adipic acid.

(G) Part (B) is repeated using 2000 parts of the acylating agent of Example 7 in lieu of the polyisobutylsuccinic anhydride.

Still further additives of the type contemplated by the present invention can be prepared by substituting other alkanedioic acids, alkylene polyamines, epoxides, or acylating agents for those used in Example 14. For example, equimolar amounts of the acylating reagents and acylating agents described in Table I can be substituted for those used in each part of Example 14. Similarly, equivalent amounts of other alkylene polyamines and alkylene oxides of the type described hereinabove may be used in lieu of those of that example.

In practicing the procedure of Example 14, a stoichiometric excess of the polyamine reactant should be used. There should be at least about one and one-half moles of polyamine for each equivalent of polycarboxylic acid

acylating reagent and preferably there will be at least about two moles. There is little advantage in using more than four moles of polyamine for each equivalent of acylating reagent. Of course, if the acylating reagent is an acyl chloride, allowances should be made for the amount of amine which will react with the hydrogen halide produced. The excess amine is used to prevent the production of large amounts of long-chain polyamides. After completion of the reaction, i.e., when substantially all the carboxyl functions have reacted with amino groups to form amide, imide, or amidine linkages, the excess amine can be removed by conventional techniques, e.g., distillation at reduced pressure, etc.

While temperatures of about 50°-300° C. are useful for the process of Example 14, it is desirable to employ temperatures of at least about 150° C. Further, it is preferred that conditions conducive to the formation of amidine linkages be employed in the reaction between the acylating reagent and the alkylene polyamine. Thus, temperatures of about 200-300° C. are preferred for this step of the reaction with temperatures of about 210-260° C. being especially suitable for this step.

The polyamine reactants used in the process illustrated by Example 14 will preferably be characterized by at least one radical of the formula $H_2N-alkylene-NH-$. Alkylene polyamines corresponding to Formulae C and D where each R' is H and the alkylene dicarboxylic acids of Formula B where R is alkylene are preferred for the first step of the process.

The following examples illustrate preferred embodiments of the invention as it relates to the additives prepared by post-treatment with aldehydes, carboxylic acids, and epoxides as discussed above.

EXAMPLE 15

(A) Into 1000 parts of a filtrate produced in accordance with the procedure of Example 3, there is introduced slowly under reflux conditions 60 parts of propylene oxide over a 2-hour period while maintaining a temperature of about 90-100° C. The resulting mixture is heated under reflux an additional two hours. The resulting reaction product is an oil-solution of an epoxide post-treated additive of this invention.

(B) The procedure of (A) is repeated using 40 parts of ethylene oxide and the reaction product of Example 4.

(C) The procedure of (A) is repeated using 120 parts of styrene oxide and a reaction temperature of about 200° C.

By substituting 0.01% to 20% by weight of other epoxides (based on the total weight of additive product exclusive of diluent) for those in Example 15(A)-(C), other epoxide post-treated products can be prepared. Similarly, other non-post-treated additives can be substituted for that of Examples 3 and 4.

EXAMPLE 16

(A) To a mixture consisting of 1000 parts of the filtrate of Example 3 there are added over a 0.5-hour period 50 parts of formic acid while maintaining a temperature of about 100-105° C. at reflux conditions. The resulting mixture is maintained under these conditions for about 3.5 hours with nitrogen blowing. Thereafter, the mass is heated to 150° C. for one hour at reduced pressure. The residue is an oil solution of the desired formic acid treated product.

(B) Part (A) is repeated using 20 parts of glacial acetic acid and 20 parts of formic acid in lieu of this 50 parts of formic acid.

(C) Part (A) is repeated using 5 parts of formic acid.

EXAMPLE 17

(A) A mixture of 1000 parts of a filtrate produced according to Example 3 and 50 parts of a 37% aqueous formalin are heated under reflux conditions at about 95-105° C. for four hours. Thereafter, the reaction mix-

ture is blown with nitrogen for an hour while maintaining a temperature of about 150° C. without reflux conditions. The resulting product is an oil solution of the desired post-treated additive.

(B) Procedure (A) is repeated using 30 parts of n-butyraldehyde in lieu of the formalin.

The general procedures of Examples 16 and 17 can be repeated using other acids, aldehydes, and non-post-treated additives described in detail hereinbefore to prepare additional post-treated additives of the type contemplated by this invention.

As mentioned above, the additives of this invention are useful in both lubricant and fuel compositions. They can be effectively employed in a variety of lubricant compositions based on diverse oils of lubricating viscosity such as a natural or synthetic lubricating oil, or suitable mixtures thereof. The lubricating compositions contemplated include principally crankcase lubricating oils for spark-ignited and compression-ignited internal combustion engines including automobile and truck engines, two-cycle engine lubricants, aviation piston engines, marine and railroad diesel engines, and the like. However, automatic transmission fluids, transaxle lubricants, gear lubricants, metal-working lubricants, hydraulic fluids, and other lubricating oil and grease compositions can benefit from the incorporation of the present additives.

Natural oils include animal oils and vegetable oils (e.g., castor oil, lard oil) as well as solvent-refined or acid-refined mineral lubricating oils of the paraffinic, naphthenic, or mixed paraffinic-naphthenic types. Oils of lubricating viscosity derived from coal or shale are also useful base oils. Synthetic lubricating oils include hydrocarbon oils and halo-substituted hydrocarbon oils such as polymerized and interpolymerized olefins (e.g., polybutylenes, polypropylenes, propylene-isobutylene copolymers, chlorinated polybutylenes, etc.); alkyl benzenes (e.g., dodecylbenzenes, tetradecylbenzene, dinonylbenzenes, dis-(2-ethylhexyl)benzenes, etc.); polyphenyls (e.g., biphenyls, terphenyls, etc.); and the like. Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc., constitute another class of known synthetic lubricating oils. These are exemplified by the oils prepared through polymerization of ethylene oxide or propylene oxide, the alkyl and aryl ethers of these polyoxyalkylene polymers, e.g., methylpolyisopropylene glycol ether having an average molecular weight of 1000, diphenyl ether of polyethylene glycol having a molecular weight of 500-1000, diethyl ether of polypropylene glycol having a molecular weight of 1000-1500, etc.) or mono- and polycarboxylic esters thereof, for example, the acetic acid esters, mixed C₃-C₉ fatty acid esters, or the C₁₃ oxo acid diester of tetraethylene glycol. Another suitable class of synthetic lubricating oils comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, etc.) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, pentaerythritol, etc.). Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid, and the like. Silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy-, or polyaryloxy-siloxane oils and silicate oils comprise another useful class of synthetic lubricants (e.g., tetraethyl-silicate, tetraisopropyl-silicate, tetra-(2-ethylhexyl)-silicate, tetra-(4-methyl-2-tetraethyl)-silicate, tetra-(p-tert-butylphenyl)-silicate, hexyl-(4-methyl-2-pentoxo) - disiloxane, poly(methyl)-siloxanes, poly(methylphenyl)-siloxanes, etc.). Other synthetic lubricating oils include liquid esters of phosphorus-containing

acids (e.g., tricresyl phosphate, trioctyl phosphate, diethyl ester of decane phosphonic acid, etc.), polymeric tetrahydrofurans, and the like.

The lubricating compositions contemplated by this invention are those containing a major amount of a lubricating oil of the type described hereinabove and a minor amount of the additives of this invention. The amount of additives employed, of course, is dependent upon the particular environment in which the lubricant is to be used and the other components of the lubricating composition, if any. However, the lubricating compositions will usually contain from about 0.01% to about 30% by weight of the present additives. Crankcase lubricants for gasoline-fueled automobile and truck engines will generally contain from about 0.1% to about 10% by weight of the additives and usually from about 0.5% to about 5% by weight. However, diesel engines, particularly railroad diesels and marine diesels, may contain up to 30% or more by weight of these additives. Similarly, gear lubricants may contain as much as 10% by weight or more of the additives.

The additives may also be used in lubricating compositions for two-cycle engines, that is, lubricating compositions which are added directly to the fuel which is to be burned in these engines. Lubricating compositions for two-cycle engines which comprise this additive will contain from about 80 to 99% of a lubricating oil and from about 1 to 20% of one or more of the additives of this invention. Ordinarily, however, the additive will not exceed about 10% by weight of the two-cycle lubricant composition.

It is also contemplated that other conventional additives will be present in the lubricating compositions of this invention. Such additives include detergents of the ash-containing type, other ashless dispersants, viscosity index improving agents, pour point depressants, anti-foam agents, extreme pressure agents, rust inhibiting agents, and other oxidation and corrosion inhibitors. Suitable ashless dispersants for use in combination with the additives of this invention are exemplified by those disclosed in the patents incorporated hereinabove for their disclosure of suitable mono- and polycarboxylic acid acylating agents for preparing the additives of this invention. Generally, these are the amides, imides, and esters, of alkylene polyamine or polyhydric alcohols.

The ash-containing detergents are exemplified by the oil-soluble neutral and basic salts of alkali or alkaline earth metals with sulfonic acids, carboxylic acids, or organic phosphorus acids. The latter are characterized by at least one direct carbon-to-phosphorus linkage such as those prepared by the treatment of an olefin polymer (e.g. polyisobutylene having an average molecular weight of about 1000) with a phosphorizing agent such as phosphorus trichloride, phosphorus heptasulfide, phosphorus pentasulfide, phosphorus trichloride and sulfur, white phosphorus and a sulfur halide, or phosphorothioic chloride. The most commonly used salts of such acids are the sodium, potassium, lithium, calcium, magnesium, strontium, and barium salts.

The term "basic salt" is used to designate those metal salts wherein the metal is present in stoichiometrically larger amounts than the organic acid radical. The commonly employed methods for preparing the basic salts involves heating a mineral oil solution of an acid with a stoichiometric excess of a metal neutralizing agent such as the metal oxide, hydroxide, carbonate, bicarbonate, or sulfide at a temperature of at least about 50° C. and filtering the resulting mass. The use of a promoter in the neutralization step to aid the incorporation of a large excess of metal is known. Examples of compounds useful as promoters include phenolic substances such as phenol, naphthol, alkylphenols, thiophenols, sulfurized alkylphenols, and condensation products of formaldehyde with a phenolic substance; alcohols such as methanol, 2-propanol, octyl alcohol, Cellosolve, Carbitol, ethylene glycol,

stearyl alcohol, and cyclohexyl alcohol; amines such as aniline, phenylene diamine, phenothiazine, and dodecyl amine. Illustrative ash-containing detergents and processes for their preparation are discussed in detail in such U.S. patents as 3,027,325; 3,312,618; 3,377,281.

Extreme pressure agents, corrosion inhibitors, oxidation inhibitors and the like such as are contemplated for use in the compositions of the present invention are also well-known in the art and include, for example, chlorinated aliphatic hydrocarbons such as chlorinated wax; organic sulfides and polysulfides such as benzyl disulfides, bis-(chlorobenzyl)disulfide, dibutyl tetrasulfide, sulfurized sperm oil, sulfurized methyl ester of maleic acid, sulfurized alkyl phenol, sulfurized dipentene, and sulfurized turpene; phosphosulfurized hydrocarbons such as the reaction product of a phosphorus sulfide with turpentine or methyloleate and the phosphorus esters including principally dihydrocarbon and trihydrocarbon phosphates such as dibutyl phosphate, diheptyl phosphite, dicyclohexyl phosphite, pentyphenyl phosphite, dipentyl phenyl phosphite, tridecyl phosphite, distearyl phosphite, dimethyl naphthyl phosphite, oleyl-4-pentyphenyl phosphite, polypropylene (molecular weight-500)-substituted phenyl phosphite, diisobutyl substituted phenyl phosphite; metal thiocarbamate such as zinc dioctyl-thiocarbamate and barium heptylphenyl dithiocarbamate; Group II metal phosphorodithioates such as zinc dicyclohexylphosphorodithioate, zinc dioctylphosphorodithioate, barium di(heptylphenyl) phosphorodithioate, cadmium dinonylphosphorodithioate, and zinc salts of a phosphorodithioic acid produced by the reaction of phosphorus pentasulfide with an equal molar mixture of isopropyl alcohol and n-hexyl alcohol.

The lubricating compositions of this invention can contain the metal containing detergents in amounts up to about 20% by weight. In some applications such as lubricants for marine diesel engines, the lubricating compositions may contain as much as 30% by weight of a metal detergent additive. The other components in the composition will be present in amounts in which such components are ordinarily used, that is, in amounts of about 0.001% to about 10% by weight.

The additives of this invention are also useful as components in fuels wherein they function as sludge dispersants, emulsion breakers and retardants, anti-screen clogging agents. In liquid fuels used in internal combustion engines, they also serve to promote the general cleanliness of the fuel system such as fuel pumps, carburetors, and the like and to reduce the deposition of deposits in the exhaust system.

The fuels contemplated for use with the additives of this invention are generally the petroleum distillate fuels including diesel fuels, furnace fuels, jet fuels, aviation fuels and include fuel oils, kerosene, and gasolines. In fuels, the additives will be used in amounts such that they comprise from about 0.0001% to about 5% by weight of the fuel composition and preferably from about 0.001% to about 1% by weight of the total fuel composition.

The fuel compositions of this invention may contain other conventional additives such as alkyl or alkenyl lead anti-knocking agents e.g., tetraethyl lead, tetramethyl lead, tetravinyl lead; corrosion inhibitors, anti-oxidants, anti-static agents, lead octane appreciators, lead scavengers, anti-icing agents, smoke suppressants, and the like.

The following compositions are illustrative of lubricants and fuels contemplated by the present invention.

Composition A

SAE-10 W-30 mineral lubricating oil containing 0.75% of an additive produced according to Example 2.

Composition B

SAE-30 mineral lubricating oil containing 2% of the product of Example 3, 0.075% of phosphorus as zinc dioctylphosphorodithioate, and 5% of the barium salt of an

acidic composition prepared by the reaction of 1000 parts of polyisobutene having the molecular weight of 60,000 with 100 parts of phosphorus pentasulfide at 200° C. and hydrolyzing the product with steam at 150° C.

Composition C

SAE-10 mineral lubricating oil containing 1.5% of the product of Example 7, 0.075% of phosphorus as the adduct obtained by heating zinc di-nonylphosphorodithioate with 0.25 mole of 1,2-hexene oxide at 120° C., 2% of a sulfurized methyl ester of tall oil acid having a sulfur content of 15%, 6% of a polyisobutene viscosity index improving agent, 0.005% of a poly-(alkylmethacrylate) anti-foam agent, and 0.5% of lard oil.

Composition D

SAE-10 mineral lubricating oil containing 2% of the product of Example 7, 0.07% of phosphorus as zinc dioctylphosphorodithioate, 2% of barium detergent prepared by neutralizing with barium hydroxide the hydrolyzed reaction product of polypropylene (molecular weight-2000) with one mole of phosphorus pentasulfide and one mole of sulfur, 3% of a barium sulfonate detergent prepared by carbonating a mineral oil solution of mahogany acid and a 500% stoichiometrically excess amount of barium hydroxide in the presence of heptylphenol as a promoter at a 180° C., 3% of a supplemental ashless detergent prepared by copolymerizing a mixture of 95% of decyl-methacrylate and 5% of diethylamino ethylacrylate.

Composition E

A synthetic lubricant which is the diphenyl ether of polyethylene glycol having a molecular weight of about 1000 and 0.5% of the additive produced according to Example 3.

Composition F

Gasoline containing 0.05% of the additive produced according to Example 3.

Composition G

Kerosene containing 0.15% of the additive produced according to Example 7.

Composition H

Diesel fuel containing 0.008% of the additive produced according to Example 4.

Composition I

Gasoline containing 0.2% of the product of Example 2.

The emulsion sludge resistance of the additives of this invention is demonstrated by the following engine test results of lubricating compositions differing only in the nature of the ashless dispersant present. Composition X is a mineral lubricating oil composition containing two prior art ashless dispersants. One is a reaction product of (1) polyisobutenyl succinic acid anhydride and (2) the reaction product of polyethylene polyamines and acrylonitrile as described in Example 3 of U.S. Pat. No. 3,278,550. The other is the reaction product of (1) polyisobutenyl succinic acid anhydride and (2) polyethylene polyamines of the type in Example 5 of U.S. Pat. No. 3,172,892. Each is present in composition in an amount of about 1.5% by weight. Composition Y is the same as Composition X but the two ashless dispersants are replaced with about 3% by weight of the additive produced according to Example 3.

Each composition is employed in test engines which are operated under identical conditions. At the end of each day of operation the emulsion sludge resistance of the lubricant is ascertained by the amount of emulsion sludge formed on the rocker arm covers. A rating of 10 represents no sludge deposit. The results achieved with Composition X and Y are tabulated below.

TABLE II

Days of engine operation	Emulsion sludge rating ¹	
	Composition X	Composition Y
1-----	5.2	6.2
2-----	3.5	5.7
3-----		6.2
4-----		6.0
5-----		5.7
6-----		5.7
7-----		5.7

¹ Ratings are the averages of two engine tests of each composition.

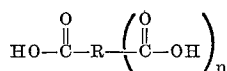
As seen by the foregoing results, the additive of Example 3 results in less sludge after seven days than is present after either the first or second day with the prior art dispersants. Yet the additive of Example 3 is also an effective ashless dispersant. These results also demonstrate another advantage of the additives of this invention, particularly those prepared from N-(hydroxyalkyl)-alkylene diamines. Their emulsion sludge resistance appears to improve somewhat with engine operation and they continue to function effectively for a long period of time.

What is claimed is:

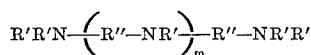
1. An oil-soluble acylated nitrogen composition produced by the process comprising reacting at a temperature of from about 75° C. up to the decomposition temperature:

(I) at least one substantially saturated aliphatic mono- or polycarboxylic acylating agent characterized by the presence of at least about thirty aliphatic carbon atoms exclusive of carboxyl carbon atoms and average molecular weight of from about 400 to about 100,000, with

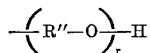
(II) at least one nitrogen-containing reactant, said reactant having been produced by reacting at a temperature of about 50° C. up to the decomposition temperature (a) a polycarboxylic acid acylating reagent selected from the class consisting of the formula



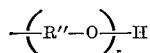
and their corresponding acyl halides, lower alkyl esters, and anhydrides where R is a polyvalent organic radical which does not contain more than twenty carbon atoms and whose valence equals n plus 1, n is a whole number of 1 to 3, with the proviso that R may also be a direct linkage between the carbon atoms, with (b) a polyamine of the formula



where R' is H, hydrocarbyl of up to ten carbon atoms, or



where r is a whole number of 1 to 10 but at least one R' per polyamine molecule is



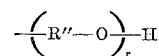
and at least one R' per polyamine molecule is H, and R'' is hydrocarbylene of up to ten carbon atoms, (a) and (b) having been reacted in a ratio of at least about one equivalent of (a) up to about one mole of (a) for each mole of (b), where (I) and (II) are reacted in amounts such that there is at least one equivalent of the acylating agent for each mole of nitrogen containing reactant.

2. A composition according to claim 1 wherein (I) and (II) as well as (a) and (b) are reacted at temperatures of at least 100° C. up to about 260° C.

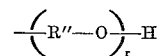
3. A composition according to claim 2 wherein said polycarboxylic acid acylating reagent (a) is a dicarboxylic acid acylating reagent selected from the class consisting

of the acids per se and their corresponding acyl halides, lower alkyl esters, and anhydrides where R is a divalent hydrocarbon radical having up to about 10 carbon atoms.

4. A composition according to claim 3 wherein said polyamine (b) is further characterized in that the R' variables are either H or

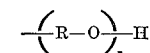


10 providing one R' is H and at least one R' is



5. A composition according to claim 4 wherein R is a divalent aliphatic hydrocarbon radical.

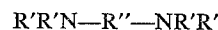
6. A composition according to claim 5 where said polyamine (b) is further characterized in that all R'' groups are alkylene of up to six carbon atoms, one R' is



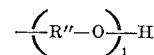
and the remaining R' groups are H.

7. A composition according to claim 6 where said dicarboxylic acid acylating reagent (a) is further characterized in that R is a straight or branched chain alkylene containing up to ten carbon atoms.

8. A composition according to claim 7 wherein all R'' groups are alkylene of two to six carbon atoms and said polyamine (b) corresponds to the formula



where one R' is



and the remaining R' groups are H.

9. A composition according to claim 8 where the dicarboxylic acid acylating reagent (a) is further characterized in that R separates the acid groups by at least four carbon atoms.

10. A composition according to claim 9 wherein all the R'' groups are ethylene or propylene.

11. A composition according to claim 2 wherein (I) has been prepared by reacting at a temperature of about 100°-300° C. (i) an ethylenically unsaturated carboxylic acid reactant of the formula $\text{R}_0(\text{COOH})_n$ or its corresponding acyl halide, ester, or anhydride, where n is one or two and R_0 is characterized by the presence of at least one ethylenic linkage in an α,β -position with respect to at least one carboxyl function, the total number of carbon atoms in $\text{R}_0(\text{COOH})_n$ not exceeding ten, with (ii) substantially saturated, substantially aliphatic polyolefins or chlorinated polyolefins having average molecular weights of about 400 to about 5000.

12. A composition according to claim 4 wherein (I) has been prepared by reacting at a temperature of about 100°-300° C. a member selected from the group consisting (i) of acrylic acid, methacrylic acid, maleic acid, maleic anhydride, fumaric acid, itaconic acid, itaconic anhydride, citraconic acid, citraconic anhydride, mesaconic acid, glutaconic acid, chloromaleic acid, aconitic acid, crotonic acid, methylcrotonic acid, sorbic acid, 3-hexenoic acid, and 10-decenoic acid with (ii) substantially saturated, substantially aliphatic polyolefins or chlorinated polyolefins having average molecular weights or about 400 to about 5000.

13. A composition according to claim 7 where (I) has been prepared by reacting at a temperature of about 100°-300° C. (i) a member selected from the class consisting of α,β -ethylenically unsaturated dicarboxylic acids and the corresponding anhydrides having up to six carbon atoms with (ii) a member selected from the group consisting of polypropylene, polyisobutylene, and their chlorinated derivatives having molecular weights of about 700 to about 5000.

14. A composition according to claim 9 where (I) has been prepared by reacting at a temperature of about 100°–300° C. (i) a member selected from the class consisting of α - β -ethylenically unsaturated dicarboxylic acids and the corresponding anhydrides having up to six carbon atoms with (ii) a member selected from the group consisting of polypropylene, polyisobutylene, and their chlorinated derivatives having molecular weights of about 700 to about 5000.

15. A composition according to claim 2 wherein the reaction product of (I) and (II) has been post-treated at a temperature of about 25° C. up to about 300° C. with at least one member selected from the group consisting of lower aliphatic acids and the corresponding acyl halides, lower alkyl esters, and anhydrides, lower aliphatic aldehydes, and alkylene oxides and mono-aryl substituted alkylene oxides, said oxides having two to eight carbon atoms in amounts such that the post-treating materials comprise from about 0.01% to about 20% by weight of the total weight of (I) and (II).

16. A composition according to claim 4 wherein the reaction product of (I) and (II) has been post-treated at a temperature of from about 50° C. up to about 200° C. with at least one member selected from the group consisting of lower aliphatic mono- and dicarboxylic acids and their corresponding acyl halides, lower alkyl esters, and anhydrides, lower alkyl monoaldehydes, 1–2 alkylene oxides, said alkylene oxides having two to eight carbon atoms, in such amounts that the post-treating materials comprise from about 0.1% to about 10% by weight of the total weight of (I) and (II).

17. A composition according to claim 7 wherein the reaction product of (I) and (II) has been post-treated at a temperature of from about 50° C. up to about 200° C. with at least one member selected from the group consisting of lower aliphatic mono- and dicarboxylic acids and their corresponding acyl halides, lower alkyl esters, and anhydrides, lower alkyl monoaldehydes, 1–2 alkylene oxides, said alkylene oxides having two to eight carbon atoms, in such amounts that the post-treating materials comprise from about 0.1% to about 10% by weight of the total weight of (I) and (II).

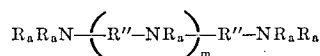
18. A composition according to claim 11 wherein the reaction product of (I) and (II) has been post-treated at a temperature of from about 50° C. up to about 200° C. with at least one member selected from the group consisting of lower aliphatic mono- and dicarboxylic acids and their corresponding acyl halides, lower alkyl esters, and anhydrides, lower alkyl monoaldehydes, 1–2 alkylene oxides, said alkylene oxides having two to eight carbon atoms, in such amounts that the post-treating materials comprise from about 0.1% to about 10% by weight of the total weight of (I) and (II).

19. A composition according to claim 12 wherein the reaction product of (I) and (II) has been post-treated at a temperature of from about 50° C. up to about 200° C. with at least one member selected from the group consisting of lower aliphatic mono- and dicarboxylic acids and their corresponding acyl halides, lower alkyl esters, and anhydrides, lower alkyl monoaldehydes, 1–2 alkylene oxides, said alkylene oxides having two to eight carbon atoms, in such amounts that the post-treating materials comprise from about 0.1% to about 10% by weight of the total weight of (I) and (II).

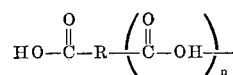
20. A composition according to claim 13 wherein the reaction product of (I) and (II) has been post-treated at a temperature of from about 50° C. up to about 200° C. with at least one member selected from the group consisting of lower aliphatic mono- and dicarboxylic acids and their corresponding acyl halides, lower alkyl esters, and anhydrides, lower alkyl monoaldehydes, 1–2 alkylene oxides, said alkylene oxides having two to eight carbon atoms, in such amounts that the post-treating materials comprise from about 0.1% to about 10% by weight of the total weight of (I) and (II).

21. A composition according to claim 14 wherein the reaction product of (I) and (II) has been post-treated at a temperature of from about 50° C. up to about 200° C. with at least one member selected from the group consisting of lower aliphatic mono- and dicarboxylic acids and their corresponding acyl halides, lower alkyl esters, and anhydrides, lower alkyl monoaldehydes, 1–2 alkylene oxides, said alkylene oxides having two to eight carbon atoms, in such amounts that the post-treating materials comprise from about 0.1 % to about 10% by weight of the total weight of (I) and (II).

22. An oil-soluble acylated nitrogen composition produced by the process comprising reacting at a temperature of at least about 50° C. up to about the decomposition temperature at least one alkylene polyamine of the formula



where R_a is H or hydrocarbyl of up to ten carbon atoms with the proviso that at least two R_a 's are H, R'' is alkylene of from two to six carbon atoms and m is 0 or a whole number of 1 to 8, with at least one polycarboxylic acid acylating reagent selected from the group consisting of those of the Formula B



and their corresponding acyl halides, lower alkyl esters, and anhydrides where R is a polyvalent organic radical which does not contain more than twenty carbon atoms and whose valence equals $n+1$, n is a whole number of 1 to 3, with the proviso that R may also be a direct linkage between the carbon atoms, in a molar ratio of acylating reagent to polyamine of at least one equivalent of acylating reagent per mole of polyamine to form a first reaction composition; reacting this first reaction composition at a temperature of from about 25° C. up to the decomposition temperature with at least one epoxide selected from the class consisting of alkylene oxides and mono-aryl-substituted alkylene oxides in an amount such that the molar ratio of epoxide to the polyamine used in preparing the first reaction composition is about 1:1 to about 10:1 to form a second reaction composition; and thereafter reacting the second reaction composition at a temperature of from about 75° C. up to the decomposition temperature with at least one substantially saturated aliphatic mono- or polycarboxylic acid acylating agent characterized by the presence within its structure of at least about thirty aliphatic carbon atoms exclusive of the carboxyl carbon atoms and average molecular weight of from about 400 to about 100,000, the amount of high molecular weight carboxylic acid being such that there is at least one equivalent of said at least one substantially saturated aliphatic mono- or polycarboxylic acid acylating agent for each mole of polyamine employed in the preparation of the first reaction composition.

23. An oil-soluble acylated nitrogen composition according to claim 22 wherein: said at least one polyamine and said acylating reagent are reacted at a temperature of at least about 100° C.; said at least one acylating reagent corresponds to Formula B where R is a divalent hydrocarbon radical of up to about ten carbon atoms and n is 1 and the corresponding lower alkyl esters and anhydrides; said first reaction mixture and said at least one epoxide are reacted at a temperature of about 40° C. to about 150° C.; said at least one substantially saturated aliphatic mono- or polycarboxylic acid acylating agent is selected from the high molecular weight mono- and polycarboxylic acids and anhydrides; and said second reaction composition and said at least one substantially saturated aliphatic mono- or polycarboxylic acid acylating agent are reacted at a temperature of at least 100° C. up to about 260° C.

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24. An oil-soluble acylated nitrogen composition according to claim 23 wherein: said at least one epoxide is 1,2-alkylene oxide; said R_a groups are H; R separates the carboxylic acid groups by at least four carbon atoms; and said at least one substantially saturated aliphatic mono- or polycarboxylic acid acylating agent is selected from those prepared by reacting at a temperature of about 100°–300° C. (i) an ethylenically unsaturated carboxylic acid reactant of the formula $R_0-(COOH)_n$ or its corresponding acyl halide, ester, or anhydride, where n is one or two and R_0 is characterized by the presence of at least one ethylenic linkage in an α,β -position with respect to at least one carboxyl function, the total number of carbon atoms in $R_0(COOH)_n$ not exceeding ten, with (ii) substantially saturated, substantially aliphatic polyolefins and chlorinated polyolefins having average molecular weights of about 400 to about 5000.

25. A lubricant or fuel comprising, respectively, a major amount of a lubricating oil or a normally liquid petroleum distillate fuel and a dispersant amount of an oil-soluble acylated nitrogen composition according to claim 1.

26. A lubricant or fuel comprising, respectively, a major amount of a lubricating oil or a normally liquid petroleum distillate fuel and a dispersant amount of an oil-soluble acylated nitrogen composition according to claim 5.

27. A lubricant or fuel comprising, respectively, a major amount of a lubricating oil or a normally liquid

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petroleum distillate fuel and a dispersant amount of an oil-soluble acylated nitrogen composition according to claim 8.

28. A lubricant or fuel comprising, respectively, a major amount of a lubricating oil or a normally liquid petroleum distillate fuel and a dispersant amount of an oil-soluble acylated nitrogen composition according to claim 15.

29. A lubricant or fuel comprising, respectively, a major amount of a lubricating oil or a normally liquid petroleum distillate fuel and a dispersant amount of an oil-soluble acylated nitrogen composition according to claim 21.

30. A lubricant or fuel comprising, respectively, a major amount of a lubricating oil or a normally liquid petroleum distillate fuel and a dispersant amount of an oil-soluble acylated nitrogen composition according to claim 22.

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U.S. Cl. X.R.

44—63, 71; 260—268 PL, 268 H, 326.5 F, 326.5 FM

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,630,904 Dated December 28, 1971

Inventor(s) Jerry L. Musser et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

At column 26, line 3, that is Claim 27, line 5,
"Claim 8" should be --Claim 11--.

Signed and sealed this 29th day of August 1972.

(SEAL)

Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents