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LUBRICANT CONTAINING NITROGEN-CONTAINING AND PHOSPHORUS-CONTAINING SUCCINIC DERIVATIVES

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14 Claims

ABSTRACT OF THE DISCLOSURE

Nitrogen- and phosphorus-containing succinic derivatives are obtained by the reaction of a high molecular weight succinic acid compound, an amine, and a phosphorizing agent. The products of such reaction are useful as additives in lubricating oils, fuels, plastics, etc.

This application is a division of parent application Ser. No. 288,481, filed June 17, 1963.

This invention relates to substituted polyamines and to processes for preparing the same. The substituted polyamines of this invention are useful as anti-wear agents, anti-rust agents, insecticides, plasticizers, detergents, etc. They are especially useful as additives in lubricating compositions, fuels, hydrocarbon oils, and power-transmitting fluids.

Deterioration of lubricating oils, especially mineral oils, has been a great concern in the formulation of lubricating compositions for internal combustion engines, transmissions, gears, etc. Deterioration of the oil results in the formation of products which are corrosive to the metal surfaces with which the oil comes into contact. It also results in the formation of products which agglomerate to form sludge- and varnish-like deposits. The deposits cause sticking of the moving metal parts and obstruct their free movement. They are a principal cause of malfunctioning and premature breakdown of the equipment which the oil lubricates.

It is known that water is a common contaminant in the crankcase lubricant of an engine. It may result from the decomposition of the lubricating oil or come from the combustion chamber as a blow-by product of the burning of the fuel. The presence of water in the lubricant seems to promote the deposition of a mayonnaise-like sludge. This type of sludge is more objectionable because it is tenacious to metal surfaces and is not removed by the oil filter. If the engine is operated under conditions such that the crankcase lubricant temperature is continuously high, the water will be eliminated about as fast as it accumulates and only a very small amount of the mayonnaise-like sludge is formed. On the other hand, if the crankcase lubricant temperature is intermittently high and low or consistently low, the water will accumulate and a substantial quantity of the mayonnaise-like sludge will be deposited in the engine.

High operating temperatures are characteristic of an engine that is consistently run at relatively high speed and continuously for a lengthy period. However, where an automobile is primarily used for trips of short distance such as is characteristic of urban, home-to-work use, a significant portion of the operation occurs before the engine has reached its optimum, high temperature. An ideal environment thus obtained for the accumulation of water in the lubricant. In this type of operation, the problem of mayonnaise sludge has been especially troublesome. Its solution has been approached by the use in the lubricant of detergents such as metal phenates and sul-

fonates which have been known to be effective in reducing deposits in engines operated primarily at high temperatures. Unfortunately, such known detergents have not been particularly effective in solving the problems associated with low temperature operation, particularly those problems which are associated with crankcase lubricants in engines which are operated at low or alternating high and low temperatures.

It is accordingly a principal object of this invention to provide novel compositions of matter.

It is also an object of this invention to provide compositions which are adapted for use as additives in hydrocarbon oils.

It is also an object of this invention to provide compositions which are effective as detergents in lubricating compositions.

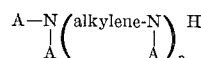
It is another object of this invention to provide novel compositions which are effective dispersants in lubricant compositions intended for use in engines operated at low or alternating high and low temperatures.

It is another object of this invention to provide improved lubricating compositions.

It is another object of this invention to provide improved fuel compositions.

These and other objects are attained in accordance with this invention by providing a process for preparing substituted polyamines comprising the reaction of 1 mole of an alkylene amine with at least about 0.25 mole of a substantially hydrocarbon-substituted succinic acid-producing compound having at least about 50 aliphatic carbon atoms in the substantially hydrocarbon substituent and at least about 0.001 mole of a phosphorus acid-producing compound selected from the class consisting of phosphoric acids, phosphorous acids, phosphonyl acids, phosphinyl acids, and the esters, the halides, and the anhydrides thereof.

The polyamines from which the products of this invention are derived include principally alkylene amines conforming for the most part to the formula



wherein n is an integer preferably less than about 10, A is a hydrogen radical or a substantially hydrocarbon preferably having up to about 30 carbon atoms, and the alkylene radical is preferably a lower alkylene radical having less than about 8 carbon atoms. The alkylene amines include principally methylene amines, ethylene amines, butylene amines, propylene amines, pentylene amines, hexylene amines, heptylene amines, octylene amines, other polymethylene amines, and also the cyclic and the higher homologues of such amines such as piperazines and amino-alkyl-substituted piperazines. They are exemplified specifically by: ethylene diamine, triethylene tetramine, propylene diamine, decamethylene diamine, octamethylene diamine, di(heptamethylene) triamine, tripropylene tetramine, tetraethylene pentamine, trimethylene diamine, pentaethylene hexamine, di(trimethylene) triamine, 2-heptyl-3-(2 - aminopropyl)imidazoline, 4-methyl-imidazoline, 1,3-bis(2 - aminoethyl)imidazoline, pyrimidine, 1-(2 - aminopropyl)piperazine, 1,4-bis(2-aminoethyl)piperazine, and 2-methyl-1-(2-aminobutyl)piperazine. Higher homologues such as are obtained by condensing two or more of the above-illustrated alkylene amines likewise are useful.

The ethylene amines are especially useful. They are described in some detail under the heading "Ethylene Amines" in Encyclopedia of Chemical Technology, Kirk and Othmer, volume 5, pages 898-905, Interscience Publishers, New York (1950). Such compounds are prepared most conveniently by the reaction of an alkylene chloride with ammonia. The reaction results in the

production of somewhat complex mixtures of alkylene amines, including cyclic condensation products such as piperazines. These mixtures find use in the process of this invention. On the other hand, quite satisfactory products may be obtained also by the use of pure alkylene amines. An especially useful alkylene amine for reasons of economy as well as effectiveness of the products derived therefrom is a mixture of ethylene amines prepared by the reaction of ethylene chloride and ammonia and having a composition which corresponds to that of tetraethylene pentamine.

Hydroxyalkyl-substituted alkylene amines, i.e., alkylene amines having one or more hydroxyalkyl substituents on the nitrogen atoms, likewise are contemplated for use herein. The hydroxyalkyl-substituted alkylene amines are preferably those in which the alkyl group is a lower alkyl group, i.e., having less than about 6 carbon atoms. Examples of such amines include N-(2-hydroxyethyl)ethylene diamine, N,N'-bis(2-hydroxyethyl)ethylene diamine, 1-(2-hydroxyethyl)piperazine, mono-hydroxypropyl-substituted diethylene triamine, 1,4-bis(2-hydroxypropyl)piperazine, di-hydroxypropyl-substituted tetraethylene pentamine, N-(3-hydroxypropyl)tetramethylene diamine, and 2-heptadecyl-1-(2-hydroxyethyl)imidazoline.

Higher homologues such as are obtained by condensation of the above illustrated alkylene amines or hydroxy alkyl-substituted alkylene amines through amino radicals or through hydroxy radicals are likewise useful. It will be appreciated that condensation through amino radicals results in a higher amine accompanied with removal of ammonia and that condensation through the hydroxy radicals results in products containing ether linkages accompanied with removal of water.

The substantially hydrocarbon-substituted succinic acid-producing compounds used in the above process include the succinic acids, anhydrides, halides, and esters. An important aspect of this invention is the size of the substantially hydrocarbon substituent on the succinic acid-producing compound. Thus, only the substituted succinic acid-producing compounds having at least about 50 aliphatic carbon atoms in the substantially hydrocarbon substituent are contemplated as being within the scope of this invention. This lower limit is based not only upon a consideration of the oil-solubility of the substituted polyamines but also upon the effectiveness of such compounds in application contemplated by this invention.

The substantially hydrocarbon substituent of the succinic compound may contain polar groups provided, however, that the polar groups are not present in proportions sufficiently large to alter significantly the hydrocarbon character of the substituent. The polar groups are exemplified by the chloro, bromo, keto, ether, aldehyde, nitro, etc. The upper limit with respect to the portion of such polar groups in the substituent is approximately 10% based on the weight of the hydrocarbon portion of the substituent.

The sources of the substantially hydrocarbon substituent include principally the high molecular weight substantially saturated petroleum fractions and substantially saturated olefin polymers, particularly polymers of mono-olefins having from 2 to 30 carbon atoms. The especially useful polymers are the polymers of 1-mono-olefins such as ethylene, propene, 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. They are illustrated by 2-butene, 3-pentene, and 4-octene.

Also useful are the interpolymers of the olefins such as those illustrated above with other interpolymerizable olefinic substances such as aromatic olefins, cyclic olefins, and polyolefins. Such interpolymers include, for example, those prepared by polymerizing isobutene with styrene;

isobutene with butadiene; propene with isoprene; ethylene with piperylene; isobutene with chloroprene; isobutene with p-methyl styrene; 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; etc.

The relative proportions of the mono-olefins to the other monomers in the interpolymers influence the stability and oil-solubility of the final products derived from such interpolymers. Thus, for reasons of oil-solubility and stability the interpolymers contemplated for use in this invention should be substantially aliphatic and substantially saturated, i.e., they should contain at least about 80%, preferably at least about 95%, on a weight basis of units derived from the aliphatic monoolefins and no more than about 5% of olefinic linkages based on the total number of carbon-to-carbon covalent linkages. In most instances, the percentage of olefinic linkages should be less than about 2% of the total number of carbon-to-carbon covalent linkages.

Specific examples of such interpolymers include copolymer of 95% (by weight) of isobutene with 5% of styrene; terpolymer of 98% of isobutene with 1% of piperylene and 1% of chloroprene; terpolymer of 95% of isobutene with 2% of 1-butene and 3% of 1-hexene, terpolymer of 80% of isobutene with 20% of 1-pentene and 20% of 1-octene; copolymer of 80% of 1-hexene and 20% of 1-heptene; terpolymer of 90% of isobutene with 2% of cyclohexene and 8% of propene; and copolymer of 80% of ethylene and 20% of propene.

Another source of the substantially hydrocarbon radical comprises saturated aliphatic hydrocarbons such as highly refined high molecular weight white oils or synthetic alkanes such as are obtained by hydrogenation of high molecular weight olefin polymers illustrated above or high molecular weight olefinic substances.

The use of olefin polymers having molecular weight of about 750-5000 is preferred higher molecular weight olefin polymers having molecular weights from about 10,000 to about 100,000 or higher have been found to impart also viscosity index improving properties to the final products of this invention. The use of such higher molecular weight olefin polymers often is desirable.

The succinic acid-producing compounds useful in the above process are preferably substantially hydrocarbon-substituted succinic acids and anhydrides. These succinic compounds are readily available from the reaction of maleic anhydride with a high molecular weight olefin or a chlorinated hydrocarbon such as the olefin polymer described hereinabove. The reaction involves merely heating the two reactants at a temperature about 100°-200° C. The product from such a reaction is an alkenyl succinic anhydride. The alkenyl group may be hydrogenated to an alkyl group. The anhydride may be hydrolyzed by treatment with water or steam to the corresponding acid. Either the anhydride or the acid may be converted to the corresponding acid halide or ester by reaction with, e.g., phosphorus halide, phenols, or alcohols.

In lieu of the olefins or chlorinated hydrocarbons, other hydrocarbons containing an activating polar substituent, i.e., a substituent which is capable of activating the hydrocarbon molecule in respect to reaction with maleic acid or anhydride, may be used in the above-illustrated reaction for preparing the succinic compounds. Such polar substituents may be illustrated by sulfide, di-sulfide, nitro, mercaptan, bromine, ketone, or aldehyde radicals. Examples of such polar-substituted hydrocarbons include polypropylene sulfide, di-polyisobutene disulfide, nitrated mineral oil, di-polyethylene sulfide, brominated polyethylene, etc. Another method useful for preparing the succinic acids and anhydrides involves the reaction of itaconic acid with a high molecular weight olefin or a polar-substituted hydrocarbon at a temperature usually

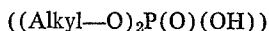
within the range from about 100° C. to about 200° C.

The acid halides of the succinic acids can be prepared by the reaction of the acids or their anhydrides with a halogenation agent such as phosphorus tri-bromide, phosphorus pentachloride or thionyl chloride. The esters of such acids can be prepared simply by the reaction of the acids or their anhydrides with an alcohol or a phenolic compound such as methanol, ethanol, octadecanol, cyclohexanol, phenol, naphthol, octylphenol, etc. The esterification is usually promoted by the use of an alkaline catalyst such as sodium hydroxide or sodium alkoxide or an acidic catalyst such as sulfuric acid. The nature of the alcoholic or phenolic portion of the ester radical appears to have little influence on the utility of such ester as reactant in the process described hereinabove.

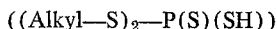
The phosphorus acid-producing reactants useful in the above process for forming the substituted polyamines of this invention may be phosphorus acids, anhydrides, esters, or halides. The phosphorus acids, as indicated previously, may be phosphoric acids, phosphorous acids, phosphinyl acids (including phosphinic acids and phosphinous acids), and phosphonyl acids (including phosphonic acids and phosphonous acids). It will be noted that the phosphorous acids include the oxyphosphorus acids, the thiophosphorus acids, as well as the mixed oxythiophosphorus acids (i.e., those containing both oxygen and sulfur). Thus, a "phosphoric acid" is used in a generic sense to denote the class consisting of phosphoric acid (H₃PO₄), phosphorotetrathioic acid (H₃PS₄), phosphoromonothioic acid.



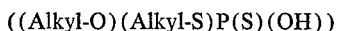
phosphorodithioic acid (H₃PO₂S₂), and phosphorotrithioic acid (H₃POS₃). It should be noted that the acids containing both oxygen and sulfur may be further characterized according to the manner in which the oxygen or sulfur is attached to the phosphorus atom of the acid. The nomenclature used here follows essentially that proposed by the American Chemical and Engineering News, volume 30, No. 43, Oct. 27, 1952. According to this nomenclature, for instance, a phosphoromonothioic acid in which the sulfur atom is attached only to the phosphorus atom (i.e., —P(S)(OH)) is a phosphorothioic acid whereas its isomer in which the sulfur atom is attached to both the phosphorus atom and a hydrogen atom (i.e., —P(O)(SH)) is a phosphorothioic acid. Also according to this nomenclature, the inclusion of thio analogs is admitted only when generic expressions are used and the specific designation of dioctylphosphoric acid refers to the oxy-acids only, i.e. (Octyl-O)₂P(O)(OH). Thus, dialkylphosphoric acids, i.e., dialkyl esters of phosphoric acids, include dialkylphosphoric acid



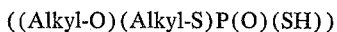
dialkylphosphorotetrathioic acid



O,S-dialkylphosphorodithioic acid



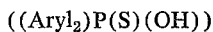
O,S-dialkylphosphorodithioic acid



O,S-dialkylphosphorotrithioic acid



etc. Similarly, diarylphosphinic acids include: diarylphosphinic acid ((Aryl)₂P(O)(OH)); diarylphosphinodithioic acid ((Aryl)₂P(S)(SH)); diarylphosphinothioic acid



and diarylphosphinothioic acid ((Aryl)₂P(O)(SH)).

Specific examples of the organic phosphonyl and phosphinyl acids include: diphenylphosphinic acid, dinaphthylphosphinodithioic acid, diheptylphosphinic acid, di(heptylphenyl)phosphinous acid, di(chlorodecyl)phosphinic acid,

phenylphosphonic acid, phenylphosphonous acid, phenylphosphonomonothioic acid, the acid obtained by the reaction of alpha-pinene with phosphorus pentasulfide, the acid obtained by the reaction of polyisobutene having a molecular weight of 1000 with phosphorus pentasulfide, the acid obtained by the reaction of a polyisobutene having a molecular weight of 500 with phosphorus trichloride and oxygen, and bis(o,p-dichlorophenyl)phosphinomonothioic acid.

The phosphorus acids, anhydrides, esters, and halides likewise are useful for preparing the substituted polyamines. The anhydrides of inorganic phosphorus acids are especially desirable. They are illustrated by phosphorus pentoxide, phosphorus pentasulfide, phosphorus heptasulfide, phosphorus sesquisulfide, and phosphorus oxysulfide. The anhydrides of organic phosphorus acids are exemplified by the anhydrides of diphenylphosphinic acid, O,O'-dioctylphosphorodithioic acid, dinaphthylphosphinodithioic acid, etc. The halides of the phosphorus acids include, for instance, phosphorus trichloride, phosphorus pentachloride, phosphorothioic trichloride, phosphorus tribromide, diphenylphosphinic chloride, di(chlorophenyl)phosphinothioic chloride, O,O'-diphenylphosphorothioic chloride, phenylphosphonic dichloride, diphenylphosphinyl chloride, diphenylphosphorus trichloride, and diphenylphosphinothioic bromide.

The esters of the phosphorus acids may be the completely esterified acids or partially esterified acids. The latter are also known as acidic esters, i.e., at least a portion of the acid is not esterified; they are illustrated by the mono- or the di-esterified phosphoric or phosphorous acids and the mono-esterified phosphonic or phosphonous acids. The ester portion may be derived from a substantially hydrocarbon radical usually one having less than about 30 and preferably from about 1 to about 24 aliphatic carbon atoms. The substantially hydrocarbon radicals are exemplified by methyl, ethyl, chloromethyl, o-chlorophenyl, p-bromophenyl, alpha-chloronaphthyl, beta-heptylnaphthyl, o,p-dimethoxyphenyl, tolyl, isobutyl, octadecyl, 4-chloro-2-heptadecyl, eicosyl, naphthyl, benzyl, chlorobenzyl, 2-phenylethyl, cyclohexyl, cyclopentyl, 2-methylcyclohexyl, the hydrocarbon radical derived from polypropene having a molecular weight of 1500, the hydrocarbon radical derived from polyisobutene having a molecular weight of 5000, behenyl, stearyl, oleyl, allyl, propargyl, o-heptylphenyl, 2,4,6-trimethylphenyl, 2-mercaptophenyl, m-nitrophenyl, methoxy-tetraethoxymethyl, 10-keto 1-octadecyl, polyisobutene (molecular weight of 1000)-substituted phenyl, xenyl, 5-naphthyl-2-decyl, 10-tolyl-1-stearyl, and 9,10-dichlorostearyl radical.

The commonly used esters are, for example, methyl ester of phosphoric acid, dimethyl ester of phosphoric acid, trimethyl ester of phosphoric acid, methyl ester of phosphorothioic acid, O-methyl ester of phosphorothioic acid, dicyclohexyl ester of phosphoric acid, O,O'-dicyclohexyl ester of phosphorodithioic acid, dicyclohexyl ester of phosphorotetrathioic acid, O-cyclohexyl-S-decyl ester of phosphoromonothioic acid, O,O'-diphenyl ester of phosphoromonothioic acid, triphenyl ester of phosphoric acid, triphenyl ester of phosphorous acid, tritoyl ester of phosphoric acid, dioctadecyl ester of phosphorus acid, trinaphthyl ester of phosphorous acid, trinaphthyl ester of phosphoric acid, O,O'-dinaphthyl ester of phosphoromonothioic acid, O,O'-dinaphthyl ester of phosphorothioic acid, di(heptylphenyl) ester of phosphoric acid, bis(dichlorophenyl) ester of phosphorous acid, S-benzyl ester of phosphoromonothioic acid, S,S'-di(phenylethyl) ester of phosphorodithioic acid, O,S-didecyl ester of phosphorotrithioic acid, S,S'-didodecyl ester of phosphorotrithioic acid, diphenyl ester of phosphorotetrathioic acid, O-dodecyl-S-phenyl ester of phosphoromonothioic acid, O,O'-diisooctyl ester of phosphorodithioic acid, di(nitrophenyl) ester of phosphoric acid, O,O'-di(nitrophenyl) ester of phosphorodithioic acid, O,O'-di(methoxyphenyl) ester of phosphorodithioic acid, di(heptylphenyl)-(O—C₂H₄)₋₂₀

ester of phosphoric acid, di(methyl-(O—C₃H₇)₂)₁₅ ester of phosphoric acid, decyl octadecyl ester of phosphoric acid, di(4-keto-1-decyl) ester of phosphoric acid, methyl ester of diphenylphosphinic acid, ethyl ester of diphenylphosphinodithioic acid, cyclohexyl ester of dinaphthylphosphinomonothioic acid, octyl ester of dicyclohexylphosphinomonothioic acid, dimethyl ester of methylphosphonic acid, dimethyl ester of ethylphosphonomonothioic acid, dodecyl ester of cyclohexylphosphonic acid, tertiary-butyl ester of di(heptylphenyl)phosphinous acid, dipentyl ester of phenylphosphonotrithioic acid, diphenyl ester of phenylphosphonous acid, di(polyisobutene (molecular weight of 1500)-substituted phenyl) ester of phosphoric acid, O,O'-di(polypropene (molecular weight of 300)-substituted naphthyl) ester of phosphorodithioic acid, and oleyl ester of phosphoric acid.

The esters of phosphoric acid and phosphorothioic acids are obtained by the reaction of phenol or an alcohol with phosphoric acid or a phosphorothioic acid, or an anhydride of the acid such as phosphorus pentoxide, phosphorus pentasulfide, or phosphorus oxy-sulfide. The reactoin is usually carried out simply by mixing the reactants at a temperature above about 50° C., preferably between about 80° C. and 150° C. In many instances, however, the esters of phosphoric acids tend to decompose at high temperatures. Thus it is often desirable to avoid prolonged exposure of the reaction mixture to temperatures above about 150° C. A solvent may be used in the reaction to facilitate mixing of the reactants and control of the reaction temperature. The solvent may be benzene, naphtha, chlorobenzene, mineral oil, kerosene, cyclohexane, or carbon tetrachloride. A solvent capable of forming a relatively low boiling azeotrope with water further aids the removal of water in the esterification of an alcohol or phenol with the phosphorus acid reactant. The relative amounts of the alcohol or phenol reactant and the acid reactant influence the nature of the ester obtained. For instance, equimolar amounts of an alcohol and phosphoric acid tend to result in the formation of a monoester of phosphoric acid whereas the use of a molar excess of the alcohol reactant in the reaction mixture tends to increase the proportion of the diester or triester in the product. In most instances the product will be a mixture of the mono-, di-, and tri-esters of the acid and such a mixture is desirable for use in this invention for reasons of economy.

The reaction of an alcohol or phenol with phosphorus pentasulfide ordinarily results in O,O'-diester of phosphorodithioic acid. Such a reaction involves four moles of the alcohol or phenol per mole of phosphorous pentasulfide and may be carried out within the temperature range from about 50° C. to about 250° C. Thus, the preparation of O,O'-di-n-hexylphosphorodithioic acid involves the reaction of phosphorus pentasulfide with four moles of n-hexyl alcohol at about 100° C. for about 2 hours. Hydrogen sulfide is liberated and the residue is the defined acid. Treatment of the phosphorodithioic acid with water or steam removes one or both sulfur atoms and converts the product to the corresponding phosphoromonothioic acid or phosphoric acid.

The esters of phosphorotetrathioic acid can be prepared by first the reaction of a mercaptan or thiophenol with PSCl₃ or PSBr₃ to produce an intermediate which is either a phosphorotrithioic halide or triester of phosphorotetrathioic acid and the subsequent reaction of the intermediate with hydrogen sulfide or sodium hydrosulfide. The esters of phosphorotrithioic acids are obtained by the treatment of the esters of the phosphorotetrathioic acids with water or steam.

The esters of phosphorous acids are obtained by the reaction of an alcohol or phenol with phosphorous acid or a phosphorus trihalide such as phosphorus tribromide or phosphorus trichloride and the above noted reaction usually requires carefully controlled conditions such as low temperature in order to give a substantial yield of the esters of phosphorous acids. Under other conditions the reaction of an alcohol or phenol with a phosphorus tri-

halide may result in a phosphonic acid or ester. Such esters are readily susceptible to rearrangement to phosphonic acids and esters.

The esters of phosphinic, phosphinous, phosphonic, and phosphonous acids obtained by either direct esterification of the acid or an anhydride with an alcohol or phenol or the reaction of an acid halid with an alcohol or phenol. They are also obtained by the rection of a salt of the acid such as sodium or ammonium salt of the acid with a suitable halogenated hydrocarbon. The methods for preparing the phosphorus acids and their anhydrides, esters, and halides are known in the art and are not discussed in further detail here.

The reaction by which the products of this invention are obtained can be effected simply by mixing a polyamine reactant with the succinic acid-producing and the phosphorus acid-producing reactants at the desired temperature. The use of an inert solvent in the reaction is not necessary but often desirable, especially when a highly viscous or solid reactant is present in the reaction mixture. The inert solvent useful in the reaction may be a hydrocarbon such as benzene, toluene, naphtha, cyclohexane, n-hexane, or mineral oil.

The chemical composition of the substituted polyamines resulting from the reaction depends primarily upon the reaction conditions employed and the nature of the reactants. Thus, a polyamine containing primary-amino groups is capable of forming salts or amides as well as imides or amidines with a succinic acid or anhydride. On the other hand, a polyamine containing secondary-amino groups is capable of forming salts and amides and a polyamine containing tertiary-amino groups is capable of deforming only salts with a succinic acid or anhydride. Similarly, a polyamine having tertiary-amino groups forms salts with a phosphorus acid whereas one having primary- or secondary-amino groups may form either salts or amides with a phosphorus acid. When an ester of a succinic acid or phosphorus acid is used as the reactant with a polyamine, the reaction proceeds by replacing the ester radical with the amino group of the polyamine to form an amide or imide. A by-product of such a reaction is a hydroxy- or thio-compound (e.g., alcohol or phenol) derived from the ester radical. The reaction of a polyamine with an acid halide may result in forming a salt, amide, or imide accompanied by the by-product of hydrogen halide.

In general, a reaction temperature below about 80°–100° C. results in products having predominantly salt linkages, whereas at a higher temperature, the product usually contains predominantly amide, imide, amidine linkages or a mixture of such linkages. The maximum temperature for the reaction is limited by the decomposition point of the reaction mixture. It usually does not exceed about 250° C.

A convenient method of carrying out the process of this invention involves first reacting a polyamine with either one of the two acid-producing reactants (ie., the succinic acid-producing reactant or the phosphorus acid-producing reactant) to form an intermediate and then reacting the intermediate with the other acid-producing reactant. For instance, an alkylene amine may be first partially acylated by reaction at 80° C., preferably at 120° C. or a higher temperature, with a substantially hydrocarbon-substituted succinic acid or anhydride to form an intermediate having at least some nitrogen-succinic groups (such as succinamides or succinimide groups) and the intermediate is then reacted at 25° C., preferably at 50° C. or a higher temperature with phosphoric acid to form the final product having both nitrogen-succinic groups and nitrogen-phosphorus groups. Alternatively, the alkylene amine may be first combined with phosphoric acid at 25° C., preferably at 50° C. or a higher temperature to form an intermediate and the intermediate is then acylated at 80° C., preferably at 120° C. or a higher temperature with a substituted succinic acid or anhydride to form the final product. Still another method

may be used which involves mixing the alkylene amine, the substituted succinic acid or anhydride, and phosphoric acid and maintaining the reaction mixture at the desired temperature such as about 10° C. or higher.

The relative proportions of the reactants to be used in the process of this invention are based on the utility of the products resulting therefrom for the purposes of this invention. For the most part, the amount of the phosphorus acid-producing reactant should be at least about 0.001 mole per mole of the alkylene amine used and the amount of the succinic acid-producing reactant should be at least about 0.25 mole per mole of the alkylene amine used. The preferred amounts of these reactants are such that there be from 1 to 3 moles of the succinic reactant and from about 0.5 to 3 moles of the phosphorus reactant for each mole of the alkylene amine used. In most instances, the practical upper limit for the amounts of the succinic reactant and the phosphorus reactant is based on the stoichiometry for the reaction in which all of the amino groups of the alkylene amine reactant are combined with the succinic and the phosphorus reactants. Thus, such practical upper limit may be as many moles of the combined succinic and phosphorus reactants as the number of amino groups in the alkylene amine. For instance, where an alkylene amine having n number of amino groups, the practical upper limit for the total amounts of the succinic and the phosphorus reactants will be n moles per mole of the alkylene amine used.

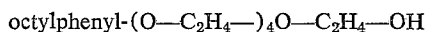
It will be noted, however, that if an excess of any reactant is used in the process, the un-used reactant may be separated from the desired product by distillation, extraction, precipitation, filtration or such ordinary means; or it may be allowed to remain in the product. It will be also noted that within the above ranges for the amounts of the reactants, the process may result in partially substituted alkylene amines, i.e., products in which some of the amino groups of the alkylene amine reactant are not combined with a succinic or phosphoric reactant. The partially substituted polyamines are contemplated within the scope of this invention.

For the purposes of this invention, the molecular weight of a succinic compound is taken to be twice the equivalent weight based on its acid number as determined by an ASTM method. The molecular weights of the alkylene amine and the phosphorus reactants likewise may be computed from the nitrogen content and the phosphorus content of such reactants, respectively.

The following examples illustrate the preparation of the compositions of this invention:

EXAMPLE 1

A mineral oil solution of a partially acylated polyamine having a nitrogen content of 2.1% is prepared by adding 553 parts of a commercial ethylene amine mixture (having an average composition corresponding to that of tetraethylene pentamine and a nitrogen content of 34.3%) to a mixture of 5000 parts (1.67 moles per mole of the amine) of a polyisobutene-substituted succinic anhydride, having an acid number of 100 (prepared by the reaction of maleic anhydride and a chlorinated polyisobutene having a molecular weight of 1000 and a chlorine content of 4.3% at 200° C.) and 3650 parts of mineral oil and heating the mixture at 155°–160° C. for 10 hours while nitrogen is bubbled through the mixture formed during the reaction is distilled off. An ester of phosphoric acid is prepared by heating a mixture of 119 parts (0.84 mole) of phosphorus pentoxide, 1332 parts (3.34 moles) of



and 485 parts of toluene (solvent) at the reflux temperature (125°–130° C.) azeotropically distilling off the water formed during the reaction within a period of 6 hours, and then removing the solvent from the product by heating the reaction mixture to 140° C./30 mm. The

ester is a mixture of the esters of phosphoric acid having a phosphorus content of 3.7% and an acid number of 65 (bromphenol blue indicator). A mixture of this ester (430 parts, 1.67 moles per mole of the amine) and the above partially acylated polyamine (1000 parts) is prepared at 60°–65° C. and then heated at 105°–110° C. for 3 hours. The product is substituted polyamine and has a phosphorus content of 1.1% and a nitrogen content of 1.5%.

EXAMPLE 2

A decyl ester of phosphoric acid is prepared by adding one mole of phosphorus pentoxide to 3 moles of decyl alcohol at a temperature within the range from 32° C. to 55° C. and then heating the mixture at 60–63° C. until reaction is complete. The product is a mixture of the decyl esters of phosphoric acid having a phosphorus content of 9.9% and an acid number of 250 (phenolphthalein indicator). To a mineral oil solution of a partially acylated polyamine (prepared by the heating of 1021 parts of the polyisobutene-substituted succinic anhydride of Example 1, 100 parts of the commercial ethylene amine described in Example 1, and 684 parts of mineral oil at 150° C. for 10 hours) there is added 137 parts of the above decyl ester at 145°–150° C. within a period of 30 minutes. The mixture is heated at 150° C. for 1 hour and filtered. The filtrate is diluted with 130 parts of mineral oil and the final oil solution has an oil content of 40%, a nitrogen content of 1.7%, and a phosphorus content of 0.67%.

EXAMPLE 3

A mineral oil solution of a partially acylated polyamine (1075 grams) having a nitrogen content of 1.9% and prepared according to the procedure described in Example 2 is mixed with 204 grams (1.4 moles per mole of the ethylene amine used) of the octadecyl ester of phosphoric acid prepared by the reaction of 3 moles of octadecyl alcohol with 1 mole of phosphorus pentoxide at a temperature of 80°–100° C. and having a phosphorus content of 6.4% and an acid number of 116. The mixture is heated at 60°–85° C. for 1 hour. The product is a 60% oil solution of a substituted polyamine having nitrogen groups attached to succinic radicals and phosphorus acid salt radicals and has a nitrogen content of 1.6% and a phosphorus content of 0.97%.

EXAMPLE 4

An ester of phosphoric acid is prepared by heating 1 mole of nonylphenyl-polyoxyethylene-ethanol having a molecular weight of 386, 0.25 mole of phosphorus pentoxide, and 140 grams of toluene at the reflux temperature while water is removed by azeotropic distillation. Toluene is distilled off by heating the residue to 150° C./30 mm. and the product is a mixture of the esters of phosphoric acid having a phosphorus content of 3.9% and an acid number of 68 (bromphenol blue indicator). A mixture of 360 grams (1.85 moles per mole of the ethylene amine used) of the ester and 840 grams of the oil solution of the partially acylated polyamine of Example 1 is prepared at 60°–65° C. and then heated at 105°–110° C. for 3 hours. The residue is an oil-soluble substituted polyamine having a phosphorus content of 1.1% and a nitrogen content of 1.2%.

EXAMPLE 5

An ester of phosphoric acid having a phosphorus content of 0.77% is obtained by reacting a polyisobutene-substituted propyl alcohol with phosphorus pentoxide in a molar ratio of 4 to 1, respectively, at 130°–140° C. and filtering the product obtained. The polyisobutene-substituted propyl alcohol is prepared by reacting a chlorinated polyisobutene having a chlorine content of 4.7% and a molecular weight of 750 with methyl acrylate at 190°–200° C. to form the methyl ester of polyiso-

butene-substituted propionic acid and reducing the ester so formed with sodium in the presence of hexyl alcohol and xylene at 140° C. The polyisobutene-substituted propyl alcohol has a hydroxyl content of 0.9%. An oil-soluble product is obtained by heating the oil solution of the partially acylated polyamine of Example 1 (385 parts), the above ester of phosphoric acid (729 parts, 1.6 moles per mole of the amine reactant), and 743 parts of mineral oil at 60°–70° C. for 4 hours. The resulting oil solution of the substituted polyamine has a nitrogen content of 0.4% and a phosphorus content of 0.3%.

EXAMPLE 6

A mixture of 190 grams (.9 mole) of a commercial ethylene amine having a nitrogen content of 33% and an average composition corresponding to that of tetraethylene pentamine and 175 grams (0.5 mole) of tritoyl ester of phosphorus acid having a phosphorus content of 8.9% is prepared at 25°–38° C., heated to 200° C. in 2.5 hours, and then heated at 200° C.–225° C. for 5 hours to distill off volatile components of the reaction mixture. The residue is an intermediate product having phosphorus acid amide linkages. This intermediate is added to 1632 grams (1.5 moles) of a polyisobutene (molecular weight of 1000)-substituted succinic anhydride having an acid number of 103 in 1000 cc. of toluene and 1313 grams of mineral oil at 80°–90° C. The mixture is heated at the reflux temperature (115°–128° C.) while water is removed by azeotropic distillation in 5 hours. The residue is heated to 190° C./9 mm. to distill off all volatile components and then filtered. The filtrate is an oil-soluble substituted polyamine having a nitrogen content of 2.1% and a phosphorus content of 0.4%.

EXAMPLE 7

An oil-soluble substituted polyamine is obtained by reacting 1005 grams of a 60% oil solution of a partially acylated polyamine having a nitrogen content of 2.8% prepared by the reaction of 1 equivalent of a polyisobutene-substituted succinic anhydride of Example 1 with 2 equivalents of a commercial ethylene amine having a nitrogen content of 34.3% and an average composition corresponding to that of tetraethylene pentamine at (150°–155° C.), 306 grams (2 moles per mole of the amine reactant) of an ester of phosphoric acid (prepared from 3 moles of tridecyl alcohol and 1 mole of phosphorus pentoxide), and 203 grams of mineral oil at 65°–85° C. The product is filtered and the filtrate is found to have a nitrogen content of 2% and a phosphorus content of 1.7%.

EXAMPLE 8

A mixed phosphoric and thiophosphoric acid ester is prepared by mixing at 58°–78° C. for 2.5 hours 64 grams (0.45 mole) of phosphorus pentoxide and 514 grams (1.4 moles) of S-hydroxypropyl-O,O'-di(4-methyl-2-pentyl) phosphorodithioate having a phosphorus content of 8.2% and filtering the product. The filtrate is the mixed acid ester having a sulfur content of 15.2%, a phosphorus content of 12%, and an acid number of 87 (bromphenol blue indicator). To 482 grams of a solution consisting of 40% of mineral oil and 60% of the partially acylated polyamine of Example 1, there is added 124 grams (0.47 mole per 0.15 mole of the amine reactant) of the above mixed ester at 55°–78° C. The mixture is heated at 85° C. for 3 hours and filtered. The filtrate is the oil-soluble product having a phosphorus content of 2.6%, a sulfur content of 3.3%, and a nitrogen content of 1.4%.

EXAMPLE 9

A mixture of 755 grams of soya lecithin having a phosphorus content of 2.1%, 491 grams of the oil solution of the partially acylated polyamine of Example 7, and 235 grams of mineral oil is heated at 165° C. for 4 hours. The residue is an oil-soluble product having a

phosphorus content of 1% and a nitrogen content of 1.2%.

EXAMPLE 10

A mixture of 207 grams of the decyl ester of phosphoric acid (prepared by the procedure described in Example 2) and 1270 grams of an oil solution containing 40% of mineral oil and 60% of the partially acylated polyamine (prepared according to the procedure of Example 7) is heated at 55°–65° C. for 1 hour. The product has an acid number of 27 (phenolphthalein indicator). It is then neutralized by treatment by barium oxide (20% in excess of the stoichiometric amount) and water at 90°–100° C. The neutralized product is dried and filtered. The filtrate is the oil-soluble product having a phosphorus content of 0.8%, a nitrogen content of 1.6%, a barium sulfate ash content of 7.5%, and an acid number of 5 (phenolphthalein indicator).

EXAMPLE 11

A mixture of 164 grams of the oil solution of the partially acylated polyamine (having a nitrogen content of 3.4% and prepared by the procedure of Example 3 from 1.5 moles of the polyisobutene substituted succinic anhydride and 0.8 mole of the commercial ethylene amine) and 36 grams of a mixture of esters of phosphoric acid prepared by the reaction of 4 moles of tertiary-pentyl-phenol with 1 mole of phosphorus pentoxide at 150°–160° C. is heated at 95° C. for 1.5 hours. The residue is an oil-soluble product having a nitrogen content of 2.7% and a phosphorus content of 1.5%.

EXAMPLE 12

The procedure of Example 3 is repeated except that the phosphoric acid ester used is derived from decyl alcohol in lieu of octadecyl alcohol. A mixture of 1670 grams of the product and 480 grams of mineral oil is heated to 80°–90° C. and 68 grams of boron trifluoride is bubbled into the mixture at this temperature throughout a period of 1.5 hours. The product is blown with nitrogen for 0.5 hour and the residue has a nitrogen content of 1.2%, a phosphorus content of 0.5%, and a boron content of 0.5%.

EXAMPLE 13

A hexyl alcohol ester of phosphoric acid is prepared as follows: phosphorus pentoxide is added in small increments to 4-methyl-2-pentyl alcohol (3 moles per mole of phosphorus pentoxide) within a period of 1 hour at 16°–28° C. The mixture is maintained at 28°–53° C. for 1 hour whereupon a homogeneous solution is obtained. It is heated to 50°–55° C., mixed with a filter aid, and filtered. The filtrate is a mixture of the hexyl esters of phosphoric acid having a phosphorus content of 14% and an acid number of 293 (phenolphthalein indicator). A mixture of 67 grams of the above ester (0.3 mole), 45 grams of mineral oil, and 1000 grams (0.3 mole of the amine reactant) of a 60% oil solution of the partially acylated polyamine prepared as is described in Example 2 is heated at 90°–100° C. for 0.5 hour. The resulting homogeneous product has a nitrogen content of 1.8% and a phosphorus content of 0.8%.

EXAMPLE 14

A butyl ester of phosphoric acid is prepared by a procedure similar to that described in Example 13 except that butyl alcohol is used in place of the hexyl alcohol. The ester is a mixture of the butyl esters of phosphoric acid having a phosphorus content of 16.4% and an acid number of 420 (phenolphthalein indicator). This ester (413 grams, 2.2 moles) is added to a mixture of 275 grams of mineral oil and a 60% oil solution of a partially acylated polyamine (1170 grams, 0.7 mole of the amine reactant); prepared by reacting 1 equivalent of the polyisobutene substituted succinic anhydride of Example 1 with 4 equivalents of a commercial ethylene amine mix-

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ture having a nitrogen content of 34% and an average composition corresponding to that of tetraethylene pentamine at 145°–165° C. for 6 hours and diluting the product with mineral oil. The mixture is stirred at 70°–90° C. for 1 hour to give a product having a nitrogen content of 3% and a phosphorus content of 2.7%.

EXAMPLE 15

861 grams (0.33 mole of the amine reactant) of a 60% mineral oil solution of the partially acylated polyamine prepared as described in Example 7 is heated to 77° C. To this solution there is added 403 grams (0.8 mole) of O,O'-di(heptylphenyl)phosphorodithioic acid having an acid number of 115 and a phosphorus content of 6.1%. An exothermic reaction occurs. The mixture is heated at 96°–100° C. for 2 hours, diluted with mineral oil to a solution containing 40% of oil and filtered at 100° C. The product has a nitrogen content of 1.5%, a sulfur content of 3.1%, and a phosphorus content of 1.6%.

EXAMPLE 16

A mixture of 134 grams (0.35 mole) of O,O'-di-isooctylphosphorodithioic acid having an acid number of 146 and 1000 grams (0.3 mole of the amine reactant) of a 60% mineral oil solution of the partially acylated polyamine prepared as described in Example 2 is maintained at 60°–80° C. for 0.5 hour, diluted with mineral oil to a solution having an oil content of 40% and filtered. The filtrate has a nitrogen content of 1.6%, a sulfur content of 2%, and a phosphorus content of 0.9%.

EXAMPLE 17

A mixture of 18.2 grams (0.17 mole) of ethyl ester of metaphosphoric acid having the empirical formula of C₂H₅OPO₂ and 421 grams (0.14 mole of the amine reactant) of a 60% oil solution (having a nitrogen content of 2.3%) of the partially acylated polyamine prepared as described in Example 1 is prepared at 50°–60° C. and heated at 70°–90° C. for 6 hours. The resulting product is a brown viscous liquid having a phosphorus content of 1.2% and a nitrogen content of 2.2%.

EXAMPLE 18

A partially acylated polyamine is prepared by the reaction of 107 grams (0.5 mole) of a commercial ethylene amine mixture having a nitrogen content of 33% and an average composition corresponding to that of tetraethylene pentamine and 1000 grams (1 mole) of a polyisobutene substituted succinic anhydride of Example 1 in 500 grams of mineral oil at 135°–160° C. To this intermediate product there is added 212 grams of O,O'-di(4-methyl-2-pentyl) phosphorodithioic acid at 69°–80° C. The mixture is heated at 90°–100° C. for 1 hour, diluted with 367 grams of mineral oil and filtered at 100° C. The filtrate has a nitrogen content of 1.6%, a sulfur content of 2.1%, and a phosphorus content of 1%.

EXAMPLE 19

An ester of thiophosphoric acid is prepared by reacting 4 moles of a commercial mixture of alcohols consisting of about 50% of cetyl alcohol and 40% of stearyl alcohol having an average molecular weight of about 260 with 1 mole of phosphorus pentasulfide at 70°–87° C. and filtering the product. The product consists essentially of the O,O'-diesterified phosphorodithioic acid having a sulfur content of 9.2, a phosphorus content of 4.8%, and an acid number of 68 (bromphenol blue indicator). To 1000 grams of a 60% mineral oil solution of the partially acylated polyamine of Example 2 there is added 290 grams of the above ester. The mixture is heated at 60°–80° C. for 0.5 hour, diluted with 193 grams of mineral oil, and filtered at 100° C. The filtrate has a sulfur content of 1.9%, a phosphorus content of 0.9%, and a nitrogen content of 1.4%.

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EXAMPLE 20

A mixture of 1057 grams of a 60% mineral oil solution (having a nitrogen content of 2.7%) of the partially acylated polyamine prepared as described in Example 7 and 394 grams (0.44 mole) of a 70% toluene solution of O,O'-di(heptylphenyl) phosphorothioyl succinic anhydride having a phosphorus content of 3.5% (obtained by the reaction of O,O'-di(heptylphenyl) phosphorodithioic acid and maleic anhydride) is heated at 150°–160° C. for 4 hours. The mixture is heated to 150° C./4 mm. to remove toluene and diluted with mineral oil to a solution containing 40% of oil. The oil solution has a sulfur content of 0.99%, a phosphorus content of 0.9%, and a nitrogen content of 1.9%.

EXAMPLE 21

An oil-soluble composition is prepared by a procedure similar to that described in Example 15 except that the maximum temperature at which the partially acylated polyamine and the O,O'-di(heptylphenyl)phosphorodithioic acid are reacted is 60° C. The product consists essentially of a salt of the phosphorodithioic acid with the amino groups of the polyamine. The product is diluted with mineral oil to a solution containing 40% of the oil and the solution has a nitrogen content of 1.6%, a sulfur content of 3.2%, and a phosphorus content of 1.1%.

EXAMPLE 22

A partially acylated polyamine is prepared by the reaction of 160 grams (0.7 mole) of a commercial ethylene amine having a nitrogen content of 33% and an average composition corresponding to that of tetraethylene pentamine and 1000 grams (1 mole) of the polyisobutene-substituted succinic anhydride of Example 1 in 500 grams of mineral oil at 148°–180° C. and removing all of the water formed from the reaction. The product is diluted with 565 grams of mineral oil to a solution having an oil content of 40%. To this solution there is added 635 grams of O,O'-di(4-methyl-2-pentyl)phosphorodithioic acid at 70°–85° C. An exothermic reaction occurs. The mixture is heated at 90° C.–100° C. for 1 hour and filtered at 150°–160° C. The filtrate has a phosphorus content of 2.1%, a sulfur content of 4.5%, and a nitrogen content of 1.6%.

EXAMPLE 23

A 60% mineral oil solution (1286 grams) of the partially acylated polyamine prepared as described in Example 2 is mixed with 300 grams of mineral oil and heated to 170° C. To this solution there is added 176 grams (0.5 mole) of tritoyl ester of phosphorus acid at 75° C. The mixture is heated at 150°–162° C./6–11 mm. for 11 hours whereupon 73 grams of a distillate is collected, which contains 67% of cresol. The residue is diluted with 373 grams of mineral oil and filtered at 160° C. The filtrate has a phosphorus content of 1.2% and a nitrogen content of 1.3%.

EXAMPLE 24

A 60% mineral oil solution (1286 grams) of the partially acylated polyamine prepared as described in Example 2 is diluted with 300 grams of mineral oil and mixed with 59 grams (0.17 mole) of tritoyl ester of phosphorous acid at 154°–170° C./2–4 mm. for 3 hours. A total of 56 grams of distillate is collected which consists substantially of cresol. The residue is diluted with 300 grams of mineral oil and the oil solution is found to have a phosphorus content of 0.3% and a nitrogen content of 1.6%.

EXAMPLE 25

A polyamine having a nitrogen content of 32% is obtained by the reaction of acrylonitrile with 216 grams of a mixture consisting of 75% (by weight) of triethylene tetramine and 25% of diethylene triamine at 110°–130° C. for 5 hours. To 713 grams of the polyisobutene sub-

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stituted succinic anhydride of Example 1 there is added 125 grams of the above polyamine at 80°–100° C. within a period of 1 hour. The mixture is heated at 100° C. for 5 hours and then mixed with 76 grams of tritoyl ester of phosphorous acid at 150° C. within a period of 1 hour. The resulting mixture is heated at 170°–200° C. for 7 hours and then to 190°–100° C./15 mm. A total of 71 grams of cresol is collected as the distillate. The residue is filtered. The filtrate has a nitrogen content of 2.4% and a phosphorus content of 0.4%.

EXAMPLE 26

A mixture of 138 grams of tritoyl ester of phosphorous acid and 250 grams of the polyamine prepared from acrylonitrile and a mixture of triethylene tetramine and diethylene triamine by the procedure described in Example 25 is prepared at 28°–32° C. and then heated at 140°–150° C./4 mm. for 3.5 hours. A total of 99 grams of distillate is collected which consists substantially of cresol. The residue is then heated to 185° C./9 mm. and is found to have a nitrogen content of 24.5% and a phosphorus content of 4.8%. The polyisobutene substituted succinic anhydride of Example 1 (740 grams) is then mixed with 153 grams of the above product of the polyamine with tritoyl ester of phosphorous acid and 355 grams of mineral oil at 160°–190° C. for 8.5 hours. A total of 11 grams of water is collected as the distillate. The product is diluted with 214 grams of mineral oil and filtered at 160° C. The filtrate has a nitrogen content of 2.6% and a phosphorus content of 0.5%.

EXAMPLE 27

An imidazole is prepared by mixing 1164 grams (5.8 moles) of lauric acid, 836 grams of an amine mixture consisting of 75% (by weight) of triethylene tetramine and 25% of diethylene triamine, and 200 grams of toluene at 25°–73° C.; refluxing the mixture at 133°–208° C. for 22.3 hours while toluene and the water formed from the reaction is gradually removed by distillation and heating the residual product to 155° C./5 mm. A total of 1641 grams of the imidazole is obtained, having a nitrogen content of 17%. A portion (378 grams) of the imidazole is added at 80° C. to 1000 grams of the polyisobutene substituted succinic anhydride of Example 1 and 450 grams of toluene and the mixture is heated at 150°–170° C. for 5 hours while water (17 grams) is removed by distillation. The residue is diluted with 153 grams of toluene and filtered at 100°. The filtrate is a toluene solution of intermediate product having a nitrogen content of 3.4%. Toluene is then replaced by mineral oil and the oil solution (oil content of 40%) of the intermediate product and 472 grams of tritoyl ester of phosphorous acid is heated at 120°–170° C./2–3 mm. for 4.5 hours whereupon a total of 98 grams of cresol is collected as the distillate. The residue is found to have a phosphorus content of 2.1% and a nitrogen content of 2.3%.

EXAMPLE 28

A partially acylated polyamine is prepared by the reaction of 1 equivalent of the polyisobutene substituted succinic anhydride of Example 1 with one equivalent of a commercial ethylene amine having a nitrogen content of 33% and an average composition corresponding to that of tetraethylene pentamine at 150°–160° C. A mixture of 933 grams of a 60% mineral oil solution (having a nitrogen content of 1.5%) of the partially acylated polyamine and 250 grams (0.77 mole) of the decyl ester of phosphoric acid having a phosphorus content of 9.5% and prepared as described in Example 2 is heated at 50°–70° C. for 1 hour. The residue is found to have a nitrogen content of 1.2% and a phosphorus content of 2.3%.

EXAMPLE 29

A mixture of 2330 grams of a 60% mineral oil solution of the partially acylated polyamine prepared as is described in Example 28 and 89 grams (0.625 mole) is

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heated at from 30° C. to 160° C. in 2 hours, blown with nitrogen at 160° C. for 3 hours, and filtered. The product has a nitrogen content of 1.4%, a phosphorus content of 0.8%, and an acid number of 45 (phenolphthalein indicator).

EXAMPLE 30

A mixture of 825 grams (0.25 mole of the amine reactant) of the oil solution of the partially acylated polyamine of Example 1 and 26 grams (0.08 mole) of a crude di(carboxyphenyl)phosphinic acid having a phosphorus content of 9.9% is heated at 150°–160° C. for 13 hours and at 160° C./20 mm. for 3 hours whereupon 7 grams of water is distilled off from the reaction mixture. The residue is filtered and the filtrate has a nitrogen content of 2% and a phosphorus content of 0.3%.

EXAMPLE 31

A mixture of 55 grams of phosphorus sesquisulfide and 1040 grams of a 60% mineral oil solution of the partially acylated polyamine of Example 7 is blown with nitrogen at 180° C. for 4 hours, mixed with 272 grams of mineral oil and blown with steam at 150°–160° C. for 4 hours to remove unstably bound sulfur and then dried at 150° C. for 1 hour. The product is filtered. The filtrate has a sulfur content of 0.3%, a nitrogen content of 2%, and a phosphorus content of 1.4%.

EXAMPLE 32

A 60% oil solution of a partially acylated polyamine having a nitrogen content of 1.14% is obtained by reacting at 160° C. 2 moles of the polyisobutene-substituted succinic anhydride of Example 1 and 0.6 mole of a commercial tetraethylene pentamine having a nitrogen content of 34% and diluting the product with mineral oil. A mixture of the solution (1230 grams) and phosphorus sesquisulfide (55 grams) is blown with nitrogen at 150° C. for 4 hours, diluted with 313 grams of mineral oil, filtered, blown with steam at 150° C. for 4 hours, dried at 150° C. for 1 hour and filtered. The filtrate has a nitrogen content of 0.9%, a sulfur content of 0.53%, and a phosphorus content of 1.4%.

EXAMPLE 33

A mixture of 570 grams of a 60% mineral oil solution of the partially acylated polyamine of Example 7 and 44 grams of phosphorus oxysulfide is heated at 180° C. for 4 hours and filtered at 150° C. The filtrate has a nitrogen content of 2.4%, a sulfur content of 1.2%, and a phosphorus content of 1.6%.

EXAMPLE 34

A mixture of 1130 grams of the 60% oil solution of the partially acylated polyamine of Example 7 and 24 grams of phosphorus pentoxide is heated at 90°–110° C. for 1 hour, at 150°–155° C. for 6 hours, and filtered. The filtrate has a phosphorus content of 0.7% and a nitrogen content of 2.1%.

EXAMPLE 35

A substituted polyamine by the procedure described in Example 31 except that 87 grams of phosphorus heptasulfide is used in place of the phosphorus sesquisulfide. The product has a nitrogen content of 1.6%, a sulfur content of 0.9%, and a phosphorus content of 2.1%.

EXAMPLE 36

A mixture is prepared from 352 grams of the oil solution of the partially acylated polyamine of Example 1 and 85 grams of a nonylphenyl ester of phosphotetrathioic acid having a phosphorus content of 5.8% and obtained by the reaction of 95°–135° C. of 4 moles of p-nonylthiophenol with 1 mole of phosphorus pentasulfide. The mixture is heated at 72°–85° C. for 4.5 hours and filtered. The filtrate has a nitrogen content of 1.6%, a phosphorus content of 1.4%, and a sulfur content of 5%.

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EXAMPLE 37

A mixture of 1140 grams of the 60% oil solution of the partially acylated polyamines of Example 7, 111 grams of phosphorus pentasulfide, and 324 grams of mineral oil is heated at 160°–170° C. for 6 hours and filtered at 160° C. The filtrate has a nitrogen content of 1.9%, a phosphorus content of 1.6%, and a sulfur content of 3.7%.

EXAMPLE 38

A 50% mineral oil solution of a substituted polyamine is prepared by the procedure of Example 37 except that the amount of phosphorus pentasulfide used is equal to 0.2 equivalent of phosphorus per equivalent of nitrogen of the partially acylated polyamine used.

EXAMPLE 39

A mixture of 1040 grams (0.3 mole of the amine reactant) of the 60% oil solution of the partially acylated polyamine of Example 1, 135 grams (0.53 mole) of crude diphenylphosphinodithioic acid having a phosphorus content of 12.1%, and 90 grams of mineral oil is heated at 90° C. for 7 hours and blown with nitrogen for 6 hours whereupon 5 grams of water is distilled off. The residue is filtered and the filtrate has a phosphorus content of 1.2%, a nitrogen content of 1.8%, and a sulfur content of 2.7%.

EXAMPLE 40

A phosphorus acid is prepared by reacting 200°–210° C. 2 moles of a commercial hexadecene with 1 mole of phosphorus pentasulfide and hydrolyzing the product by blowing it with steam at 160° C. and diluted with an equal weight of mineral oil. The acid is a mixture of phosphonothioic and phosphinothioic acids and has a phosphorus content of 5.4%, a sulfur content of 5% and an acid number of 146. A mixture of 384 grams (0.67 mole) and 0.4 mole of the amine as the partially acylated polyamine of Example 7 is heated at 100° C.–120° C. for 1.5 hours, dissolved in 243 grams of mineral oil and filtered. The filtrate has a sulfur content of 1.2%, a phosphorus content of 1.3%, and a nitrogen content of 1.4%.

EXAMPLE 41

The oil solution of the partially acylated polyamine of Example 28 is mixed with 1% of its weight (0.006 mole) per mole of the amine as the partially acylated polyamine intermediate of phosphorus pentoxide and the mixture is heated at 158°–160° C. for 1 hour. The resulting product has a phosphorus content of 0.0045% and a nitrogen content of 1.4%.

EXAMPLE 42

A phosphorus acid is obtained by heating a polyisobutene having a molecular weight of 1000 with 10% of its weight of phosphorus pentasulfide at 260° C., and then blowing the product with steam at 160° C. The acid has a phosphorus content of 2.3% and an acid number of 41 (phenolphthalein indicator). A mixture of 1550 grams of a 60% oil solution of the partially acylated polyamine prepared as is described in Example 1 and 1220 grams is heated at 140° C. for 4 hours and filtered. The filtrate has a nitrogen content of 1%, a phosphorus content of 1%, and a sulfur content of 1%.

EXAMPLE 43

A substituted polyamine is prepared by the procedure of Example 2 except that the commercial ethylene amine mixture is replaced on an equivalent nitrogen basis with ethylene diamine.

EXAMPLE 44

A substituted polyamine is prepared by the procedure of Example 1 except that the commercial ethylene amine mixture is replaced on an equivalent nitrogen basis with triethylene tetramine.

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EXAMPLE 45

The process of Example 2 is repeated except that the polyisobutene-substituted succinic anhydride used in preparing the partially acylated polyamine intermediate is replaced on a chemical equivalent basis with polypropene (molecular weight of 5000)-substituted succinic acid.

EXAMPLE 46

The process of Example 2 is repeated except that the polyisobutene-substituted succinic anhydride and in preparing the partially acylated polyamine intermediate is replaced on a chemical equivalent basis with a dimethyl ester of the anhydride.

EXAMPLE 47

A substituted polyamine is obtained by first partially acylating ethylene diamine with the polyisobutene-substituted succinic anhydride of Example 1 to form a mono-succinimide of the diamine and then reacting the mono-succinimide with dioctylphosphoric acid at room temperature to form a salt between the free amino group of the mono-succinimide and the acid.

EXAMPLE 48

A mixture is prepared from 1 mole of nitrogen as N-piperazinyloethyl alkenylsuccinimide in which the alkenyl radical is derived from a polyisobutene having a molecular weight of 1000 and 1 mole of phosphorus as dicyclohexylphosphoric acid. The mixture is maintained at 50°–70° C. for 4 hours to form a substituted N-aminoethyl piperazine in which a nitrogen group is attached to the succinic radical by a succinimide linkage and a nitrogen group is attached to dicyclohexylphosphoric radical by ammonium-phosphoric acid salt linkage.

EXAMPLE 49

A partially acylated hexamethylene diamine having a nitrogen group attached to a polyisobutene (molecular weight of 60,000)-substituted succinic radical by an amide linkage is treated at 50°–80° C. with phenylphosphoric acid (1 mole per mole of the amine as the partially acylated diamine). The product is a substituted hexamethylene diamine containing both the above-noted succinic radical and a phosphoric acid radical attached to a nitrogen group of the diamine by a salt linkage.

EXAMPLE 50

A succinic anhydride is obtained by reacting at 200°–220° C. for 20 hours one mole of maleic anhydride with one mole of a copolymer having a molecular weight of 1200 and prepared by copolymerizing 95 parts (by weight) of isobutene with 5 parts of styrene at –25° C.–0° C. in the presence of n-hexene as the solvent and aluminum chloride as the polymerization initiator. The succinic anhydride so obtained (0.5 mole) is mixed at 200° C. with diethylene triamine (0.3 mole) for 6 hours while the water formed by the reaction is distilled off. The product consists substantially of the mono-succinimide of the triamine. A mixture of the mono-succinimide (2 moles of the amine) and tri-tolyl ester of phosphoric acid (1 mole) dissolved in twice its weight of mineral oil is heated at 100°–200° C./2 mm. while cresol is distilled off from the reaction mixture. The residue is a substituted polyamine having above-described succinimide linkage and a nitrogen group attached to a ditolylphosphoric radical by an amide linkage.

EXAMPLE 51

A partially acylated polyamine is obtained by heating at 70°–80° C. menthane diamine (1 mole) and an isobutene-isoprene copolymer-substituted succinic acid (0.5 mole, the copolymer has a molecular weight of 2000 and is obtained by copolymerizing a mixture of 99 parts (by weight) of isobutene and 1 part of isoprene). The prod-

uct is a salt of the acid and menthane diamine having an average of one free amino group per menthane diamine radical. This product is then heated with dicyclohexylphosphinodithioic acid (1 mole per mole of the diamine reactant as the partially acylated amine) at 50°–80° C. The product is a substituted polyamine having salt linkages between the nitrogen groups with both the succinic acid and the phosphinodithioic acid groups.

EXAMPLE 52

A polyisobutene (molecular weight of 6,000)-substituted N,N'-dibutyl p-phenylenediamine is obtained by the reaction of two moles of the phenylene-diamine with a suitably substituted succinic anhydride. The product comprises principally the amide derived by the amidation of one of the amino groups of the phenylenediamine. The succinamide is mixed with ditridecyl ester of phosphoric acid (1 mole per 0.1 mole of the amine reactant) at 50°–80° C. for 5 hours so that a salt is formed between the two free amino groups in the succinamide and the phosphoric acid. The product thus is a substituted polyamine having a nitrogen group attached to the succinoyl radicals (i.e., succinic radical through a succinamide linkage) and a nitrogen group attached to a phosphoric acid through a salt linkage.

EXAMPLE 53

The procedure of Example 2 is repeated except that the commercial ethylene amine used in preparing the partially acylated polyamine is replaced with N-hydroxyethyl ethylene diamine.

EXAMPLE 54

The procedure of Example 2 is repeated except that the commercial ethylene amine used in preparing the partially acylated polyamine is replaced with N-aminoethyl morpholine.

EXAMPLE 55

The procedure of Example 2 is repeated except that the commercial ethylene amine used in preparing the partially acylated polyamine is replaced with melamine.

EXAMPLE 56

The procedure of Example 2 is repeated except that the commercial ethylene amine used in preparing the partially acylated polyamine is replaced with N,N,N',N'-tetramethyl hexamethylene diamine.

EXAMPLE 57

The procedure of Example 2 is repeated except that the commercial ethylene amine used in preparing the partially acylated polyamine is replaced with o-phenylenediamine.

EXAMPLE 58

A substituted polyamine is obtained by the reaction at 150°–180° C. of the partially acylated ethylene amine of Example 1 with methyl ester of diphenylphosphoric acid (1 mole per mole of the ethylene amine as the partially acylated intermediate) until the methyl alcohol formed is distilled off from the reaction mixture. The product contains nitrogen groups attached to diphenylphosphinic radicals through amide linkages.

EXAMPLE 59

The procedure of Example 58 is repeated except that phenyl ester of diphenylphosphinodithioic acid and that the reaction temperature is 180°–200° C./25 mm. The by-product is thiophenol. The substituted polyamine contains both succinic radicals and phosphinic radicals (amide) attached to nitrogen groups.

EXAMPLE 60

A mixture of N-octadecyl trimethylene diamine (1 mole), the polyisobutene-substituted succinic anhydride of

Example 1 (0.5 mole) and bis(di(heptylphenyl) phosphorothioic)sulfide (i.e., the anhydride of di(heptyl) phosphorodithioic acid obtained by heating the acid to split off hydrogen sulfide) (1 mole) is heated at 150°–200° C. for 10 hours. The product is a substituted polyamine having nitrogen groups attached to the succinic and phosphorothioic radicals through amide linkages.

The substituted polyamines of this invention are useful for a wide variety of purposes including pesticides, plasticizers, rust inhibiting agents for treatment of metals, corrosion-inhibiting agents, extreme pressure agents, anti-wear agents, and detergents.

A principal utility of such products is as additives in lubricants. It has been discovered in accordance with this invention that when used for such purpose their effectiveness to impart a specific property to a lubricant is closely related to the size of the substantially hydrocarbon substituent in the succinic radical attached to the nitrogen groups of the substituted polyamines. More particularly it has been found that products in which the substantially hydrocarbon substituent contains more than about 50 aliphatic carbon atoms are effective to impart oxidation-inhibiting, corrosion-inhibiting, and detergent properties to a lubricant. It has also been found that the detergent properties of the products diminish sharply with a decrease in the size of the substantially hydrocarbon substituent having less than about 50 aliphatic carbon atoms so that products having less than about 35 aliphatic carbon atoms in this substituent are ineffective as detergent additives in lubricants. The presence of the phosphorus radicals in the substituted polyamines further enhance the effectiveness of the products even though such radicals are attached to only a portion of the nitrogen groups of the substituted polyamines.

The lubricating oils in which the substituted polyamines of this invention are useful as additives may be of synthetic, animal, vegetable, or mineral origin. Ordinarily mineral lubricating oils are preferred by reason of their availability, general excellence, and low cost. For certain applications, oils belonging to one of the other three groups may be preferred. For instance, synthetic polyesters oil such as didodecyl adipate and di-2-ethylhexyl sebacate are often preferred as jet engine lubricants. Normally the lubricating oils preferred will be fluid oils, ranging in viscosity from about 40 Saybolt Universal seconds at 100° F. to about 200 Saybolt Universal seconds at 210° F.

The concentration of the substituted polyamines as additives in lubricants usually ranges from about 0.01% to about 10% by weight. The optimum concentrations for a particular application depend to a large measure upon the type of service to which the lubricants is to be subjected. Thus, for example, lubricants for use in gasoline internal combustion engines may contain from about 0.5 to about 5% of the additive, whereas lubricating compositions for use in gears and diesel engines may contain as much as 10% or even more of the additive.

This invention contemplates also the presence of other additives in the lubricating compositions. Such additives include, for example, supplemental detergents of the ash-containing type, viscosity index improving agents, pour point depressing agents, anti-foam agents, extreme pressure agents, rust-inhibiting agents, and supplemental oxidation and corrosion-inhibiting agents.

The ash-containing detergents are exemplified by oil-soluble neutral and basic salts of alkali or alkaline earth metals with sulfonic acids, carboxylic acids, or organic phosphorus acids characterized by at least one direct carbon-to-phosphorus linkage such as those prepared by the treatment of an olefin polymer (e.g., polyisobutene having a molecular weight of 1000) with an 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 those of sodium, potassium, lithium, calcium, magnesium, strontium, and barium.

The term "basic salt" is used to designate the 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 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 likewise is known. Examples of compounds useful as the promoter include phenolic substances such as phenol, naphthol, alkylphenol, thiophenol, sulfurized alkylphenol, and condensation products of formaldehyde with a phenolic substance; alcohols such as methanol, 2-propanol, octyl alcohol, Cellosolve, carboto, ethylene glycol, stearyl alcohol, and cyclohexyl alcohol; amines such as aniline, phenylenediamine, phenothiazine, phenyl-beta-naphthylamine, and dodecylamine. A particularly effective method for preparing the basic salts comprises mixing an acid with an excess of a basic alkaline earth metal neutralizing agent, a phenolic promoter compound, and a small amount of water and carbonating the mixture at an elevated temperature such as 60°-200° C.

The preparation of a basic sulfonate detergent is illustrated as follows: A mixture of 490 parts (by weight) of a mineral oil, 110 parts of water, 61 parts of heptylphenol, 340 parts of barium mahogany sulfonate, and 227 parts of barium oxide is heated at 100° C. for 0.5 hour and then to 150° C. Carbon dioxide is then bubbled into the mixture until the mixture is substantially neutral. The mixture is filtered and the filtrate found to have a sulfate ash content of 25%.

The preparation of a basic barium salt of a phosphorus acid is illustrated as follows: A polyisobutene having a molecular weight of 50,000 is mixed with 10% by weight of phosphorus pentasulfide at 200° C. for 6 hours. The resulting product is hydrolyzed by treatment with steam at 160° C. to produce an acidic intermediate. The acidic intermediate is then converted to a basic salt by mixing twice its volume of mineral oil, 2 moles of barium hydroxide and 0.7 mole of phenol and carbonating the mixture at 150° C. to produce a fluid product.

The substituted polyamines are especially adapted for use in combination with extreme pressure and corrosion-inhibiting additives such as metal dithiocarbamates, xanthates, the Group II metal phosphorodithioates and their epoxide adducts, hindered phenols, sulfurized cycloalkanes, di-alkyl polysulfides, sulfurized fatty esters, phosphosulfurized fatty esters, alkaline earth metal salts of alkylated phenols, dialkyl phosphites, triaryl phosphites, and esters of phosphorodithioic acids. Combinations of the substituted polyamines of this invention with any of the above-mentioned additives are especially desirable for use in lubricants which must have superior extreme pressure and oxidation-inhibiting characteristics.

The Group II metal phosphorodithioates are the salts of acids having the formula



in which R₁ and R₂ are substantially hydrocarbon radicals. The metals for forming such salts are exemplified by barium, calcium, strontium, zinc, and cadmium. The barium and zinc phosphorodithioates are especially preferred. The substantially hydrocarbon radicals in the phosphorodithioic acid are preferably low or medium molecular weight alkyl radicals and alkylphenyl radicals, i.e., those having from about 1 to about 30 carbon atoms in the alkyl group. Illustrative alkyl radicals include methyl, ethyl, isopropyl, isobutyl, n-butyl, sec-butyl, the various amyl alcohols, n-hexyl, methylisobutyl carbonyl, heptyl,

2-ethylhexyl, diisobutyl, isooctyl, nonyl, behenyl, decyl, etc. Illustrative lower alkylphenyl radicals include butylphenyl, amylphenyl, di-amylphenyl, octylphenyl, etc. Cycloalkyl radicals likewise are useful and these include chiefly cyclohexyl and the lower alkyl-cyclohexyl radicals. Other substantially hydrocarbon radicals likewise are useful such as tetradecyl, octadecyl, eicosyl, butyl-naphthyl, hexyl-naphthyl, octyl-naphthyl, cyclohexylphenyl, naphthyl, etc. Many substituted hydrocarbon radicals may also be used, e.g., chlorophenyl, dichlorophenyl, and dichlorodecyl.

The availability of the phosphorodithioic acids from which the Group II metal salts of this invention are prepared is well known. They are prepared by the reaction of phosphorus pentasulfide with an alcohol or phenol. The reaction involves four moles of the alcohol or phenyl per mole of phosphorus pentasulfide, and may be carried out within the temperature range from about 50° C. to about 200° C. Thus the preparation of O,O-di-n-hexyl phosphorodithioic acid involves the reaction of phosphorus pentasulfide with four moles of n-hexyl alcohol at about 100° C. for about 2 hours. Hydrogen sulfide is liberated and the residue is the defined acid. The preparation of the zinc or barium salt of this acid may be effected by reaction with zinc oxide or barium oxide. Simply mixing and heating these two reactants is sufficient to cause the reaction to take place and the resulting product is sufficiently pure for the purposes of this invention.

Especially useful Group II metal phosphorodithioates can be prepared from phosphorodithioic acids which in turn are prepared by the reaction of phosphorus pentasulfide with mixtures of alcohols. The use of such mixtures enables the utilization of cheaper alcohols which in themselves do not yield oil-soluble phosphorodithioic acids. Thus a mixture of isopropyl and hexyl alcohols can be used to produce a very effective, oil-soluble metal phosphorodithioate. For the same reason mixtures of simple phosphorodithioic (i.e., acids prepared from one alcohol) acids can be reacted with zinc oxide or barium oxide to produce less expensive, oil-soluble salts.

Another class of the phosphorothioate additives contemplated for use in the lubricating compositions of this invention comprises the adducts of the metal phosphorodithioates described above with an epoxide. The metal phosphorodithioates useful in preparing such adducts are for the most part the zinc phosphorodithioates. The epoxides may be alkylene oxides or arylalkylene oxides. The arylalkylene oxides are exemplified by styrene oxide, p-ethylstyrene oxide, alpha-methylstyrene oxide, 3-beta-naphthyl-1,3-butylene oxide, m-dodecylstyrene oxide, and p-chlorostyrene oxide. The alkylene oxides include principally the lower alkylene oxides in which the alkylene radical contains 6 or less carbon atoms. Examples of such lower alkylene oxides are ethylene oxide, propylene oxide, 1,2-butene oxide, trimethylene oxide, tetramethylene oxide, butadiene monoepoxide, 1,2-hexene oxide, and propylene epichlorohydrin. Other epoxides useful herein includes, for example, butyl 9,10-epoxy-stearate, epoxide soybean oil, epoxidized tung oil, and epoxidized copolymer of styrene with butadiene.

The adduct may be obtained by simply mixing the phosphorodithioate and the epoxide. The reaction is usually exothermic and may be carried out within wide temperature limits from about 0° C. to about 200° C. Because the reaction is exothermic it is best carried out by adding one reactant, usually the epoxide, in small increments to the other reactant in order to obtain convenient control of the temperature of the reaction. The reaction may be carried out in a solvent such as benzene, mineral oil, naphtha, or n-hexane.

The chemical structure of the adduct is not known. More than one mole, sometimes as many as four moles, of the epoxide can be made to combine with the phosphorodithioate to form products useful herein. However, adducts obtained by the reaction of one mole of the phos-

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phorodithioate with from about 0.25 mole to about 1 mole of a lower alkylene oxide, particularly ethylene oxide and propylene oxide, have been found to be especially useful and therefore are preferred.

The lubricating compositions may contain metal detergent additives in amounts usually within the range of about 0.1% to about 20% by weight. In some applications such as in lubricating marine diesel engines the lubricating compositions may contain as much as 30% of detergent additives. They may contain extreme pressure addition agents, viscosity index improving agents, and pour point depressing agents, each in amounts within the range from about 0.1% to about 10%.

The following examples are illustrative of the lubricating compositions of this invention: (all percentages are by weight).

EXAMPLE I

SAE 20 mineral lubricating oil containing 0.5% of the product of Example 1.

EXAMPLE II

SAE 30 mineral lubricating oil containing 0.75% of the product of Example 2 and 0.1% of phosphorus as the barium salt of di-n-nonylphosphorodithioic acid.

EXAMPLE III

SAE 10W-30 mineral lubricating oil containing 0.4% of the product of Example 3.

EXAMPLE IV

SAE 90 mineral lubricating oil containing 0.1% of the product of Example 4 and 0.15% of the zinc salt of an equimolar mixture of di-cyclohexylphosphorodithioic acid and di-isobutyl phosphorodithioic acid.

EXAMPLE V

SAE 30 mineral lubricating oil containing 2% of the product of Example 30.

EXAMPLE VI

SAE 20W-30 mineral lubricating oil containing 5% of Example 39.

EXAMPLE VII

SAE 10W-30 mineral lubricating oil containing 1.5% of the product of Example 2 and 0.05% of phosphorus as the zinc salt of a phosphorodithioic acid prepared by the reaction of phosphorus pentasulfide with a mixture of 60% (mole) of p-butylphenol and 40% (mole) of n-pentyl alcohol.

EXAMPLE VIII

SAE 50 mineral lubricating oil containing 3% of the product of Example 40 and 0.1% of phosphorus as the calcium salt of di-hexylphosphorodithioate.

EXAMPLE IX

SAE 10W-30 mineral lubricating oil containing 2% of the product of Example 2, 0.06% of phosphorus as zinc di-n-octylphosphorodithioate, and 1% of sulfate ash as barium mahogany sulfonate.

EXAMPLE X

SAE 30 mineral lubricating oil containing 5% of the product of Example 10, 0.1% of phosphorus as the zinc salt of a mixture of equimolar amounts of diisopropylphosphorodithioic acid and di-n-decylphosphorodithioic acid, and 2.5% of sulfate ash as a basic barium detergent prepared by carbonating at 150° C. a mixture comprising mineral oil, barium di-dodecylbenzene sulfonate and 1.5 moles of barium hydroxide in the presence of a small amount of water and 0.7 mole of octylphenol as the promoter.

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EXAMPLE XI

SAE 10W-30 mineral lubricating oil containing 6% of the product of Example 17, 0.075% of phosphorus as zinc di-n-octylphosphorodithioate, and 5% of the barium salt of an acidic composition prepared by the reaction of 100 parts of a polyisobutene having a molecular weight of 60,000 with 100 parts of phosphorus pentasulfide at 200° C. and hydrolyzing the product with steam at 150° C.

EXAMPLE XII

SAE 10 mineral lubricating oil containing 2% of the product of Example 25, 0.075% of phosphorus as the adduct of zinc di-cyclohexylphosphorodithioate treated with 0.3 mole of ethylene oxide, 2% of a sulfurized sperm oil having a sulfur content of 10%, 3.5% of a poly-(alkyl methacrylate) viscosity index improver, 0.02% of a poly-(alkyl methacrylate) pour point depressant, 0.003% of a poly-(alkyl siloxane) anti-foam agent.

EXAMPLE XIII

SAE 10 mineral lubricating oil containing 1.5% of the product of Example 27, 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., a sulfurized methyl ester of tall oil acid having a sulfur content of 15%, 6% of a polybutene viscosity index improver, 0.005% of a poly-(alkyl methacrylate) anti-foam agent, and 0.5% of lard oil.

EXAMPLE XIV

SAE 20 mineral lubricating oil containing 1.5% of the product of Example 2, 0.5% of di-dodecyl phosphite, 2% of the sulfurized sperm oil having a sulfur content of 9%, a basic calcium detergent prepared by carbonating a mixture comprising mineral oil, calcium mahogany sulfonate and 6 moles of calcium hydroxide in the presence of an equi-molar mixture (10% of the mixture) of methyl alcohol and n-butyl alcohol as the promoter at the reflux temperature.

EXAMPLE XV

SAE 10 mineral lubricating oil containing 25% of the product of Example 33, 0.07% of phosphorus as zinc di-octylphosphorodithioate, 2% of a barium detergent prepared by neutralizing with barium hydroxide the hydrolyzed reaction product of a polypropylene (molecular weight 2000) with 1 mole of phosphorus pentasulfide and 1 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 phenol as the promoter at 180° C., 3% of a supplemental ashless detergent prepared by copolymerizing a mixture of 95% (weight) of decyl-methacrylate and 5% (weight) of diethylaminoethylacrylate.

EXAMPLE XVI

SAE 80 mineral lubricating oil containing 2% of the product of Example 20, 0.1% of phosphorus as zinc di-n-hexylphosphorodithioate, 10% of a chlorinated paraffin wax having a chlorine content of 40%, 2% of di-butyl tetrasulfide, 2% of sulfurized dipentene, 0.2% of oleyl amide, 0.003% of an anti-foam agent, 0.02% of a pour point depressant, and 3% of a viscosity index improver.

EXAMPLE XVII

SAE 10 mineral lubricating oil containing 3% of the product of Example 2, 0.075% of phosphorus as the zinc salt of a phosphorodithioic acid prepared by the reaction of phosphorus pentasulfide with an equimolar mixture of

n-butyl alcohol and dodecyl alcohol, 3% of a barium detergent prepared by carbonating a mineral oil solution containing 1 mole of sperm oil, 0.6 mole of octylphenol, 2 moles of barium oxide, and a small amount of water at 150° C.

EXAMPLE XVIII

SAE 20 mineral lubricating oil containing 2% of the product of Example 12 and 0.07% of phosphorus as zinc di-n-octylphosphorodithioate.

EXAMPLE XIX

SAE 30 mineral lubricating oil containing 3% of the product of Example 14 and 0.1% of phosphorus as zinc di-(isobutylphenyl)-phosphorodithioate.

EXAMPLE XX

SAE 50 mineral lubricating oil containing 2% of the product of Example 35.

EXAMPLE XXI

SAE 90 mineral lubricating oil containing 3% of the product of Example 46 and 0.2% of phosphorus as the reaction product of 4 moles of turpentine with 1 mole of phosphorus pentasulfide.

EXAMPLE XXII

SAE 90 mineral lubricating oil containing 3% of the product of 45 and 0.2% of 4,4'-methylene-bis-(2,6-di-tert-butylphenol).

EXAMPLE XXIII

SAE 30 mineral lubricating oil containing 2% of the product of Example 30 and 0.1% of phosphorus as phenylethyl di-cyclohexylphosphorodithioate.

EXAMPLE XXIV

SAE 90 mineral lubricating oil containing 5% of the product of Example 2 and 1% of the calcium salt of the sulfurized phenol obtained by the reaction of 2 moles of heptylphenol with 1 mole of sulfur.

The above lubricants are merely illustrative and the scope of invention includes the use of all the additives previously illustrated as well as others within the broad concept of this invention described herein.

The utility of the oil-soluble compositions of this invention as additives in lubricating compositions is illustrated by the results from an oxidation and detergency test in which a 350 cc. sample of a lubricant containing 0.001% of iron naphthenate and 1.5% by weight of the solvent-free additive to be tested is placed in a 2 x 15 (inches) borosilicate tube. A 1 3/8 x 5/8 (inches) SAE 1020 steel panel is immersed in oil. The sample then is heated at 300° F. for a specified period while air is bubbled through it at the rate of 10 liters per hour. The oxidized sample is cooled to 120° F., homogenized with 0.5% of water allowed to stand at room temperature for 24 hours, and then filtered through two layers of No. 1 Whatman filter paper at 20 mm. Hg pressure. The weight of the precipitate, washed with naphtha and dried, is taken as a measure of the effectiveness of the additive to inhibit oxidation and disperse the sludge formed during the test. The greater the weight of the precipitate the less effective the additive. The test is adapted to evaluate the corrosiveness of the lubricant by the following modification: a clean copper-lead bearing is immersed in the lubricant during the air blowing step. After the test, the bearing is scrubbed with naphtha, dried, and weighed and its weight loss (in milligrams) and is taken as an indication of the corrosiveness of the lubricant. The results of the test are indicated in the following Table I. The base oil of the lubricant sample employed in the test is a Mid-Continent, conventionally refined mineral oil having a viscosity of about 200 Saybolt Universal seconds at 100° F.

Product of this invention	Test procedure	Hours of test	Sludge (mg. per 100 cc. of sample)	Bearing weight loss (mg.)
None	A	48	250-400	-----
Do	A	96	800-1,200	-----
Do	B	48	1,200-1,600	10-30
Product of Ex. 10	A	96	15.8	-----
	B	48	2.1	2
Product of Ex. 20	A	96	2.3	-----
Product of Ex. 28	A	96	6.1	-----
Product of Ex. 21	A	48	5.3	-----
Product of Ex. 15	B	48	2.2	None
Product of Ex. 23	A	96	2.3	-----
Product of Ex. 3	A	96	2.6	-----
Product of Ex. 9	A	96	3.4	-----
Product of Ex. 22	B	48	1.9	5.9
Product of Ex. 24	A	96	1.5	-----
Product of Ex. 26	A	96	1.2	-----
Product of Ex. 25	A	96	2.7	-----
Product of Ex. 27	A	48	1.3	-----
Product of Ex. 29	A	96	2.7	-----
Product of Ex. 32	A	96	2.6	-----
Product of Ex. 33	A	96	1.8	-----
Product of Ex. 34	A	96	1.7	-----
Product of Ex. 37	A	96	23	-----
Product of Ex. 42	A	96	8.3	-----

Procedure A: Copper-lead bearing not present in test sample.

Procedure B: Copper-lead bearing present in test sample.

Further illustration of the effectiveness of the substituted polyamines of this invention as lubricant additives is had by the modified CRC-EX-3 engine test (the modification consists of extending the test period from the specified 96 hours to 144 hours, thus making the test more severe). This test is recognized in the field as an important test by which lubricants can be evaluated for use under relatively light duty or intermittently high and low temperature service conditions such as are encountered in the operation of automobiles in urban use. In this test, the lubricant is used in the crankcase of a 1954 6-cylinder Chevrolet Powerglide engine operated for 144 hours under recurring cyclic conditions, each cycle consisting of: 2 hours at engine speed of 500 r.p.m. under no load, oil sump temperature of 100°-125° F., and air:fuel ratio of 10:1; and 2 hours at an engine speed of 2500 r.p.m. under a load of 40 brake horsepower, oil sump temperature of 240°-280° F., and an air:fuel ratio of 16:1. At the end of the test, the lubricant is rated in terms of (1) the extent of piston filling, (2) the amount of sludge formed in the engine (rating scale of 80-0, 80 being indicative of no sludge and 0 being indicative of extremely heavy sludge), and (3) the total amount of engine deposits, i.e., sludge and varnish formed in the engine (rating scale of 100-0, 100 being indicative of no deposit and 0 being indicative of extremely heavy deposit). The results of the test are summarized in Table II.

The SAE 20 lubricating compositions referred to in Lubricants A-E are composed of an SAE 20 mineral lubricating oil containing 0.3% of barium sulfate ash as a basic barium detergent obtained by carbonating a mixture of an excess of barium hydroxide, heptylphenol (promoter), and a hydrolyzed acidic product of a chlorinated polyisobutene (chlorine content of 4.7% and a molecular weight of 1000), heptylphenol, and phosphorus trichloride; 0.06% of phosphorus as the zinc salt of a phosphorodithioic acid obtained by the reaction of phosphorus pentasulfide with a mixture of isobutyl alcohol and primary-pentyl alcohol; and 3 parts per million of a polymeric dialkylsiloxane anti-foam agent. Such lubricating compositions are suitable for use under consistently high temperature service conditions and are not entirely satisfactory for use under intermittently high and low temperature service conditions. By the CRC-EX-3 test, they show test results no better than: percent ring filling, 16%; sludge rating, 68.5; and total deposit rating, 84.0. 16; sludge rating, 68.5; and total deposit rating, 84.0.

The efficacy of the substituted polyamines of this invention as detergent additives in lubricants for diesel engines operated under relatively severe conditions is demonstrated by the results (Table III) of the CRC-L-1 En-

gine test (also known as Caterpillar 1E test). In this test, the lubricating composition is used in the crankcase of a 4-stroke diesel engine having a compression ratio of 15:1 operated for 120 hours under the following conditions: speed, 1000 r.p.m.; B.t.u. input per minute, 2900-3000; load, 20 brake horsepower; water jacket temperature, 175-180° F.; oil temperature, 140-150° F. A diesel fuel having a sulfur content of either 1% or 0.4% is used. The lubricant is evaluated according to (1) the piston cleanliness (rating scale of 0-100, 100 being indicative of no deposit and 0 being indicative of heavy deposit) and (2) the amount of ring filling.

TABLE II

Lubricant tested	Percent ring filling	Sludge rating	Total deposit rating
(A) SAE 20 lubricating composition containing 0.41% of the product of Example 6	2	76.9	93.6
(B) SAE 20 lubricating composition containing 0.81% of the product of Example 18	2	73.7	91.5
(C) SAE 20 lubricating composition containing 1.35% of the product of Example 16	2	75.1	91.9
(D) SAE 20 lubricating composition containing 0.41% of the product of Example 25	3	67.0	84.5
(E) SAE 20 lubricating composition containing 1.35% of the product prepared by the procedure of Example 29 except that 0.33 equivalent of phosphorus as phosphorus pentoxide is used per equivalent of nitrogen as the partially acylated polyamine	2	72.8	89.8
(F) SAE 20 mineral lubricating oil containing 2.5% of the product of Example 2, 1.2% of a sulfurized dipentene having a sulfur content of 35%, and 3 parts per million of a polymeric dialkylsiloxane anti-foam agent	1	78.3	97.1

TABLE III

Lubricant tested	Percent ring filling	Piston cleanliness rating
(G) SAE 30 mineral lubricating oil containing 1.48% of the product of Example 2 and 1.16% of a sulfurized dipentene having a sulfur content of 35%	3	96.0
(H) Same as Lubricant E of Table II	3	97.5
(I) SAE 20 mineral lubricating oil containing 3% of the product of Example 32	None	94.0
(J) SAE 30 mineral lubricating oil containing the product of Example 38	2	96.0
(K) SAE 30 mineral lubricating oil containing the product of Example 6	5	97.0

What is claimed is:

1. A composition comprising a major proportion of a lubricating oil and a minor proportion of a substituted polyamine prepared by the process comprising the reaction at a temperature of from about 80° C. up to the decomposition point of 1 mole of an alkylene polyamine with at least about 0.25 mole of a hydrocarbon-substituted succinic acid-producing compound selected from the class consisting of acids, anhydrides, esters and halides having at least about 50 aliphatic carbon atoms in the hydrocarbon substituent and at least about 0.001 mole of a phosphorus acid-producing compound selected from the class consisting of phosphoric acids, phosphorous acids, phosphonyl acids, phosphinyl acids, and the esters, the halides, and the anhydrides thereof.

2. The composition of claim 1 wherein the alkylene polyamine is a hydroxy alkyl-substituted alkylene polyamine.

3. The composition of claim 1 wherein the alkylene amine is an ethylene polyamine, the succinic acid-producing compound is a hydrocarbon-substituted succinic acid or anhydride and the phosphorus acid-producing compound is a partially esterified phosphoric acid in which the ester portion contains from 1 to about 30 carbon atoms.

4. The composition of claim 1 wherein the alkylene amine is an ethylene polyamine, the succinic acid-producing

compound is an olefin polymer-substituted succinic acid or anhydride in which the olefin polymer substituent has a molecular weight of from about 700 to 5000, and the phosphorus acid-producing compound is an alkylphosphoric acid obtained by the reaction of phosphorus pentoxide with from about 1 to 4 moles of an alcohol having up to about 30 carbon atoms.

5. The composition of claim 4 wherein the olefin polymer substituent is a polymer of isobutene.

6. A composition comprising a major proportion of a lubricating oil and a minor proportion of a substituted polyamine prepared by the process comprising (A) forming a partially acylated polyamine intermediate by reacting at a temperature from about 80° C. to about 250° C. 1 mole of an ethylene polyamine with at least about 0.25 mole of an olefin polymer-substituted succinic acid or anhydride in which the olefin polymer substituent has a molecular weight of from about 700 to 5000 and (B) reacting at a temperature from about 25° C. to about 100° C. said intermediate with at least about 0.001 mole of phosphorus pentoxide.

7. A composition comprising a major proportion of a lubricating oil and a minor proportion of a substituted polyamine prepared by the process comprising (A) forming a partially acylated polyamine intermediate by reacting at a temperature from about 80° C. to about 250° C. a polyethylene polyamine with from about 1 to 3 moles of a polyisobutene-substituted succinic acid or anhydride in which the polyisobutene substituent has a molecular weight of from about 700 to 5000 and (B) reacting at a temperature from about 25° C. to about 100° C. said intermediate with from about 0.5 to 3 moles of an alkylphosphoric acid obtained by the reaction of phosphorus pentoxide with from about 1 to 4 moles of an alcohol having from about 8 to 24 carbon atoms.

8. A composition comprising a major proportion of a lubricating oil and a minor proportion of a substituted polyamine prepared by the process comprising (A) forming a partially acylated polyamine intermediate by reacting at a temperature from about 80° C. to 250° C. 1 mole of a polyethylene polyamine having from 2 to about 10 amino groups with from about 1 to 3 moles of a polyisobutene-substituted succinic acid or anhydride in which the polyisobutene substituent has a molecular weight from about 700 to 5000 and (B) reacting at a temperature from about 50° C. to about 100° C. said intermediate with from about 0.5 to 3 moles of an alkylphosphoric acid obtained by the reaction of phosphorus pentoxide with 3 moles of decyl alcohol.

9. A composition comprising a major proportion of a lubricating oil and a minor proportion of a substituted polyamine prepared by the process comprising (A) forming a partially acylated polyamine intermediate by reacting at a temperature from about 80° C. to about 250° C. 1 mole of an alkylene polyamine with at least about 0.25 mole of a hydrocarbon-substituted succinic acid or anhydride in which the hydrocarbon substituent has a molecular weight of from about 700 to 5000 and (B) reacting at a temperature from about 25° C. to about 100° C. said intermediate with at least about 0.001 mole of phosphorus pentasulfide.

10. A composition comprising a major proportion of a lubricating oil and a minor proportion of a substituted polyamine prepared by the process comprising (A) forming a partially acylated polyamine intermediate by reacting at a temperature from about 80° C. to about 250° C. 1 mole of an alkylene polyamine in which the alkylene group is ethylene or propylene with at least about 0.25 mole of a hydrocarbon-substituted succinic acid or anhydride in which the hydrocarbon substituent has a molecular weight of from about 700 to 5000 and (B) reacting at a temperature from about 25° C. to about 100° C. said intermediate with at least about 0.001 mole of phosphorus pentasulfide.

11. A composition comprising a major amount of a substance selected from the group consisting of lubricating oils and normally liquid hydrocarbon fuels and a minor amount of a reaction product obtained by reacting a phosphosulfurized hydrocarbon with a condensation reaction product of a hydrocarbon-substituted succinic anhydride and an amine selected from the group consisting of alkylene polyamines and N-aminoalkyl piperazines, said hydrocarbon substituent having at least about 50 carbon atoms.

12. The composition of claim 1 wherein the phosphorus acid-producing compound is selected from the class consisting of (a) oxy-phosphoric acids; (b) oxy-phosphorous acids, thio-phosphorous acids, and mixed oxy-thio-phosphorous acids; (c) oxy-phosphinyl acids, thio-phosphinyl acids, and mixed oxy-thio-phosphinyl acids; (d) oxy-phosphonyl acids, thio-phosphonyl acids, and mixed oxy-thio-phosphonyl acids; and (e) the esters,

the halides, and the anhydrides of the foregoing oxy-, thio-, and mixed oxy-thio-phosphorus acids.

13. The composition of claim 1 wherein the phosphorus acid-producing compound is an anhydride or halide of an inorganic phosphorus acid.

14. The composition of claim 1 wherein the phosphorus acid-producing compound is an ester of a phosphorothioic acid.

References Cited

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