United States Patent Office 3,390,082
Patented June 25, 1968

3,390,082

LUBRICANTS CONTAINING METAL-FREE DISPERSANTS AND INHIBITORS

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No Drawing. Continuation-in-part of application Ser. No. 102,638, Apr. 13, 1961. This application Sept. 19, 1967, Ser. No. 668,921
12 Claims. (Cl. 252—32.7)

ABSTRACT OF THE DISCLOSURE

The invention relates to a lubricant, such as is prepared from a petroleum lubricating oil or synthetically prepared lubricating oil, which contains at least one metal-free dispersant and at least one corrosion- and/or oxidation inhibitor. The metal-free dispersant is an oil-soluble acylated amine wherein the acyl group is illustrated by a relatively high molecular weight substituted succinic group having at least about 50 aliphatic carbon atoms in the substituent. The inhibitor is illustrated by a phosphorus-containing substance such as a metal phosphorodithioate or an adduct of such phosphorodithioate with an epoxide.

This application is a continuation-in-part of application Ser. No. 102,638, filed Apr. 13, 1961 and now abandoned, which was a continuation-in-part of applications Ser. No. 802,667, filed Mar. 30, 1959, now Ser. No. U.S. 3,172,892, and Ser. No. 808,889, filed Apr. 27, 1959 and now abandoned.

This invention relates to chemical compositions which are especially useful in lubricants. It relates in particular to lubricants containing such compositions.

This composition consists of a metal-free composition which acts in a lubricant to disperse insoluble particles so that they do not settle out and form sludge, varnish or other deposits, and a metal-containing composition which acts in a lubricant to inhibit the decomposition of the motor oil and also to prevent corrosion of the relatively moving metal parts of the engine which is being lubricated. The first of these compositions is not described in the prior art, but the second class of compositions is represented by a metal salt of a phosphorodithioic acid or a derivative of such metal salt.

The first-mentioned additive is notably effective as a dispersing agent in lubricating oils when used alone, but the present invention is concerned with a marked enhancement of its effectiveness when it is used in combination with the second of the additives referred to above. The composition of this invention has been found to be much more effective and versatile than any similar composition heretofore known.

It is accordingly a principal object of this invention to provide a novel composition which is effective to improve lubricants.

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

These and other objects of this invention are achieved by a lubricating composition comprising a major proportion of a lubricating oil and (a) from about 0.1% to about 10% by weight of an oil-soluble acylated nitrogen-containing composition characterized by the presence within its structure of a substituted succinic radical selected from the class consisting of succinoyl, succinoyloxy, and succinimidoyl radicals in which the substituent is substantially hydrocarbon radical having at least about 50 aliphatic carbon atoms and a nitrogen radical characterized by a nitrogen atom attached directly to said succinic

radical, said nitrogen radical being derived from an amine selected from the class consisting of alkylene amines and hydroxyalkyl-substituted alkylene amines, and (b) from about 0.001% to about 2% by weight of phosphorus as a phosphorothioate selected from the class consisting of oil-soluble Group II metal phosphorodithioates and adducts of oil-soluble Group II metal phosphorodithioates with an epoxide.

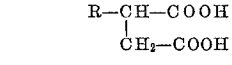
It will be readily appreciated that the linkage between a nitrogen atom and a succinoyl radical is representative of an amide or an imide structure, that the linkage between a nitrogen atom and a succinimidoyl radical is representative of an amidine or imidazoline structure, and that the linkage between a nitrogen atom and a succinoyloxy radical is representative of quaternary ammonium-carboxylic acid salt structure. Thus the acylated nitrogen-containing composition of this invention is characterized by amide, imide, amidine, imidazoline, or salt linkages and in many instances it contains a mixture of such linkages.

A critical aspect of this invention is the size of the substantially hydrocarbon substituent in the substituted succinic radical. Only acylated nitrogen-containing compositions having at least about 50 aliphatic carbon atoms in the substituent in the succinic radical 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 acylated nitrogen-containing compositions but also upon the effectiveness of such compositions as additives in hydrocarbon oils for the purposes of this invention. It has now been discovered that while acylated nitrogen-containing compositions having less than the minimum number of such aliphatic carbon atoms in the substituent may be sufficiently oil-soluble, they nevertheless are not sufficiently effective to be useful as additives of this invention. Furthermore, it has been discovered that their effectiveness diminishes sharply with a corresponding decrease in the size of the substituent, so that acylated nitrogen-containing compositions having less than about 35 aliphatic carbon atoms in such substituent either are ineffective or produce detrimental results when added to a hydrocarbon oil.

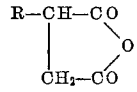
Another important aspect of this invention is the structural constitution of the substantially hydrocarbon substituent in the succinic radical. Thus, the substituent is preferably substantially saturated, i.e., at least about 99% of the total number of carbon-to-carbon covalent linkages are saturated linkages. If excessive unsaturation is present, the substituent becomes susceptible to oxidation, decomposition, or polymerization and the final acylated nitrogen-containing compositions in many instances will not be sufficiently stable for use in hydrocarbon oils.

The substituent may contain polar groups provided, however, that such polar groups are not present in proportions sufficiently large to alter significantly the hydrocarbon character of the substituent. The polar group which may be present are exemplified by chloro, bromo, keto, aldehyde, and nitro radicals. The maximum proportion of such polar groups in the substituent is approximately 10% based upon the weight of the hydrocarbon portion of the substituent.

A particularly convenient method for preparing the acylated nitrogen-containing compositions of this invention comprises reacting a substituted succinic compound selected from the class consisting of substituted succinic acids having the structural formula



and the substituted succinic anhydrides having the structural formula

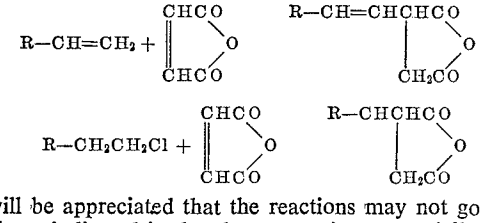


in which structural formulas R is a substantially hydrocarbon radical having at least about 50 aliphatic carbon atoms, with at least about one-half an equivalent amount of an amine selected from the class consisting of alkylene amines and hydroxyalkyl-substituted alkylene amines, and heating the resulting mixture to effect acylation and to remove the water formed thereby.

It will be seen that the reaction by which the acylated nitrogen-containing composition of (a) is prepared involves a reaction of a dicarboxylic acid (or anhydride thereof) with a polyamine and can result in a simple acyclic diamide, a cyclic diamide, a polymeric amide, an amidine, an imidazoline, or products having a combination of any of these types of structures. It is believed that a substantial amount of imide formation takes place in the process. Furthermore there is reason to believe that in certain instances there is present in the product an appreciable proportion of amine carboxylate salt.

The size and the chemical constitution of the substituent of the succinic acid or anhydride are of major importance in the process because they allow the preparation of a product which satisfies the objects of the invention, i.e., one which is effective as a dispersant in the lubricants of this invention. It is critically important that this substituent be large, that it have at least about 50 aliphatic carbon atoms in its structure, and that it preferably be substantially saturated. These substituent groups are substantially aliphatic hydrocarbon radicals, including both alkyl and alkenyl radicals. They are commonly derived from polyolefins such as polyethylene, polypropylene, polybutylene, etc., although they may be derived from any substantially aliphatic hydrocarbon.

The substituted succinic acids and anhydrides which are contemplated as a reactant in the process are readily available from the reaction of maleic anhydride with a high molecular weight substantially hydrocarbon reactant such as an olefin polymer or a chlorinated high molecular weight substantially saturated hydrocarbon. The product from such a reaction is the corresponding alkenyl succinic anhydride. The reaction involves merely heating the two reactants at a temperature of about 100°–300° C. The reactions in each case are illustrated by the following equations.



It will be appreciated that the reactions may not go precisely as indicated in the above equations, especially with respect to the particular carbon atom of the olefin or the chloride reactant which ultimately becomes attached to the maleic acid or anhydride reactant, but the equations are believed to be illustrative. Furthermore although the product of this reaction has been indicated as being an alkenyl succinic anhydride it is apparent that similar products can be prepared by this process in which the substituent is something other than an alkenyl group. For the purposes of this invention this substituent preferably should be a substantially saturated aliphatic group and in most cases it will be an alkyl or alkenyl group. In some cases, however, it may well be desirable to employ a substituted succinic anhydride in which the substituent is derived, for example, from a copolymer of styrene and isobutylene or of a substituted styrene and some other lower aliphatic olefin. In these latter cases the copolymer

will be substantially aliphatic, i.e., more than about 90% of the monomeric units in the copolymer will be those of the aliphatic monomer.

As mentioned earlier the size of this substituent group appears to determine the effectiveness of the product of the process of the invention as a dispersant in motor oils. Substituted succinic anhydrides and their derivatives have been known for some time and it likewise has been known that these compounds are useful in lubricants, but their utility heretofore has been predicated upon their rust-preventing properties, corrosion-inhibiting properties, viscosity-temperature characteristics, etc. The usefulness of compositions of this type as dispersants has never been realized and an important aspect of this invention resides in the discovery that by increasing the size of this particular substituent an entirely new property, i.e., dispersancy, can be incorporated into the composition.

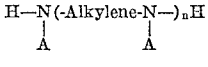
It is also important that the substituent in the succinic acid reactant preferably be substantially saturated. As indicated previously, excess unsaturation in the molecule is harmful to the stability of the product. In most instances the maximum degree of unsaturation permissible in the molecule appears to be about 5% of olefinic linkages based upon the total number of carbon-to-carbon covalent linkages. Preferably such percentage of olefin linkages should be less than about 2%.

The most commonly used sources of these substantially hydrocarbon substituents are the polymers of aliphatic monoolefins. They are illustrated by polymers of 1-butene, 2-butene, isobutene, 1-pentene, 1-hexene, 1-octene, 1-nonene, cyclohexene, 2-methyl-1-pentene, and 2,3-diethyl-1-octene. They include also interpolymers of the aliphatic mono-olefins illustrated above with a minor amount of aromatic olefins or polyolefins provided that the interpolymers are composed of no more than about 5% by weight of polyolefin units. Examples of such interpolymers of 95% (by weight) of isobutene with 5% of styrene; terpolymer of 98% of isobutene with 1% of piperylene and 1% of chloroprene; copolymers of 95% of isobutene with 2% of 1-butene and 3% of 1-hexene; terpolymers of 60% of isobutene with 20% of 1-pentene and 20% of 1-octene; copolymers of 1-hexene and 20% of 1-heptene; 90% of isobutene, 2% of cyclohexene, and 8% of propene; and copolymers of 80% of ethylene and 20% of propene.

The molecular weight of the polymers useful for this purpose should be at least about 700, preferably within the range from about 750 to about 5000. Higher molecular weight polymers such as those having molecular weights above about 10,000 or 100,000 are capable of imparting viscosity index improving properties to the product and in many instances they are preferred for this reason.

The substituted succinic anhydride ordinarily is reacted directly with the amine although in some circumstances it may be desirable first to convert the anhydride to the acid before the reaction. In other circumstances it may be desirable to prepare the substituted succinic acid by some other means and to use an acid prepared by such other means in the process. In any event either the acid or the anhydride may be used in the process of this invention.

The alkylene amines useful in the above process are the polyamines conforming for the most part to the structure



in which *n* is an integer preferably less than about 10 and A is a hydrocarbon amine-substituted hydrocarbon or hydrogen radical. The alkylene radical usually has up to about 8 carbon atoms and is exemplified by an ethylene, propylene, butylene, trimethylene, tetramethylene, pentamethylene, hexamethylene, octamethylene, or decamethylene radical. Specific examples of such alkylene amines are ethylenediamine, diethylenetriamine, triethylenetetramine, propylenediamine, tripropylenetetramine, tetra-

ethylenepentamine, trimethylenediamine, pentaethylenetetramine, di(trimethylene)triamine, tri(hexamethylene)-tetramine, decamethylenediamine, N-octyl trimethylenediamine, N,N'-dioctyl propylenediamine, N-dodecyl ethylenediamine, and N,N'-dimethyl propylenediamine.

The alkylene amines include also those containing cyclic linkages such as are found in imidazolidines, imidazolines, and piperazines. Cyclic polyamines in which the amino nitrogen atoms are separated by at least one and no more than 3 carbon atoms are especially useful. Such amines may be illustrated by imidazoline, piperazine, 2-methylimidazoline, 2-heptyl-1-(2-aminopropyl) imidazolidine, 4-methyl-imidazoline, 1,3-bis(2-aminoethyl)imidazoline, pyrimidine, 1-(2-iminopropyl piperazine, 1,4-bis (2-aminoethyl)piperazine, 1-(2-(2 aminoethylamino)ethyl)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.

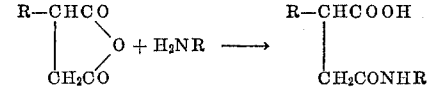
Alkylene amines having one or more hydroxyalkyl substituents on the nitrogen atoms also are contemplated for use in preparing the acylated nitrogen-containing compositions of (a) of this invention. Those having one hydroxyalkyl substituent on a nitrogen atom in which the alkyl group is a lower alkyl group, i.e., having less than about 6 carbon atoms, are especially useful. Examples include N-(2-hydroxyethyl)ethylenediamine, N,N'-bis(2-hydroxy ethyl)ethylenediamine, 1-(2-hydroxyethyl) piperazine, monohydroxypropyl-substituted diethylenetriamine, 1,4-bis(2-hydroxypropyl)piperazine, di(hydroxypropyl-substituted)tetraethylenepentamine, N-(3-hydroxypropyl)tetramethylenediamine, and 2-heptadecyl-1-(2-hydroxyethyl)imidazoline.

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

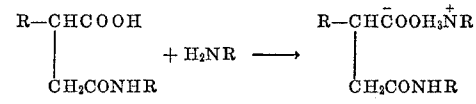
The ethylene amines are preferred. They are discussed in some detail under the heading "Ethylene Amines" in "Encyclopedia of Chemical Technology," Kirk and Othmer, vol. 5, pp. 898–905, Interscience Publishers, New York (1950). Such compounds are prepared most conveniently by the reaction of ethylene or propylene dichloride with ammonia. This process results in the production of somewhat complex mixtures of ethylene amines including cyclic condensation products such as piperazines and 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 ethylene amines. An especially useful ethylene amine, for reasons of economy as well as effectiveness as a dispersant, is a mixture of ethylene amines prepared by the reaction of ethylene chloride with ammonia having a composition which corresponds to that of tetraethylene pentamine. This is available in the trade under the trade name "Polyamine H."

It has been noted that at least one-half of a chemical equivalent amount of the amine per equivalent of substituted succinic anhydride must be used in the process to produce a satisfactory product with respect to dispersant properties and generally it is preferred to use these reactants in equivalent amounts. Amounts up to 2.0 chemical equivalents (per equivalent of substituted succinic anhydride) have been used with success, although there appears to be no advantage attendant upon the use of more than this amount. Based on the stoichiometry for the formation of amidine linkages, two moles of the amine may be used for each equivalent of the succinic reactant. The chemical "equivalency" of the amine reactant is based upon the nitrogen content, i.e., one having four nitrogens per molecule has four equivalents per mole.

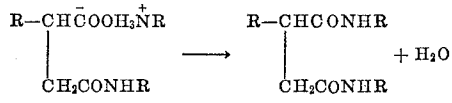
The reaction of the process involves a splitting out of water and the reaction conditions are such that this water is removed as it is formed. Presumably the first principal reaction that occurs, following salt formation, is the formation of a half amide.



followed then by salt formation

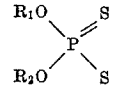


and involving finally dehydration of this salt to form the product



The first two of these reactions appear to take place spontaneously (when a substituted succinic anhydride is used) upon mixing, but the third requires heating. Temperatures within the range of about 80° C. to about 200° C. are satisfactory, and within this range it is preferred to use a reaction temperature of from about 100° C. to about 160° C. A useful method of carrying out this step is to add some toluene to the reaction mixture and to remove the water by azeotropic distillation. As indicated before there is also some imide-formation. When a hydroxyalkyl-substituted alkylene amine is used in the process, a certain amount of ester linkages may be formed between the acid radical of the succinic reactant and the hydroxy radical of the amine. Such ester linkages are not formed in appreciable amounts and apparently are not detrimental to the effectiveness of the products of the process.

Component (a) is unique in that it acts as a dispersant in lubricant compositions although it contains no metal within its molecular structure. Component (b) on the other hand may be any of several well known inhibitors all of which are phosphorothioates. They include the Group II metal salts of phosphorodithioic acids having the structure



in which R_1 and R_2 are substantially hydrocarbon radicals. The metals for forming such salts are exemplified by barium, calcium, strontium, zinc, and cadmium. A preferred class of the phosphorodithioates are those having at least about 7.6 carbon atoms in the hydrocarbon radicals per atom of phosphorus in the phosphorodithioate molecular structure. The barium and zinc phosphorodithioates are especially preferred. These 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 carbinyl, heptyl, 2-ethylhexyl, diisobutyl, isooctyl, nonyl, behenyl, decyl, etc. Illustrative lower alkylphenyl radicals include butylphenyl, amylphenyl, diamylphenyl, 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, butylnaphthyl, hexylnaphthyl, octylnaphthyl, cyclohexylphenyl, naphthenyl, etc. Many substituted hydrocarbon radicals may also be used, e.g., chloropentyl, 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 phenol 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 phosphrous pentasulfide with four moles of n-hexyl alcohol at about 100° C. for about two hours. Hydrogen sulfied 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 i.e., acids prepared from 1 alcohol, phosphorodithioic 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 composition 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 8 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 include, for example, butyl 9,10-epoxy-stearate, epoxidized soya bean 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 300° C. Because the reaction is exothermic it is best carried out by adding on 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-hexene.

The chemical structure of the adduct is not known. For the purpose of this invention adducts obtained by the reaction of one mole of the phosphorodithioate with from about 0.25 mole to 5 moles, usually up to about 0.75 mole or about 0.5 mole of a lower alkylene oxide, particularly ethylene oxide and propylene oxide, have been found to be especially useful and therefore are preferred.

The preparation of such adducts is more specifically illustrated by the following example: To 394 parts (by weight) of zinc dioctylposphorodithioate having a phosphorus content of 7% there is added at 75°–85° C., 13 parts of propylene oxide (0.5 mole per mole of the zinc phosphorodithioate) throughout a period of 20 minutes. The mixture is heated at 82°–85° C. for 1 hour and filtered. The filtrate (399 parts) is found to contain 6.7% of phosphorus, 7.4% of zinc, and 4.1% of sulfur.

In lieu of the phosphorodithioate inhibitor, other inhibitors may be used in conjunction with the acylated amine in a lubricant. Such other inhibitors are exemplified by alkylated phenols or naphthols preferably hindered phenols such as 4-methylene bis - (2,6-di-tertiary-butylphenol) or 2,6-di-tertiarybutyl - 4 - octylphenol; sulfurized hydrocarbons such as sulfurized terpentine, dibutyl disulfide, or dipentene disulfide; sulfurized fatty materials such as sulfurized sperm oil or sulfurized methyl oleate; phosphosulfurized hydrocarbon or fatty materials such as the reaction products of dipentene with phosphorus pentasulfide, oleic acid with phosphorus pentasulfide or tall oil with phosphorous sesquesulfide; any other known inhibitors.

The combination of additives of this invention have been found to be effective in many different types of lubricating oils. Oils derived from paraffinic and asphaltic crudes are benefited thereby as well as all of the ordinarily available synthetic lubricants. These latter include the polyethers, vegetable oils, polyesters, silicones, etc.

The following examples illustrate the process for preparing the acylated nitrogen-containing compositions.

Example 1

A polyisobutenyl succinic anhydride was prepared by the reaction of a chlorinated polyisobutylene with maleic anhydride at 200° C. The polyisobutenyl radical had an average molecular weight of 850 and the resulting alkenyl succinic anhydride was found to have an acid number of 113 (corresponding to an equivalent weight of 500). To a mixture of 500 grams (1 equivalent) of this polyisobutenyl succinic anhydride and 160 grams of toluene there was added at room temperature 35 grams (1 equivalent) of diethylene triamine. The addition was made portionwise throughout a period of 15 minutes, and an initial exothermic reaction caused the temperature to rise to 50° C. The mixture then was heated and a water-toluene azeotrope distilled from the mixture. When no more water would distill the mixture was heated to 150° C. at reduced pressure to remove the toluene. The residue was diluted with 350 grams of mineral oil and this solution was found to have a nitrogen content of 1.6%.

Example 2

The procedure of Example 1 was repeated using 31 grams (1 equivalent) of ethylene diamine as the amine reactant. The nitrogen content of the resulting product was 1.4%.

Example 3

The procedure of Example 1 was repeated using 55.5 grams (1.5 equivalents) of an ethylene amine mixture having a composition corresponding to that of triethylene tetramine. The resulting product had a nitrogen content of 1.9%.

Example 4

The procedure of Example 1 was repeated using 55.0 grams (1.5 equivalents) of triethylene tetramine as the amine reactant. The resulting product had a nitrogen content of 2.5%.

Example 5

To a mixture of 140 grams of toluene and 400 grams (0.78 equivalent) of a polyisobutenyl succinic anhydride (having an acid number of 109 and prepared from maleic anhydride and the chlorinated polyisobutylene of example 1) there was added at room temperature 63.6 grams (1.55 equivalents) of an ethylene amine mixture having an average composition corresponding to that of tetraethylene pentamine and available from Carbide and Carbon under the trade name "Polyamine H." The mixture was heated to distill the water-toluene azeotrope and then to 150° C. at reduced pressure to remove the remaining toluene. The residual polyamide had a nitrogen content of 4.7%

Example 6

The procedure of Example 1 was repeated using 46 grams (1.5 equivalents) of ethylene diamine as the amine reactant. The product which resulted had a nitrogen content of 1.5%.

Example 7

A polyisobutenyl succinic anhydride having an acid number of 105 and an equivalent weight of 540 was prepared by the reaction of a chlorinated polyisobutylene (having an average molecular weight of 1,050 and a chlorine content of 4.3%) and maleic anhydride. To a mixture of 300 parts by weight of the polyisobutenyl succinic anhydride and 160 parts by weight of mineral oil there was added at 65–95° C. an equivalent amount (25 parts by weight) of Polyamine H (identified in Example 5). This mixture then was heated to 150° C. to distill all of the water formed in the reaction. Nitrogen was bubbled through the mixture at this temperature to insure removal of the last traces of water. The residue was diluted by 79 parts by weight of mineral oil and this oil solution found to have a nitrogen content of 1.6%.

Example 8

A mixture of 2,112 grams (3.9 equivalents) of the polyisobutenyl succinic anhydride of Example 7, 136 grams (3.9 equivalents) of diethylene triamine, and 1,060 grams of mineral oil was heated at 140–150° C. for one hour. Nitrogen was bubbled through the mixture at this temperature for four more hours to aid in the removal of water. The residue was diluted with 420 grams of mineral oil and this oil solution was found to have a nitrogen content of 1.3%.

Example 9

To a solution of 1,000 grams (1.87 equivalents) of the polyisobutenyl succinic anhydride of Example 7, in 500 grams of mineral oil there was added at 85–95° C., 70 grams (1.87 equivalents) of tetraethylene pentamine. The mixture then was heated at 150–165° C. for four hours, blowing with nitrogen to aid in the removal of water. The residue was diluted with 200 grams of mineral oil and the oil solution found to have a nitrogen content of 1.4%.

Example 10

A polypropenyl succinic anhydride was prepared by the reaction of a chlorinated polypropylene (having a molecular weight of about 900 and a chlorine content of 4%) and maleic anhydride at 200° C. The product had an acid number of 75. To a mixture of 390 grams (0.52 equivalent) of this polypropenyl succinic anhydride, 500 grams of toluene, and 170 grams of mineral oil there was added portionwise 22 grams (0.52 equivalent) of Polyamine H. The reaction mixture was heated at reflux temperature for three hours and water removed from an azeotrope with toluene. The toluene then was removed heating to 150° C./20 millimeters. The residue was found to contain 1.3% of nitrogen.

Example 11

A substituted succinic anhydride was prepared by reacting maleic anhydride with a chlorinated copolymer of isobutylene and styrene. The copolymer consisted of 94 parts by weight of isobutylene units and 6 parts by weight of styrene units, had an average molecular weight of 1,200, and was chlorinated to a chlorine content of 2.8% by weight. The resulting substituted succinic anhydride had an acid number of 40. To 710 grams (0.51 equivalent) of this substituted succinic anhydride and 500 grams of toluene there was added portionwise 22 grams (0.51 equivalent) of Polyamide H. The mixture was heated at reflux temperature for three hours to remove by azeotropic distillation all of the water formed in the reaction, and then at 150° C./20 millimeters to remove the toluene. The residue contained 1.1% by weight of nitrogen.

Example 12

A substituted succinic anhydride was prepared by reacting maleic anhydride with a chlorinated copolymer of isobutylene and isoprene. The copolymer consisted of 99 parts by weight of isobutylene units and 1% by weight of isoprene units. The molecular weight of the copolymer was 28,000 and the chlorine content of the chlorinated copolymer was 1.95%. The resulting alkenyl succinic anhydride had an acid number of 54. A stirred mixture of 228 grams (0.22 equivalent) of an oil solution of this alkenyl succinic anhydride, 58 grams of additional mineral oil, 500 grams of toluene and 9.3 grams (0.22 equivalent) of Polyamine H was heated at 110–120° C. for three hours, water being removed from an azeotrope with toluene. When all of the water had thus been removed the toluene was distilled by heating to 150° C./20 millimeters. The residue was found to have a nitrogen content of 1.1%.

Example 13

A polyisobutenyl succinic anhydride was prepared by the reaction of a chlorinated polyisobutylene with maleic anhydride. The chlorinated polyisobutylene had a chlorine content of 2% and an average molecular weight of 11,000. The polyisobutenyl succinic anhydride had an acid number of 48. A mixture of 410 grams (0.35 equivalent) of this anhydride, 15 grams (0.35 equivalent) of Polyamine H and 500 grams of toluene was heated at reflux temperature for four hours to remove water from an azeotrope with toluene. The toluene then was removed by heating to 150° C./20 millimeters. The nitrogen content of the residue was 1.3%.

Example 14

The procedure of Example 5 was repeated except that 0.94 equivalent of Polyamine H was used instead of 1.55 equivalents. The nitrogen content of the product was 3%.

Example 15

A polyisobutenyl-substituted succinic acid was prepared by hydrolysis of the corresponding anhydride (prepared in turn by the condensation of a chlorinated polyisobutylene and maleic anhydride). To 1152 grams (1.5 equivalents) of a 70% mineral oil solution of this polyisobutenyl succinic acid having an acid number of 62 there was added at room temperature 59.5 grams (1.5 equivalents) of Polyamine H. This mixture was heated at 150–167° C. for 7 hours during which time a total of 19.5 grams of water was distilled from the mixture. The residue was diluted with 174 grams of mineral oil and then filtered at 150° C. The filtrate had a nitrogen content of 1.6%.

Example 16

A mixture of 1,056 grams (2.0 equivalents) of the polyisobutenyl succinic anhydride of the preceding example (in which the polyisobutenyl group has a molecular weight of 850), 89 grams (2.0 equivalents) of di-(1,2-propylene) triamine (having a nitrogen content of 31.3%), 370 grams of mineral oil and 100 grams of toluene was heated at reflux temperature (180–190° C.) for 5 hours. A total of 18 grams of water was collected from the water-toluene azeotrope. The residue was heated to 150° C. 20 mm. to remove any last traces of water which might have remained. The nitrogen analysis of this residue was 1.9%.

Example 17

A polyisobutylene having an average molecular weight of 50,000 was chlorinated to a chlorine content of 10% by weight. This chlorinated polyisobutylene was reacted with maleic anhydride to produce the corresponding polyisobutenyl succinic anhydride having an acid number of 24. To 6,000 grams (2.55 equivalents) of this anhydride there was added portionwise at 70–105° C., 108 grams (2.55 equivalents) of Polyamine H over a period of 45 minutes. The resulting mixture was heated for four

hours at 160–180° C. while nitrogen was bubbled throughout to remove water. When all of the water had been removed the product was filtered and the filtrate found to have a nitrogen content of 0.6%.

Example 18

A mixture of 1,000 grams (1.89 equivalents) of a polyisobutenyl succinic anhydride in which the polyisobutenyl group has an average molecular weight of 850, 60 grams (1.45 equivalents) of an ethylene amine mixture having a nitrogen content of 33.9%, 15 grams (0.44 equivalent) of diethylene triamine, and 161 grams of toluene was heated at 112–174° C. (reflux temperature) for 9 hours. A total of 17 ml. of water was removed from the toluene-water azeotrope. The residual product was found to have a nitrogen analysis of 1.4%.

Example 19

To a mixture of 396 grams of the polyisobutene-substituted succinic anhydride of Example 1 and 282 grams of mineral oil there was added 34 grams of N-methyl-trimethylene diamine at 60° C. within a period of one hour. The mixture was blown with nitrogen at 150°–155° C. for 5 hours. The residue was found to have a nitrogen content of 1.41%.

Example 20

A mixture of 308 grams of mineral oil, 400 grams of the polyisobutene-substituted succinic anhydride of Example 1, and 70 grams of N-(2-ethylhexyl)-trimethylenediamine was prepared at 60° C. The mixture was heated to 250° C. and was then blown with nitrogen at 150°–155° C. for 5 hours. The residue had a nitrogen content of 1.4%.

Example 21

A mixture of 386 grams of mineral oil, 528 grams of the polyisobutene-substituted succinic anhydride of Example 1, and 59 grams of N-(2-hydroxyethyl)-trimethylenediamine was prepared at 60° C. The mixture was blown with nitrogen at 150°–155° C. for 5 hours. The residue had a nitrogen content of 1.56%.

Example 22

A mixture of 185 grams of mineral oil, 330 grams of the polyisobutene-substituted succinic anhydride of Example 1, and 88.5 grams of 1,4-bis(2-hydroxypropyl)-2-methylpiperazine was prepared at 60° C. The mixture was heated at 180°–276° C./40 mm. for 14.5 hours. The residue had a nitrogen content of 1.12%.

Example 23

To a mixture of 314 grams of mineral oil and 430 grams of the polyisobutene-substituted succinic anhydride of Example 1 there was added at 60° C., 49 grams of 1-(2-hydroxyethyl)piperazine. The mixture was heated to 150° C. and blown with nitrogen at this temperature for 5 hours. The residue had a nitrogen content of 1.38%.

Example 24

A mixture of 382 grams of mineral oil, 528 grams of the polyisobutene-substituted succinic anhydride of Example 1, and 53 grams of 1-methyl-4-(3-aminopropyl) piperazine was prepared at 60° C., heated to 150° C., and blown with nitrogen at 150°–155° C. for 5 hours. The residue had a nitrogen content of 1.57%.

Example 25

A mixture of 355 grams of mineral oil, 430 grams of the polyisobutene-substituted succinic anhydride of Example 1, and 108 grams of N-(3-aminopropyl)morpholine was heated to 150° C. and blown with nitrogen at this temperature for 5 hours whereupon a total of 6 cc. of water was collected as the distillate. The residue had a nitrogen content of 2.3%.

Example 26

To a mixture of 800 grams of the polyisobutene-substituted succinic anhydride of Example 1 and 175 grams of toluene there was added 77 grams of a commercial mixture of alkylene amines and hydroxy alkyl-substituted amines consisting of approximately 2% (by weight) of diethylene triamine, 36% of 1-(2-aminoethyl) piperazine, 11% of 1-(2-hydroxyethyl)piperazine, 11% of N-(2-hydroxyethyl)ethylenediamine, and 40% of higher homologues obtained as a result of condensation of the above-indicated amine components. The resulting mixture was heated at the reflux temperature for 16.5 hours whereupon 12 cc. of water was collected as the distillate. The residue was then heated to 160° C./25 mm. and diluted with 570 grams of mineral oil. The final product was found to have a nitrogen content of 1.57%.

Example 27

A mixture of 920 grams of the polyisobutene-substituted succinic anhydride of Example 1, 249 grams of bis-(3-aminopropyl)amine, and 266 grams of toluene was heated at the reflux temperature for 6 hours and then to 220° C./3 mm. The residue had a nitrogen content of 4%.

Example 28

To a mixture of 1000 grams of the polyisobutene-substituted succinic anhydride of Example 1 and 500 grams of mineral oil there was added at 70°–95° C. 159 grams of methane diamine. The reaction was exothermic. The mixture was heated at 150°–190° C. for 10 hours, diluted with 258 grams of mineral oil and filtered at 160° C. The filtrate had a nitrogen content of 1.37%.

Example 29

A mixture of 333 grams of bis-(3-aminopropyl)ether of ethylene glycol, 1000 grams of the polyisobutene-substituted succinic anhydride of Example 1, and 500 grams of mineral oil was prepared at 65°–90° C. The mixture was heated at 140°–170° C. for 5 hours whereupon a total of 17.5 cc. of water was collected as the distillate. The residue was diluted with 380 grams of mineral oil and filtered at 160° C. The filtrate had a nitrogen content of 2.4%.

Example 30

A mixture of 418 grams of bis-(3-aminopropyl)ether of diethylene glycol, 1000 grams of the polyisobutene-substituted succinic anhydride of Example 1, and 500 grams of mineral oil was prepared at 70°–100° C. The mixture was heated at 150°–170° C. for 4 hours whereupon 16.7 cc. of water was collected as the distillate. The residue was diluted with 433 grams of mineral oil and filtered at 160° C. The filtrate had a nitrogen content of 2.27%.

As indicated previously the acylated nitrogen-containing composition is usually present in lubricating oils in amounts ranging from about 0.1% to about 10% by weight and the phosphorothicate additive is usually present in amounts such as to impart from about 0.001% to about 2% by weight of phosphorus to the final lubricating composition. The optimum amounts for a particular application depend to a large measure upon the type of surface to which the lubricating composition is to be subjected. Thus, for example, lubricating compositions for use in gasoline internal combusion engines may contain from about 0.01% to about 0.5% of phosphorus and the phosphorothioate additive whereas lubricating compositions for use in gears and diesel engines may contain as much as 1% or 2% of phosphorus as the additive. On the other hand, lubricating compositions for use in a 2-cycle outboard motor engines may contain as little as 0.005% or even less of phosphorus as the additive. Similarly, lubricating compositions for use in gasoline

internal combustion engines may contain from about 0.5 to about 5% of an acylated nitrogen-containing 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, 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 a phosphorizing agent such as phosphorus trichloride, phosphorus heptasulfide, phosphorus pentasulfide, phosphorus trichloride and sulfur, white phosphorus and a sulfur halide, or phosphrothoric 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 above 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 formaledhyde with a phenolic substance; alcohols such as methanol, 2-propanol, octyl alcohol, Cellosolve, carbitol, ethylene glycol, stearyl alcohol, and cyclohexyl alcohol; amines such as aniline, 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, as a small amount of water and carbonating the mixture at an elevated temperature such as 60°–200° C.

Extreme pressure addition agents are exemplified by chlorinated aliphatic hydrocarbons such as chlorinated wax; organic sulfides and polysulfides such as benzyl disulfide, bis-(chlorobenzyl) disulfide, dibutyl tetrasulfide, sulfurized sperm oil, sulfurized methyl ester of oleic acid, sulfurized algylphenol, sulfurized dipentene, and sulfurized terpene; phosphosulfurized hydrocarbons such as the reaction product of a phosphorus sulfide with turpentine or methyl oleate; phosphorous esters including principally dihydrocarbon and trihydrocarbon phosphites such as dibutyl phosphite, diheptyl phosphite, dicyclohexyl phosphite, pentyl phenyl phosphite, diphenyl phenyl phosphite, tridecyl phosphite, distearyl phosphite, dimethyl naphthyl phosphite, oleyl 4-pentylphenyl phosphite, polypropylene (molecular weight 500)-substituted phenyl phosphite, diisobutyl substituted phenyl phosphite; metal triocarbamates such as zinc dioctyl-dithiocarbamate, and barium heptylphenyl dithiocarbamate.

The lubricating compositions may also contain 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 a detergent additive. They may also 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 and 0.05% of phosphorus as the zinc salt of a phosphorodithioic acid prepared by the reaction of phosphorus pentasulfide with an equimolar mixture of methyl alcohol an n-octyl alcohol.

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 7 and 0.075% of phosphorus as zinc di-n-octyl-phosphorodithioic acid.

Example IV

SAE 90 mineral lubricating oil containing 0.1% of the products of Example 7 and 0.15% of the zinc salt of an equimolar mixture of di-cyclohexylphosphorodithioic and di-isobutylphosphorodithioic acid.

Example V

SAE 30 mineral lubricating oil containing 2% of the product of Example 3, 0.02% of phosphorous as zinc dicyclohexylphosphorodithioate and 0.04% of phosphorus as zinc di-dodecylphosphorodithioate.

Example VI

SAE 20W–30 mineral lubricating oil containing 5% of the product of Example 4 and 0.05% of phosphorus as barium di-heptyl-phenylphosphorodithioate.

Example VII

SAE 10W–30 mineral lubricating oil containing 1.5% of the product of Example 5 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 6 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 8, 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 9, 0.1% of phosphorus as the zinc salt of a mixture of equimolar amounts of di-isopropylphosphorodithioic 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.

Example XI

SAE 10W–30 mineral lubricating oil containing 6% of the product of Example 25, 0.075% of phosphorus as the adduct obtained by treating zinc di-n-octylphosphorodithioate with 0.5 mole of propylene oxide at room

temperature, and 5% of the barium salt of an acidic composition prepared by the reaction of 1000 parts of a polyisobutene having a molecular weight of 60,000 with 1 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 24, 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 products of Example 30, 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 13, 0.05% of phosphorus as the adduct of zinc di-heptylphosphorodithioate with 0.5 mole of 1,2-butene oxide, 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 pressure 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 2% of the product of Example 14, 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 15, 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 16, 0.075% of phosphorus as the adduct of 0.5 mole of propylene oxide with 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 30 mineral lubricating oil containing 2% of the product of Example 17 and 0.07% of phosphorus as the adduct of zinc di-n-octylphosphorodithioate with 0.25 mole of propylene oxide.

Example XIX

SAE 30 mineral lubricating oil containing 3% of the product of Example 18 and 0.1% of phosphorus as the adduct of zinc di-(isobutylphenyl)-phosphorodithioate with 0.4 mole of epichlorohydrin.

Example XX

SAE 50 mineral lubricrating oil containing 2% of the product of Example 19 and 15% of phosphorus as the adduct of zinc di-primary-pentylphosphorodithioate with 0.3 mole of styrene oxide.

Example XXI

SAE 90 mineral lubricating oil containing 3% of the product of Example 20 and 0.2% of phosphorus as the adduct of zinc di-dodecylphosphorodithioate with 0.25 mole of 3,4-hexene oxide.

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

The usefulness of the combination of additives of this invention in motor oils is illustrated by the results obtained from an Oxidation-Dispersancy test in which a 350-ml. sample of a mineral oil containing 0.001% of iron naphthenate and the additive to be tested is heated at 300° F. for 48 hours in a 2 x 15" borosilicate tube. A clean copper-lead bearing is immersed in this solution along with an SAE 1020 steel test panel. Air is bubbled through the solution at the rate of 10 liters per hour. The oxidized sample is allowed to cool to 122° F. whereupon 0.5% (by volume) of water is added and dispersed into the sample. The sample is allowed to stand for 16 hours at room temperature and then filtered through dry, number one Whatman paper (double thickness) under slightly reduced pressure. The precipitant is washed with naphtha to constant weight and reported as mgs. of sludge per 100 ml. of oil. The bearing is scrubbed with naphtha, dried and weighed, and the bearing weight change is reported in mgs.

The performance of the additive combinations of this invention in this test is shown in the following table:

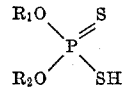
Lubricant	Additives	Bearing Weight Change (mgs.)	Sludge (mgs.)
1	1.5% of product of Example 7. 0.06% (as phosphorus) of a zinc salt of a phosphorodithioic acid prepared from a 65-35 molar mixture of isobutyl alcohol and mixed primary amyl alcohols.	−8.3	100
2	1.5% of the product of Example 7.	−206.2	102
3	2.5% of the product of Example 7.	−201.7	2.2
4	0.06% (as phosphorus) of the zinc phosphorodithioate of Lubricant 1.	+0.4	990
5	0.31% (as phosphorus) of the zinc phosphorodithioate of Lubricant 1.	0	1,124
6	1.5% of the product of Example 7. 0.1% (as phosphorus) of the barium salt of a phosphorodithioic acid prepared by the reaction of phosphorus pentasulfide with a 50-37-13 molar mixture of octyl, methyl-cyclohexyl and hexyl alcohols.	−3.6	0.7
7L	0.9% of the product of Example 7. 0.1% (as phosphorus) of the barium phosphorodithioate of Lubricant 6.	−6.5	20
8	0.1% (as phosphorus) of the barium phosphorodithioate of Lubricant 6.	−2.7	834
9	0.19% (as phosphorus) of the barium phosphorodithioate of Lubricant 6.	−11.9	1,215

Lubricant	Additives	Bearing Weight Change (mgs.)	Sludge (mgs.)
10	1.5% of the product of Example 7. 0.07% (as phosphorus) of zinc di-(heptylphenyl) phosphorodithioate.	−10.9	0.7
11	1.5% of the product of Example 7. 0.018% (as phosphorus) of zinc di-(heptylphenyl) phosphorodithioate.	−7.4	16.4
12	0.07% (as phosphorus) of zinc di-(heptylphenyl) phosphorodithioate.	1.1	850
13	1.5% of the product of Example 7. 0.04% (as phosphorus) of zinc di-(methylcyclohexyl) phosphorodithioate.	−2.8	32.1
14	0.04% (as phosphorus) of zinc di-(methylcyclohexyl) phosphorodithioate.	−0.5	365
15	1.5% of the product of Example 13. 0.1% (as phosphorus) of the barium phosphorodithioate of Lubricant 6.	−2.2	23.9
16	1.5% of the product of Example 13.	−117.6	16.8
17	0.1% (as phosphorus) of the barium phosphorodithioate of Lubricant 6.	−2.7	834
18	1.5% of a product prepared in Example 17 except that the chlorinated polyisobutylene contained 3.5% Cl. 0.1% (as phosphorus) of the barium phosphorodithioate of Lubricant 6.	−3.4	3.1
19	1.5% of a product prepared as in Example 17 except that the chlorinated polyisobutylene contained 3.5% Cl.	−91.4	3.8
20	1.5% of the product of Example 14. 0.1% of the barium phosphorodithioate of Lubricant 6.	−21.5	3.3
21	1.5% of the product of Example 14.	−145.9	4.6
22	1.5% of a product prepared as in example 2 except that the succinic anhydride: diethylene triamine equivalent ratio was 1:1.2. 0.1% (as phosphorus) of the barium phosphorodithioate of Lubricant 6.	1.7	6.6
23	1.5% of a product prepared as in Example 2 except that the succinic anhydride: diethylene triamine equivalent ratio was 1:1.2.	----------	----------
24	2.5% of a product prepared as in Example 2 except that the succinic anhydride: diethylene triamine equivalent ratio was 1:1.2.	−244.8	1.5
25	1.5% of the product of Example 7. 0.06% (as phosphorus) of the adduct of zinc di-n-octylphosphorodithioate with 0.5 mole of propylene oxide.	−1.8	120
26	0.06% (as phosphorus) of the adduct of barium phosphorodithioate of Lubricant 6 with 0.5 mole of propylene oxide.	−8.3	680
27	1.5% of the product of Example 7. 0.06% (as phosphorus) of the adduct of barium phosphorodithioate of Lubricant 6 with 0.5 mole of propylene oxide.	−9.8	4.8
28	0.06% (as phosphorus) of the adduct of zinc di(4-methyl-2-pentyl)-phosphorodithioate with 0.5 mole of propylene oxide.	−1	570
29	1.5% of the product of Example 7. 0.06% (as phosphorus) of the adduct of zinc di-(4-methyl-2-pentyl)-phosphorodithioate with 0.5 mole of propylene oxide.	−2.9	25.2
30	0.06% (as phosphorus) of the adduct of zinc di-n-octylphosphorodithioate with 0.5 mole of propylene oxide.	−1.8	415
31	0.06% (as phosphorus) of the adduct of zinc di-n-octylphosphorodithioate with 0.5 mole of 1,2-octylene oxide.	−1.5	820
32	1.5% of the product of Example 7. 0.06% (as phosphorus) as the adduct of zinc di-n-octylphosphorodithioate with 0.5 mole of 1,2-octylene oxide.	−5.3	34.2

It will be noted from the data of the above table that only a combination of additives is effective in meeting both requirements of the test, i.e., a minimum weight loss of the copper-lead bearing and of sludge formation. The use even of very large amounts of either additives alone, as in lubricants 3, 5, 9 and 24, does not provide a satisfactory lubricant. It is necessary to use both of these additives.

What is claimed is:

1. A lubricating composition comprising a major proportion of a lubricating oil and a minor proportion of each of: (a) an oil-soluble acylated nitrogen composition characterized by the presence within its structure of (A) a substantially saturated hydrocarbon-substituted polar group containing a radical selected from the class consisting of succinoyl, succinimidoyl and succinoyloxy radicals wherein said substantially saturated hydrocarbon substituent contains at least about 50 aliphatic carbon atoms, and (B) a nitrogen-containing group characterized by a nitrogen atom attached directly to said polar group, said nitrogen containing group being derived from an alkylene polyamine or a hydroxyalkyl-substituted alkylene polyamine; and (b) a phosphorodithioate selected from the class consisting of oil-soluble Group II metal salts of phosphorodithioic acids having the structural formula



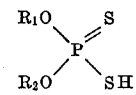
wherein R_1 and R_2 are hydrocarbon radicals each having from 1 to about 30 aliphatic carbon atoms and adducts of said metal salts with a lower alkylene oxide having up to about 8 carbon atoms.

2. The lubricating composition of claim 1 wherein the nitrogen-containing group of (a)(B) is derived from an alkylene polyamine having up to about 11 amino groups and R_1 and R_2 of the structural formula of (b) are selected from the class consisting of alkyl radicals and alkylphenyl radicals.

3. The lubricating composition of claim 1 wherein the substantially saturated hydrocarbon substituent of (a)(A) is a butene polymer radical having a molecular weight within the range of from about 700 to about 5000; the nitrogen containing group of (a)(B) is derived from an alkyklene polyamine having up to about 11 amino groups; and the phosphorodithioate of (b) is a zinc dialkylphosphorodithioate.

4. The lubricating composition of claim 1 wherein the substantially saturated hydrocarbon substiutent of (a)(A) (is a polyisobutene radical having a molecular weight of from about 700 to about 5000; a nitrogen containing group of (a)(B) is derived from a polyethylene polyamine having up to about 11 amino groups; and the phosphorodithioate of (b) is a zinc dialkylphosphorodithioate.

5. A lubricating composition comprising a major proportion of a lubricating oil and (a) from about 0.1% to about 10% by weight of an oil-soluble acylated nitrogen composition prepared by the process which comprises the reaction of a substantially saturated hydrocarbon substituted succinic acid or anhydride wherein the substantially saturated hydrocarbon substituent has at least about 50 aliphatic carbon atoms with at least about 0.5 equivalent of an alkylene polyamine or hydroxyalkyl substituted alkylene polyamine and (b) from about 0.001% to about 2% by weight as phosphorus of a phosphorodithioate selected from the class consisting of oil-soluble Group II metal salts of phosphorodithioic acids having the structural formula



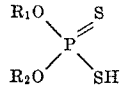
wherein R_1 and R_2 are hydrocarbon radicals each having from 1 to about 30 aliphatic carbon atoms and adducts of said metal salts with a lower alkylene oxide having up to about 8 carbon atoms.

6. The lubricating composition of claim 5 wherein the substantially saturated hydrocarbon substituent of (a) is a polyisobutene radical having a molecular weight of from about 700 to about 5000; the amine of (a) is a polyethylene polyamine having up to about 11 amino groups; and the phosphorodithioate of (b) is a zinc di-

alkylphosphorodithioate or zinc dialkylphenylphosphorodithioate.

7. A lubricating composition comprising a major proportion of a lubricating oil and (a) from about 0.1 to 10% by weight of an oil-soluble acylated nitrogen composition prepared by the process comprising reacting a polyisobutene substituted succinic anhydride or acid wherein the polyisobutene substituent has a molecular weight of from about 700 to about 5000 with from about 0.5 equivalent to 2 moles, per equivalent of the succinic reactant, of an alkylene polyamine having up to about 11 amino groups and (b) from about 0.001% to about 2% by weight as phosphorus of a zinc dialkylphosphorodithioate wherein the alkyl radicals contain a total of at least about 7.6 carbon atoms per phosphorus atom in the phosphorodithioate, or an adduct of said phosphorodithioate with up to about 0.75 mole, per mole of said phosphorodithioate, of ethylene oxide or propylene oxide.

8. A lubricating composition comprising a major proportion of a lubricating oil and (a) from about 0.1% to about 10% by weight of an oil-soluble acylated nitrogen-containing composition prepared by the process comprising reacting maleic anhydride with an olefin polymer or a chlorinated olefin polymer, wherein the polymer has a molecular weight of from about 700 to about 100,000, to form a substituted carboxylic anhydride, mixing said carboxylic anhydride or the corresponding acid thereof with an alkylene polyamine or hydroxyalkyl-substituted alkylene polyamine, and heating the resulting mixture to effect acylation; and (b) from about 0.001% to about 2% be weight as phosphorus of a phosphorodithioate selected from the class consisting of oil-soluble Group II metal salts of phosphorodithioic acids having the structural formula

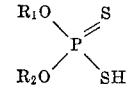


wherein R_1 and R_2 are hydrocarbon radicals each having from 1 to about 30 aliphatic carbon atoms and adducts of said metal salts with a lower alkylene oxide having up to about 8 carbon atoms.

9. The lubricating composition of claim 8 wherein the polymer of (a) is a polymer of butene; the polyamine of (a) is a polyethylene polyamine having up to about 11 amino groups; and the phosphorodithioate of (b) is a zinc dialkylphosphorodithioate.

10. The lubricating composition of claim 8 wherein the polymer of (a) is a polyisobutene having a molecular weight of from about 700 to about 5000; the polyamine of (a) is a polyethylene polyamine having up to about 11 amino groups; and the phosphorodithioate of (b) is a zinc dialkylphosphorodithioate.

11. The lubricating composition of claim 8 wherein the oil-soluble acylated nitrogen-containing composition of (a) is prepared by the process comprising reacting maleic anhydride with a homopolymer of isobutylene having an average molecular weight of from about 750 to about 5000 to form a substituted carboxylic anhydride, mixing said substituted carboxylic anhydride with from about 0.4 to about 1.5 moles of a polyethylene polyamine and heating the resulting mixture to effect acylation and to remove the water formed thereby; and the phosphorodithioate of (b) is a zinc salt of a phosphorodithioic acid having the structural formula



wherein R_1 and R_2 are alkyl radicals each having from 1 to about 30 carbon atoms, the total of said carbon atoms being at least about 7.6 per phosphorus atom.

12. A lubricating oil composition comprising a major proportion of mineral lubricating oil and from about 0.1 to 5.0 percent by weight of a dispersant formed by the reaction of maleic anhydride with a material selected from the class consisting of aliphatic olefin polymers and chlorinated aliphatic hydrocarbons to form a substituted carboxylic acid anhydride having from 50 to 200 aliphatic carbon atoms in the substituent group with further reaction of said acid anhydride with at least an equivalent amount of an alkylene amine having up to 10 alkylene groups and from 2 to 10 carbon atoms in each alkylene group and heating the resulting mixture to effect acylation and remove the water formed thereby, and, in an amount sufficient to further enhance the wear and dispersant characteristics of the composition, of an oil-soluble zinc di-lower-alkyl phosphorodithioate.

References Cited

UNITED STATES PATENTS

2,689,220	9/1954	Mulvany.	
2,723,235	11/1955	Asseff et al.	
2,838,555	6/1958	Goldsmith.	
2,977,334	3/1961	Zopf et al.	252—56 XR
3,018,247	1/1962	Anderson et al.	

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