It is another object of this invention to provide additives adapted especially for use with metal phosphorodithioates in hydrocarbon oils.

It is also an object of this invention to provide lubricating compositions containing metal phosphorodithioates which compositions are characterized by an improved resistance to thermal deterioration.

These and other objects are attained in accordance with this invention by providing a process for preparing acylated amines which comprises heating at a temperature above about 80°C an alkylene amine with from about 0.5 to about 1 equivalent for each equivalent of the alkylene amine used of an acidic mixture consisting of a hydrocarbon-substituted succinic acid having at least about 50 aliphatic carbon atoms in the hydrocarbon radical and an aliphatic mono-carboxylic acid, the ratio of equivalents of said succinic acid to said mono-carboxylic acid in said acidic mixture being from about 1:1 to about 1:1 and removing the water formed thereby.

The term "alkylene amine" is used herein in a general sense to denote a class of polyamines conforming for the most part to the structure

\[ \text{H}_2\text{N}-(\text{Alkylene NH})_{\text{x}}\text{H} \]

in which \( x \) is an integer preferably less than about six and the alkylene radical is preferably a lower alkylene radical such as ethylene, propylene, trimethylene, tetra-ethylene, or the like. Thus, it includes, for example, ethylene diamine, diamethylene diamine, triethylene tetramine, tetraethylene pentamine, trimethylene diamine, propylene diamine, tetramethylene diamine, butylene diamine, N-aminoethyl trimethylene diamine, N-dodecyl propylene diamine, di-(trimethylene) triamine, penta- ethylene hexamine, etc. It includes also higher and cyclic homologues of such amines such as piperazines. The alkylene amines are especially useful. They are discussed in some detail under the heading "Ethylene Amines" in "Encyclopedia of Chemical Technology" by K. E. Othmer, volume 5, pages 998-995, Interscience Publishers, New York (1950). Such compounds are prepared most conveniently by the reaction of alkylene dihalides, e.g., ethylene dichloride, with ammonia or primary amines. This reaction results in the production of somewhat complex mixtures of alkylene amines including cyclic condensation products such as piperazine, N-aminoethyl-piperazine, etc. 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 having a composition which corresponds to that of tetraethylene pentamine.

The aliphatic mono-carboxylic acids contemplated for use in the process of this invention include saturated and unsaturated acids. Examples of useful acids are acetic acid, chloroacetic acid, dodecanolic acid, butanolic acid, palmitic acid, decanoic acid, oleic acid, stearic acid, linoleic acid, linolenic acid, naphthenic acid, chlorostearic acid, formic acid, tallow acid, etc. Acids having 12 or more aliphatic carbon atoms, particularly stearic acid and oleic acid, are especially useful.

Aliphatic mono-carboxylic acids useful in the process of this invention may be iso-aliphatic acids, i.e., acids having one or more lower acyclic pendant alkyl groups. The iso-aliphatic acids result in products which are more readily soluble in hydrocarbon oils at relatively high concentrations and more readily miscible with other additives in the oil. Hence, they are preferred especially when the products of the process are to be used in lubricants.
containing other additives. Such acids often contain a principal chain having from 14 to 20 saturated, aliphatic carboxy-ethyl, isobutyl, isovaleryl, lauryl, or other radical groups having no more than 4 pendant acyclic alkyl groups. The principal chain of the acid is exemplified by radicals derived from tetradecane, pentadecane, hexadecane, heptadecane, octadecane, and eicosane. The pendant group is preferably a lower alkyl radical such as methyl, ethyl, n-propyl, iso-propyl, terti-butyl, isovaleryl, lauryl, or other radical having less than about 6 carbon atoms. The pendant group may also be a polar-substituted alkyl radical such as chloromethyl, bromomethyl, methoxyethyl, or the like, but it preferably contains no more than one polar substituent per radical. Specific examples of such acids are iso-aliphatic acids such as 10-methyl-tetradecanoic acid, 11-methyl-pentadecanoic acid, 3-ethylhexadecanoic acid, 15-methyl-heptadecanoic acid, 16-methyl-heptadecanoic acid, 6-methyl-octadecanoic acid, 8-methyl-octadecanoic acid, 10-methyl-octadecanoic acid, 14-methyl-octadecanoic acid, 16-methyl-octadecanoic acid, 15-ethyl-heptadecanoic acid, 3-chloromethyl-nonadecanoic acid, 2-methyl-cyclohexadienyl-oxo-9,10,13,16-tetramethyl-octadecanoic acid, and 2,9,10-trimethyl-octadecanoic acid.

An especially useful class of iso-aliphatic acids are the mixtures of branch-chain acids prepared by the isomerization of commercial fatty acid. A particularly useful method comprises the isomerization of an unsaturated fatty acid having from 16 to 20 carbon atoms, by heating it at a temperature above about 250°C and at a pressure between about 200 and 700 p.s.i. (pounds per square inch), distilling the crude isomerized acid, and hydrogenating the distillate to produce a substantially saturated isomerized acid. The isomerization is promoted by a catalyst such as zinc chloride, ferric chloride, or some other Friedel-Crafts catalyst. The concentration of the catalyst may be as low as 0.01%, but more often from 0.1% to 3% by weight of the isomerization mixture. Water also promotes the isomerization and a small amount, from 0.1% to 5% by weight, of water may thus be advantageously added to the isomerization mixture.

A by-product of the isomerization process is a polymerized unsaturated fatty acid. This product can be removed as the residue by distillation or as the insoluble fraction by solvent extraction, precipitation, or filtration of the reaction mixture. On the other hand, the desired isomerized product can be recovered, as above, as the distillate, usually by heating the reaction mixture under vacuum. The distillate may contain also the unreacted portion of the unsaturated fatty acid. However, upon hydrogenation, the isomerized acid and the unused starting acid yield significantly different products which can be separated by solvent extraction and precipitation. Thus, the hydrogenated product of the unreacted starting acid will be considerably higher melting and less soluble in a solvent such as acetone. The hydrogenation can be effected by any one of the well known methods such as catalytic hydrogenation in the presence of Raney nickel or platinum. The product of the hydrogenation should have an iodine number less than about 10.

The mechanism of the isomerization is not known. It is known, however, that the product of the isomerization is monomeric but structurally different from the starting acid in that its hydrocarbon radical now contains at least one branch chain.

The unsaturated fatty acids from which the iso-aliphatic acid mixture is derived include, in addition to oleic acid mentioned above, linoleic acid, linolenic acid, or commercial fatty acid mixtures such as tall oil acids containing a substantial portion of unsaturated fatty acids. The term "succi acid" as used herein includes both the succinic acids and the anhydrides of the acids. The anhydrides are preferred because of their greater reactivity. The hydrocarbon-substituted succinic acids useful in the process of this invention are those in which the hydrocarbon radical may be exemplified by an alkyl or alkenyl group containing at least 50 carbon atoms. They are commonly derived from polyolefins such as polyethylene, polypropylene, polybutene, etc. having molecular weights of 750 or higher. They may be likewise derived from substantially aliphatic hydrocarbon substances such as copolymers of isobutene with styrene. In the latter case the copolymers will be substantially aliphatic i.e., they will contain at least about 95% by weight of the units derived from aliphatic olefinic monomers.

The hydrocarbon-substituted succinic anhydrides are readily available from the reaction of maleic anhydride with a high molecular weight olefin or a chlorinated high molecular weight hydrocarbon. The reaction involves merely heating the two reactants at a temperature about 150°-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. A particularly preferred source of the hydrocarbon-substituted in the succinic acid is a polymer of lower mono-olefins having up to 6 carbon atoms such as polybutenes. The use of polyolefins having molecular weights of 1000-5000 is preferred. Higher molecular weight polyolefins are still more desirable. A particularly useful polymer is polyethylene having molecular weights from about 10,000 to about 100,000 or even higher have been found to impart also viscoelasticity improving properties to the product of this invention.

In many instances, the use of such higher molecular weight polyolefins is desirable. Other sources of the hydrocarbon substituent include petroleum fractions such as waxes, mineral oils, still bottoms, etc.

The size of the hydrocarbon substituent in the succinic acid molecule appears to determine the effectiveness of the product of this process as an additive in hydrocarbon oils for the purpose of this invention. Substituted succinic acids and their derivatives have been known for some time. It has likewise been known that these compounds are useful lubricants, but their utility heretofore has been predicated upon their rust-preventing properties, corrosion-inhibiting properties, etc. The usefulness of compositions of this type for the purpose of this invention 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 can be incorporated into the composition.

The process of this invention comprises essentially the acylation of the alkylenic amine with all of the acid radicals in both the hydrocarbon-substituted acid and the mono-carboxylic acid used. The acylation is accompanied by the formation of approximately one mole of water for each equivalent of the acid radical used. The product resulting from the process is substantially non-acidic, i.e., it has an acid number as determined by ASTM Procedure D974-58T less than 10. The precise composition of the product is not known. It appears that the product comprises predominantly amides and imides and may contain cyclic or polyamide linkages. The relative proportions of these substances in the product are not known. Also, a very small amount of amine carboxylic salts, imidazolines and polyamides may be formed but these do not amount to an appreciable proportion in the product.

The relative proportions of the reactants to be used in the process of this invention are such that for each equivalent of the alkylenic amine used, there is employed from about 0.5 to about 1 molar equivalent of hydrocarbon-substituted succinic acid and a mono-carboxylic acid in respective ratios of equivalents within the range from about 1:0.1 and about 1:1. It will be noted that the equivalent weight of the alkylenic amine is based upon its nitrogen content and that the equivalent weight of the acid reactant is based upon the number of acid
radicals in the molecule. Thus, one mole of alkylene amine has as many equivalents as there are nitrogen atoms in the molecule, one mole of the succinic acid or anhydride has two equivalents and one mole of the mono-carboxylic acid has one equivalent. The above limits with respect to the relative proportions of reactants are predicated upon the stoichiometry of the reaction involved in the process and also the utility of the products for the purposes of this invention. For example, the use of more than one equivalent of the acidic mixture for one equivalent of the alkylene amine used results in products having excessive acidity and corrosive tendencies. On the other hand, the use of lesser amounts of the acidic mixture limited by a minimum of 0.83 equivalent for each equivalent of the alkylene amine used and the preferred ratio of equivalents of the hydrocarbon-substituted succinic acid and the mono-carboxylic acid in the acidic mixture are within the range from 1:0.25 to 1:0.5.

The process of this invention may be carried out in either of two ways. It may be carried out by heating a mixture of the hydrocarbon-substituted succinic acid, the mono-carboxylic acid and the alkylene amine. Alternatively it may be carried out by first reacting the alkylene amine with the hydrocarbon-substituted succinic acid to form an intermediate product and then reacting further the intermediate product with the mono-carboxylic acid. A critical aspect in carrying out the process is that the alkylene amine should not be allowed to react with the mono-carboxylic acid in the absence of the succinic acid reactant. If such reaction is allowed to take place, the final product, i.e., the final product obtained by reacting further such product with the hydrocarbon-substituted succinic acid is unsatisfactory. Thus, for example, such final product has been found not to possess no detergent properties but to be capable of promoting the tendency to form harmful deposits of hydrocarbon compositions to which it has been added. The reason for the critical difference between such product and the products obtained by the process of this invention is not known.

The acylation reaction which characterizes the herein described process requires a minimum temperature of about 80° C. The preferred temperature is between 150° and 250° C. Higher temperatures may be used, provided that such temperatures do not cause decomposition of the components of reaction mass.

As indicated previously, the reaction involved in the process of this invention is accompanied by the formation of approximately one mole of water for each equivalent of the acid radical used. The removal of the water formed may be effected conveniently by heating the product at a temperature above about 100° C. preferably in the neighborhood of about 150° C. The removal of water may be facilitated by blowing the reaction mixture with an inert gas such as nitrogen during such heating. It may likewise be facilitated by the use of a solvent which forms an azeotrope with water. Such solvents are exemplified by benzene, toluene, naphtha, n-hexane, xylene, etc. The use of such solvent permits the removal of water at a lower temperature, e.g., 80° C.

The following examples illustrate in greater detail the processes of this invention.

EXAMPLE 1

A mixture of 140 parts (by weight) of a mineral oil, 174 parts of a polyisobutene (molecular weight 1000)-substituted succinic anhydride having an acid number of 105 and 23 parts of stearic acid is prepared at 90° C. To this mixture there is added 17.6 parts of a mixture of polyalkylene amines having an overall composition corresponding to that of tetraethylene pentamine at 80°-100° C. throughout a period of 1.3 hours. The reaction is exothermic. The mixture is blown at 225° C. with nitrogen at a rate of 5 pounds per hour for 3 hours whereupon 47 parts of an aqueous distillate is obtained. The mixture is dried at 225° C. for 1 hour, cooled to 110° C. and filtered. The filtrate is found to have the following analysis:

Percent N .................................................. 1.7
Acid number ............................................... 4.5

EXAMPLE 2

A mixture of 600 grams (1.14 equivalents) of the polyisobutene-substituted succinic anhydride of Example 1 and 161 grams (0.57 equivalent) of stearic acid in 540 grams of mineral oil is prepared and heated to 80° C., whereupon 73 grams (1.7 equivalents) of the polyalkylene polyamine mixture of Example 1 is added to the mixture at 80°-90° C. throughout a period of 45 minutes. The resulting mixture is heated gradually to 210° C. and then at 210°-225° C. for 1 hour while being purged with nitrogen. A total of 30 cc. of an aqueous distillate is collected. The residue is cooled and filtered. The filtrate is found to have the following analysis:

Percent N .................................................. 1.83
Acid number ............................................... 8

EXAMPLE 3

A mixture of 600 grams (1.14 equivalents) of the polyisobutene-substituted succinic anhydride of Example 1 and 81 grams (0.28 equivalent) of stearic acid in 474 grams of mineral oil is prepared and heated to 85° C. A commercial ethyleneamine mixture having a composition corresponding to that of tetraethylene pentamine (60 grams, 1.4 equivalents) is added to the mixture at 85°-95° C. The mixture is heated at 200-220° C. for 3 hours and then at 210°-220° C./30 mm. The residue is cooled and filtered. The filtrate is found to have the following analysis:

Percent N .................................................. 1.89
Acid number ............................................... 5

EXAMPLE 4

A mixture of 528 grams (1 equivalent) of the polyisobutene-substituted succinic anhydride of Example 1, 295 grams (1 equivalent) of a fatty acid derived from distillation of tall oil and having an acid number of 190, 200 grams of toluene and 85 grams (2 equivalents) of the polyalkylene polyanamine mixture of Example 1 is heated at the reflux temperature while water is removed by azeotropic distillation. The toluene is removed by distillation and the mixture heated at 180°-190° C. for 2 hours, then to 150° C./20 mm. The residue is found to have the following analyses:

Percent N .................................................. 3.3
Acid number ............................................... 9.8

EXAMPLE 5

A mixture of 33.2 grams (0.93 equivalent) of diethylenetriamine, 100 grams (2.77 equivalents) of triethylene tetramine, 1000 grams (1.85 equivalents) of the polyisobutene substituted succinic anhydride of Example 1 and 500 grams of mineral oil is prepared at 100°-109° C. and heated at 160°-170° C. for 1 hour. The mixture is cooled and mixed with 266 grams (1.85 equivalents) of 2-ethyl hexanoic acid at 75°-80° C. and the resulting mixture is heated at 160°-165° C. for 12 hours. A total of 64 grams of water is removed as distillate. The residue is diluted with 390 grams of mineral oil, heated to 160° C. and filtered. The filtrate is found to have the following analysis:

Percent N .................................................. 2.3
EXAMPLE 6
A mixture of 100 grams (2.77 equivalents) of triethylene tetramine, 30 grams (0.96 equivalent) of diethylene triamine, 1000 grams (1.85 equivalents) of the polyisobutene-substituted succinic anhydride of Example 1, 266 grams (1.85 equivalents) of 2-ethyl hexanoic acid and 500 grams of mineral oil is prepared at 50–90° C. and heated at 145°–180° C. for 11 hours while nitrogen is passed through the mixture throughout the period. A total of 37 grams of water is collected as distillate. The residue is diluted with 403 grams of mineral oil, heated to 160° C. and filtered. The filtrate is found to have the following analysis:

Percent N ----------------------------------------------- 2.3

EXAMPLE 7
To a mixture of 528 grams (1 equivalent) of the polyisobutene-substituted succinic anhydride of Example 1, 30 grams (0.5 equivalent) of glacial acetic acid in 402 grams of mineral oil there is added 64 grams (1.5 equivalents) of the polyleylene polyamine mixture of Example 1 at 70°–85° C. in ¾ hour. The mixture is purged with nitrogen 20°–220° C. for 3 hours and then heated to 210° C./50 mm. The residue is cooled and filtered at 70°–90° C. The filtrate is found to have a nitrogen content of 2% and an acid number of 2.

EXAMPLE 8
To a solution of 815 grams (1.5 equivalents) of the polyisobutene-substituted succinic anhydride of Example 1 and 148 grams (0.5 equivalent) of the tall oil fatty acid of Example 4 in 750 cc. of toluene there is added 85 grams (2 equivalents) of the polyleylene polyamine mixture of Example 1 throughout a period of 1 hour. The mixture is heated at reflux temperature (130° C.) for 5 hours whereupon 8 cc. of water is collected in an azotropic mixture with toluene. The residue is then heated to 150° C./20 mm. to remove toluene. The residue is found to have a nitrogen content of 2.85%.

EXAMPLE 9
A mixture of 792 grams (1.5 equivalents) of the polyisobutene-substituted succinic anhydride of Example 1, 148 grams (0.5 equivalent) of the tall oil fatty acid of Example 4, 85 grams (2 equivalents) of the polyleylene polyamine mixture of Example 1 and 150 cc. of toluene is heated at 180° C. 5 hours. A total of 22 grams of water is collected as the distillate. The residue is heated to 150° C./20 mm. The residue is found to have a nitrogen content of 2.9%.

EXAMPLE 10
A mixture of 100 parts of tall oil fatty acids and 2 parts of water is heated in an autoclave at 370° C. at a pressure of 550 p.s.i. for 1.5 hours and then subjected to distillation under vacuum. The distillate, 96.5 parts, is hydrogenated with a Raney nickel catalyst until its iodine number is reduced to about 7. The hydrogenated product is dissolved in a mixture of 90 parts of acetone and 10 parts of water and the solution is chilled to precipitate as a solid the hydrogenated product of the unused part of the starting acid. The solvent in the liquid product is allowed to evaporate and the residue is a liquid isomerized acid (34 parts) having an iodine number of 10 and at least one branched chain (shown by infrared analysis). A mixture of 200 parts (by weight) of toluene, 340 parts (0.1 equivalents) of diethylene triamine, 112 parts (3.6 equivalents) of diethylene triamine, 1897 parts (6.3 equivalents) of the iso-aliphatic acid having an acid number of 186 and 3300 parts (6.3 equivalents) of the polyisobutene substituted succinic anhydride of Example 1 is heated at 140°–210° C. for 20 hours whereupon water and toluene are removed by distillation. The residue is mixed with an equal volume of mineral oil and heated to 170° C./1 mm. and filtered.

EXAMPLE 11
A mixture of 100 parts of tall oil acids, 2 parts of water, and 2 parts of mineral clay is heated at 230° C. for 3 hours and then subjected to distillation under vacuum. The distillate, 58 parts, has an iodine number of 103 and is hydrogenated in the presence of a Raney nickel catalyst until the iodine number is reduced to 8. The liquid isomerized acid product (obtained by the solvent extraction and precipitation method as described in Example 1) is found to have an iodine number of 11 at least one branched chain (shown by infrared analysis). An oil-soluble composition is prepared by reaction of this acid with the polyisobutene-substituted succinic anhydride and the amine mixture of Example 1, in accordance with the procedure of Example 1.

EXAMPLE 12
A mixture of 100 parts of oleic acid, 2 parts of water, and 4 parts of a mineral clay is heated at 230° C. for 3 hours and then subjected to distillation under vacuum. The distillate is hydrogenated in the presence of a Raney nickel catalyst until the iodine number is reduced to 6. The liquid isomerized acid product (obtained by solvent extraction and precipitation as described in Example 1) is found to have an iodine number of 8 and at least one branched chain (shown in infrared analysis). An oil-soluble, nitrogen-containing composition is prepared by reaction of this acid with the polyisobutene-substituted succinic anhydride and the amine mixture of Example 1, in accordance with the procedure of Example 1.

EXAMPLE 13
An iso-aliphatic acid (42 parts by weight) obtained by a procedure substantially the same as is described in Example 10 and having an acid number of 176, and the isobutene substituted succinic anhydride of Example 1 (456 parts), are mixed with 186 parts of mineral oil. The mixture is added at 85–107° C. to 182 parts of mineral oil and 78 parts of the amine of Example 1. The resulting mixture is blown with nitrogen at 205°–210° C. for 8 hours whereupon volatile components are distilled off. The residue is cooled and filtered at 138° C. The filtrate, 904 parts (representing 97% of the theoretical yield), is the desired product and has a nitrogen content of 7.9%.

The products of the process of this invention are for the most part liquids or semi-solids. They are soluble in hydrocarbon oils and are useful as additives in hydrocarbon oils such as fuel oils, gasoline, metal working oils, lubricating oils, etc. They are especially effective as additives to impart detergent properties to the oil, and thus to prevent the deposition of sludge or varnish-like substances from the oil. They are also effective in improving the thermal stability of hydrocarbon oils containing metal phosphorodithiates. The metal phosphorodithiates which are most commonly used in hydrocarbon oils include the salts of metals in group II of the Periodic Table, particularly barium and zinc, of phosphorodithioic acids having the formula

wherein R₁ and R₂ are organic radicals such as alkyl, alkenyl, arylalkyl, and cycloalkyl radicals. Those metal phosphorodithioic acids in which the metal radicals contain a minimum 7.5 aliphatic carbon atoms per each phosphorus atom are most readily soluble in oils and are, therefore, preferred for such use. For reasons of economy, the R₁ and R₂ radicals in the phosphorodithioic acids are preferably low molecular weight alky radicals and lower alkylaryl radicals include methyl, ethyl, isopropyl, isobutyl, n-butyl, sec-butyl, n-pentyl, neopentyl, 3-methyl-butyl, n-heptyl,
methyl-isobutyl, 2-ethyl-hexyl, di-isobutyl, iso-octyl, decyl, etc. Illustrative cycloalkyl radicals and lower alkylphenyl radicals include cyclohexyl, cyclohexyl, methyl-cyclohexyl, butyl-phenyl, amyphenyl, dialkylphenyl, octyl-phenyl, polyisobutyl (molecular weight 1000)-substituted phenyl, etc. Other hydrocarbon radicals such as tetra-decyl, octadecyl, decyl, butylphosphinyl, hexylphosphinyl, cyclohexylphenyl, napthphenyl, etc. likewise are useful. Many substituted hydrocarbon radicals such as chloro-alkyl, dichlorophenyl and chloroalkylphenyl radicals may also be used.

The availability of the phosphorodithioic acids from which the metal salts are readily well known. They are prepared for example, by the reaction of phosphorus pentasulfide with an alcohol or phenol. The reaction involves 4 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 and preferably from about 80°C to about 120°C. Thus, the preparation of di-n-hexylphosphorodithioic acid involves the reaction of phosphorus pentasulfide with 4 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 metal salt of this acid may be effected by reaction of the acid with a metal neutralizing agent such as zinc oxide. Simply mixing and heating these reactants is sufficient to cause the neutralization to take place and the resulting product is sufficiently pure for the purpose of this invention.

Especially useful 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 mixtures of alcohols enables the utilization of cheaper alcohols which in themselves do not yield oil-soluble phosphorodithioate acid salts. 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 acids i.e., acids prepared from a single alcohol, can be reacted with the metal neutralizing agent to produce less expensive oil-soluble metal salts.

The amount of the products of this invention to be used is sufficient to improve the thermal stability of hydrocarbon compositions containing metal phosphorodithioate additives will vary according to the amount of the metal phosphorodithioate additive present therein. In most compositions such as those useful as lubricants for internal combustion engines, gears, power-transmitting units, the phosphorodithioate additive should be present in amounts to impart from about 0.01% to about 0.5% by weight of phosphorus to the compositions. It has been found that from about 0.05% to about 5% by weight of the products of this invention usually will suffice to improve the thermal stability of such compositions. When used as additives to impart detergent properties to hydrocarbon oils, the products of this invention may be used in amounts ranging from about 0.001% to about 10% by weight or even more. Further, for use in fuel oils, the concentration should be within the range from about 0.001% to about 0.5%, and when used in lubricating oils, the amount may be from about 0.1% to about 10%.

The effectiveness of the products of this invention in improving the thermal stability of lubricating compositions containing metal phosphorodithioates is shown by data obtained from a test in which a 20 cc. sample of a lubricating composition placed in a 5% inch glass test tube having immersed therein a strip (2 x 0.5 inch) of 10-20 steel as a catalyst to promote deterioration is maintained at 295°F until the first appearance of haze or sediment. The thermal stability of the lubricating composition is measured by the time in hours required for this appearance of haze or sediment. The results are summarized in Table I. The lubricating base oil used in this test is a SAE 90 grade mineral lubricating oil. All percentages are by weight.

The efficacy of the products of this invention as additives which impart detergent to hydrocarbon oils is shown by the comparative data of Table II. This data was acquired from a test in which a 350 cc. sample of a Mid- Continent, conventionally refined lubricating oil having a viscosity of 200 SUS/100°F. F. containing 0.001% by weight of iron naphthenate (as a promoter of oil degradation) and a specified amount of the detergent additive to be tested, is placed in a borosilicate tube. A 13" x 5¾" SAE 10-20 steel panel is immersed in the oil. The sample is then heated at 300°F. for 48 hours while air is bubbled through the oil at a rate of 10 liters per hour. The oxidized sample is cooled to 120°F., mixed with 0.5% by weight of water, homogenized, allowed to stand at room temperature for 24 hours and then filtered through 2 layers of number 1 Whatman filter paper at 20 mm. mercury pressure. The precipitate is washed with naptha and dried. The weight of the precipitate expressed as milligrams per 100 cc. of the oil is taken as a measure of the detergent properties of the lubricating composition, i.e., the greater the weight of the precipitate the less effective the detergent properties. The appearance of the steel panel is also noted and rated on a numerical scale from 0 indicating a heavy deposit to 10 indicating no deposit.

Table I

<table>
<thead>
<tr>
<th>Lubricant Sample No.</th>
<th>Additives in Lubricant</th>
<th>Test Result—Hours to Development of Haze or Sediment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Metal Phosphorodithioate</td>
<td>Acylated Alkylene Amine</td>
</tr>
<tr>
<td>1</td>
<td>0.3% of phosphorus as zinc di(4-methyl-2-pentyl) phosphorodithioate</td>
<td>None</td>
</tr>
<tr>
<td>2</td>
<td>0.1% of phosphorus as zinc di(4-methyl-2-pentyl) phosphorodithioate</td>
<td>0.25% of Product of Example 1</td>
</tr>
<tr>
<td>3</td>
<td>0.1% of phosphorus as zinc di(4-methyl-2-pentyl) phosphorodithioate</td>
<td>0.5% of Product of Example 1</td>
</tr>
<tr>
<td>4</td>
<td>0.1% of phosphorus as zinc di(4-methyl-2-pentyl) phosphorodithioate</td>
<td>None</td>
</tr>
<tr>
<td>5</td>
<td>0.1% of phosphorus as zinc di(4-methyl-2-pentyl) phosphorodithioate</td>
<td>0.5% of Product of Example 1</td>
</tr>
<tr>
<td>6</td>
<td>0.1% of phosphorus as zinc di(4-methyl-2-pentyl) phosphorodithioate</td>
<td>None</td>
</tr>
<tr>
<td>7</td>
<td>0.1% of phosphorus as zinc di(4-methyl-2-pentyl) phosphorodithioate</td>
<td>0.5% of Product of Example 1</td>
</tr>
</tbody>
</table>

Table II

<table>
<thead>
<tr>
<th>Lubricant Sample No.</th>
<th>Acylated Alkylene Amine Additive (% by weight)</th>
<th>Test Result</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sludge (mg./100 cc. Oil)</td>
<td>Panel Rating (0-10)</td>
</tr>
<tr>
<td>1</td>
<td>None</td>
<td>177-400</td>
</tr>
<tr>
<td>2</td>
<td>1.5% of Product of Example 2</td>
<td>7.8</td>
</tr>
<tr>
<td>3</td>
<td>1.5% of Product of Example 3</td>
<td>13.4</td>
</tr>
<tr>
<td>4</td>
<td>1.5% of Product of Example 4</td>
<td>3.4</td>
</tr>
<tr>
<td>5</td>
<td>1.5% of Product of Example 5</td>
<td>9.8</td>
</tr>
<tr>
<td>6</td>
<td>1.5% of Product of Example 6</td>
<td>1.4</td>
</tr>
<tr>
<td>7</td>
<td>1.5% of Product of Example 7</td>
<td>11.8</td>
</tr>
<tr>
<td>8</td>
<td>1.5% of Product of Example 8</td>
<td>3.4</td>
</tr>
</tbody>
</table>
The products of this invention are also useful as pour point depressants in mineral oils. For instance, the pour point of a SAE 10W 30 base oil is lowered from 10° F. to 0° F. by the incorporation therein of 1% by weight of a 60% oil solution of the reaction product of the polyisobutene-substituted succinic anhydride of Example 1 (6 equivalents), stearic acid (1 equivalent), and the polyethylene polyamine of Example 1 (14 equivalents).

The following examples illustrate the lubricating compositions containing metal phosphorodithioates which may be improved by the addition thereto of products of this invention (all percentages are by weight):

**LUBRICANT 1**

SAE 20 mineral lubricating oil containing 0.05% of phosphorus as zinc di(cyclohexylphosphorodithioate) and 0.1% of the product of Example 1.

**LUBRICANT 2**

SAE 90 mineral lubricating oil containing 0.06% of phosphorus as zinc di(isopropylphenyl)phosphorodithioate and 0.05% of the product of Example 2.

**LUBRICANT 3**

SAE 90 mineral lubricating oil containing 0.2 of phosphorus as zinc salt of an equimolar mixture of di-isopropylphosphorodithioic acid and di-hexyl phosphorodithioic acid and 0.5% of the product of Example 3.

**LUBRICANT 4**

SAE 10W-30 mineral lubricating oil containing 0.15% of phosphorus as barium di-octylphosphorodithioate, 2% as sulfate ash of barium mahogany sulfonate and 0.4% of the product of Example 5.

**LUBRICANT 5**

SAE 10W-20 mineral lubricating oil containing 0.1% of phosphorus as zinc salt of a phosphorodithioic acid prepared by the reaction of P$_2$S$_5$ with an equimolar mixture of iso-octyl alcohol and cyclohexyl alcohol, 0.1% of sulfate ash of a barium salt of an acidic composition prepared by hydrolyzing the reaction product of a polyisobutene (having a molecular weight of 1000) with P$_2$S$_5$ and 0.5% of the product of Example 7.

**LUBRICANT 6**

SAE 90 mineral gear lubricating oil containing 0.3% of phosphorus as zinc dibehyl phosphorodithioate, 5% of a chlorinated eicosane having a chlorine content of 50%, 4% of dibutyl tetrasulfide, and 0.4% of the product of Example 9.

The products of this invention are also useful in the oil-fuel mixtures for two-cycle internal combustion engines. In this application they are effective to reduce the engine wear and minimize the tendency of the oil-fuel mixture to cause spark plug fouling and to form harmful engine deposits. Their effectiveness is shown by the results (Table III) of a two-cycle engine test in which a 60-horsepower, two-cycle, three-cylinder outboard motor is subjected to cycling operations, each cycle consisting of 55 minutes of full throttle operation (5500–5600 r.p.m.) and 5 minutes of idling at 600–700 r.p.m. under the following conditions: water inlet temperature, 78–82° F.; water outlet temperature, 140–180° F.; and tank temperature, 95–105° F. The test period of 50 or 100 hours unless excessive spark plug fouling is observed. The oil-fuel mixture used in the test consists of 720 (parts by volume) of a regular, leaded gasoline having an octane number of 93–94 and 18 parts of a SAE 40 mineral lubricating oil containing the chemical additive. The effectiveness of the additive is measured in terms of the piston cleanliness on a scale of 0 to 10 (0 being indicative of extremely heavy deposits and 10 being indicative of no deposit) and the average life of the spark plugs, i.e., the number of changes of spark plugs made necessary by fouling during the test period.

The gasolines useful as the fuels for two-cycle engines may be of regular or premium grade having an octane number from about 80 to about 110. They may contain an anti-knock agent such as tetraethyl lead or tetramethyl lead and a scavenger such as ethylene dibromide or ethylene dichloride. In lieu of the gasolines, diesel fuel likewise is useful in two-cycle internal combustion engines. The lubricating base oils useful in the oil-fuel mixture for two-cycle engines are usually characterized by viscosity values from about 30 to about 200 SUS (Saybolt Universal Seconds) at 210° F. The most commonly used oils are the mineral lubricating oils having viscosity values from about 40 to about 120 SUS at 210° F. They are exemplified by mineral lubricating oils of SAE 10 to SAE 50 grades.

The relative proportions of the lubricating oil to the gasoline in the oil-fuel mixture may vary within wide ranges such as from a ratio of about 1:120 to a ratio of about 1:5, respectively, by volume. The preferred ratio is from about 1:10 to about 1:60, respectively, of the lubricating oil to the gasoline.

The oil-fuel mixtures for two-cycle engines may contain other additives such as metal-containing detergents, corrosion-inhibiting agents, oxidation-inhibiting agents, etc. The metal-containing detergents are exemplified by the alkaline earth metal salts of oil-soluble acids, e.g., mahogany sulfonic acid and didodecylbenzenesulfonic acid. The metal salts include both the normal salts and the basic salts, the latter describing the metal salts in which the metal is present in a stoichiometrically greater amount than the organic acid radical. Specific examples of the metal-containing detergents are calcium salt of mahogany sulfonic acid, strontium salt of mahogany sulfonic acid, basic barium salt of didodecylbenzenesulfonic acid obtained by carbonating a mixture of a mineral oil, a sulfonic acid and barium hydroxide (5 chemical equivalents per equivalent of the acid) in the presence of a promoting agent such as octylphenol (one equivalent per equivalent of the acid). Other metal-containing detergents include the alkaline earth metal salts of organic phosphorus acids prepared by the treatment of an olefin polymer (such as polyisobutene having a molecular weight of about 1000) with a phosphorus sulfide (such as phosphorus pentasulfide or phosphorus heptasulfide). These metal salts likewise may be normal or basic salts.

The corrosion-inhibiting agents and the oxidation-inhibiting agents are exemplified by phenolic compounds such as 2,6-dibutyl-4-methylphenol, 4,4'-methylenebis(2-tet-butyl - 6 - isopropylphenol), 2-methyl-6-tert-butyl-4-heptylphenol, and sulfured heptylphenol. Arylamines and sulfured hydrocarbons likewise are useful as inhibiting agents. They include, for example, sulfurred dipentene (obtained by the reaction of two moles of dipentene with one mole of sulfur at 150° C.), the reaction product of turpentine (4 moles) with phosphorus pentasulfide (1 mol).
The concentrations of the chemical additives in the oil-fuel mixtures depend to some extent upon the oils and fuels used and the types of service to which the oil-fuel mixtures are to be subjected. In most applications the nitrogen-containing composition of the invention is present in the oil-fuel mixture at concentrations ranging from 0.001% to about 2%, preferably from 0.01% to 3% by weight of the mixture. The concentration of the other additives may each range from 0.0001% to 2% by weight of the mixture.

The following examples illustrate further the fuel-oil mixtures containing the oil-soluble, nitrogen-containing compositions of the invention (the relative proportions of the fuel and the lubricating oil are expressed in parts by volume whereas the concentration of the additives are expressed in percentages by weight of the oil-fuel mixture).

**EXAMPLE A**

| SAE 20 mineral lubricating oil | Parts | 1 |
| Gasoline having an octane number of 98 | Do | 20 |
| The product of Example 1 | Percent | 0.15 |

**EXAMPLE B**

| SAE 30 mineral lubricating oil | Parts | 1 |
| Gasoline having an octane number of 100 | Do | 16 |
| The product of Example 2 | Percent | 0.05 |

**EXAMPLE C**

| SAE 50 mineral lubricating oil | Parts | 1 |
| Gasoline having an octane number of 85 | Do | 30 |
| The product of Example 3 | Percent | 0.1 |

**EXAMPLE D**

| SAE 40 mineral lubricating oil | Parts | 1 |
| Gasoline having an octane number of 95 | Do | 50 |
| The product of Example 4 | Percent | 0.05 |
| 4,4'-methylene-bis(2,6-di-tert-butylphenol) | Do | 1 |

What is claimed is:

1. A process for preparing acylated amines by the reaction of an alkylene amine having the structural formula

   \[ H_2N-(R-NH)_xH \]

   in which \( x \) is an integer less than about 6 and \( R \) is a lower alkylene radical with a substituted succinic compound selected from the class consisting of olefin polymer substituted succinic acid and anhydrides having at least about 50 aliphatic carbon atoms in the olefin polymer substituent and an aliphatic hydrocarbon mono-carboxylic acid having up to about 22 carbon atoms, the total amounts of the succinic compound and the mono-carboxylic acid being from about 0.5 to about 1 equivalent per equivalent of the alkylen amine used and the ratio of equivalents of the succinic compound to the mono-carboxylic acid being from 1:0.1 to about 1:1; said process comprising the steps of preparing a mixture of the alkylen amine with the substituted succinic compound, heating said mixture at a temperature of from about 80°C to about 250°C to form an acylated intermediate, preparing a second mixture of the acylated intermediate with an aliphatic hydrocarbon mono-carboxylic acid, heating said second mixture at a temperature of from about 80°C to about 250°C to cause further acylation and removing the water formed thereby.

2. A process for preparing acylated amines by the reaction of an alkylene amine having the structural formula

   \[ H_2N-(R-NH)_xH \]

   in which \( x \) is an integer less than about 6 and \( R \) is a lower alkylene radical with a substituted succinic compound selected from the class consisting of olefin polymer substituted succinic acids and anhydrides having at least about 50 aliphatic carbon atoms in the olefin polymer substituent and an aliphatic hydrocarbon mono-carboxylic acid having up to about 22 carbon atoms, the total amounts of the succinic compound and the mono-carboxylic acid used being from about 0.5 to about 1 equivalent per equivalent of the alkylen amine used and the ratio of equivalents of the succinic compound to the mono-carboxylic acid being from 1:0.1 to about 1:1; said process comprising the steps of preparing a mixture of the substituted succinic compound and the aliphatic hydrocarbon mono-carboxylic acid and heating said mixture with the alkylen amine at a temperature of from about 80°C to about 250°C.

3. The process of claim 2 wherein the alkylen amine is an ethylene amine.

4. The process of claim 2 wherein the alkylen amine is a polyethylene polyamine.

5. The process of claim 2 wherein the alkylen amine is an ethylene amine mixture having an average of from about 2 to about 7 amino groups.

6. The process of claim 2 wherein the substituted succinic compound is a polybutene-substituted succinic anhydride wherein the polybutene substituent has a molecular weight above about 750.

7. The process of claim 2 wherein the aliphatic hydrocarbon mono-carboxylic acid is an iso-fatty acid having at least about 12 aliphatic carbon atoms.

8. The process of claim 2 wherein the aliphatic hydrocarbon mono-carboxylic acid is an iso-fatty acid having at least about 12 aliphatic carbon atoms.

9. A process for preparing acylated amines which comprises the steps of preparing a mixture of a polyethylene polyamine having up to about 5 amino groups with a polyisobutene substituted succinic anhydride wherein the polyisobutene radical has a molecular weight of from about 750 to about 5000, heating said mixture at a temperature from about 80°C to about 250°C to form an acylated intermediate, preparing a second mixture of said acylated intermediate with a fatty acid having from about 12 to about 22 carbon atoms, heating said second mixture at a temperature from about 80°C to about 250°C to cause further acylation and removing the water formed thereby, the total amounts of the succinic anhydride and the fatty acid being from 0.5 to about 1 equivalent per equivalent of the polyethylene polyamine and the ratio of equivalents of the succinic anhydride to the fatty acid being from about 1:0.25 to about 1:1.

10. A process for preparing acylated amines which comprises the steps of preparing a mixture of a polyethylene polyamine having up to about 5 amino groups with a polyisobutene substituted succinic anhydride wherein the polyisobutene radical has a molecular weight of from about 750 to about 5000, heating said mixture at a temperature from about 80°C to about 250°C to form an acylated intermediate, preparing a second mixture of said acylated intermediate with an iso-fatty acid having from about 12 to about 22 carbon atoms, heating said second mixture at a temperature from about 80°C to about 250°C to cause further acylation and removing the water formed thereby, the total amounts of the succinic anhydride and the iso-fatty acid being from 0.5 to about 1 equivalent per equivalent of the polyethylene polyamine and the ratio of equivalents of the succinic anhydride to the iso-fatty acid being from about 1:0.25 to about 1:1.

11. The process of claim 10 wherein the iso-fatty acid
is obtained by the isomerization of an unsaturated fatty acid having from about 16 to 20 carbon atoms.

12. The product of the process of claim 2.

13. The product of the process of claim 11.

14. A hydrocarbon oil composition comprising a major proportion of a hydrocarbon oil and a minor amount, sufficient to improve the detergent property of said composition, of the product of claim 11.

15. A hydrocarbon oil composition comprising a major proportion of a hydrocarbon oil and a minor amount, sufficient to improve the detergent property of said composition, of the product of claim 12.

16. A lubricating composition comprising a major proportion of a mineral lubricating oil, from about 0.01% to about 0.5% of phosphorus as a Group II metal phosphorodithioate and a small amount, sufficient to reduce the tendency of said composition to develop haze or sediment at elevated temperatures due to the presence therein of said metal phosphorodithioate, of the product of claim 12.

17. The lubricating composition of claim 16 characterized further in that the Group II metal phosphorodithioate is a zinc phosphorodithioate.

18. The lubricating composition of claim 16 characterized further in that the Group II metal phosphorodithioate is a zinc salt of a phosphorodithioic acid having the formula

\[
\begin{align*}
\text{R}_1 & \text{O} \quad \text{S} \\
\text{S} & \quad \text{R}_2 \\
\text{SH} & 
\end{align*}
\]

wherein \( \text{R}_1 \) and \( \text{R}_2 \) each contain up to about 10 aliphatic carbon atoms and are selected from the group consisting of alkyl, alkaryl, arylalkyl, and cycloalkyl radicals.

19. An oil-fuel mixture suitable for use in two-cycle engines comprising from about 5 to about 120 parts by weight of gasoline, one part of a mineral lubricating oil, and a small amount, sufficient to improve the detergent property of said mixture, of the product of the process of claim 2.

20. An oil-fuel mixture suitable for use in two-cycle engines comprising from about 5 to about 120 parts by weight of gasoline, one part of a mineral lubricating oil, and a small amount, sufficient to improve the detergent property of said mixture, of the product of the process of claim 11.

References Cited by the Examiner

UNITED STATES PATENTS

<table>
<thead>
<tr>
<th>Patent Number</th>
<th>Date</th>
<th>Inventor(s)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,568,876</td>
<td>9/61</td>
<td>White et al.</td>
<td>252—51.5</td>
</tr>
<tr>
<td>3,018,247</td>
<td>1/62</td>
<td>Anderson et al.</td>
<td>260—32.7</td>
</tr>
<tr>
<td>3,083,162</td>
<td>3/63</td>
<td>Lawrence</td>
<td>44—58 X</td>
</tr>
</tbody>
</table>

DANIEL E. WYMAN, Primary Examiner.