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REACTION PRODUCT OF AN ALIPHATIC OLEFIN-POLYMER-SUCCINIC ACID PRODUCING COMPOUND WITH AN AMINE AND REACTING THE RESULTING PRODUCT WITH A BORON COMPOUND

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This invention relates to oil-soluble nitrogen- and boron-containing compositions and to the process of preparing the same. The compositions of this invention are useful as additives in lubricants, especially lubricants intended for use in internal combustion engines, gears, and power transmitting units.

One of the principal problems associated with present day automobile crankcase lubricants is that posed by the inevitable presence in the lubricant of foreign particles such as dirt, soot, water, and decomposition products resulting from breakdown of the lubricating oil. Even if there were none of this latter contaminant present the very nature of the design of the modern internal combustion engine is such that a significant amount of foreign matter will accumulate in the crankcase. Perhaps the most important of these contaminants is water because it seems to be responsible for the deposition of a mayonnaise-like sludge. It appears that if there were no water present the solid components of the mayonnaise-like sludge would circulate with the oil and be removed by the oil filter. It will be readily appreciated that the deposition of the sludge presents a serious problem with respect to the efficient operation of the engine and that it is desirable to prevent such deposition of sludge-like material.

The presence of water and the precursors of sludge in a lubricating oil is dependent largely upon the operating temperature of the oil. If the oil is operated at a high temperature the water, of course, will be eliminated by evaporation about as fast as it accumulates. In the absence of water as stated above the other foreign particles will be removed by the filter. At low oil temperatures, on the other hand, water will accumulate and so consequently will sludge. It is apparent that the environment in which a crankcase lubricant is maintained will determine to a large extent the ultimate performance of that lubricant.

High operating temperatures are characteristic of a lubricant in an engine that is run at relatively constant high speed. Thus, in an engine that is run at 60 miles per hour for a long period of time it is very unlikely that there will be any accumulation of water and it is similary unlikely that there will be any formation and deposition of sludge, but in ordinary stop-and-go driving such as is the case with taxicabs, delivery trucks, police cruisers, etc., the crankcase lubricant will be alternately hot and cold, an ideal environment for the accumulation of water. In such cases the formation of sludge is a serious problem. This problem has been with the automotive industry for many years and its solution has been approached by the use of known detergents such as metal phenates and sulfonates but without notable success. Although such known detergents are very effective in solving the detergency problems associated with motor oils at high temperatures they have not been particularly effective in solving the problems associated with low temperature operation or, to put it better, those problems which are associated with crankcase lubricants in engines which are operated at alternating high and low temperatures.

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

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

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

It is another object of this invention to provide a novel process for the preparation of products which are effective as dispersants in lubricant compositions.

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

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

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

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

These and other objects are achieved in accordance with this invention by providing a process for preparing oil-soluble nitrogen- and boron-containing compositions comprising treating an acylated nitrogen composition characterized by the presence within its structure of (A) a substatnially hydrocar-substituted succinic radical selected from the class consisting of succinoyl, succinimidoyl, and succinoyloxy radicals wherein the substantially 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 succinic radical, with a boron compound selected from the class consisting of boron oxide, boron halides, boron acids, and esters of boron acids in an amount to provide from about 0.1 atomic proportion of boron for each mole of said acylated nitrogen composition to about 10 atomic proportions of boron for each atomic proportion of nitrogen of said acylated nitrogen composition.

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

The sources of the substantially hydrocarbon substituent include principally the high molecular weight substantially saturated petroleum fractions and substantially saturated olefin polymers, particularly polymers of mono-olefins having from 2 to 30 carbon atoms. The especially useful polymers are the polymers of 1-mono-olefins such as ethylene, propene, 1-butene, isobutene, 1-hexene, 1-octene, 2-methyl-1-heptene, 3-cyclohexyl-1-butene, and 2-methyl-5-propyl-1-hexene. Polymers of medial olefins, i.e., olefins in which the olefinic linkage is not at the terminal position, likewise are useful. They are illustrated by 2-butene, 3-penetne, and 4-octene.

Also useful are the interpolymers of the olefins such as those illustrated above with other interpolymerizable olefinic substances such as aromatic olefins, cyclic olefins, and polyolefins. Such interpolymers include, for example, those prepared by polymerizing isobutene with styrene; isobutene with butadiene; propene with isoprene; ethylene with piperylene; isobutene with chloroprene; isobutene with p-methyl styrene; 1-hexene with 1,3-hexadiene; 1 octene with 1-hexene; 1 heptene with 1-pentene;

3-methyl-1-butene with 1-octene; 3,3-dimethyl-1-pentene with 1-hexene; isobutene with styrene and piperylene, etc.

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

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

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

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

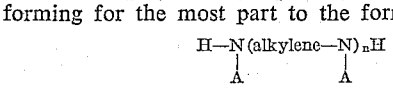
The nitrogen-containing group of the acylated nitrogen compositions of this invention is derived from compounds characterized by a radical having the structural configuration

The two remaining valences of the nitrogen atom of the above

radical preferably are satisfied by hydrogen, amino, or organic radicals bonded to said nitrogen atom through direct carbon-to-nitrogen linkages. Thus, the compounds from which the nitrogen-containing group may be derived include principally ammonia, aliphatic amines, aromatic amines, heterocyclic amines, or carbocyclic amines. The amines may be primary or secondary amines and may also be polyamines such as alkylene amines, arylene amines, cyclic polyamines, and the hydroxy-substituted derivatives of such polyamines.

Specific amines of these types are methylamine, N-methylethylamine, N-methyl-octylamine, N-cyclohexyl-aniline, dibutylamine, cyclohexylamine, aniline, di(p-methylphenyl)amine, dodecylamine, octadecylamine, o-phenylenediamine, N,N′-di-n-butyl-p-phenylenediamine, morpholine, piperazine, tetrahydropyrazine, indole, hexahydro-1,3,5-triazine, 1-H-1,2,4-triazole, melamine, bis-(p-aminophenyl)methane, phenyl-methylenimine, menthanediamine, cyclohexamine, pyrrolidine, 3-amino-5,6-diphenyl-1,2,4-triazine, ethanolamine, diethanolamine, quinonediimine, 1,3-indandiimine, 2-octadecylimidazoline, 2-phenyl-4-methyl-imidazolidine, oxazolidine, and 2-heptyl-oxazolidine.

A preferred source of the nitrogen-containing group consists of polyamines, especially alkylene amines conforming for the most part to the formula



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

The ethylene amines are especially useful. They are described in some detail under the heading "Ethylene Amines" in "Encyclopedia of Chemical Technology," Kirk and Othmer, volume 5, pages 898–905, Interscience Publishers, New York (1950). Such compounds are prepared most conveniently by the reaction of an alkylene chloride with ammonia. The reaction results in the production of somewhat complex mixtures of alkylene amines, including cyclic condensation products such as piperazines. These mixtures find use in the process of this invention. On the other hand, quite satisfactory products may be obtained also by the use of pure alkylene amines. An especially useful alkylene amine for reasons of economy as well as effectiveness of the products derived therefrom is a mixture of ethylene amines prepared by the reaction of ethylene chloride and ammonia and having a composition which corresponds to that of tetraethylene pentamine.

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

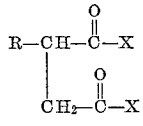
Higher homologues such as are obtained by condensation of the above-illustrated alkylene amines or hydroxy alkyl-substituted alkylene amines through amino radicals or through hydroxy radicals are likewise useful. It will be appreciated that condensation through amino radicals results in an higher amine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

Other sources of the nitrogen-containing group include ureas, thioureas, hydrazines, guanidines, amidines, amides, thioamides, cyanamides, etc. Specifice examples illustrating such compounds are: hydrazine, phenylhydrazine, N,N′-diphenylhydrazine, octadecylhydrazine, benzoylhydrazine, urea, thiourea, N-butylurea, stearylamide, oleylamide, guanidine, 1,3-diphenylguanidine,

1,2,3 - tributylguanidine, benzamidine, octadecamidine, N,N'-dimethylstearamidine, cyanamide, dicyandiamide, guanylurea aminoguanidine, etc.

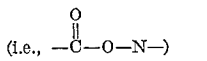
As indicated previously, the nitrogen-containing group in the acylated nitrogen compositions of this invention is characterized by a nitrogen atom attached directly to the scuccinic radical. It will be apperciated, of course, that the linkage between a nitrogen atom and a succinoyl radical is representative of an amide or an imide structure, that the linkage between a nitrogen atom and a succinimidoyl radical is representative of an amidine structure, and that the linkage between a nitrogen atom and a succinoyloxy radical is representative of an ammonium-carboxylic acid salt structure. Thus, the acylated nitrogen compositions of this invention are characterized by amide, amide-salt, imide, amidine, or salt linkages and in many instances a mixture of such linkages.

A convenient method for preparing the acylated nitrogen compositions comprises reacting a high molecular weight succinic acid-producing compound characterized by the presence within its structure of a high molecular weight oil-solubilizing group having at least about 50 aliphatic carbon atoms and at least one succinic acid-producing group. Such compounds are illustrated by one having the structural configuration

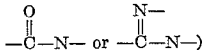


wherein R is a subsantially hydrocarbon radical having at least about 50 aliphatic carbon atoms and X is selected from the class consisting of halogen, hydroxy, hydrocarbon-oxy, and acyloxy radicals, with a least about one-half an equivalent amount of a nitrogen-containing compound characterized by the presence within its structure of at least one radical having the structural configuration

The above process involves a reaction between the succinic acid-producing group with the nitrogen-containing radical to result in the direct attachment of the nitrogen atoms to the succinic radical, i.e., succinoyl, succinimidoyl, or succinolyloxy radical. The linkage formed between the nitrogen atom and the succinic radical may thus be that representative of a salt, amide, imide, or amidine radical. In most instances the product of the above process contains a mixture of linkages representative of such radicals. The precise relative proportions of such radicals in the product usually are not known as they depend to a large measure upon the type of the acid-producing group and the nitrogen-containing radical involved in the reaction and also upon the environment (e.g., temperature) in which the reaction is carried out. To illustrate, the reaction involving an acid or anhydride group with an amino nitrogen-containing radical at relatively low temperatures such as below about 60° C. results predominantly in a salt linkage



but at relatively high temperatures such as above about 80° C. results predominantly in an amide, imide, or amidine linkage



In any event, however, the products obtained by the above process, irrespective of the nature or relative proportions of the linkages present therein, have been found to be effective as additives in hydrocarbon oils for the purposes of this invention.

The substantially saturated, aliphatic hydrcarbon-substituted succinic acids and anhydrides are especially preferred for use as the acid-producing reactant of this process for reasons of the particular effectiveness of the products obtained from such compounds as additives in hydrocarbon oils. The succinic compounds are readily available from the reaction of maleic anhydride with a high molecular weight olefin or a chlorinated hydrocarbon such as the olefin polymer described hereinabove. The reaction involves merely heating the two reactants at a temperature about 100°–200° C. The product from such a reaction is an alkenyl succinic anhydride. The alkenyl group may be hydrogenater to an alkyl group. The anhydride may be hydrolyzed by treatment with water or steam to the corresponding acid. Either the anhydride or the acid may be converted to the corresponding acid halide or ester by reaction with, e.g., phosphorus halide, phenols, or alcohols.

In lieu of the olefins or chlorinated hydrocarbons, other hydrocarbons containing an activating polar substituent, i.e., a substituent which is capable of activating the hydrocarbon molecule in respect to reaction with maleic acid or anhydride, may be used in the above-illustrated reaction for preparing the succinic compounds. Such polar substituents may be illustrated by sulfide, disulfide, nitro, mercaptan, bromine, ketone, and aldehyde radicals. Examples of such polar-substituted hydrocarbons include polypropene sulfide, di-polyisobutene disulfide, nitrated mineral oil, di-polyethylene sulfide, brominated polyethylene, etc. Another method useful for preparing the succinic acids and anhydrides involves the reaction of itaconic acid with a high molecular weight olefin or a polar-substituted hydrocarbon at a temperature usually within the range from about 100° C. to about 200° C.

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

The nitrogen-containing reactants useful in the above process are the compounds, described previously in this specification, from which the nitrogen-containing group the acylated nitrogen compositions of this invention can be derived.

The above process is usually carried out by heating a mixture of the acid-producing compound and the nitrogen-containing reactant at a temperature above 80° C., preferably within the range from about 100° C., to about 250° C. However, when an acid or anhydride is employed in reactions with an amino nitrogen-containing reactant, the process may be carried out at a lower temperature such as room temperature to obtain products having predominantly salt linkages or mixed salt-amide linkages. Such products may be converted, if desired, by heating to above 80° C. to products having predominantly amide, imide, or amidine linkages. The use of a solvent such as benzene, toluene, naphtha, mineral oil, xylene, n-hexane, or the like is often desirable in the above process to facilitate the control of the reaction temperature.

The relative proportions of the acid-producing compounds and the nitrogen-containing reactants to be used in the above process are such that at least about one-half of a stoichiometrically equivalent amount of the nitrogen-containing reactant is used for each equivalent of the acid-producing compound used. In this regard it will be noted that the equivalent weight of the nitrogen-containing reactant is based upon the number of the nitrogen-con-

taining radicals. Similarly the equivalent weight of the acid-producing compound is based upon the number of the acid-producing radicals defined by the structural configuration

Thus, ethylene diamine has two equivalents per mole; amino guanidine has four equivalents per mole; a succinic acid or ester has two equivalents per mole, etc.

The upper limit of the useful amount of the nitrogen-containing reactant appears to be about two equivalents for each equivalent of the acid-producing compound used. Such amount is required, for instance, in the formation of products having predominantly amidine linkages. Beyond this limit, the excess amount of the nitrogen-containing reactant appears not to take part in the reaction and thus simply remains in the product apparently without any adverse effects. On the other hand, the lower limit of about one-half equivalent of the nitrogen-containing reactant used for each equivalent of the acid producing compound is based upon the stoichiometry for the formation of products having predominantly imide linkages. In most instances, the preferred amount of the nitrogen-containing reactant is approximately one equivalent for each equivalent of the acid-producing compound used.

The following examples illustrate the processes useful for preparing the acylated nitrogen compositions useful in the process of this invention:

Example 1

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

Example 2

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

Example 3

The procedure of Example 1 is 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 has a nitrogen content of 1.9%.

Example 4

The procedure of Example 1 is repeated using 55.0 grams (1.5 equivalents) of triethylene tetramine as the amine reactant. The resulting product has a nitrogen content of 2.9%.

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 is added at room temperature 63.6 grams (1.55 equivalents) of a commercial ethylene amine mixture having an average composition corresponding to that of tetraethylene pentamine. The mixture is heated to distill the water-toluene azeotrope and then to 150° C. at reduced pressure to remove the remaining toluene. The residual polyamide has a nitrogen content of 4.7%.

Example 6

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

Example 7

A polyisobutenyl succinic anhydride having an acid number of 105 and an equivalent weight of 540 is 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 is added at 65–95° C. an equivalent amount (25 parts by weight) of the commercial ethylene amine mixture of Example 5. This mixture then is heated to 150° C. to distill all of the water formed in the reaction. Nitrogen is bubbled through the mixture at this temperature to insure removal of the last traces of water. The residue is 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 1060 grams of mineral oil is heated at 140–150° C. for one hour. Nitrogen is bubbled through the mixture at this temperature for four more hours to aid in the removal of water. The residue is diluted with 420 grams of mineral oil and this oil solution is 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 is added at 85–95° C. 70 grams (1.87 equivalents) of tetraethylene pentamine. The mixture then is heated at 150°–165° C. for four hours, blowing with nitrogen to aid in the removal of water. The residue is 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 is 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 has 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 is added portionwise 22 grams (0.52 equivalent) the commercial ethylene amine mixture of Example 5. The reaction mixture is heated at reflux temperature for three hours and water removed from an azeotrope with toluene. The toluene then is removed by heating to 150° C./20 millimeters. The residue was found to contain 1.3% of nitrogen.

Example 11

A substituted succinic anhydride is prepared by reacting maleic anhydride with a chlorinated copolymer of isobutylene and styrene. The copolymer consists of 94 parts by weight of isobutylene units and 6 parts by weight of styrene units, has an average molecular weight of 1,200, and is chlorinated to a chlorine content of 2.8% by weight. The resulting substituted succinic anhydride has an acid number of 40. To 710 grams (0.51 equivalent) of this substituted succinic anhydride and 500 grams of toluene there is added portionwise 22 grams (0.51 equivalent) of

the commercial ethylene amine mixture of Example 5. The mixture is 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 contains 1.1% by weight of nitrogen.

Example 12

A substituted succinic anhydride is prepared by reacting maleic anhydride with a chlorinated copolymer of isobutylene and isoprene. The copolymer consists of 99 parts by weight of isobutylene units and 1% by weight of isoprene units. The molecular weight of the copolymer is 28,000 and the chlorine content of the chlorinated copolymer is 1.95%. The resulting alkenyl succinic anhydride had an acid number of 54. To a 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 the commercial ethylene amine mixture of Example 5 is heated at 110°–120° C. for three hours, water being removed from an azeotrope with toluene. When all of the water has thus been removed the toluene is distilled by heating to 150° C./20 millimeters. The residue is found to have a nitrogen content of 1.1%.

Example 13

A polyisobutenyl succinic anhydride is prepared by the reaction of a chlorinated polyisobutylene with maleic anhydride. The chlorinated polyisobutylene has a chlorine content of 2% and an average molecular weight of 11,000. The polyisobutenyl succinic anhydride has an acid number of 48. A mixture of 410 grams (0.35 equivalent) of this anhydride, 15 grams (0.35 equivalent) of the commercial ethylene amine mixture of Example 5 and 500 grams of toluene is heated at reflux temperature for four hours to remove water from an azeotrope with toluene. The toluene then is removed by heating to 150° C./20 millimeters. The nitrogen content of the residue is 1.3%.

Example 14

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

Example 15

A polyisobutenyl-substituted succinic acid is 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 is added at room temperature 59.5 grams (1.5 equivalents) of the commercial ethylene amine mixture of Example 5. This mixture is heated at 150°–167° C. for 7 hours during which time a total of 19.5 grams of water is distilled from the mixture. The residue is diluted with 174 grams of mineral oil and then filtered at 150° C. The filtrate has a nitrogen content of 1.6%.

Example 16

A mixture of 1056 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 is heated at reflux temperature (180°–190° C.) for 5 hours. A total of 18 grams of water is collected from the water-toluene azeotrope. The residue is heated to 150° C./20 mm. to remove any last traces of water which might have remained. The nitrogen analysis of this residue is 1.9%.

Example 17

A polyisobutylene having an average molecular weight of 50,000 is chlorinated to a chlorine content of 10% by weight. This chlorinated polyisobutylene is 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 is added portionwise at 70–105° C. 108 grams (2.55 equivalents) of the commercial ethylene amine mixture of Example 5 over a period of 45 minutes. The resulting mixture is heated for four hours at 160–180° C. while nitrogen is bubbled throughout to remove water. When all of the water has been removed the product is filtered and the filtrate found to have a nitrogen content of 0.6%.

Example 18

A mixture of 1 equivalent of a polyisobutene-substituted succinic anhydride having an acid number of 98 (prepared according to the procedure described in Example 1) and 1 equivalent of an acrolein-ammonia (molar ratio of 1:1) interpolymer having a nitrogen content of 23% by weight is diluted with 40% by its weight of a mineral oil. The resulting mixture is heated to 155° C. and nitrogen is bubbled through the mixture at this temperature for 5 hours. The residue is found to have a nitrogen content of 1.35%.

Example 19

A cyanoethyl-substituted ethylene amine is prepared by mixing 212 grams of acrylonitrile with 216 grams of an ethylene amine mixture consisting of 75% by weight of triethylene tetramine and 25% by weight of diethylene triamine at room temperature and heating the mixture at 110°–130° C. for 5 hours and then to 125° C./30 mm. To a mixture of 1110 grams of the polyisobutene-substituted succinic anhydride of Example 1 and 825 grams of mineral oil there is added at 60° C. 143 grams dropwise of the above cyanoethyl-substituted ethylene amine (having a nitrogen content of 31.8%). The mixture is heated at 150°–160° C. for 5 hours while being purged with nitrogen. A total of 6 cc. of water is removed by distillation. The residue has a nitrogen content of 1.66%.

Example 20

To a mixture of 430 grams of the polyisobutene-substituted succinic anhydride of Example 1 and 355 grams of mineral oil there is added at 60°–80° C. 108 grams of N-aminopropyl morpholine throughout a period of 1 hour. The mixture is heated at 150°–155° C. for 5 hours until no more distills. The residue is found to have a nitrogen content of 2.3%.

Example 21

To a mixture of 430 grams of the polyisobutene-substituted succinic anhydride of Example 1 and 304 grams of mineral oil there is added at 60°–80° C. 33 grams of dipropylene triamine. The mixture is then heated at 150°–155° C. for 5 hours until no more water distills. The residue is found to have a nitrogen content of 1.45%.

Example 22

To a mixture of 1000 grams of the polyisobutene-substituted succinic anhydride of Example 1 and 500 grams of mineral oil there is introduced at 150°–160° C. beneath its surface a sufficient quantity of ammonia for formation of an imide within a period of 1 hour. The mixture is diluted with 169 grams of mineral oil, heated to 150° C. and filtered. The filtrate is found to have a nitrogen content of 0.77%.

Example 23

A mixture of 286 grams of polyisobutene-substituted succinic anhydride of Example 1, 96 grams of N,N-dibutyl ethylene diamine and 252 grams of mineral oil is prepared at 60° C. and heated at 150°–165° C. for 5 hours while being purged with nitrogen. The residue is found to have a nitrogen content of 2.24%.

Example 24

A mixture of 417 grams of polyisobutene-substituted succinic anhydride of Example 1, 30 grams of N-(2-aminoethyl) trimethylene diamine and 293 grams of mineral oil is prepared at 60°–80° C. for 5 hours while being purged with nitrogen. The residue is found to have a nitrogen content of 1.51.

Example 25

A mixture of 430 grams of the polyisobutene-substituted succinic anhydride of Example 1, 64 grams of 1,1-(dimethylaminoethyl)-4-methyl-piperazine and 324 grams of mineral oil is prepared at 60° C. and then heated at 150°–155° C. while being blown with nitrogen. The residue is found to have a nitrogen content of 1.81%.

Example 26

A mixture of 416 grams of polyisobutene-substituted succinic anhydride of Example 1, 124 grams of N-phenyl piperazine and 356 grams of mineral oil is prepared at 60° C. and then heated at 150–155° C. for 5 hours while being purged with nitrogen. No water is removed by such heating. The residue is found to have a nitrogen content of 2.07%.

Example 27

A mixture of 1110 grams of polyisobutene-substituted succinic anhydride of Example 1, 105 grams of anthranilic acid and 844 grams of mineral oil is heated at 100° C. for 2 hours. The mixture is cooled and is mixed with 72 grams of a mixture consisting of 75% by weight of triethylene tetramine and 25% by weight of diethylenetriamine at 60°–80° C. The resulting mixture is heated at 150°–155° C. for 5 hours while being purged with nitrogen. The residue is found to have a nitrogen content of 1.72%.

Example 28

A diisobutenyl-substituted ethylene amine is prepared by reacting 590 grams of diisobutenyl chloride and 264 grams of a mixture consisting of 75% by weight of triethylene tetramine and 20% by weight of diethylene triamine in the presence of 264 grams of potassium hydroxide (85% purity) and 2200 grams of isopropyl alcohol at 85°–90° C. A mixture of 528 grams of polyisobutene-substituted succinic anhydride of Example 1, 101 grams of the above diisobutenyl-substituted ethylene amine and 411 grams of mineral oil is heated at 150°–160° C. while being purged with nitrogen until no more water distills. The residue has a nitrogen content of 1.98%.

Example 29

A mixture of 45 grams of di-(polypropoxy)cocoamine having a molecular weight of 2265, 22 grams of polyisobutene-substituted succinic anhydride of Example 1 and 44 grams of mineral oil is heated at 150°–155° C. for 7 hours. The residue is found to have a nitrogen content of 0.25%.

Example 30

A mixture of 1000 grams of the polyisobutene-substituted succinic anhydride of Example 1, 159 grams of menthane diamine and 500 grams of mineral oil is prepared at 70°–100° C. and heated at 150°–190° C. while being blown with nitrogen until no water distills. The residue is diluted with 258 grams of mineral oil and the solution is found to have a nitrogen content of 1.32.

Example 31

A polypropylene-substituted succinic anhydride having an acid number of 84 is prepared by the reaction of a chlorinated polypropylene having a chlorine content of 3% and molecular weight of 1200 with maleic anhydride. A mixture of 813 grams of the polypropylene-substituted succinic anhydride, 50 grams of a commercial ethylene amine mixture having an average composition corresponding to that of tetraethylene pentamine and 566 grams of mineral oil is heated at 150° C. for 5 hours. The residue is found to have a nitrogen content of 1.18%.

Example 32

A mixture of 206 grams of N,N'-disecondary-butyl p-phenylene diamine, 1000 grams of the polyisobutene-substituted succinic anhydride of Example 1 and 500 grams of mineral oil is prepared at 85° C. and heated at 150°–200° C. for 9.5 hours. The mixture is diluted with 290 grams of mineral oil, heated to 160° C. and filtered. The filtrate is found to have a nitrogen content of 1.29%.

Example 33

To 1000 grams of the polyisobutene-substituted succinic anhydride of Example 1 and 500 grams of mineral oil there is added 17.6 grams of hydrazine at 70°–80° C. The reaction is exothermic. The mixture is heated at 140°–150° C. for 1 hour whereupon 9 grams of water is collected as the distillate. To the residue there is then added 40 grams of an ethylene amine mixture having an average composition corresponding to that of tetraethylene pentamine at 70°–80° C. The mixture is then heated at 150°–160° C. while being purged with nitrogen until no more water is removed by distillation. The residue is diluted with 200 grams of mineral oil, heated to 160° C. and filtered. The filtrate has a nitrogen content of 1.16%.

Example 34

To a solution of 1000 grams of the polyisobutene-substituted succinic anhydride of Example 1 in 500 grams of mineral oil there is added 28 grams of 1,1-dimethyl hydrazine at 50°–60° C. The mixture is heated at 60°–95° C. for 3 hours and then mixed with 40 grams of an ethylene amine mixture having an average composition corresponding to that of tetraethylene pentamine at 85°–95° C. The mixture is then heated at 150°–185° C. for 6 hours whereupon 14 grams of water is collected as the distillate. The residue is diluted with 197 grams of mineral oil, heated to 160° C. and filtered. The filtrate has a nitrogen content of 1.53%.

Example 35

A mixture of 1000 grams of the polyisobutene-substituted succinic anhydride of Example 1, 333 grams of 1,2-di(3-aminopropoxy) ethane and 500 grams of mineral oil is heated at 140°–170° C. for 5 hours whereupon 18 grams of water is collected as the distillate. The residue is diluted with 380 grams of mineral oil, heated to 160° C. and filtered. The filtrate has a nitrogen content of 2.3%.

Example 36

A mixture of 1000 grams of the polyisobutene-substituted succinic anhydride of Example 1, 418 grams of di(3-aminopropoxy ethyl) ether and 500 grams of mineral oil is heated at 150°–170° C. for 4 hours. A total of 17 grams of water is collected as the distillate. The residue is diluted with 433 grams of mineral oil heated to 160° C. and filtered. The filtrate has the nitrogen content of 2.18%.

Example 37

A mixture of 1000 grams of the polyisobutene-substituted succinic anhydride of Example 1 and 361 grams of a technical tertiary-alkyl primary amine wherein the tertiary-alkyl radical contains 12–14 carbon atoms and 500 grams of mineral oil is heated at 155°–250° C. for 13 hours while being urged with nitrogen. The reisdue is then heated to 150° C./1 mm., diluted with 337 grams of mineral oil, heated to 160° C. and filtered. The filtrate has a nitrogen content of 0.87%.

Example 38

A mixture of 1000 grams of the polyisobutene-substituted succinic anhydride of Example 1, 254 grams of aminoguanidine bicarbonate and 500 grams of mineral

oil is prepared at 80° C. and heated at 130°–165° C. for 5 hours. The residue is mixed with 223 grams of mineral oil, heated to 150° C., and filtered. The filtrate has the nitrogen content of 3.38%.

Example 39

A mixture of 1000 grams of the polyisobutene-substituted succinic anhydride of Example 1, 178 grams of 2-amino-pyridine and 500 grams of mineral oil is heated at 140°–175° C. for 10 hours while being purged with nitrogen. A total of 16 grams of water is collected as the distillate. The residue is diluted wtih 273 grams of mineral oil and filtered. The filtrate has a nitrogen content of 2.55%.

Example 40

A mixture of 1000 grams of the polyisobutene-substituted succinic anhydride of Example 1, 103 grams of 2,6-diamino-pyridine and 500 grams of mineral oil is heated at 140°–180° C. for 11 hours while being purged with nitrogen. A total of 16 grams of water is collected as the distillate. The residue is diluted with 223 grams of mineral oil, heated to 150° C. and filtered. The filtrate has a nitrogen content of 2.15%.

Example 41

A mixture of 1000 grams of polyisobutene-substituted succinic anhydride of Example 1 159 grams of cyanoguanidine and 233 grams of toluene is heated at the reflux temperature for 14 hours while 7.15 grams of water is removed by azeotropic distillation. The mixture is diluted with 740 grams of mineral oil and toluene is then removed by heating the mixture to 150° C. The residue is filtered and the filtrate has the nitrogen content of 4.74%.

Example 42

A mixture of 1632 grams of polyisobutene-substituted succinic anhydride of Example 1 207 grams of a condensation product of acrolein with ammonia (molar ratio of 1:1) having a nitrogen content of 20%, 604 grams of mineral oil and 1750 grams of toluene is heated at the reflux temperature for 3 hours. A total of 31 grams of water is removed as the distillate. Toluene is then removed by heating the mixture to 150° C./20 mm. The residue is found to have a nitrogen content of 1.89%.

Example 43

A nitrogen-containing compound is prepared by mixing 100 grams of cyanoguanidine with 500 grams of ethylene amine mixture having an average composition corresponding to that of tetraethylene pentamine and heating the mixture at 70°–80° C. for 3 hours to obtain a homogeneous mass and filtering the mass. A mixture of 1000 grams of the polyisobutene-substituted succinic anhydride of Example 1 96 grams of the above filtrate and 164 grams of toluene is heated at the reflux temperature for 10 hours. Toluene is then removed by heating the mixture to 150° C./20 mm. The residue is diluted with 400 grams of mineral oil and filtered. The filtrate has a nitrogen content of 3.43%.

Example 44

To a mixture of 544 grams of the polyisobutene-substituted succinic anhydride of Example 1 283 grams of mineral oil and 281 grams of toluene there is added 30 grams of urea at 45° C. The resulting mixture is heated at 130°–135° C. for 11 hours whereupon 2.5 cc. of water is removed as the distillate. The residue is then heated to 140° C./20 mm. and filtered. The filtrate has a nitrogen content of 1%.

Example 45

A mixture of 1088 grams of the polyisobutene-substituted succinic anhydride of Example 1, 106 grams of dipropylene triamine, 500 grams of toluene is heated at the reflux temperature for 4 hours until no more water distills. The residue is then heated to 150° C./20 mm. and diluted with 392 grams of mineral oil. The oil solution is found to have a nitrogen content of 1.74%.

Example 46

A mixture of 1000 grams of the polyisobutane-substituted succinic anhydride of Example 1, 174 grams of phenylbiguanide and 270 grams of toluene is heated at the reflux temperature for 6.5 hours whereupon 25 grams of water is removed by distillation. The residue is diluted with 500 grams of mineral oil and heated to 160° C./20 mm. to distill off toluene. The residue is diluted further with 265 grams of mineral oil, heated to 150° C. and filtered. The filtrate has a nitrogen content of 3.4%.

Example 47

A mixture of 920 grams of the polyisobutene-substituted succinic anhydride of Example 1, and 249 grams of bis-(dimethylaminopropyl)amine is heated at the reflux temperature until no more water distills. The residue has a nitrogen content of 4%.

Example 48

A mixture of 1000 grams of the polyisobutene-substituted succinic anhydride of Example 1, 363 grams of aminopropyl octadecylamine and 1314 grams of mineral oil is heated at 2000° C. for 24 hours. The residue is filtered. The filtrate has a nitrogen content of 1.02%.

Example 49

A mixture of 1000 grams of the polyisobutene-substituted succinic anhydride of Example 1, and 258 grams of di-n-butylamine is heated at 185° C. for 12 hours and then to 200° C./25 mm. The residue is diluted with 1157 grams of mineral oil and filtered. The filtrate has a nitrogen content of 0.8%.

Example 50

A mixture of 297 grams of the polyisobutene-substituted succinic anhydride of Example 1, 25 grams of melamine and 200 grams of mineral oil is heated at 190°–250° C. for 9 hours and then at 290°–295°C. for 7 more hours. The residue is mixed with 50 grams of water, heated at reflux for 7 hours, dried and filtered. The filtrate has a nitrogen content of 2%.

Example 51

A mixture of 100 grams of the polyisobutene-substituted succinic anhydride of Example 1 and 67 grams of mineral oil is heated to 50°C. To this mixture there is added 59 grams of a 85% aqueous solution of hydrazine hydrate. The mixture is heated at 100°–110° C. for 1.25 hours, diluted with toluene, and heated at 107° C. until no more water distills. Toluene is removed by distillation. The residue has a nitrogen content of 0.8%.

Example 52

A mixture of 1.0 equivalent of the dimethyl ester of the polyisobutene substituted succinic anhydride of Example 1 and 1.0 equivalent of N,N-dibutyl thiourea is dissolved in five times its volume of xylene. The resulting mixture is heated at the reflux temperature until no more water is removed by azeotropic distillation. The mixture is heated further and the xylene is removed by distillation. The residue is the acylated nitrogen compound.

Example 53

A product is obtained by the procedure of Example 1, except that pyrrolidine (1 equivalent) is used in lieu of the diethylene triamine used.

Example 54

A product is obtained by the procedure of Example 1, except that hexahydro-1,3,5-triazine (1 equivalent) is used in lieu of the diethylene triamine used.

Example 55

A product is obtained by the procedure of Example 1, except that 1,3,4-dithiazolidine (1 equivalent) is used in lieu of the diethylene triamine used.

Example 56

A product is obtained by the procedure of Example 1, except that hexamethylene tetramine (2 equivalents) is used in lieu of the diethylene triamine used.

Example 57

A product is obtained by the procedure of Example 1, except that tripentylene tetramine (3 equivalents) is used in lieu of the diethylene triamine used.

Example 58

An equi-molar mixture of the polyisobutene-substituted succinic anhydride of Example 1 and N-octyl thiourea is diluted with an equal volume of xylene. The resulting mixture is heated at the reflux temperature for 30 hours. The residue is a xylene solution of the product.

Example 59

A product is obtained by the procedure of Example 58 except that oleylamide is used in lieu of the thiourea used.

Example 60

A product is obtained by the procedure of Example 58 except that 1,3-diphenyl guanidine is used in lieu of the thiourea used.

Example 61

A product is obtained by the procedure of Example 58 except that octadecamidine is used in lieu of the thiourea used.

Example 62

A product is obtained by the procedure of Example 58 except that guanylurea is used in lieu of the thiourea used.

Example 63

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 64

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)-trimethylene diamine 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 65

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 66

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-methyl piperazine was prepared at 60° C. The mixture was heated at 180°–276° C./40 mm. for 14.5 hours. The residue has a nitrogen content of 1.12%.

Example 67

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 68

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 has a nitrogen content of 1.57%.

Example 69

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 alkylene 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 70

A product is obtained by the procedure of Example 58 except that an equimolar mixture of ammonia and bis(2-hydroxyethyl)amine is used in lieu of the thiourea used.

Example 71

A product is obtained by the procedure of Example 58 except that benzidine is used in lieu of the thiourea used.

Example 72

An acylated nitrogen composition is prepared according to the procedure of Example 1 except that the reaction mixture consists of 3880 grams of the polyisobutenyl succinic anhydride, 376 grams of a mixture of triethylene tetramine and diethylene triamine (75:25 weight ratio), and 2785 grams of mineral oil. The product is found to have a nitrogen content of 2%.

Example 73

An acylated nitrogen composition is prepared according to the procedure of Example 1 except that the reaction mixture consists of 1385 grams of the polyisobutenyl succinic anhydride, 179 grams of a mixture of triethylene tetramine and diethylene triamine (75:25 weight ratio), and 1041 grams of mineral oil. The product is found to have a nitrogen content of 2.55%.

Example 74

An acylated nitrogen composition is prepared according to the procedure of Example 31 except that the polyisobutene-substituted succinic anhydride of Example 1 (1 equivalent for 1.5 equivalents of the amine reactant) is substituted for the polypropylene-substituted succinic anhydride used.

Example 75

An acylated nitrogen composition is prepared according to the procedure of Example 31 except that the polyisobutene-substituted succinic anhydride of Example 1, (1 equivalent for 2 equivalents of the amine reactant) is substituted for the polypropylene-substituted succinic anhydride used.

Example 76

An acylated nitrogen composition is prepared according to the procedure of Example 4 except that the commercial ethylene amine mixture (1.5 equivalent per equivalent of the anhydride) of Example 7 is substituted for the triethylene tetramine used.

Example 77

An acylated nitrogen composition is prepared according to the procedure of Example 31 except that the polyisobutene-substituted succinic anhydride of Example 1 (1 equivalent for 1 equivalent of the amine reactant) is substituted for the polypropylene-substituted succinic anhydride. The composition is found to have a nitrogen content of 1.5%.

The boron compounds useful in reaction with the acylated nitrogen compositions include boron oxide, boron oxide hydrate, boron trifluoride, boron tribromide, boron trichloride, boron acids such as boronic acid (e.g., alkyl-$B(OH)_2$ or aryl-$B(OH)_2$), boric acid (i.e., H_3BO_3), tetraboric acid (i.e., $H_2B_4O_7$), metaboric acid (i.e. HBO_2), and esters of such boron acids. The use of complexes of a boron trihalide with ethers, organic acids, inorganic acids, or hydrocarbons is a convenient means of introducing the boron reactant into the reaction mixture. Such complexes are known and are exemplified by boron-trifluoride-diethyl ester, boron trifluoride-phosphoric acid, boron trichloride-chloroacetic acid, boron tribromide-dioxane, and boron trifluoride-methyl ethyl ether.

Specific examples of boronic acids include methyl boronic acid, phenyl-boronic acid, cyclohexyl boronic acid, p-heptylphenyl boronic acid and dodecyl boronic acid.

The boron acid esters include especially mono-, di-, and tri-organic esters of boric acid with alcohols or phenols such as, e.g., methanol, ethanol, isopropanol, cyclohexanol, cyclopentanol, 1-octanol, 2-octanol, dodecanol, behenyl alcohol, oleyl alcohol, stearyl alcohol, benzyl alcohol, 2-butyl cyclohexanol, ethylene glycol, propylene glycol, trimethylene glycol, 1,3-butanediol, 2,4-hexanediol, 1,2-cyclohexanediol, 1,3-octanediol, glycerol, pentaerythritol diethylene glycol, carbitol, Cellosolve, triethylene glycol, tripropylene glycol, phenol, naphthol, p-butylphenol, o,p-diheptylphenol, n-cyclohexylphenol, 2,2-bis-(p-hydroxyphenyl)propane, polyisobutene (molecular weight of 1500)-substituted phenol, ethylenechlorohydrin, o-chlorophenol, m-nitrophenol, 6-bromo-octanol, and 7-keto-decanol. Lower alcohols, 1,2-glycols, and 1-3-glycols, i.e., those having less than about 8 carbon atoms are especially useful for preparing the boric acid esters for the purpose of this invention.

Methods for preparing the esters of boron acid are known and disclosed in the art (such as "Chemical Reviews," pages 959–1064, volume 56). Thus, one method involves the reaction of boron trichloride with 3 moles of an alcohol or a phenol to result in a tri-organic borate. Another method involves the reaction of boric oxide with an alcohol or a phenol. Another method involves the direct esterification of tetra boric acid with 3 moles of an alcohol or a phenol. Still another method involves the direct esterification of boric acid with a glycol to form, e.g., a cyclic alkylene borate.

The reaction of the acylated nitrogen compositions with the boron compounds can be effected simply by mixing the reactants at the desired temperature. The use of an inert solvent is optional although it is often desirable, especially when a highly viscous or solid reactant is present in the reaction mixture. The inert solvent may be a hydrocarbon such as benzene, toluene, naphtha, cyclohexane, n-hexane, or mineral oil. The temperature of the reaction may be varied within wide ranges. Ordinarily it is preferably between about 50° C. and about 250° C. In some instances it may be 25° C. or even lower. The upper limit of the temperature is the decomposition point of the particular reaction mixture.

The reaction is usually complete within a short period such as 0.5 to 6 hours. After the reaction is complete, the product may be dissolved in the solvent and the resulting solution purified by centrifugation or filtration if it appears to be hazy or contain insoluble substances. Ordinarily the product is sufficiently pure so that further purification is unnecessary or optional.

The reaction of the acylated nitrogen compositions with the boron compounds results in a product containing boron and substantially all of the nitrogen originally present in the nitrogen reactant. It is believed that the reaction results in the formation of a complex between boron and nitrogen. Such complex may involve in some instances more than one atomic proportion of boron with one atomic proportion of nitrogen and in other instances more than one atomic proportion of nitrogen with one atomic proportion of boron. The nature of the complex is not clearly understood. Evidence appears to indicate that the complex results from a direct linkage between boron and nitrogen and that in most instances, the radicals originally present in the boron and the nitrogen atoms do not take part directly in the complex formation. However, in the case of a boron acid as the reactant, the reaction is often accompanied with the formation of water.

Inasmuch as the precise stoichiometry of the complex formation is not known, the relative proportions of the reactants to be used in the process are based primarily upon the consideration of utility of the products for the purposes of this invention. In this regard, useful products are obtained from reaction mixtures in which the reactants are present in relative proportions as to provide from about 0.1 atomic proportions of boron for each mole of the acylated nitrogen composition used to about 10 atomic proportions of boron for each atomic proportion of nitrogen of said acylated nitrogen composition used. The preferred amounts of reactants are such as to provide from about 0.5 atomic proportion of boron for each mole of the acylated nitrogen composition to about 2 atomic proportions of boron for each atomic proportion of nitrogen used. To illustrate, the amount of a boron compound having one boron atom per molecule to be used with one mole of an acylated nitrogen composition having five nitrogen atoms per molecule is within the range from about 0.1 mole to about 50 moles, preferably from about 0.5 mole to about 10 moles.

The following examples are illustrative of the process for preparing the nitrogen- and boron-containing compositions of this invention.

Example A

To 600 grams (1 atomic proportion of nitrogen) of the acylated nitrogen composition prepared according to the process of Example 77 there is added 45.5 grams (0.5 atomic proportion of boron) of boron trifluoride-diethyl ether complex (1:1 molar ratio) at 60°–75° C. The resulting mixture is heated to 103° C. and then at 110° C./30 mm. to distill off all volatile components. The residue is found to have a nitrogen content of 1.44% and a boron content of 0.49%.

Example B

A mixture of 62 grams (1 atomic proportion of boron) of boric acid and 1645 grams (2.35 atomic proportions of nitrogen) of the acylated nitrogen composition obtained by the process of Example 72 is heated at 150° C. in nitrogen atmosphere for 6 hours. The mixture is then filtered and the filtrate is found to have a nitrogen content of 1.94% and a boron content of 0.33%.

Example C

An oleyl ester of boric acid is prepared by heating an equi-molar mixture of oleyl alcohol and boric acid in toluene at the reflux temperature while water is removed azeotropically. The reaction mixture is then heated to 150° C./20 mm. and the residue is the ester having a boron content of 3.2% and a saponification number of

62. A mixture of 344 grams (1 atomic proportion of boron) of the ester and 1645 grams (2.35 atomic proportions of nitrogen) of the acylated nitrogen composition obtained by the process of Example 72 is heated at 150° C. for 6 hours and then filtered. The filtrate is found to have a boron content of 0.6% and a nitrogen content of 1.74%.

Example D

A mixture of 344 grams (1 atomic proportion of boron) of the oleyl ester of boric acid of Example C and 1112 grams (2.86 atomic proportions of nitrogen) of the acylated nitrogen composition obtained by the process of Example 73 is heated at 150° C. for 6 hours and filtered. The filtrate is found to have a nitrogen content of 1.94% and a boron content of 0.81%.

Example E

Tri-isobutylborate is prepared by heating a mixture of 620 grams (10 moles) of boric acid, 2220 grams (30 moles) of isobutyl alcohol, and 800 grams of toluene at the reflux temperature while water formed during esterification is being removed by azeotropic distillation. The reaction mass is then heated at 100° C./20 mm. to distill off toluene and the borate is recovered by distillation at 105°–110° C./20 mm. The distillate is found to have a boron content of 5.2%. A mixture of 57 grams (0.27 atomic proportion of boron), 13 grams of mineral oil, and 1045 grams (1.56 atomic proportions of nitrogen) of the product obtained by the process of Example 74 is heated at 150°–160° C. for 3 hours and then blown with nitrogen at 170° C. (no volatile substance is formed). The mixture is then heated to 150° C./20 mm. and the residue is found to have a boron content of 0.39% and a nitrogen content of 1.98%.

Example F

Boron trifluoride (34 grams, 0.5 atomic proportion of boron) is bubbled into 1400 grams (1.5 atomic proportion of nitrogen) of the product prepared according to the process of Example 77 at 80° C. within a period of 3 hours. The resulting mixture is blown with nitrogen at 70°–80° C. for 2 hours and diluted with 23 grams of mineral oil. The residue is found to have a boron content of 0.42%, a fluorine content of 1.58%, and a nitrogen content of 1.41%.

Example G

A mixture of 31 grams (0.5 atomic proportion of boron) of boric acid and 1175 grams (1.75 atomic proportions of nitrogen) of the acylated nitrogen composition prepared by the process of Example 74 is heated at 150° C. for 3 hours and filtered. The filtrate is found to have a boron content of 0.43% and a nitrogen content of 1.85%.

Example H

A complex of phosphoric acid with 3 moles of boron trifluoride (67.3 grams, 0.62 atomic proportion of boron) is added dropwise to a mixture of 1344 grams (1.92 atomic proportions of nitrogen) of the acylated nitrogen composition of Example 74 and 432 grams of mineral oil. An exothermic reaction occurs. The mixture is heated at 80°–90° C. for 0.5 hour and mixed with 520 cc. of benzene. The resulting solution is washed with, successively, 500 cc. of water, a mixture of 500 cc. of water and 250 cc. of isopropyl alcohol, 50 cc. of a saturated sodium chloride solution, and a mixture of 750 cc. of water and 250 cc. isopropyl alcohol. The washed product is heated to 150° C./38–68 mm. within a period of 6 hours, cooled, and filtered. The filtrate is found to have a nitrogen content of 1.34% and a boron content of 0.1%.

Example I

A mixture of 12 grams (0.38 mole) of sulfur, 124 grams (2 atomic proportions of boron) of boric acid, and 1018 grams (2 atomic proportions of nitrogen) of the acylated nitrogen composition of Example 75 is heated at 150° C. for 3 hours and filtered. The filtrate is found to have a nitrogen content of 2.4%, a boron content of 1.68%, and a sulfur content of 0.5%.

Example J

The process of Example I is repeated except that thiourea (38 grams, 0.5 mole) is substituted for the sulfur used. The product is found to have a nitrogen content of 3.3%, a sulfur content of 1.44%, and a boron content of 1.75%.

Example K

A mixture of 55 grams (0.39 atomic proportion of boron) of boron trifluoride-diethyl ether complex (1:1 molar ratio) and 480 grams (0.77 atomic proportion of nitrogen) of the product of Example 76 is heated at 80°–90° C. for 0.5 hour and then to 120° C./30 mm. The residue is found to have a nitrogen content of 2.08% and a boron content of 0.76%.

Example L

A mixture of 372 (6 atomic proportions of boron) of boric acid and 3111 grams (6 atomic proportions of nitrogen) of the acylated nitrogen composition obtained by the process of Example 75 is heated at 150° C. for 3 hours and then filtered. The filtrate is found to have a boron content of 1.64% and a nitrogen content of 2.56%.

Example M

Boron trifluoride (272 grams, 4 atomic proportions of boron) is bubbled slowly into a mixture of 1790 grams of mineral oil and 5370 grams (7.3 atomic proportions of nitrogen) of the acylated nitrogen composition prepared by the process of Example 74. The mixture is then blown with nitrogen for 0.5 hour. The product, weighing 7426 grams (99% of theoretical yield), is found to have a nitrogen content of 1.38% and a boron content of 0.54%.

Example N

Boric acid (124 grams, 2 atomic proportions of boron) is added to the acylated nitrogen composition (556 grams, 1 atomic proportion of nitrogen) obtained according to the procedure of Example 75. The resulting mixture is heated at 150° C. for 3.5 hours and filtered at that temperature. The filtrate is found to have a boron compound of 3.23% and a nitrogen content of 2.3%.

Example O

A mixture of boric acid and the acylated nitrogen composition prepared according to the procedure of Example 17 in relative proportions such as to provide 1 atomic proportion of boron per atomic proportion of nitrogen is diluted with twice its volume of xylene and the resulting mixture heated at 150° C. for 3 hours and filtered. Xylene is removed by heating the filtrate to 150° C./0.25 mm. The residue is found to have a boron content of 0.42% and a nitrogen content of 0.44%.

Example P

A mixture of boric acid and the acylated nitrogen composition obtained according to the procedure of Example 44 in relative proportions such as to provide 1 atomic proportion of boron per atomic proportion of nitrogen is heated at 150° C. for 3 hours and filtered. The filtrate is found to have a boron content of 0.2%.

Example Q

A mixture of boric acid and an acylated nitrogen composition obtained by the procedure of Example 41 in relative proportions such as to provide 1 atomic proportion of boron per atomic proportion of nitrogen is heated at

150° C. for 3 hours and filtered at this temperature. The filtrate is found to have a boron content of 3.1% and a nitrogen content of 4.1%.

Example R

A mixture of boron trifluoride-diethyl ether complex and a polyisobutene-substituted succinimide derived from a polyisobutene having an average molecular weight of 1000 in relative proportions such as to provide 1 atomic proportion of boron per atomic proportion of nitrogen is heated at 150° C. for 3 hours and filtered at this temperature.

Example S

A mixture of boric acid and the acylated nitrogen composition obtained by the procedure of Example 37 in relative proportions such as to provide 1 atomic proportion of boron per atomic proportion of nitrogen is heated at 150° C. for 3 hours and filtered.

Example T

A mixture of boric acid and the acylated nitrogen composition obtained according to the procedure of Example 25 in relative proportions such as to provide 1 atomic proportion of boron per atomic proportion of nitrogen is heated at 150° C. for 3 hours and filtered.

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

A principal utility of such products is as additives in lubricants. It has been discovered in accordance with this invention that when used for such purpose the effectiveness of the nitrogen- and boron-containing products to impart a specific property to a lubricant is closely related to the size of the substantially hydrocarbon substituent in the succinic radical of the acylated nitrogen composition from which such products are derived. More particularly it has been found that products in which the substantially hydrocarbon substitutent contains more than about 50 aliphatic carbon atoms are effective to impart oxidation-inhibiting, corrosion-inhibiting, and detergent properties to a lubricant. It has also been found that the detergent properties of the products diminish sharply with a decrease in the size of the substantially hydrocarbon substituent having less than about 50 aliphatic carbon atoms so that products having less than about 35 aliphatic carbon atoms in this substituent are ineffective as detergent additives in lubricant.

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

The concentration of the nitrogen- and boron-containing compositions as additives in lubricants usually ranges from about 0.1% to about 10% by weight. The optimum concentrations for a particular application depend to a large measure upon the type of service to which the lubricants is to be subjected. Thus, for example, lubricants for use in gasoline internal combustion engines may contain from about 0.5 to about 5% of the additive, whereas lubricating compositions for use in gears in diesel engines may contain as much as 10% or even more of the additive.

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

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

The term "basic salt" is used to designate the metal salts wherein the metal is present in stoichiometrically larger amounts than the organic acid radical. The commonly employed methods for preparing the basic salts involves heating a mineral oil solution of an acid with a stoichiometric excess of a metal neutralizing agent such as the metal oxide, hydroxide, carbonate, bicarbonate, or sulfide at a temperature about 50° C. and filtering the resulting mass. The use of a "promoter" in the neutralization step to aid the incorporation of a large excess of metal likewise is known. Examples of compounds useful as the promoter include phenolic substances such as phenol, naphthol, alkylphenol, thiophenol, sulfurized alkylphenol, and condensation products of formaldehyde with a phenolic substance; alcohols such as methanol, 2-propanol, octyl alcohol, Cellosolve, 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, and a small amount of water and carbonating the mixture at an elevated temperature such as 60°–200° C.

Extreme pressure agents and corrosion-inhibiting and oxidation-inhibiting 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 alkylphenol, sulfurized dipentene, and sulfurized terpene; phosphosulfurized hydrocarbons such as the reaction product of a phosphorus sulfide with turpentine or methyl oleate; phosphorus esters including principally dihydrocarbon and trihydrocarbon phosphites such as dibutyl phosphite, diheptyl phosphite, dicyclohexyl phosphite, pentyl phenyl phosphite, dipentyl 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 thiocarbamates such as zinc dioctyl-dithiocarbamate, and barium heptylphenyl dithiocarbamate: Group II metal phosphorodithioates such as zinc dicyclohexylphosphorodithioate, zinc dioctylphosphorodithioate, barium di(heptylphenyl)phosphorodithioate, cadmium dinonylphosphorodithioate, and zinc salt of a phosphorodithioic acid produced by the reaction of phosphorus pentasulfide with an equimolar mixture of isopropyl alcohol and n-hexyl alcohol.

The lubricating compositions may also contain metal detergent additives in amounts usually within the range of about 0.1% to about 20% by weight. In some applications such as in lubricating marine diesel engines the lubricating compositions may contain as much as 30% of the metal detergent additive. They may also contain extreme pressure addition agents, viscosity in-

dex 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 A.

Example II

SAE 30 mineral lubricating oil containing 0.75% of the product of Example B 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 C.

Example IV

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

Example V

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

Example VI

SAE 20W–30 mineral lubricating oil containing 5% of the product of Example M.

Example VII

SAE 10W–30 mineral lubricating oil containing 1.5% of the product of Example E 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 F 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 G, 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 H, 0.1% of phosphorus as the zinc salt of a mixture of equimolar amounts of di-isopropyl-phosporodithioic 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 I, 0.075% of phosphorus as zinc di-n-octylphosphorodithioate, 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 100 parts of phosphorus pentasulfide at 200° C. and hydrolyzing the product with steam at 150° C.

Example XII

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

Example XV

SAE 10 mineral lubricating oil containing 2% of the product of Example N, 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 M, 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 O, 0.075% of phosphorus as the zinc salt of a phosphorodithioic acid prepared by the reaction of phosphorus pentasulfide with an equimolar mixture of n-butyl alcohol and dodecyl alcohol, 3% of a barium detergent prepared by carbonating a mineral oil solution containing 1 mole of sperm oil, 0.6 mole of octylphenol, 2 moles of barium oxide, and a small amount of water at 150° C.

Example XVIII

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

Example XIX

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

Example XX

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

Example XXI

SAE 90 mineral lubricating oil containing 3% of the

product of Example S and 0.2% of phosphorus as the reaction product of 4 moles of turpentine with 1 mole of phosphorus pentasulfide.

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 this invention described herein.

The effectiveness of the nitrogen- and boron-containing compositions as additives in lubricants to impart oxidation-inhibiting, corrosion-inhibiting, and detergent properties is illustrated by the results obtained from an inhibition-detergency test in which a 350 cc. sample of a lubricant containing 0.001% of iron naphthenate and 1.5% by weight of 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 the lubricant along with an SAE 1020 steel test panel. Air is bubbled through the lubricant 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 15 hours at room temperature and then filtered through dry No. 1 Whatman paper (double thickness) under slightly reduced pressure. The precipitant is washed with naphtha to constant weight and reported as milligrams of sludge per 100 ml. of oil. The bearing is scrubbed with naphtha, dried, and weighed, and the bearing weight change is reported in milligrams. The viscosity at 100° F. and 210° F. of the lubricant before and after the test is noted. Thus, the quantity of sludge is an indication of the ability of the additive to prevent the formation of harmful deposits; the bearing weight change is an indication of the corrosiveness of the lubricant; and the viscosity change of the lubricant is an indication of the oxidation resistance of the lubricant. The lubricant base employed in the test is a Mid-Continent, conventionally refined mineral oil having a viscosity of about 200 Saybolt Universal seconds at 100° F. The results of the test are summarized in Table I below.

Further illustration of the usefulness of the additive of this invention in lubricants is gained from a modified version (the modification consists of extending the test period from the usual 96 hours to 144 hours) of the CRC–EX–3 engine test. This test is recognized in the field as an important test by which lubricants can be evaluated for use under light-duty service conditions. In this particular test the lubricant is used in the crankcase of a 1954 6-cylinder Chevrolet Powerglide engine operated for 144 hours under recurring cycling conditions, each cycle consisting of 2 hours at an engine speed of 500±25 r.p.m. under 0 load and at an oil sump temperature of 100°–125° F. and air fuel ratio of 10:1; 2 hours at an engine speed of 2500±25 r.p.m. under a load of 40 brake-horse power and at an oil sump temperature of 150–170° F. and air-fuel ratio of 16:1; and 2 hours at an engine speed of 2500±25 r.p.m. under a load of 40 brake-horsepower and at an oil sump temperature of 240°–250° F. and air-fuel ratio of 16:1.

Table I

Additive (1.5% by weight of diluent-free chemical)	Viscosity Increase		Bearing Weight change (milligrams)	Sludge (milligrams per 100 ml. of Lubricant)
	100° F.	210° F.		
	Percent	*Percent*		
None	13.2	3.1	−53.5	1,145
The acylated nitrogen compositions from which the N- and B-containing additives are derived	>30	>10	−200	>100
Product of Example F	1.3	0.9	−13.9	1.8
Product of Example A	11.1	2.8	+0.9	2.0
Product of Example K	8.9	2.1	+3.3	2.4
Product of Example N	11.2	4.1	−1.6	18.7
Product of Example Q	15.2	3.2	−1.7	60

After completion of the test the engine is dismantled and various parts of the engine are examined for deposit. The lubricant is then rated according to (1) the extent of piston ring-filling, (2) the amount of sludge formed in the engine (on a scale of 80–0, 80 being indicative of no sludge and 0 being indicative of extremely heavy sludge), and (3) the total amount of deposits, i.e., sludge and varnish, formed in the engine (on a scale of 100–0, 100 being indicative of no deposit and 0 being indicative of extremely heavy deposits). The lubricant used in the test comprises an SAE 20 mineral oil containing 1.41% by weight of the product of Example L. The lubricant is found to pass the test with the following result: ring filling, 1%; sludge rating, 75.3; total deposit rating, 93.4.

The efficacy of the nitrogen- and boron-containing compositions as additives in lubricants for use under conditions of high speed and high temperature operation is shown by the results of an engine test carried out in accordance with U.S. Army Ordnance tentative specification AXS–1551. This is known as the Caterpillar CRC–L–1 engine test and the particular test to which the lubricant is subjected is a modification of test, the modification consisting of the use of a fuel having a sulfur content of 1% (significantly higher than that of the specified fuel). In this test the lubricant is used in the crankcase of the 4-stroke diesel engine having a 5¾" x 8" stroke and a compression ratio of 15 to 1 which is operated for 480 hours under the following conditions; speed, 100 r.p.m.; BTU input per minute, 2900–3000; load, 20 brake-horsepower; water jacket outlet temperature, 175°–180° F.; and oil temperature, 145°–150° F. The lubricant is evaluated in terms of (1) the piston cleanliness rating on a scale of 0–100 (100 being perfectly clean and 0 representing maximum deposit) and (2) percent ring filling. A lubricant comprising a SAE 10W–30 mineral oil containing 2% by weight of the product of Example L is found to pass this test with the following result: ring filling, 19%; piston cleanliness, 96.0.

The effectiveness of the nitrogen- and boron-containing compositions of this invention as additives in lubricants for internal combustion engines is evaluated further by the CRC–L–4–545 engine test. This test involves the operation of a 6-cylinder gasoline automobile engine for 36 hours under the following conditions: engine speed, 3150 r.p.m.; engine load, 30 brake-horsepower; jacket coolant temperature, outlet 200° F., inlet 190° F.; oil sump temperature, 265° F.; and air-fuel ratio, 14.5:1. The lubricant is rated in terms of the weight loss of bearings, the cleanliness of the pistons and the overall varnish and sludge deposits on the various parts of the engine. By this test, a lubricant comprising a SAE 10W–30 mineral oil containing 2.08% by weight of the product of Example L is found to pass the test with the following results: piston cleanliness rating of 9.5 (10 being perfectly clean), overall varnish and sludge rating of 96.7 (100 being perfectly clean), and an average weight loss per bearing of 2.5 milligrams.

The utility of the nitrogen- and boron-containing compositions of this invention as additives in lubricants for use in 2-cycle internal combustion engines illustrated by the results of an engine test in which a 7-horsepower chain saw engine (McCulloch model No. 1–80) is operated for 25 hours under the following recurring cycling conditions, each cycle consisting of 15 minutes at zero load and 1800–2200 r.p.m. and 5 minutes at adjustable load and 5000 r.p.m. The lubricant comprises a SAE 30 mineral oil containing 7% by volume of the product of Example M and is incorporated in the fuel mixture consisting of 20 parts by volume of a leaded gasoline having an octane number of 95 and 1 part by volume of the lubricant. The lubricant is found to give by this test a piston varnish rating of 7.0 (on a scale of 0–10, 10 being indicative of no varnish and 0 being indicative of extremely heavy varnish) and a crankcase cover varnish rating of 10.0 (on the same scale as above) whereas the base

oil, i.e., SAE 30 mineral oil, gives a piston varnish rating of 2.5 and a crankcase cover varnish rating of 8.

What is claimed is:

1. A process for preparing oil-soluble nitrogen- and boron-containing compositions comprising forming an acylated nitrogen intermediate by the reaction at a temperature within the range of from about 80° to about 250° C., of a substantially aliphatic olefin polymer-substituted succinic acid-producing compound having at least about 50 aliphatic carbon atoms in the polymer substituent with at least about one-half equivalent of an amine, for each equivalent of the acid-producing compound used, selected from the class consisting of alkylene amines and hydroxy-substituted alkylene amines, and reacting, at a temperature between about 50° C. and about 250° C., said acylated nitrogen intermediate with a boron compound selected from the class consisting of boron oxide, boron halide, boron acids, and esters of boron acids in an amount to provide from about 0.1 atomic proportion of boron for each mole of said acylated nitrogen intermediate to about 10 atomic proportions of boron for each atomic proportion of nitrogen of said acylated nitrogen intermediate.

2. A process of claim 1 wherein the polymer substituent of the succinic acid-producing compound is derived from a polyisobutene having an average molecular weight within the range from about 700 to about 5000.

3. The process of claim 1 wherein the amine is a polyethylene polyamine.

4. The process of claim 1 wherein the boron compound is boric acid.

5. An oil-soluble nitrogen- and boron-containing composition prepared by the process comprising forming an acylated nitrogen intermediate by the reaction at a temperature within the range of from about 80° C. to about 250° C., of a substantially aliphatic olefin polymer-substituted succinic acid-producing compound having at least about 50 aliphatic carbon atoms in the polymer substituent with at least about one-half equivalent of an amine for each equivalent of acid-producing compound used, selected from the class consisting of alkylene amines and hydroxy-substituted alkylene amines, and reacting at a temperature between about 50° C. and about 250° C. said acylated nitrogen intermediate with a boron compound selected from the class consisting of boron oxide, boron halide, boron acids, and esters of boron acids in an amount to provide from about 0.1 atomic proportion of boron for each mole of said acylated nitrogen intermediate to about 10 atomic proportions of boron for each atomic proportion of nitrogen of said acylated nitrogen intermediate.

6. The oil-soluble nitrogen- and boron-containing composition of claim 5 wherein the polymer substituent of the succinic acid-producing compound is derived from a polymer of isobutene.

7. The oil-soluble nitrogen- and boron-containing composition of claim 5 wherein the polymer substituent of the succinic acid-producing compound is derived from a polyisobutene having an average molecular weight within the range of from about 700 to about 5000.

8. The oil-soluble nitrogen, and boron-containing composition of claim 5 wherein the amine is a polyethylene polyamine.

9. The oil-soluble nitrogen- and boron-containing composition of claim 5 wherein the boron compound is boric acid.

10. The oil-soluble nitrogen- and boron-containing composition of claim 5 wherein the boron compound is boron trifluoride.

References Cited in the file of this patent

UNITED STATES PATENTS

2,052,192	Piggott	Aug. 25, 1936
2,216,618	Katz	Oct. 1, 1940
2,234,581	Rosen	Mar. 11, 1941
2,422,278	Young et al.	June 17, 1947
2,611,746	Kipp	Sept. 23, 1952
3,000,916	Klass et al.	Sept. 19, 1961
3,018,250	Anderson et al.	Jan. 23, 1962
3,018,291	Anderson et al.	Jan. 23, 1962