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(71) Applicant : **ETHYL PETROLEUM ADDITIVES, INC.**
20 South Fourth Street
St. Louis Missouri 63102-1886 (US)

(72) Inventor : **Papay, Andrew George**
897 Rustic Manor Circle
Manchester, Missouri 63011 (US)
Inventor : **Hartley, Rolfe John**
4387 Westminster Place
St. Louis, Missouri 63108 (US)

(74) Representative : **Collier, Jeremy Austin Grey**
J.A.Kemp & Co., 14 South Square, Gray's Inn
London WC1R 5LX (GB)

(54) Oil additive concentrates and lubricants of enhanced performance capabilities.

(57) Additive concentrates and lubricant compositions containing a combination of additives which result in enhanced performance particularly as regards extreme pressure and antiwear performance. The combination of additives so utilized comprise

a-1) at least one oil-soluble additive composition formed by heating concurrently or in any sequence at least one ashless dispersant which contains basic nitrogen and/or at least one hydroxyl group with (i) at least one inorganic phosphorus acid or anhydride, or at least one partial or total sulfur analog thereof, or any combination of the foregoing, and (ii) at least one boron compound ; such that a liquid composition is formed ; or

a-2) at least one oil-soluble boron-free additive composition formed by heating (i) at least one boron-free oil-soluble ashless dispersant containing basic nitrogen and/or at least one hydroxyl group, with (ii) at least one inorganic phosphorus acid such that a liquid boron-free phosphorus-containing composition is formed ; or a-3) one or more oil-soluble additive compositions formed by heating concurrently or in any sequence at least one ashless dispersant which contains basic nitrogen and/or at least one hydroxyl group with (i) at least one water-hydrolyzable organic phosphorus compound and water ; and (ii) at least one boron compound ; such that a liquid phosphorus- and boron-containing composition is formed ; or a-4) one or more oil-soluble boron-free additive compositions formed by heating concurrently or in any sequence (i) at least one boron-free oil-soluble ashless dispersant which contains basic nitrogen and/or at least one hydroxyl group, with (ii) -at least one water-hydrolyzable organic phosphorus compound and water ; such that a liquid boron-free phosphorus-containing composition is formed ; and

b) at least one oil-soluble metal-free sulfur-containing antiwear and/or extreme pressure agent having a sulfur content of at least 20% by weight ; components a-1), a-2), a-3) or a-4) and b) being proportioned such that the mass ratio (wt :wt) of sulfur in component b) to phosphorus in component a-1), a-2), a-3) or a-4) is in the range of 8 :1 to 30 :1.

Jouve, 18, rue Saint-Denis, 75001 PARIS

This invention relates to additive concentrates and oleaginous compositions (i.e., lubricating oils and functional fluids) having enhanced performance properties.

Heretofore a number of additive concentrates containing, inter alia, sulfur-containing antiwear and/or extreme pressure additives, phosphorus-containing antiwear and/or extreme pressure additives, and other additive components have been proposed and used. Among such other additive components are acidic components such as carboxylic acids, hydrocarbyl phosphoric acids, and hydrocarbyl thiophosphoric acids; basic components such as amines; and ashless dispersants such as boronated succinimides.

In order to qualify for premium automotive gear oil usage, the finished lubricating oil composition and additive concentrate from which it is made must be formulated to meet the American Petroleum Institute GL-5 requirements. This involves passing a battery of standard tests. In addition, the provision of clean gears in the L-60 test is an important consideration in the marketplace. So far as is known, only a very limited number of lubricant additive packages have received GL-5 approval. Thus there is a need for additional automotive gear oil packages which give good performance in the GL-5 qualification tests, and especially for packages capable of satisfying the GL-5 requirements.

There is, additionally, a need for automotive gear oil formulations which not only meet the GL-5 requirements but which afford superior results in the standard planetary spur gear test.

Still another need is for an ashless or low-ash lubricant additive package affording high dispersancy and high wear resistance to lubricants, such as crankcase lubricants, gear lubricants, manual and automatic transmission fluids, oil-based hydraulic fluids, wet brake fluids, and similar lubricants and functional fluids.

Yet another need is for an automotive or industrial gear oil package which performs well in synthetic base oils.

In accordance with one embodiment of this invention, there is provided an additive concentrate which comprises a minor proportion of diluent oil and a major proportion of additive components, said additive components comprising:

a-1) at least one oil-soluble additive composition formed by heating concurrently or in any sequence at least one ashless dispersant which contains basic nitrogen and/or at least one hydroxyl group with (i) at least one inorganic phosphorus acid or anhydride, or at least one partial or total sulfur analog thereof, or any combination of the foregoing, and (ii) at least one boron composed; such that a liquid composition is formed; or

a-2) at least one oil-soluble boron-free additive composition formed by heating (i) at least one boron-free oil-soluble ashless dispersant containing basic nitrogen and/or at least one hydroxyl group, with (ii) at least one inorganic phosphorus acid such that a liquid boron-free phosphorus-containing composition is formed; or

a-3) one or more oil-soluble additive compositions formed by heating concurrently or in any sequence at least one ashless dispersant which contains basic nitrogen and/or at least one hydroxyl group with (i) at least one water-hydrolyzable organic phosphorus compound and water; and (ii) at least one boron compound; such that a liquid phosphorus- and boron-containing composition is formed; or

a-4) one or more oil-soluble boron-free additive compositions formed by heating concurrently or in any sequence (i) at least one boron-free oil-soluble ashless dispersant which contains basic nitrogen and/or at least one hydroxyl group, with (ii) -at least one water-hydrolyzable organic phosphorus compound and water, such that a liquid boron-free phosphorus-containing composition is formed; and

b) at least one oil-soluble metal-free sulfur-containing antiwear and/or extreme pressure agent having a sulfur content of at least 20% by weight.

The term "component a)" as used hereinafter refers collectively to the above components a-1), a-2), a-3) and a-4).

The cooperation between components a) and b) of such compositions makes it possible to achieve performance levels (reduction in sludge formation and/or deposition and reduction in wear in gears and/or other relatively moveable metal surfaces in contact with each other) normally achieved, if at all, by higher concentrations of component b).

More particularly, the cooperation between components a) and b) can provide these important performance-improving effects:

1) inhibition of scoring or scuffing such as results from micro-welding of asperities between relatively moving metallic mechanical energy transferring surfaces in close proximity to each other, particularly under conditions of high speed and shock;

2) inhibition of ridging and rippling such as results from metal deformation or surface flow of relatively moving metallic surfaces in close proximity to each other, particularly under conditions of low speed and high torque;

3) inhibition of pitting and spalling such as results from metal fatigue in relatively moving metallic surfaces

in close proximity to each other, particularly under conditions of low speed and high torque; and

4) inhibition of sludge and varnish formation in base oils and/or deposition of sludge and/or varnish on both stationary and relatively moving parts of engines, hydraulic systems, gear boxes, power transmissions or like mechanisms, especially when operated under high temperature conditions.

Thus, the additive combinations of this invention have the capability of contributing greatly improved performance properties to base oils of lubricating viscosity, including animal, vegetable, mineral, and synthetic oils. For example, significantly improved properties can be achieved in lubricant compositions of this invention when subjected to various API GL-5 test procedures, such as enhanced extreme pressure properties as seen in the standard L-42 test, improved antirust performance as seen in the standard L-33 test, and/or clean gears as seen in the standard L-60 test. Indeed, particularly preferred compositions of this invention are those which satisfy all of the requirements of the API GL-5 test procedures. In addition, particularly preferred compositions of this invention exhibit superior performance in the standard planetary spur gear test.

In order to achieve optimum beneficial performance effects such as those referred to above, components a) and b) should be proportioned such that the mass ratio (wt:wt) of sulfur in component b) to phosphorus in component a) is in the range of 8:1 to 30:1, more preferably in the range of 10:1 to 20:1, and most preferably in the range of 14:1 to 20:1. The finished lubricating oils of this invention will usually contain at least about 0.5 wt % of sulfur as component b) and preferably will contain an amount of component b) to provide a sulfur content in the finished lubricant in the range of 1 to 3 wt %, and more preferably in the range of 1.5 to 3 wt %, of the total weight of the composition.

In preferred embodiments, the foregoing additive concentrates further comprise one or more of the following additive components:

c) at least one oil-soluble amine salt of a mono- or dihydrocarbyl ester of a monomeric pentavalent acid of phosphorus, preferably wherein the acid is phosphoric acid or a monothiophosphoric acid; and/or
d) at least one oil-soluble trihydrocarbyl ester of a dithiophosphoric acid; and/or
e) at least one oil-soluble amine salt of a carboxylic acid; and/or
f) at least one oil-soluble demulsifying agent; and/or
g) at least one oil-soluble copper corrosion inhibitor.

When component a-2) or a-4) is used, the following additive component can also be used in preferred embodiments:

h) at least one oil-soluble or oil-dispersible boron-containing additve composition.

Also provided by this invention are lubricant compositions which comprise a major proportion of at least one oil of lubricating viscosity and a minor amount of the various additive combinations referred to hereinabove.

Preferably, the compositions of this invention are ashless compositions (i.e., they contain no metal-containing additive components) or are low-ash compositions (i.e., base oil containing an additive concentrate or a combination of additives pursuant to this invention at a total concentration of 10% by weight will contain no more than 100 parts by weight, and more preferably no more than 50 parts by weight, of added metal per million parts by weight of the total composition.

Component a) -- i.e., a-1), a-2), a-3) or a-4) -- is one indispensable additive ingredient of the compositions of this invention.

Component a-1) - Phosphorylated & Boronated Ashless Dispersant

These oil-soluble additive compositions are formed by heating concurrently or any sequence at least one ashless dispersant which contains basic niaogen and/or at least one hydroxyl group with (i) at least one inorganic phosphorus acid or anhydride or at least one partial or total sulfur analog thereof, or any combination of the foregoing, and (ii) at least one boron compound, such that a liquid composition is formed. The ashless dispersant which is heated concurrently or in any sequence with components (i) and (ii) is preferably a preformed ashless dispersant containing basic nitrogen and/or at least one hydroxyl group. Thus, for example, any suitable ashless dispersant formed in the customary manner can be heated with one or more boron compounds to cause boronation to occur and the resultant product mixture can then be heated with one or more inorganic phosphorus compounds such that a liquid phosphorus- and boron-containing composition [component a-1)] is formed. Conversely, a preformed ashless dispersant can be heated with one or more inorganic phosphorus compounds and thereafter the product mixture can be heated with one or more boron compounds so that a liquid phosphorus- and boron-containing composition is formed. The preferred way of forming component a-1) is to heat a preformed ashless dispersant with a combination of one or more inorganic phosphorus compounds and one or more boron compounds to form a liquid phosphorus- and boron-containing composition. In other words, to form component a-1) in the preferred manner, the preformed ashless dispersant is concurrently heated with one or more inorganic phosphorus compounds and one or more boron compounds. In all cases, the resulting liquid product composition when subjected to chemical analysis reveals the presence of both phosphorus and boron.

Rather than utilizing a preformed ashless dispersant containing basic nitrogen and/or at least one hydroxyl group, it is possible to produce component a-1) by:

1) forming the ashless dispersant in the presence of one or more suitable boron compounds (e.g., boron ester or boron oxide) and then heating the resultant composition with one or more inorganic phosphorus compounds; or

2) forming the ashless dispersant in the presence of one or more suitable inorganic phosphorus compounds (e.g., a phosphorus oxide or sulfide) and then heating the resultant composition with one or more boron compounds; or

3) forming the ashless dispersant in the presence of one or more suitable boron compounds (see 1) above) and one or more suitable inorganic phosphorus compounds (see 2) above); or

4) heating one or more boron compounds with a basic nitrogen-containing and/or hydroxyl group-containing reactant used in forming the ashless dispersant, using the resultant boronated reactant to form the ashless dispersant and then heating the resultant ashless dispersant with one or more inorganic phosphorus compounds; or

5) heating one or more inorganic phosphorus compounds with a basic nitrogen-containing and/or hydroxyl group-containing reactant used in forming the ashless dispersant, using the resultant phosphorylated reactant to form the ashless dispersant and then heating the resultant ashless dispersant with one or more boron compounds; or

6) heating one or more inorganic phosphorus compounds and one more boron compounds with a basic nitrogen-containing and/or hydroxyl group-containing reactant used in forming the ashless dispersant, and using the resultant phosphorylated and boronated reactant to form the ashless dispersant.

In all cases, the final product composition [component a-1)] should be a liquid composition that on analysis reveals the presence of boron and phosphorus.

Component a-2) - Phosphorylated Ashless Dispersant

These oil-soluble additive compositions are formed by heating (i) at least one boron-free oil-soluble ashless dispersant containing basic nitrogen and/or at least one hydroxyl group, with (ii) at least one inorganic phosphorus acid such that a liquid boron-free phosphorus-containing composition is formed.

The ashless dispersant which is used in the process is preferably a preformed ashless dispersant containing basic nitrogen and/or at least one hydroxyl group. Thus, for example, any suitable boron-free ashless dispersant formed in the customary manner can be heated with one or more inorganic phosphorus acids to cause phosphorylation to occur. The resulting liquid product composition when subjected to chemical analysis reveals the presence of phosphorus.

Rather than utilizing a preformed ashless dispersant containing basic nitrogen and/or at least one hydroxyl group, it is possible to produce component a-2) by:

1) forming the ashless dispersant in the presence of one or more suitable inorganic phosphorus acids; or

2) heating one or more inorganic phosphorus acids with a basic nitrogen-containing and/or hydroxyl group-containing reactant used in forming the ashless dispersant, and using the resultant phosphorylated reactant to form the ashless dispersant.

In all such cases, the final product composition [component a-2)] should be a liquid that on analysis reveals the presence of phosphorus.

Component a-3) - Phosphorylated & Boronated Ashless Dispersant

These oil-soluble additive compositions are formed by heating concurrently or any sequence at least one ashless dispersant which contains basic nitrogen and/or at least one hydroxyl group with (i) at least one water-hydrolyzable organic compound of phosphorus -- preferably a water-hydrolyzable ester of an acid of phosphorus -- and water, and (ii) at least one boron compound, such that a liquid phosphorus- and boron-containing composition is formed, and from which water has been removed. The ashless dispersant which is heated concurrently or in any sequence with components (i) and (ii) is preferably a preformed ashless dispersant containing basic nitrogen and/or at least one hydroxyl group. Thus, for example, any suitable ashless dispersant formed in the customary manner can be heated with one or more boron compounds to cause boronation to occur and the resultant product mixture can then be heated with water and one or more water-hydrolyzable organic phosphorus compounds such that a liquid phosphorus- and boron-containing composition [component a-3)] is formed. Conversely, a preformed ashless dispersant can be heated with water and one or more water-hydrolyzable organic phosphorus compounds and thereafter the product mixture can be heated with one or more boron compounds so that a liquid phosphorus- and boron-containing composition is formed. The preferred way of forming component a-3) is to heat a preformed ashless dispersant with a combination of water, one or more water-hydrolyzable organic phosphorus compounds and one or more boron compounds to form a liquid phosphorus- and boron-containing composition. In other words, to form component a-3) in the preferred manner, the preformed ashless dispersant is concurrently heated with water, one or more water-hydrolyzable organic phosphorus compounds and one or more boron compounds. In all cases, the resulting liquid product composition when subjected to chemical analysis reveals the presence of both phosphorus and boron.

In the formation of the liquid phosphorus- and boron-containing composition, water is removed at least during or after the heating with (i) and (ii) (if conducted concurrently) or at least during or after the heating with (i) (if conducted sequentially). Such heating is conducted under conditions such that partial or total hydrolysis of the water-hydrolyzable organic phosphorus compound occurs.

Rather than utilizing a preformed ashless dispersant containing basic nitrogen and/or at least one hydroxyl group, it is possible to produce component a-3) by:

1) forming the ashless dispersant in the presence of one or more boron compounds (e.g., boron ester or boron oxide) and then heating the resultant composition in the presence of water with one or more water-hydrolyzable organic phosphorus compounds; or
2) forming the ashless dispersant in the presence of one or more water-hydrolyzable organic phosphorus compounds and then heating the resultant composition with one or more boron compounds in the presence of water; or
3) forming the ashless dispersant in the presence of one or more boron compounds and one or more water-hydrolyzable organic phosphorus compounds and heating the ashless dispersant in the presence of water either during or after the formation of the ashless dispersant; or
4) heating one or more boron compounds with a basic nitrogen-containing and/or hydroxyl group-containing reactant used in forming the ashless dispersant, using the resultant boronated reactant to form the ashless dispersant and then heating the resultant ashless dispersant in the presence of water with one or more water-hydrolyzable organic phosphorus compounds; or
5) heating one or more water-hydrolyzable organic phosphorus compounds in the presence of water with a basic nitrogen-containing and/or hydroxyl group-containing reactant used in forming the ashless dispersant, using the resultant phosphorylated reactant to form the ashless dispersant and then heating the resultant ashless dispersant with one or more boron compounds; or
6) heating in the presence of water one or more water-hydrolyzable organic phosphorus compounds and one more boron compounds with a basic nitrogen-containing and/or hydroxyl group-containing reactant used in forming the ashless dispersant, and using the resultant phosphorylated and boronated reactant to form the ashless dispersant.

In all cases, the final product composition [component a-3)] should be a liquid composition that on analysis reveals the presence of boron and phosphorus.

Component a-4) - Phosphorylated Ashless Dispersant

These oil-soluble boron-free additive compositions are formed by heating (i) at least one boron-free oil-soluble ashless dispersant which contains basic nitrogen and/or at least one hydroxyl group, with (ii) at least one water-hydrolyzable organic phosphorus compound and water such that a liquid boron-free phosphorus-containing composition is formed.

The ashless dispersant which is used in the process is preferably a preformed ashless dispersant containing basic nitrogen and/or at least one hydroxyl group. Thus, for example, any suitable boron-free ashless dispersant formed in the customary manner can be heated with water and one or more water-hydrolyzable organic phosphorus compounds to cause phosphorylation to occur. The resulting liquid product composition when subjected to chemical analysis reveals the presence of phosphorus.

Rather than utilizing a preformed ashless dispersant containing basic nitrogen and/or at least one hydroxyl group, it is possible to produce component a-4) by:

1) forming the ashless dispersant in the presence of water and one or more suitable water-hydrolyzable organic phosphorus compounds (e.g., a phosphorus oxide or sulfide); or
2) heating water and one or more water-hydrolyzable organic phosphorus compounds with a basic nitrogen-containing and/or hydroxyl group-containing reactant used in forming the ashless dispersant, and using the resultant phosphorylated reactant to form the ashless dispersant.

In all such cases, the final product composition [component a-4)] should be a liquid composition that on analysis reveals the presence of phosphorus.

Various methods can be used for removing water from component a-3) or a-4) during or after its formation. The preferred method involves applying a suitable vacuum to the reaction system while heating the water-containing mixture to a suitably elevated temperature. In this way the water is readily stripped off. When conducting the phosphorylation using a phosphorus ester made from a lower alcohol such as methanol, ethanol, propanol, 2-propanol, butanol, or isobutyl alcohol, both lower alcohol liberated in the process and water can be stripped off from the product mixture during or on completion of the heating operation.

In any case wherein an ashless dispersant used in forming component a) is not a liquid but rather is in whole or in part in the solid state of aggregation at room temperature (e.g., 25°C), it is preferable to dissolve such dispersant in a suitable solvent or diluent (polar or non-polar, as may be required to dissolve the dispersant) before the dispersant is subjected to phosphorylation and/or boronation (as the case may be) in forming component a-1) or a-3) or phosphorylation in forming component a-2) or a-4). In this connection, the phrase "such that a liquid composition is formed" as used herein in connection with such solid state dispersants means that component a), including such solvent or diluent, is in the liquid state of aggregation at room temperature (e.g., 25°C), even though at a lower temperature the dispersant may revert in whole or in part to the solid state. Of course in any case, component a-1) must be oil-soluble within the meaning of such term as set forth hereinafter.

Irrespective of the method used in forming component a), in any instance wherein macro (i.e., non-dispersible) solids are formed or remain in the liquid composition after it has been formed, such solids should be removed, and can be readily removed, by any of a variety of conventional separation techniques such as filtration, centrifugation, or decantation.

The actual chemical structures of all of the final product compositions used as component a) in the practice of this invention, however prepared, are not known with absolute certainty. While it is believed, and in some cases known, that phosphorus-containing moieties and boron-containing moieties are chemically bonded to the ashless dispersant, it is possible that in some cases component a) is in whole or in part a micellar structure containing phosphorus- and/or boron-containing species or moieties. Thus, this invention is not limited to, and should not be construed as being limited to, any specific structural configurations with respect to component a). As noted above, all that is required is that component a) is a liquid that is oil soluble and that if subjected to analysis reveals the presence of phosphorus and, in the case of a-1) and 1-3), boron. In addition, component a) should possess dispersant properties.

Although any of a variety of standard methods can be used to analyze the dispersant for the presence of phosphorus or boron therein, it is desirable to use the analytical procedure set forth in ASTM D-4951. In this procedure it is convenient to use a Perkin-Elmer Plasma 40 Emission Spectrometer. The analyzing wavelengths for acceptable measurements are 213.618 nm and 249.773 nm for phosphorus and boron, respectively.

Component a) may contain chemical species and/or moieties besides the phosphorus- and boron-containing species or moieties of a-1) or a-3) or the phosphorus-containing species and/or moieties of a-2) or a-4), such as, for example, nitrogen- and/or oxygen- and/or sulfur-containing species or moieties over and above the basic nitrogen and/or hydroxyl group(s) forming an essential part of the initial ashless dispersant itself. It is to be understood that organic phosphorus-containing compounds may be used along with inorganic phosphorus compounds in making component a-1) or a-2) and that inorganic phosphorus-containing compounds may be used along with water and one or more water-hydrolyzable organic phosphorus compounds in making component a-3) or a-4). Further, the inorganic phosphorus compound or compounds can be formed in situ, as, for example, by heating a mixture of phosphorus and sulfur to form a phosphorus sulfide, or by treating one or more organic phosphorus compounds to convert the same in whole or in part into one or more inorganic phosphorus compounds. The water-hydrolyzable organic phosphorus compound or compounds can also be formed in situ, as, for example, by heating a mixture of one or more alcohols or phenols with one or more phosphorus halides (e.g., PCl_3, $POCl_3$, $PSCl_3$, $RPCl_2$, $ROPCl_2$, $RSPCl_2$, $RPOCl_2$, $ROPOCl_2$, $RSPOCl_2$, $RPSCl_2$, $ROPSCl_2$, $RSPSCl_2$, R_2PCl, $(RO)_2PCl$, $(RS)_2PCl$, $(RO)(RS)PCl$, R_2POCl, $(RO)_2POCl$, $(RS)_2POCl$, $(RO)(RS)POCl$, R_2PSCl, $(RO)_2PSCl$, $(RS)_2PSCl$, where each R is, independently a hydrocarbyl group) and introducing water into the system in order to hydrolyze the water-hydrolyzable phosphorus ester so formed.

As used herein, the term "phosphorylated" means that the ashless dispersant has been heated with one or more inorganic phosphorus compounds [components a-1) and a-2)] or with one or more water-hydrolyzable organic phosphorus compounds and water [components a-3) and a-4)] such that the resultant product, on analysis, reveals the presence of phosphorus. Likewise, as used herein, the term "boronated" means that the ashless dispersant has been heated with one or more boron compounds such that the resultant product, on analysis, reveals the presence of boron. The terms "phosphorylated" and "boronated" are not to be construed as requiring that the resultant composition contain chemically bound phosphorus or boron.

Any of a variety of ashless dispersants can be utilized in forming component a) of the compositions of this invention. These include the following types:

Type A - Carboxylic Ashless Dispersants.

These are reaction products of (i) an acylating agent such as a monocarboxylic acid, or a dicarboxylic or other polycarboxylic acid, or a derivative thereof, with (ii) one or more compounds which contain amine groups and/or hydroxyl groups, such that the acylated reaction product contains basic nitrogen and/or at least one hydroxyl group. These products, herein referred to as carboxylic ashless dispersants, are described in many patents, including British patent specification No. 1,306,529 and the following U.S. Patents: 3,163,603; 3,184,474; 3,215,707; 3,219,666; 3,271,310; 3,272,746; 3,281,357; 3,306,908; 3,311,558; 3,316,177; 3,340,281; 3,341,542; 3,346,493; 3,381,022; 3,399,141; 3,415,750, 3,433,744; 3,444,170; 3,448,048; 3,448,049; 3,451,933; 3,454,607; 3,467,668; 3,522,179; 3,541,012; 3,542,678; 3,574,101; 3,576,743; 3,630,904; 3,632,510; 3,632,511; 3,697,428; 3,725,441; 3,868,330; 3,948,800; 4,234,435; and Re 26,433.

There are a number of sub-categories of carboxylic ashless dispersants. One such sub-category which constitutes a preferred type for use in the formation of component a) is composed of the polyamine succinamides and more preferably the polyamine succinimides in which the succinic group contains a hydrocarbyl substituent containing at least 30 carbon atoms. The polyamine used in forming such compounds contains at least one primary amino group capable of forming an imide group on reaction with a hydrocarbon-substituted succinic acid or acid derivative thereof such an anhydride, lower alkyl ester, acid halide, or acid-ester. Representative examples of such dispersants are given in U.S. Pat. Nos. 3,172,892; 3,202,678; 3,216,936; 3,219,666; 3,254,025; 3,272,746; and 4,234,435. The alkenyl succinimides may be formed by conventional methods such as by heating an alkenyl succinic anhydride, acid, acid-ester, acid halide, or lower alkyl ester with a polyamine containing at least one primary amino group. The alkenyl succinic anhydride may be made readily by heating a mixture of olefin and maleic anhydride to 180°-220°C. The olefin is preferably a polymer or copolymer of a lower monoolefin such as ethylene, propylene, 1-butene, and isobutene. The more preferred source of alkenyl group is from polyisobutene haring a number average molecular weight of up to 100,000 or higher. In a still more preferred embodiment the alkenyl group is a polyisobutenyl group having a number average molecular weight (determined using the method described in detail hereinafter) of 500-5,000, and preferably 700-2,500, more preferably 700-1,400, and especially 800-1,300. The isobutene used in making the polyisobutene is usually (but not necessarily) a mixture of isobutene and other C_4 isomers such as 1-butene. Thus, strictly speaking the acylating agent formed from maleic anhydride and "polyisobutene" made from such mixtures of isobutene and other C_4 isomers such as 1-butene, can be termed a "polybutenyl succinic anhydride" and a succinimide made therewith can be termed a "polybutenyl succinimide". However, it is common to refer to such substances as "polyisobutenyl succinic anhydride" and "polyisobutenyl succinimide", respectively. As used herein "polyisobutenyl" is used to denote the alkenyl moiety whether made from a highly pure isobutene or a more impure mixture of isobutene and other C_4 isomers such as 1-butene.

Polyamines which may be employed in forming the ashless dispersant include any that have at least one primary amino group which can react to form an imide group. A few representative examples include branched-chain alkanes containing two or more primary amino groups such as tetraamino-neopentane polyaminoalkanols such as 2-(2-aminoethylamino)-ethanol and 2-[2-(2-aminoethylamino)-ethylamino]-ethanol; heterocyclic compounds containing two or more amino groups at least one of which is a primary amino group such as 1-(β-aminoethyl)-2-imidazolidone, 2-(2-aminoethylamino)-5-nitropyridine, 3-amino-N-ethylpiperidine, 2-(2-aminoethyl)-pyridine, 5-aminoindole, 3-amino-5-mercapto- 1,2,4-triazole, and 4-(aminomethyl)-piperidine; and the alkylene polyamines such as propylene diamine, dipropylene triamine, di-(1,2-butylene)triamine, N-(2-aminoethyl)-1,3-propanediamine, hexamethylenediamine and tetra-(1,2-propylene)pentamine.

The most preferred amines are the ethylene polyamines which can be depicted by the formula

$$H_2N(CH_2CH_2NH)_nH$$

wherein n is an integer from one to ten. These include: ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, including mixtures thereof in which case n is the average value of the mixture. The ethylene polyamines which have a primary amine group at each end can form mono-alkenylsuccinimides and bis-alkenylsuccinimides. Commercially available ethylene polyamine mixtures usually contain minor amounts of branched species and cyclic species such as N-aminoethyl piperazine, N,N′-bis(aminoethyl)piperazine, N,N′-bis(piperazinyl)ethane, and like compounds. The preferred commercial mixtures have approximate overall compositions falling in the range corresponding to diethylene triamine to pentaethylene hexamine, mixtures generally corresponding in overall makeup to tetraethylene pentamine being most preferred. Methods for the production of polyalkylene polyamines are known and reported in the literature. See for example U.S. Pat. Nos. 4,827,037; and 4,983,736; and EP Pub. Nos. 412,611; 412,612; 412,613; 412,614; and 412,615, and references cited therein.

Thus especially preferred ashless dispersants for use in the present invention are the products of reaction of a polyethylene polyamine, e.g., mixture known in the trade as "triethylene tetramine" or "tetraethylene pentamine", with a hydrocarbon-substituted carboxylic acid or anhydride (or other suitable acid derivative) made by reaction of a polyolefin, preferably polyisobutene, having a number average molecular weight of 500 to 5,000, preferably 700 to 2,500, more preferably 700 to 1,400 and especially 800 to 1,300, with an unsaturated polycarboxylic acid or anhydride, e.g., maleic anhydride, maleic acid, or fumaric acid, including mixtures of two or more such substances.

As used herein the term "succinimide" is meant to encompass the completed reaction product from reaction between the amine reactant(s) and the hydrocarbon-substituted carboxylic acid or anhydride (or like acid derivative) reactant(s), and is intended to encompass compounds wherein the product may have amide, amidine, and/or salt linkages in addition to the imide linkage of the type that results from the reaction of a primary amino group and an anhydride moiety.

Residual unsaturation in the alkenyl group of the alkenyl succinimide may be used as a reaction site, if desired. For example the alkenyl substituent may be hydrogenated to form an alkyl substituent. Similarly the olefinic bond(s) in the alkenyl substituent may be sulfurized, halogenated, or hydrohalogenated. Ordinarily, there is little to be gained by use of such techniques, and thus the use of alkenyl succinimides as the precursor of component a) is preferred.

Another sub-category of carboxylic ashless dispersants which can be used in forming component a) includes alkenyl succinic acid esters and diesters of polyhydric alcohols containing 2-20 carbon atoms and 2-6 hydroxyl groups. Representative examples are described in U.S. Pat. Nos. 3,331,776; 3,381,022; and 3,522,179. The alkenyl succinic portion of these esters corresponds to the alkenyl succinic portion of the succinimides described above including the same preferred and most preferred subgenus, e.g., alkenyl succinic acids and anhydrides, where the alkenyl group contains at least 30 carbon atoms and notably, polyisobutenyl succinic acids and anhydrides wherein the polyisobutenyl group has a number average molecular weight of 500 to 5,000, preferably 700 to 2,500, more preferably 700 to 1,400, and especially 800 to 1,300. As in the case of the succinimides, the alkenyl group can be hydrogenated or subjected to other reactions involving olefinic double bonds.

Alcohols useful in preparing the esters include ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol, tripropylene glycol, glycerol, sorbitol, 1,1,1-trimethylol ethane, 1,1,1-trimethylol propane, 1,1,1-trimethylol butane, pentaerythritol, and dipentaerythritol.

The succinic esters are readily made by merely heating a mixture of alkenyl succinic acid, anhydrides or lower alkyl (e.g., C_1-C_4) ester with the alcohol while distilling out water or lower alkanol. In the case of acid-esters less alcohol is used. In fact, acid-esters made from alkenyl succinic anhydrides do not evolve water.

Still another sub-category of carboxylic ashless dispersants useful in forming component a) comprises an alkenyl succinic ester-amide mixture. These may be made by heating the above-described alkenyl succinic acids, anhydrides or lower alkyl esters with an alcohol and an amine either sequentially or in a mixture. Alcohols and amines such as those described above are also useful in this embodiment. Additionally, linear and/or branched chain monohydric alcohols such as 1-butanol, 2-butanol, 2-methyl-1-propanol, pentanol, hexanol, octanol, decanol, lauryl alcohol, oleyl alcohol, eicosanol, or ethylene glycol monomethyl ether, can be used provided they are used with one or more polyamines. Alternatively, amino alcohols can be used alone or with the alcohol and/or amine to form the ester-amide mixtures. The amino alcohol can contain 2-20 carbon atoms, 1-6 hydroxy groups and 1-4 amine nitrogen atoms. Examples are ethanolamine, diethanolamine, N-ethanol-diethylene triamine, and trimethylol aminomethane.

Here again, the alkenyl group of the succinic ester-amide can be hydrogenated or subjected to other reactions involving olefinic double bonds.

Representative examples of suitable ester-amide mixtures are described in U.S. Pat. Nos. 3, 184,474; 3,576,743; 3,632,511; 3,804,763; 3,836,471; 3,862,981; 3,936,480; 3,948,800; 3,950,341; 3,957,854; 3,957,855; 3,991,098; 4,071,548; and 4,173,540.

Yet another sub-category of carboxylic ashless dispersants useful in forming component a) comprises the Mannich-based derivatives of hydroxyaryl succinimides. Such compounds can be made by reacting a polyalkenyl succinic anhydride with an aminophenol to produce an N-(hydroxyaryl) hydrocarbyl succinimide which is then reacted with an alkylene diamine or polyalkylene polyamine and an aldehyde (e.g., formaldehyde), in a Mannich-base reaction. Details of such synthesis are set forth in U.S. Pat. No. 4,354,950. As in the case of the other carboxylic ashless dispersants discussed above, the alkenyl succinic anhydride or like acylating agent is derived from a polyolefin, preferably a polyisobutene, having a number average molecular weight of 500 to 5,000, preferably 700 to 2,500, more preferably 700 to 1,400, and especially 800 to 1,200. Likewise, residual unsaturation in the polyalkenyl substituent group can be used as a reaction site as for example, by hydrogenation or sulfurization.

Type B - Hydrocarbyl Polyamine Dispersants.

This category of ashless dispersants which can be used in forming component a) is likewise well known to those skilled in the art and fully described in the literature. The hydrocarbyl polyamine dispersants are generally produced by reacting an aliphatic or alicyclic halide (or mixture thereof) containing an average of at least about 40 carbon atoms with one or more amines, preferably polyalkylene polyamines. Examples of such hydrocarbyl polyamine dispersants are described in U.S. Pat. Nos. 3,275,554; 3,438,757; 3,454,555; 3,565,804; 3,671,511; 3,821,302; 3,394,576; and in European Patent Publication No. 382,405.

In general, the hydrocarbyl-substituted polyamines are high molecular weight hydrocarbyl-N-substituted polyamines containing basic nitrogen in the molecule. The hydrocarbyl group typically has a number average molecular weight in the range of 750-10,000, more usually in the range of 1,000-5,000.

The hydrocarbyl radical may be aliphatic or alicyclic and, except for adventitious amounts of aromatic components in petroleum mineral oils, will be free of aromatic unsaturation. The hydrocarbyl groups will normally be branched-chain aliphatic, having 0-2 sites of unsaturation, and preferably from 0-1 site of ethylene unsaturation. The hydrocarbyl groups are preferably derived from petroleum mineral oil, or polyolefins, either homopolymers or higher-order polymers, or 1-olefins of from 2-6 carbon atoms. Ethylene is preferably copolymerized with a higher olefin to insure oil solubility.

Illustrative polymers include polypropylene, polyisobutylene, or poly-1-butene. The polyolefin group will normally have at least one branch per six carbon atoms along the chain, preferably at least one branch per four carbon atoms along the chain. These branched-chain hydrocarbons are readily prepared by the polymerization of olefins of from 3-6 carbon atoms and preferably from olefins of from 3-4 carbon atoms.

In preparing the hydrocarbyl polyamine dispersants, rarely will a single compound having a defined structure be employed. With both polymers and petroleum-derived hydrocarbon groups, the composition is a mixture of materials having various structures and molecular weights. Therefore, in referring to molecular weight, number average molecular weights are intended. Furthermore, when speaking of a particular hydrocarbon group, it is intended that the group include the mixture that is normally contained within materials which are commercially available. For example, polyisobutylene is known to have a range of molecular weights and may include small amounts of very high molecular weight materials.

Particularly preferred hydrocarbyl-substituted amines or polyamines are prepared from polyisobutenyl chloride.

The polyamine employed to prepare the hydrocarbyl-substituted polyamine is preferably a polyamine having from 2 to 12 amine nitrogen atoms and from 2 to 40 carbon atoms. The polyamine is reacted with a hydrocarbyl halide (e.g., chloride) to produce the hydrocarbyl-substituted polyamine. The polyamine preferably has a carbon-to-nitrogen ratio of from 1:1 to 10:1.

The amine portion of the hydrocarbyl-substituted amine may be substituted with substituents selected from (A) hydrogen, and (B) hydrocarbyl groups of from 1 to 10 carbon atoms.

The polyamine portion of the hydrocarbyl-substituted polyamine may be substituted with substituents selected from (A) hydrogen, (B) hydrocarbyl groups of from 1 to 10 carbon atoms, (C) acyl groups of from 2 to 10 carbon atoms, and (D) monoketo, monohydroxy, mononitro, monocyano, lower alkyl and lower alkoxy derivatives of (B) and (C). "Lower" as used in terms like lower alkyl or lower alkoxy, means a group containing from 1 to 6 carbon atoms.

At least one of the nitrogens in the hydrocarbyl-substituted amine or polyamine is a basic nitrogen atom, i.e., one titratable by a strong acid.

Hydrocarbyl, as used in describing the substituents in the amine or polyamine used in forming the dispersants, denotes an organic radical composed of carbon and hydrogen which may be aliphatic, alicyclic, aromatic or combinations thereof e.g., aralkyl. Preferably, the hydrocarbyl group will be relatively free of aliphatic unsaturation, i.e., ethylenic and acetylenic, particularly acetylenic unsaturation. The hydrocarbyl substituted polyamines used in forming the dispersants are generally, but not necessarily, N-substituted polyamines. Exemplary hydrocarbyl groups and substituted hydrocarbyl groups which may be present in the amine portion of the dispersant include alkyls such as methyl, ethyl, propyl, butyl, isobutyl, pentyl, hexyl, octyl, etc., alkenyls such as propenyl, isobutenyl, hexenyl, octenyl, etc., hydroxyalkyls, such as 2-hydroxyethyl, 3-hydroxypropyl, hydroxyisopropyl, 4-hydroxybutyl, etc., ketoalkyls, such as 2-ketopropyl, 6-ketooctyl, etc., alkoxy and lower alkenoxy alkyls, such as ethoxyethyl, ethoxypropyl, propoxyethyl, propoxypropyl, 2-(2-ethoxyethoxy)ethyl, 2-(2-(2-ethoxyethoxy)ethoxy)ethyl, 3,6,9,12-tetraoxytetradecyl,2-(2-ethoxyethoxy)hexyl, etc.

Typical amines useful in preparing the hydrocarbyl-substituted amines include methylamine, dimethylamine, ethylamine, diethylamine, n-propylamine, di-n-propylamine, etc. Such amines are either commercially available or are prepared by art recognized procedures.

The polyamine component may also contain heterocyclic polyamines, heterocyclic substituted amines and substituted heterocyclic compounds, wherein the heterocyclic comprises one or more 5-6 membered rings containing oxygen and/or nitrogen. Such heterocyclics may be saturated- or unsaturated and substituted with groups selected from the aforementioned (A), (B), (C), and (D). The heterocyclis are exemplified by piperazines, such as 2-methylpiperazine, 1,2-bis(N-piperazinyl-ethane), and N,N′-bis(N-piperazinyl)piperazine, 2-methylimidazoline, 3-aminopiperidine, 2-aminopyridine, 2-(β-aminoethyl)-3-pyrroline, 3-aminopyrrolidine, N-(3-aminopropyl)morpholine, etc. Among the heterocyclic compounds, the piperazines are preferred.

Typical polyamines that can be used to form the hydrocarbyl polyamine dispersants include the following: ethylene diamine, 1,2-propylene diamine, 1,3-propylene diamine, diethylene triamine, triethylene tetramine, hexamethylene diamine, tetraethylene pentamine, methylaminopropylene diamine, N-(β-aminoethyl)piperazine, N,N′-di(β-aminoethyl)piperazine, N,N′-di(β-aminoethyl)imidazolidone-2, N-(β-cyanoethyl)ethane- 1,2-diamine, 1,3,6,9-tetraaminooctadecane, 1,3,6-triamino-9-oxadecane, N-methyl-1,2-propanediamine, and 2-(2-aminoethylamino)ethanol.

Another group of suitable polyamines are the polyalkylene amines in which the alkylene groups differ in carbon content, such as for example bis(aminopropyl)ethylenediamine. Such compounds are prepared by the reaction of acrylonitrile with an ethyleneamine, for example, an ethyleneamine having the formula $H_2H(CH_2CH_2NH)_nH$ wherein n is an integer from 1 to 5, followed by hydrogenation of the resultant intermediate. Thus, the product prepared from ethylene diamine and acrylonitrile has the formula $H_2N-(CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_2$.

In many instances the polyamine used as a reactant in the production of the hydrocarbyl-substituted polyamine is not a single compound but a mixture in which one or several compounds predominate with the average composition indicated. For example, tetraethylene pentamine prepared by the polymerization of aziridine or the reaction of 1,2-dichloroethane and ammonia will have both lower and higher amine members, e.g., triethylene tetramine, substituted piperazines and pentaethylene hexamine, but the composition will be largely tetraethylene pentamine and the empirical formula of the total amine composition will closely approximate that of tetraethylene pentamine. Finally, in preparing the hydrocarbyl-substituted polyamines for use in this invention, where the various nitrogen atoms of the polyamine are not geometrically equivalent, several substitutional isomers are possible and are encompassed with the final product. Methods of preparation of polyamines and their reactions are detailed in Sidgewick, The Organic Chemistry of Nitrogen, Clarendon Press, Oxford, 1966; Nollier, Chemistry of Organic Compounds, Saunders Philadelphia, 2nd Ed., 1957; and Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, especially volume 2, pp. 99-116.

The preferred hydrocarbyl-substituted polyalkylene polyamines for use in this invention may be represented by the formula

$$R_1NH\text{-}(\text{-}R_2\text{-}NH\text{-})_\alpha\text{-}H$$

wherein R_1 is hydrocarbyl having an average molecular weight of from 750 to 10,000; R_2 is alkylene of from 2 to 6 carbon atoms; and α is an integer of from 0 to 10.

Preferably, R_1 is hydrocarbyl having an average molecular weight of from 1,000 to 10,000. Preferably, R_2 is alkylene of from 2 to 3 carbon atoms and α is preferably an integer of from 1 to 6.

Type C - Mannich polyamine dispersants.

This category of ashless dispersant which can be utilized in the formation of component a) is comprised of reaction products of an alkyl phenol, with one or more aliphatic aldehydes containing from 1 to 7 carbon atoms (especially formaldehyde and derivatives thereof), and polyamines (especially polyalkylene polyamines of the type described hereinabove).

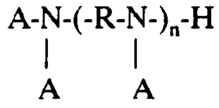
Examples of Mannich condensation products, and methods for their production are described in the following U.S. Patents: 2,459,112; 2,962,442; 2,984,550; 3,036,003; 3,166,516; 3,236,770; 3,368,972; 3,413,347; 3,442,808; 3,448,047; 3,454,497; 3,459,661; 3,493,520; 3,539,633; 3,558,743; 3,586,629; 3,591,598; 3,600,372; 3,634,515; 3,649,229; 3,697,574; 3,703,536; 3,704,308; 3,725,277; 3,725,480; 3,726,882; 3,736,357; 3,751,365; 3,756,953; 3,793,202; 3,798,165; 3,798,247; 3,803,039; 3,872,019; 3,904,595; 3,957,746; 3,980,569; 3,985,802; 4,006,089; 4,011,380; 4,025,451; 4,058,468; 4,083,699; 4,090,854; 4,354,950; and 4,485,023.

The polyamine group of the Mannich polyamine dispersants is derived from polyamine compounds characterized by containing a group of the structure -NH- wherein the two remaining valances of the nitrogen are satisfied by hydrogen, amino, or organic radicals bonded to said nitrogen atom These compounds include aliphatic, aromatic, heterocyclic and carbocyclic polyamines. The source of the oil-soluble hydrocarbyl group in the Mannich polyamine dispersant is a hydrocarbyl-substituted hydroxy aromatic compound comprising the reaction product of a hydroxy aromatic compound, according to well known procedures, with a hydrocarbyl donating agent or hydrocarbon source. The hydrocarbyl substituent provides substantial oil solubility to the hydroxy aromatic compound and, preferably, is substantially aliphatic in character. Commonly, the hydrocarbyl substituent is derived from a polyolefin having at least about 40 carbon atoms. The hydrocarbon source should be substantially free from pendant groups which render the hydrocarbyl group oil insoluble. Examples of acceptable substituent groups are hide, hydroxy, ether, carboxy, ester, amide, nitro and cyano. However, these substituent groups preferably comprise no more than about 10 weight percent of the hydrocarbon source.

The preferred hydrocarbon sources for preparation of the Mannich polyamine dispersants are those derived from substantially saturated petroleum fractions and olefin polymers, preferably polymers of mono-olefins having from 2 to 30 carbon atoms. The hydrocarbon course can be derived, for example, from polymers of olefins such as ethylene, propene, 1-butene, isobutene, 1-octene, 1-methylcyclohexene, 2-butene and 3-pentene. Also useful are copolymers of such olefins with other polymerizable olefinic substances such as styrene. In general, these copolymers should contain at least 80 percent and preferably 95 percent, on a weight basis, of units derived from the aliphatic mono-olefins to preserve oil solubility. The hydrocarbon source generally contains at least 40 and preferably at least 50 carbon atoms to provide substantial oil solubility to the dispersant. The olefin polymers having a number average molecular weight between 600 and 5,000 are preferred for reasons of easy reactivity and low cost. However, polymers of higher molecular weight can also be used. Especially suitable hydrocarbon sources are isobutylene polymers.

The Mannich polyamine dispersants are generally prepared by reacting a hydrocarbyl-substituted hydroxy aromatic compound with an aldehyde and a polyamine. The aldehyde is typically an aliphatic aldehyde containing 1 to 7 carbon atoms, and in most cases is formaldehyde or a compound such as formalin or a polyformaldehyde from which formaldehyde is derived during the reaction. Typically, the substituted hydroxy aromatic compound is contacted with from 0.1 to 10 moles of polyamine and 0.1 to 10 moles of aldehyde per mole of substituted hydroxy aromatic compound. The reactants are mixed and heated to a temperature above about 80°C. to initiate the reaction. Preferably, the reaction is carried out at a temperature from 100° to 250°C. The resulting Mannich product has a predominantly benzylamine linkage between the aromatic composed and the polyamine. The reaction can be carried out in an inert diluent such as mineral oil, benzene, toluene, naphtha, ligroin, or other inert solvents to facilitate control of viscosity, temperature, and reaction rate.

Polyamines are preferred for use in preparing the Mannich polyamine dispersants, and suitable polyamines include, but are not limited to, alkylene diamines and polyalkylene polyamines (and mixtures thereof) of the formula:



$$A\text{-}\underset{\underset{A}{|}}{N}\text{-}(\text{-}R\text{-}\underset{\underset{A}{|}}{N}\text{-})_n\text{-}H$$

wherein n is an integer from 1 to 10, R is a divalent hydrocarbyl group of from 1 to 18 carbon atoms, and each A is independently selected from the group consisting of hydrogen and monovalent aliphatic groups containing up to 10 carbon atoms which can be substituted with one or two hydroxyl groups. Most preferably, R is a lower alkylene group of from 2 to 6 carbon atoms and A is hydrogen.

Suitable polyamines for use in preparation of the Mannich polyamine dispersants include, but are not limited to, methylene polyamines, ethylene polyamines, butylene polyamines, propylene polyamines, pentylene polyamines, hexylene polyamines and heptylene polyamines. The higher homologs of such amines and related aminoalkyl-substituted piperazines are also included. Specific examples of such polyamines include ethylene diamine, triethylene tetramine, tris(2-aminoethyl)amine, propylene diamine, pentamethylene diamine, hexamethylene diamine, heptamethylene diamine, octamethylene diamine, decamethylene diamine, di(heptamethylene) triamine, pentaethylene hexamine, di(trimethylene) triamine, 2-heptyl-3-(2-aminopropyl)imidazoline, 1,3-bis(2-aminoethyl)imidazoline, 1-(2-aminopropyl)piperazine, 1,4-bis(2-aminoethyl)piperazine and 2-methyl-1-(2-aminobutyl)piperazine. Higher homologs, obtained by condensing two or more of the above mentioned amines, are also useful as are the polyoxyalkylene polyamines.

The polyalkylene polyamines, examples of which are set forth above, are especially useful in preparing the Mannich polyamine dispersants for reasons of cost and effectiveness. Such polyamines are described in detail under the heading "Diamines and Higher Amines" in Kirk-Othmer, Encyclopedia of Chemical Technology, Second Edition, Vol. 7, pp. 22-39. They are prepared most conveniently by the reaction of an ethylene imine with a ring-opening reagent such as ammonia. These reactions result in the production of somewhat complex mixtures of polyalkylene polyamines which include cyclic condensation products such as piperazines. Because of their availability, these mixtures are particularly useful in preparing the Mannich polyamine dispersants. However, it will be appreciated that satisfactory dispersants can also be obtained by use of pure polyalkylene polyamines.

Alkylene diamines and polyalkylene polyamines having one or more hydroxyalkyl substituents on the nitrogen atom are also useful in preparing the Mannich polyamine dispersants. These materials are typically obtained by reaction of the corresponding polyamine with an epoxide such as ethylene oxide or propylene oxide. Preferred hydroxyalkyl-substituted diamines and polyamines are those in which the hydroxyalkyl groups have less than about 10 carbon atoms. Examples of suitable hydroxyalkyl-substituted diamines and polyamines include, but are not limited to, N-(2-hydroxyethyl)ethylenediamine, N,N′-bis(2-hydroxyethyl)ethylenediamine, mono(hydroxypropyl)diethlenetriamine, (di(hydroxypropyl)tetraethylenepentamine and N-(3-hydroxybutyl)tetramethylenediamine. Higher homologs obtained by condensation of the above mentioned hydroxyalkyl-substituted diamines and polyamines through amine groups or through ether groups are also useful.

Any conventional formaldehyde yielding reagent is useful for the preparation of the Mannich polyamine dispersants. Examples of such formaldehyde yielding reagents are trioxane, paraformaldehyde, trioxymethylene, aqueous formalin and gaseous formaldehyde. Other aldehydes which can be used include acetaldehyde, propionaldehyde, butyraldehyde, isobutyraldehyde, valeraldehyde, hexanal, heptanal, and mixtures of two or more of these.

The most preferred Mannich base dispersants for use in this invention are Mannich base ashless dispersants formed by condensing about one molar proportion of long chain hydrocarbon-substituted phenol with from 1 to 2.5 moles of formaldehyde and from 0.5 to 2 moles of polyalkylene polyamine.

Type D - Polymeric polyamine dispersants.

Also suitable for preparing component a) of the compositions of this invention are polymers containing basic amine groups and oil solubilizing groups (for example, pendant alkyl groups having at least about 8 carbon atoms). Such polymeric dispersants are herein referred to as polymeric polyamine dispersants. Such materials include, but are not limited to, interpolymers of decyl methacrylate, vinyl decyl ether or a relatively high molecular weight olefin with aminoalkyl acrylates and aminoalkyl acrylamides. Examples of polymeric polyamine dispersants are set forth in the following patents: U.S. Pat. Nos. 3,329,658; 3,449,250; 3,493,520; 3,519,565; 3,666,730; 3,687,849; 3,702,300.

Type E - Post-treated basic nitrogen-containing and/or hydroxyl-containing ashless dispersants.

As is well known in the art, any of the ashless dispersants referred to above as types A-D can be subjected to post-treatment with one or more suitable reagents such as urea, thiourea, carbon disulfide, aldehydes, ketones, carboxylic acids, anhydrides of low molecular weight dibasic acids, nitriles, and epoxides. Such post-treated ashless dispersants can be used in forming component a) of the compositions of this invention provided that the post-treated dispersant contains residual basic nitrogen and/or one or more residual hydroxyl groups. Alternatively, the phosphorylated or the phosphorylated and boronated dispersant can be subjected to post-treatment with such reagents. Likewise, in the case of components a-1) and a-3) the post-treatment can be conducted in between the phosphorylation and boronation or conversely, between the boronation and the phosphorylation. Examples of post-treatment procedures and post-treated ashless dispersants are set forth in the following U.S. Patents: U.S. Pat. Nos. 3,036,003; 3,087,936; 3,200,107; 3,216,936; 3,254,025; 3,256,185; 3,278,550; 3,218,428; 3,280,234; 3,281,428; 3,282,955; 3,312,619; 3,366,569; 3,367,943; 3,373,111; 3,403,102; 3,442,808; 3,455,831; 3,455,832; 3,493,520; 3,502,677; 3,513,093; 3,533,945; 3,539,633; 3,573,010; 3,579,450; 3,591,598; 3,600,372; 3,639,242; 3,649,229; 3,649,659; 3,658,836; 3,697,574; 3,702,757; 3,703,536; 3,704,308; 3,708,422; 4,025,445; and 4,857,214.

Mannich-based derivatives of hydroxyaryl succinimides that have been post-treated with C_5-C_9 lactones such as ϵ-caprolactone and optionally with other post-treating agents as described for example in U.S. Pat. No. 4,971,711 can also be utilized in forming component a) for use in the practice of this invention, provided that such post-treated Mannich-based derivatives of hydroxyaryl succinimides contain basic nitrogen, and/or at least one hydroxyl group. See also U.S. Pat. Nos. 4,820,432; 4,828,742; 4,866,135; 4,866,139; 4,866,140; 4,866,141; 4,866,142; 4,906,394; and 4,913,830 as regards additional suitable basic nitrogen-containing and/or hydroxyl group-containing ashless dispersants which may be utilized in forming component a).

One preferred category of post-treated ashless dispersants is comprised of basic nitrogen-containing and/or hydroxyl group-containing ashless dispersants which have been heated with (1) a phosphorus compound such that they contain phosphorus, or (2) a boron compound such that they contain boron, all with the proviso that such post-treated products contain residual basic nitrogen and/or one or more residual hydroxyl groups. Numerous examples of such dispersants and methods for their production are described in the patent literature. See for example U.S. Pat. Nos. 3,087,936; 3,184,411; 3,185,645; 3,235,497; 3,254,025; 3,265,618; 3,281,428; 3,282,955; 3,284,410; 3,324,032; 3,325,567; 3,338,832; 3,344,069; 3,403,102; 3,502,677;

3,511,780; 3,513,093; 3,533,945; 3,623,985; 3,718,663; 3,865,740; 3,950,341; 3,991,056; 4,097,389; 4,234,435; 4,338,205; 4,428,849; 4,554,086; 4,615,826; 4,634,543; 4,648,980; 4,747,971; 4,857,214; and 4,873,004. The boron-containing post-treated ashless dispersants of the prior art type can be converted into a material suitable for use as component a-1) or a-3) simply by conducting a phosphorylation in the manner described herein. If desired, additional boron can also be incorporated into a prior art type post-treated boron-containing ashless dispersant by conducting a boronation in the manner described herein either before, during or after the phosphorylation. It is also possible by using the phosphorylation and/or boronation procedures described herein to phosphorylate and/or boronate a post-treated ashless dispersant that already contains phosphorus and/or boron, provided that such initial post-treated ashless dispersant contains at least some residual basic nitrogen and/or at least some residual hydroxyl substitution.

The ashless dispersant(s) used in forming component a) can be any mixture containing any two or more ashless dispersants containing basic nitrogen and/or at least one hydroxyl group.

Because of environmental and conservational concerns it is desirable to employ ashless dispersants which contain little, if any, halogen atoms such as chlorine atoms. Thus, in order to satisfy such concerns, it is desirable (although not necessary from a performance standpoint) to select ashless dispersants (as well as the other components used in the compositions of this invention) such that the total halogen content, if any, of the overall lubricant or functional fluid composition does not exceed 100 ppm. Indeed, the lower the better. Likewise, it is preferable in accordance with this invention, to provide additive concentrates which, when dissolved in a halogen-free base oil, at a concentration of 10% by weight, yield an oleaginous composition in which the total halogen content, if any, is 100 ppm or less.

Production of Component a-1):

Typical procedures for producing component a-1) phosphorylated and boronated ashless dispersants involve concurrently or sequentially heating one or more ashless dispersants of the types described above with at least one inorganic phosphorus compound and at least one boron compound under conditions yielding a liquid phosphorus- and boron-containing composition. Examples of inorganic phosphorus compounds which are useful in forming such products include phosphorous acid (H_3PO_3, sometimes depicted as $H_2(HPO_3)$, and sometimes called ortho-phosphorous acid or phosphonic acid), phosphoric acid (H_3PO_4, sometimes called orthophosphoric acid), hypophosphoric acid ($H_4P_2O_6$), metaphosphoric acid (HPO_3), pyrophosphoric acid ($H_4P_2O_7$), hypophosphorous acid (H_3PO_2, sometimes called phosphinic acid), pyrophosphorous acid ($H_4P_2O_5$, sometimes called pyrophosphonic acid), phosphinous acid (H_3PO), tripolyphosphoric acid ($H_5P_3O_{10}$), tetrapolyphosphoric acid ($H_6P_4O_{13}$), trimetaphosphoric acid ($H_3P_3O_9$), phosphorus trioxide, phosphorus tetraoxide, and phosphorus pentoxide. Partial or total sulfur analogs such as phosphorotetrathioic acid (H_3PS_4), phosphoromonothioic acid (H_3PO_3S), phosphorodithioic acid ($H_3PO_2S_2$), phosphorotrithioic acid (H_3POS_3), phosphorus sesquisulfide, phosphorus heptasulfide, and phosphorus pentasulfide (P_2S_5, sometimes referred to as P_4S_{10}) can also be used in forming products suitable for use as component a-1) in the practice of this invention. Also usable, though less preferred, are the inorganic phosphorus halide compounds such as PCl_3, PBr_3, $POCl_3$, $PSCl_3$, etc. The preferred phosphorus reagent is phosphorous acid, (H_3PO_3).

It will be understood and appreciated by those skilled in the art that the form or composition of the inorganic compound(s) as charged into the mixture to be heated or being heated may be altered in situ. For example, the action of heat and/or water can transform certain inorganic phosphorus compounds into other inorganic phosphorus compounds or species. Any such in situ transformations that may occur are within the purview of this invention provided that the liquid phosphorylated ashless dispersant reveals on analysis the presence therein of phosphorus (as well as boron).

Suitable compounds of boron useful in forming the phosphorylated and boronated ashless dispersants for use as component a-1) include, for example, boron acids, boron oxides, boron esters, and amine or ammonium salts of boron acids. Illustrative compounds include boric acid (sometimes referred to as orthoboric acid), boronic acid, tetraboric acid, metaboric acid, pyroboric acid, esters of such acids, such as mono-, di-, and tri-organic esters with alcohols or polyols having up to 20 or more carbon atoms (e.g., methanol, ethanol, 2-propanol, propanol, butanols, pentanols, hexanols, ethylene glycol, propylene glycol, trimethylol propane, diethanol amine, etc.), boron oxides such as boric oxide and boron oxide hydrate, and ammonium salts such as ammonium borate, ammonium pyroborate, etc. While usable, boron halides such as boron trifluoride, and boron trichloride, are undesirable as they tend to introduce halogen atoms into the boronated dispersant, a feature which is detrimental from the environmental, toxicological and conservational standpoints. Amine borane addition compounds and hydrocarbyl boranes can also be used, although they tend to be relatively expensive. The preferred boron reagent is boric acid, H_3BO_3.

Optionally, additional sources of basic nitrogen can be included in the inorganic phosphorus compound-ashless dispersant-boron compound mixture so as to provide a molar amount (atomic proportion) of basic nitrogen up to that equal to the molar amount of basic nitrogen contributed by the ashless dispersant. Preferred auxiliary nitrogen compounds are long chain primary, secondary and tertiary alkyl amines containing from 12 to 24 carbon atoms, including their hydroxyalkyl and aminoalkyl derivatives. The long chain alkyl group may optionally contain one or more ether groups. Examples of suitable compounds are oleyl amine, N-oleyltrimethylene diamine, N-tallow diethanolamine, N,N-dimethyl oleylamine, and myristyloxapropyl amine.

Other materials normally used in lubricant additives which do not interfere with the process may also be added, for example, a benzotriazole, including lower (C_1-C_4) alkyl-substituted benzotriazoles, which function to protect copper surfaces.

The concurrent heating step or the combination of sequential heating steps is conducted at temperatures sufficient to produce a final liquid composition which contains both phosphorus and boron. The heating can be carried out in the absence of a solvent by heating a mixture of the ashless dispersant and one or more suitable inorganic phosphorus compounds, or one or more suitable boron compounds, or, preferably, a combination of one or more suitable inorganic phosphorus compounds and one or more suitable boron compounds. The temperatures used will vary somewhat depending upon the nature of the ashless dispersant and the inorganic phosphorus and/or boron reagent being utilized. Generally speaking however, the temperature will usually fall within the range of 40 to 200°C. The duration of the heating is likewise susceptible to variation, but ordinarily will fall in the range of 1 to 3 hours. When conducting the heating in bulk, it is important to thoroughly agitate the components to insure intimate contact therebetween. When utilizing the preferred phosphorus and boron reagents (phosphorous acid and boric acid), it is preferable to add water to facilitate initial dissolution of the boric acid. Alternatively, the phosphorous acid may be utilized in the form of an aqueous solution thereby introducing water into the system to facilitate dissolution of the boric acid. Water (and when using boron esters, alcohol) formed in the process and any added water is preferably removed from the heated mixture by vacuum distillation at temperatures of from 100 to 140°C. Preferably the heating step or steps will be conducted in a diluent oil or other inert liquid medium such as light mineral oils, etc.

The amount of phosphorus compound employed in the heating process ranges from 0.001 mole to 0.999 mole per mole of basic nitrogen and free hydroxyl in the mixture being heated, up to one half of which may be contributed by an auxiliary nitrogen compound. The amount of boron compound employed ranges from 0.001 mole to 1 mole per mole of basic nitrogen and/or hydroxyl in the mixture which is in excess of the molar amount of inorganic phosphorus compound. When conducting the phosphorylation and boronation on a sequential basis (or when conducting one of these operations on a dispersant which has previously been subjected to the other such operation), the last-to-be-used reagent(s) -- inorganic phosphorus compound(s) or boron compound(s), as the case may be -- can be used in an amount equivalent to (or even in excess of) the amount of basic nitrogen and/or hydroxyl groups in the dispersant being heated with such last-to-be-used reagent(s).

When used, the amount of added water is not particularly critical as it is removed by distillation during the course of, or at the end of, the heating step. Amounts of up to 1% by weight of the mixture being heated are preferred. When used, the amount of diluent usually ranges from 10 to 50% by weight of the mixture being subjected to heating.

When conducting the preferred concurrent heating step for prodution of component a-1), it is desirable to employ procedures such as described in U.S. Pat. No. 4,857,214.

For further details concerning procedures for conducting the boronation operation apart from the phosphorylation operation, reference may be had, for example, to the disclosures of U.S. Pat. Nos. 3,087,936; 3,254,025; 3,281,428; 3,282,955; 3,284,410; 3,338,832; 3,344,069; 3,533,945; 3,718,663; 4,097,389; 4,554,086; and 4,634,543.

The phosphorylated and boronated dispersants utilized as component a-1) in the compositions of this invention when in their undiluted state should have on a weight basis a phosphorus content of at least 100 parts per million (ppm) (preferably at least 500 ppm and more preferably at least 1,000 ppm) and a boron content of at least 100 ppm (preferably at least 500 ppm and more preferably at least 1,000 ppm). When forming component a-1) in part by use of one or more organic phosphorus compounds such as one or more organic phosphates (e.g., trihydrocarbyl phosphates, dihydrocarbyl monoacid phosphates, monohydrocarbyl diacid phosphates, or mixtures thereof), phosphites (e.g., trihydrocarbyl phosphites, dihydrocarbyl hydrogen phosphites, hydrocarbyl diacid phosphites, or mixtures thereof), phosphonates (e.g., hydrocarbyl phosphonic acids, mono- and/or dihydrocarbyl esters of phosphonic acids, or mixtures thereof), phosphonites (e.g., hydrocarbyl phosphinic acids, mono- and/or dihydrocarbyl esters of phosphinic acids, or mixtures thereof), etc., or the partial or total sulfur analogs thereof, and in part by use of one or more inorganic phosphorus compounds, the latter should be used in an amount sufficient to provide at least 10% (preferably at least 50% and more preferably at least 75%) of the total content of phosphorus in the phosphorylated and boronated dispersant. For crankcase lubricant usage, component a-1) when in the undiluted state preferably contains at least 3,000 ppm (more preferably at least 5,000 ppm and most preferably at least 7,000 ppm) of phosphorus and at least 1,500 ppm (more preferably at least 2,500 ppm and most preferably at least 3,500 ppm) of boron.

The preparation of phosphorylated and boronated ashless dispersants suitable for use as component a-1) in the compositions of this invention is illustrated by the following Examples 1-50 in which all parts and percentages are by weight unless otherwise clearly specified.

EXAMPLE 1

A mixture is formed from 260 parts of a commercial succinimide ashless dispersant (HiTEC® 644 dispersant; Ethyl Petroleum Additives, Inc.; Ethyl Petroleum Additives, Ltd.; Ethyl S.A.; Ethyl Canada Limited), 100 parts of a 100 Solvent Neutral refined mineral oil diluent, 8 parts of phosphorous acid, 3.5 parts of tolutriazole, 8 parts of boric acid, and 3.0 parts of water. The mixture is heated at 100°C for two hours until all of the solid materials are dissolved. A vacuum of 40 mm Hg is gradually drawn on the product to remove the water while the temperature is slowly raised to 100°C. A clear solution or composition is obtained which is soluble in oil and suitable for use as component a-1).

EXAMPLE 2

The procedure of Example 1 is repeated except that the succinimide ashless dispersant used is derived from polybutene having a number average molecular weight of 1,100. The average number of succinic groups per alkenyl group in the succinimide is approximately 1.2.

EXAMPLE 3

The procedure of Example 1 is repeated except that the succinimide ashless dispersant used is derived from polybutene having a number average molecular weight of 2,100.

EXAMPLE 4

The procedure of Example 1 is repeated except that the succinimide ashless dispersant is replaced by an equal amount of a Mannich polyamine dispersant (AMOCO® 9250 dispersant; Amoco Corporation). The Amoco 9250 dispersant as supplied by the manufacturer is believed to be a boronated dispersant and in such case, another material suitable for use as component a-1) can be formed by eliminating the boric acid and water from the procedure used in this example and thereby conducting phosphorylation on an already boronated dispersant.

EXAMPLE 5

The procedure of Example 1 is repeated except that the succinimide ashless dispersant is replaced by an equal amount of a commercial ashless dispersant of the pentaerythritol succinic ester type (Lubrizol® 936 dispersant; The Lubrizol Corporation). As in the case of Example 4, the initial dispersant as supplied by the manufacturer is believed to be a boronated dispersant. In such cases, the dispersant can, if desired, be subjected just to phosphorylation to thereby form still another product suitable for use as component a-1).

EXAMPLE 6

The procedure of Example 1 is repeated except that 11 parts of phosphorus pentasulfide is used in place of the phosphorous acid, the P_2S_5 is added to the mixture after water distillation, and the mixture is then heated for an additional hour at 100°C to provide a clear, oil-soluble composition suitable for use as component a-1).

EXAMPLE 7

The procedure of Example 1 is repeated except that the P_2S_5 is replaced by 7 parts of phosphorus pentoxide (P_2O_5).

EXAMPLE 8

The procedures of Examples 1 through 7 are repeated except that the tolutriazole is omitted from the initial mixtures subjected to the thermal processes.

EXAMPLE 9

A mixture of 11,904 parts of a commercial boronated succinimide (HiTEC® 648 dispersant; Ethyl Petroleum Additives, Inc.; Ethyl Petroleum Additives, Ltd.; Ethyl S.A.; Ethyl Canada Limited) and 96 parts of phosphorous acid is heated to 100-110°C for 2 hours to form a homogeneous liquid composition suitable for use as component a-1) in the practice of this invention. For convenience in handling, 100 Solvent Neutral mineral oil can be added to form an 80% solution of the additive in the oil.

EXAMPLE 10

A mixture of 260 parts of a commercial succinimide (HiTEC® 644 dispersant), and 8 parts of phosphorous acid is heated to 100°C for 2 hours. To this product is added 8 parts of orthoboric acid and 4 parts of water, and the resultant mixture is heated at 100°C for another 2 hours. Water present in the reaction mixture is removed by applying a vacuum of 40 mm of Hg and gradually raising the temperature to 110°C. The resultant homogeneous liquid composition is suitable for use as component a-1).

EXAMPLE 11

A mixture of 260 parts of a commercial succinimide (HiTEC® 644 dispersant), 8 parts of orthoboric acid and 4 parts of water is heated to 100°C for 2 hours. Then 8 parts of phosphorous acid is added to the reaction mixture and the temperature of the mixture is held at 100°C for another 2 hours. Water present in the reaction mixture is removed by applying a vacuum of 40 mm of Hg and gradually raising the temperature to 110°C. The resultant homogeneous liquid composition is suitable for use as component a-1).

EXAMPLE 12

A mixture of 260 parts of a commercial succinic pentaerythritol ester ashless dispersant (Lubrizol® 936 dispersant), and 8 parts of phosphorous acid is heated to 100°C for 2 hours. To this product is added 8 parts of orthoboric acid and 4 parts of water, and the resultant mixture is heated at 100°C for another 2 hours. Water present in the reaction mixture is removed by applying a vacuum of 40 mm of Hg and gradually raising the temperature to 110°C. The resultant homogeneous liquid composition is suitable for use as component a-1).

EXAMPLE 13

A mixture of 260 parts of a commercial succinic pentaerythritol ester ashless dispersant (Lubrizol® 936 dispersant), 8 parts of orthoboric acid and 4 parts of water is heated to 100°C for 2 hours. Then 8 parts of phosphorous acid is added to the reaction mixture and the temperature of the mixture is held at 100°C for another 2 hours. Water present in the reaction mixture is removed by applying a vacuum of 40 mm of Hg and gradually raising the temperature to 110°C. The resultant homogeneous liquid composition is suitable for use as component a-1).

EXAMPLE 14

A mixture of 260 parts of a commercial Mannich polyamine dispersant (AMOCO® 9250 dispersant), and 8 parts of phosphorous acid is heated to 100°C for 2 hours. To this product are added 8 parts of orthoboric acid and 4 parts of water, and the resultant mixture is heated at 100°C for another 2 hours. Water present in the reaction mixture is removed by applying a vacuum of 40 mm of Hg and gradually raising the temperature to 110°C. The resultant homogeneous liquid composition is suitable for use as component a-1).

EXAMPLE 15

A mixture of 260 parts of a commercial Mannich polyamine dispersant (AMOCO® 9250 dispersant), 8 parts of orthoboric acid and 4 parts of water is heated to 100°C for 2 hours. Then 8 parts of phosphorous acid is added to the reaction mixture and the temperature of the mixture is held at 100°C for another 2 hours. Water present in the reaction mixture is removed by applying a vacuum of 40 mm of Hg and gradually raising the temperature to 110°C. The resultant homogeneous liquid composition is suitable for use as component a-1).

EXAMPLE 16

(a) A mixture of 1,000 parts (0.495 mole) of polyisobutene ($\overline{M}n$ = 2020; $\overline{M}w$ = 6049, both determined using the methodology of U.S. Pat. No. 4,234,435) and 115 parts (1.17 moles) of maleic anhydride is heated to 110°C. This mixture is heated to 184°C in 6 hours during which 85 parts (1.2 moles) of gaseous chlorine is added beneath the surface. At 184-189°C, an additional 59 parts (0.83 mole) of chlorine is added over 4 hours. The reaction mixture is stripped by heating at 186-190°C with nitrogen purged for 26 hours. The residue is predominantly polyisobutenyl succinic anhydride acylating agent.

(b) A mixture is prepared by the addition of 57 parts (1.38 equivalents) of a commercial mixture of ethylene polyamines having the approximate overall composition of tetraethylene pentamine to 1,067 parts of mineral oil and 893 parts (1.38 equivalents) of substituted succinic acylating agent prepared as in (a) while maintaining the temperature at 140-145°C. The reaction mixture is then heated to 155°C over a three hour period and stripped by blowing with nitrogen. The reaction mixture is filtered to yield the filtrate as an oil solution of the desired product composed predominantly of polyisobutenyl succinimides.

(c) A mixture is formed from 250 parts of the polyisobutenyl succinimide product solution formed as in (b), 8 parts of phosphorous acid, 3.5 parts of tolutriazole, 8 parts of boric acid, and 3.0 parts of water. The mixture is heated at 100°C for two hours until all of the solid materials are dissolved. A vacuum of 40 mm Hg is gradually drawn on the product to remove the water while the temperature is slowly raised to 100°C. A clear solution or composition is obtained which is soluble in oil and suitable for use as component a-1).

EXAMPLE 17

The procedure of Example 16 is repeated except that the tolutriazole is eliminated from the reaction mixture of (c).

EXAMPLE 18

The procedure of Example 16 is repeated except that 11 parts of phosphorus pentasulfide is used in place of the phosphorous acid, the P_2S_5 is added to the mixture after water distillation, and the mixture is then heated for an additional hour at 100°C to provide a clear, oil-soluble composition suitable for use as component a-1).

EXAMPLE 19

The procedure of Example 18 is repeated except that the P_2S_5 is replaced by 7 parts of phosphorus pentoxide (P_2O_5).

EXAMPLE 20

(a) A mixture of 1,000 parts (0.495 mole) of polyisobutene ($\overline{M}n$ = 2020; $\overline{M}w$ = 6049, both determined using the methodology of U.S. Pat. No. 4,234,435) and 115 parts (1. 17 moles) of maleic anhydride is heated to 110°C. This mixture is heated to 184°C in 6 hours during which 85 parts (1.2 moles) of gaseous chlorine is added beneath the surface. At 184-189°C, an additional 59 parts (0.83 mole) of chlorine is added over 4 hours. The reaction mixture is stripped by heating at 186-190°C with nitrogen purged for 26 hours. The residue is predominantly polyisobutenyl succinic anhydride acylating agent.

(b) A mixture is prepared by the addition of 18.2 parts (0.433 equivalents) of a commercial mixture of ethylene polyamines having the approximate overall composition of tetraethylene pentamine to 392 parts of mineral oil and 348 parts (0.52 equivalent) of substituted succinic acylating agent prepared as in (a) while maintaining the temperature at 140°C. The reaction mixture is then heated to 150°C in 1.8 hours and stripped by blowing with nitrogen. The reaction mixture is filtered to yield the filtrate as an oil solution of the desired product composed predominantly of polyisobutenyl succinimides.

(c) A mixture is formed from 250 parts of the polyisobutenyl succinimide product solution formed as in (b), 8 parts of phosphorous acid, 3.5 parts of tolutriazole, 8 parts of boric acid, and 3.0 parts of water. The mixture is heated at 100°C for two hours until all of the solid materials are dissolved. A vacuum of 40 mm Hg is gradually drawn on the product to remove the water while the temperature is slowly raised to 100°C. A clear solution or composition is obtained which is soluble in oil and suitable for use as component a-1).

EXAMPLE 21

The procedure of Example 20 is repeated except that the tolutriazole is eliminated from the reaction mixture of (c).

EXAMPLE 22

The procedure of Example 20 is repeated except that 11 parts of phosphorus pentasulfide is used in place of the phosphorous acid, the P_2S_5 is added to the mixture after water distillation, and the mixture is then heated for an additional hour at 100°C to provide a clear, oil-soluble composition suitable for use as component a-1).

EXAMPLE 23

The procedure of Example 20 is repeated except that the P_2S_5 is replaced by 7 parts of phosphorus pentoxide (P_2O_5).

EXAMPLE 24

(a) A mixture of 1,000 parts (0.495 mole) of polyisobutene ($\overline{M}n$ = 2020; $\overline{M}w$ = 6049, both determined using the methodology of U.S. Pat. No. 4,234,435) and 115 parts (1.17 moles) of maleic anhydride is heated to 110°C. This mixture is heated to 184°C in 6 hours during which 85 parts (1.2 moles) of gaseous chlorine is added beneath the surface. At 184-189°C, an additional 59 parts (0.83 mole) of chlorine is added over 4 hours. The reaction mixture is stripped by heating at 186-190°C with nitrogen purged for 26 hours. The residue is predominantly polyisobutenyl succinic anhydride acylating agent.

(b) A mixture of 334 parts (0.52 equivalents) of the polyisobutene substituted succinic acylating agent prepared as in (a), 548 parts of mineral oil, 30 parts (0.88 equivalent) of pentaerythritol and 8.6 parts (0.0057 equivalent) of Polyglycol 112-2 demulsifier (Dow Chemical Company) is heated at 150°C for 2.5 hours. The reaction mixture is then heated to 210°C over a period of 5 hours and then held at 210°C for an additional 3.2 hours. The reaction mixture is cooled to 190°C and 8.5 parts (0.2 equivalent) of a commercial mixture of ethylene polyamines having an overall composition approximating that of tetraethylene pentamine is added. The reaction mixture is stripped by heating at 205°C with nitrogen blowing for 3 hours, and then filtered to yield the filtrate as an oil solution of the desired ashless dispersant product.

(c) A mixture is formed from 300 parts of the ashless dispersant product solution formed as in (b), 8 parts of phosphorous acid, 3.5 parts of tolutriazole, 8 parts of boric acid, and 3.0 parts of water. The mixture is heated at 100°C for two hours until all of the solid materials are dissolved. A vacuum of 40 mm Hg is gradually drawn on the product to remove the water while the temperature is slowly raised to 100°C. A clear solution or composition is obtained which is soluble in oil and suitable for use as component a-1).

EXAMPLE 25

The procedure of Example 24 is repeated except that the tolutriazole is eliminated from the reaction mixture of (c).

EXAMPLE 26

The procedure of Example 24 is repeated except that 11 parts of phosphorus pentasulfide is used in place of the phosphorous acid, the P_2S_5 is added to the mixture after water distillation, and the mixture is then heated for an additional hour at 100°C to provide a clear, oil-soluble composition suitable for use as component a-1).

EXAMPLE 27

The procedure of Example 24 is repeated except that the P_2S_5 is replaced by 7 parts of phosphorus pentoxide (P_2O_5).

EXAMPLE 28

(a) A mixture of 1,000 parts (0.495 mole) of polyisobutene ($\overline{M}n$ = 2020; $\overline{M}w$ = 6049, both determined using the methodology of U.S. Pat. No. 4,234,435) and 115 parts (1.17 moles) of maleic anhydride is heated to

110°C. This mixture is heated to 184°C in 6 hours during which 85 parts (1.2 moles) of gaseous chlorine is added beneath the surface. At 184-189°C, an additional 59 parts (0.83 mole) of chlorine is added over 4 hours. The reaction mixture is stripped by heating at 186-190°C with nitrogen purged for 26 hours. The residue is predominantly polyisobutenyl succinic anhydride acylating agent.

(b) A mixture of 3225 parts (5.0 equivalents) of the polyisobutene-substituted succinic acylating agent prepared as in (a), 289 parts (8.5 equivalents) of pentaerythritol and 5204 parts of mineral oil is heated at 225-235°C for 5.5 hours. The reaction mixture is filtered at 130°C to yield an oil solution of the desired ashless dispersant product.

(c) A mixture is formed from 300 parts of the ashless dispersant product solution formed as in (b), 8 parts of phosphorous acid, 3.5 parts of tolutriazole, 8 parts of boric acid, and 3.0 parts of water. The mixture is heated at 100°C for two hours uni all of the solid materials are dissolved. A vacuum of 40 mm Hg is gradually drawn on the product to remove the water while the temperature is slowly raised to 100°C. A clear solution or composition is obtained which is soluble in oil and suitable for use as component a-1).

EXAMPLE 29

The procedure of Example 28 is repeated except that the tolutriazole is eliminated from the reaction mixture of (c).

EXAMPLE 30

The procedure of Example 28 is repeated except that 11 parts of phosphorus pentasulfide is used in place of the phosphorous acid, the P_2S_5 is added to the mixture after water distillation, and the mixture is then heated for an additional hour at 100°C to provide a clear, oil-soluble composition suitable for use as component a-1).

EXAMPLE 31

The procedure of Example 28 is repeated except that the P_2S_5 is replaced by 7 parts of phosphorus pentoxide (P_2O_5).

EXAMPLE 32

(a) A mixture of 1,000 parts (0.495 mole) of polyisobutene ($\overline{M}n$ = 2020; $\overline{M}w$ = 6049, both determined using the methodology of U.S. Pat. No. 4,234,435) and 115 parts (1.17 moles) of maleic anhydride is heated to 110°C. This mixture is heated to 184°C in 6 hours during which 85 parts (1.2 moles) of gaseous chlorine is added beneath the surface. At 184-189°C, an additional 59 parts (0.83 mole) of chlorine is added over 4 hours. The reaction mixture is stripped by heating at 186-190°C with nitrogen purged for 26 hours. The residue is predominantly polyisobutenyl succinic anhydride acylating agent.

(b) A mixture of 322 parts (0.5 equivalent) of the polyisobutene-substituted succinic acylating agent prepared as in (a), 68 parts (2.0 equivalents) of pentaerythritol and 508 parts of mineral oil is heated at 204-227°C for 5 hours. The reaction mixture is cooled to 162°C and 5.3 parts (0.13 equivalent) of a commercial ethylene polyamine mixture having an overall composition approximating that of tetraethylene pentamine is added. The reaction mixture is heated at 162-163°C for 1 hour, then cooled to 130°C and filtered. The filtrate is an oil solution of the desired ashless dispersant product.

(c) A mixture is formed from 350 parts of the ashless dispersant product solution formed as in (b), 8 parts of phosphorous acid, 3.5 parts of tolutriazole, 8 parts of boric acid, and 3.0 parts of water. The mixture is heated at 100°C for two hours until all of the solid materials are dissolved. A vacuum of 40 mm Hg is gradually drawn on the product to remove the water while the temperature is slowly raised to 100°C. A clear solution or composition is obtained which is soluble in oil and suitable for use as component a-1).

EXAMPLE 33

The procedure of Example 32 is repeated except that the tolutriazole is eliminated from the reaction mixture of (c).

EXAMPLE 34

The procedure of Example 32 is repeated except that 11 parts of phosphorus pentasulfide is used in place of the phosphorous acid, the P_2S_5 is added to the mixture after water distillation, and the mixture is then heated for an additional hour at 100°C to provide a clear, oil-soluble composition suitable for use as component a-1).

EXAMPLE 35

The procedure of Example 32 is repeated except that the P_2S_5 is replaced by 7 parts of phosphorus pentoxide (P_2O_5).

EXAMPLE 36

(a) A mixture of 510 parts (0.28 mole) of polysobutene ($\overline{M}n$ = 1845; $\overline{M}n$ = 5325, both determined using the methodology of U.S. Pat. No. 4,234,435) and 59 parts (0.59 mole) of maleic anhydride is heated to 110°C. This mixture is heated to 190°C in 7 hours during which 43 parts (0.6 mole) of gaseous chlorine is added beneath the surface. At 190-192°C, an additional 11 parts (0.16 mole) of chlorine is added over 3.5 hours. The reaction mixture is stripped by heating at 190-193°C with nitrogen blowing for 10 hours. The residue is predominantly polyisobutenyl succinic anhydride acylating agent.

(b) A mixture of 334 parts (0.52 equivalents) of the polyisobutene substituted succinic acylating agent prepared as in (a), 548 parts of mineral oil, 30 parts (0.88 equivalent) of pentaerythritol and 8.6 parts (0.0057 equivalent) of Polyglycol 112-2 demulsifier is heated at 150°C for 2.5 hours. The reaction mixture is then heated to 210°C over a period of 5 hours and then held at 210°C for an additional 3.2 hours. The reaction mixture is cooled to 190°C and 8.5 parts (0.2 equivalent) of a commercial mixture of ethylene polyamines having an overall composition approximating that of tetraethylene pentamine is added. The reaction mixture is stripped by heating at 205°C with nitrogen blowing for 3 hours, and then filtered to yield the filtrate as an oil solution of the desired ashless dispersant product.

(c) A mixture is formed from 260 parts of the ashless dispersant product solution formed as in (b), 8 parts of phosphorous acid, 3.5 parts of tolutriazole, 8 parts of boric acid, and 3.0 parts of water. The mixture is heated at 100°C for two hours until all of the solid materials are dissolved. A vacuum of 40 mm Hg is gradually drawn on the product to remove the water while the temperature is slowly raised to 100°C. A clear solution or composition is obtained which is soluble in oil and suitable for use as component a-1).

EXAMPLE 37

The procedure of Example 36 is repeated except that the tolutriazole is eliminated from the reaction mixture of (c).

EXAMPLE 38

The procedure of Example 36 is repeated except that 11 parts of phosphorus pentasulfide is used in place of the phosphorous acid, the P_2S_5 is added to the mixture after water distillation, and the mixture is then heated for an additional hour at 100°C to provide a clear, oil-soluble composition suitable for use as component a-1).

EXAMPLE 39

The procedure of Example 36 is repeated except that the P_2S_5 is replaced by 7 parts of phosphorus pentoxide (P_2O_5).

EXAMPLE 40

(a) A mixture of 510 parts (0.28 mole) of polyisobutene ($\overline{M}n$ = 1845; $\overline{M}w$ = 5325, both determined using the methodology of U.S. Pat. No. 4,234,435) and 59 parts (0.59 mole) of maleic anhydride is heated to 110°C. This mixture is heated to 190°C in 7 hours during which 43 parts (0.6 mole) of gaseous chlorine is added beneath the surface. At 190-192°C, an additional 11 parts (0.16 mole) of chlorine is added over 3.5 hours. The reaction mixture is stripped by heating at 190-193°C with nitrogen blowing for 10 hours. The residue is predominantly polyisobutenyl succinic anhydride acylating agent.

(b) A mixture is prepared by the addition of 10.2 parts (0.25 equivalent) of a commercial mixture of ethylene polyamines having the approximate overall composition of tetraethylene pentamine to 113 parts of mineral oil and 161 parts (0.25 equivalent) of the substituted succinic acylating agent prepared as in (a) while maintaining the temperature at 138°C. The reaction mixture is heated to 150°C over a 2 hour period and stripped by blowing with nitrogen. The reaction mixture is filtered to yield the filtrate as an oil solution of the desired ashless dispersant product.

EXAMPLE 41

The procedure of Example 40 is repeated except that the tolutriazole is eliminated from the reaction mixture of (c).

EXAMPLE 42

The procedure of Example 40 is repeated except that 11 parts of phosphorus pentasulfide is used in place of the phosphorous acid, the P_2S_5 is added to the mixture after water distillation, and the mixture is then heated for an additional hour at 100°C to provide a clear, oil-soluble composition suitable for use as component a-1).

EXAMPLE 43

The procedure of Example 40 is repeated except that the P_2S_5 is replaced by 7 parts of phosphorus pentoxide (P_2O_5).

EXAMPLE 44

To a reactor are charged under a nitrogen atmosphere 67.98 parts of a commercially-available polyisobutenyl succinimide of a mixture of polyethylene polyamines having the approximate overall composition of tetraethylene pentamine (the polyisobutenyl group derived from polyisobutene having a number average molecular weight of about 900; the succinimide product having a ratio of about 1.15 succinic groups per alkenyl group) and 26.14 parts of a 100 Solvent neutral refined mineral oil. After raising the temperature of the resulting solution to 100-105 C, 2.09 parts of boric acid and 2.09 parts of phosphorous acid are introduced into the reactor, followed by 0.92 part of tolutriazole (Cobratec TT- 100; PMC Specialties Group, Cincinnati, Ohio) and then 0.78 part of water. The resultant mixture is heated at 100-105°C for two hours and then the temperature is gradually raised to 115°C with the application of a vacuum to 40 mm Hg. Stripping is continued for 90 minutes and until 120°C/40 mm Hg has been reached. A flow of dry nitrogen is then applied to the system and the product mixture is allowed to cool. The product mixture is suitable for use as component a-1) in the compositions of this invention.

EXAMPLE 45

The procedure of Example 44 is repeated except that the tolutriazole is omitted from the reaction mixture.

EXAMPLE 46

(a) A mixture of 322 parts of the polyisobutene-substituted succinic acylating agent prepared as in Example 40(a), 68 parts of pentaerythritol and 508 parts of mineral oil is heated at 204-227°C for 5 hours. The reaction mixture is cooled to 162°C and 5.3 parts of a commercial ethylene polyamine mixture having the approximate overall composition corresponding to tetraethylene pentamine is added. The reaction mixture is heated at 162-163°C for 1 hour, then cooled to 130°C and filtered. The filtrate is an oil solution of the desired product.

(b) A mixture is formed from 275 parts of the product solution formed as in (a), 8 parts of phosphorous acid, 3.5 parts of tolutriazole, 8 parts of boric acid, and 3.0 parts of water. The mixture is heated at 100°C for two hours until all of the solid materials are dissolved. A vacuum of 40 mm Hg is gradually drawn on the product to remove the water while the temperature is slowly raised to 100°C. A clear solution or composition is obtained which is soluble in oil and suitable for use as component a-1).

EXAMPLE 47

The procedures of Examples 1 through 8 are repeated except that in each case a chemically equivalent amount of trimethyl borate is substituted for the boric acid, and the water used with the boric acid is omitted.

EXAMPLE 48

The procedures of Examples 1 through 5, and 10 through 15 are repeated except that in each case the boronating agent consists of a chemically equivalent amount of trimethyl borate in lieu of boric acid, the water used with the boric acid is omitted, and the phosphorylating agent consists of a chemically equivalent amount of a mixture consisting of an equimolar mixture of phosphorous acid and dibutyl hydrogen phosphite.

EXAMPLE 49

(a) To 120 parts of chlorinated polyisobutylene having a number average molecular weight of about 1,300 and containing about 2.8 weight percent chlorine are added 21.7 parts of pentaethylene hexamine and 5.6 parts of sodium carbonate. The reaction mixture is heated to about 205°C and maintained at this temperature for about 5 hours. A stream of nitrogen is passed through the reaction mixture to remove the water of reaction. The reaction mixture is diluted with 60 parts of light mineral oil and hexane, filtered and extracted with methanol to remove excess pentaethylene hexamine. The hexane is stripped from the product by heating the mixture to 120°C under a suitable vacuum. The product should have a nitrogen content of approximately 1.0 to 1.5 weight percent.

(b) A mixture is formed from 80 parts of a diluted reaction product formed as in (a), 20 parts of a 100 Solvent Neutral refined mineral oil diluent, 2.1 parts of phosphorous acid, 4.6 parts of boric acid, and 1.5 parts of water. The resultant mixture is heated at 100-105°C for 2 hours and then the temperature is gradually raised to 115°C with the application of a vacuum to 40 mm Hg. Stripping is continued for 90 minutes and until 120°C/40 mm Hg has been reached. A flow of dry nitrogen is then applied to the system and the product mixture is allowed to cool. The product mixture is suitable for use as component a-1) in the compositions of this invention.

(c) 2 Parts of powdered anhydrous boric acid is added with stirring to 80 parts of a 50 weight percent mineral oil solution of a reaction product formed as in (a) heated to 90°C. The temperature of the mixture is then increased to 150°C and maintained at this temperature for 4 hours while collecting the water of reaction overhead. The mixture is then filtered and mixed with 10 parts of a 100 Solvent Neutral refined mineral oil diluent, and 1.5 parts of phosphorous acid. The resultant mixture is heated at 100-105°C for 2 hours and then the temperature is gradually raised to 115°C with the application of a vacuum to 40 mm Hg. Stripping is continued for 90 minutes and until 120°C/40 mm Hg has been reached. A flow of dry nitrogen is then applied to the system and the product mixture is allowed to cool. The product mixture is suitable for use as component a-1).

EXAMPLE 50

(a) Into a reactor are placed 220 parts of p-nonylphenol and 465 parts of diethylenetriamine. The mixture is heated to 80°C and 152 parts of 37% formalin is added dropwise over a period of about 30 minutes. The mixture is then heated to 125 °C for several hours until the evolution of water has ceased. The resultant product should contain approximately 16-20% nitrogen.

(b) Into a reactor are placed 202 parts of styrene-maleic anhydride resin (having a number average molecular weight in the range of 600-700 and a mole ratio of styrene to maleic anhydride of 1:1), 202.5 parts of octadecyl amine and 472 parts of a 95 VI lubricating oil having a viscosity at 100°F of 150 SUS. The mixture is heated to 225°C for several hours. To this mixture is added dropwise over a period of about 30 minutes, 85 parts of the product formed as in (a). The resulting mixture is heated for 6 hours at 210-230°C while collecting the water formed during reaction. The polymeric product so formed should have a nitrogen content of about 2.1 weight percent.

(c) To a reactor are charged 200 parts of the basic nitrogen polymer produced as in (b) and 50 parts of a 100 Solvent Neutral refined mineral oil. After raising the temperature of the resulting mixture to 100-105°C, 5.7 parts of boric acid, 4.0 parts of phosphorous acid, and 2.0 parts of water are added. The resultant mixture is heated at 100-105°C for two hours and then the temperature is gradually raised to 115°C with the application of a vacuum to 40 mm Hg. Stripping is continued for 90 minutes and until 120°C/40 mm Hg has been reached. A flow of dry nitrogen is then applied to the system and the product mixture is allowed to cool. The product mixture is suitable for use as component a-1) in the compositions of this invention.

Production of Component a-2):

Typical procedures for producing component a-2) phosphorylated ashless dispersants involve heating one or more ashless dispersants of the types described above with at least one inorganic phosphorus acid under conditions yielding a liquid phosphorus-containing composition. Examples of inorganic phosphorus acids which are useful in forming such products include phosphorous acid (H_3PO_3, sometimes depicted as $H_2(HPO_3)$, and sometimes called ortho-phosphorous acid), phosphoric acid (H_3PO_4, sometimes called orthophosphoric acid), hypophosphoric acid ($H_4P_2O_6$), metaphosphoric acid (HPO_3), pyrophosphoric acid ($H_4P_2O_7$), hypophosphorous acid (H_3PO_2, sometimes called phosphinic acid), pyrophosphorous acid ($H_4P_2O_5$, sometimes called pyrophosphonic acid), phosphinous acid (H_3PO), tripolyphosphoric acid ($H_5P_3O_{10}$), tetrapolyphosphoric acid ($H_6P_4O_{13}$), trimetaphosphoric acid ($H_3P_3O_9$), phosphoramidic acid ($H_2O_3PNH_2$), phosphoramidous acid (H_4NO_2P), and the like. Partial or total sulfur analogs such as phosphorotetrathioic acid (H_3PS_4), phosphoromonothioic acid (H_3PO_3S), phosphorodithioic acid ($H_3PO_2S_2$), phosphorotrithioic acid (H_3POS_3), can also be used in forming products suitable for use as component a-2). The preferred phosphorus reagent is phosphorous acid, (H_3PO_3).

It will be understood that the form or composition of the inorganic acid(s) as charged into the mixture to be heated or being heated may be altered in situ. For example, the action of heat and/or water can transform certain inorganic phosphorus compounds into other inorganic phosphorus compounds or species. Any such in situ transformations that may occur are within the purview of this invention provided that the liquid phosphorylated ashless dispersant reveals on analysis the presence therein of phosphorus.

Optionally, additional sources of basic nitrogen can be included in the inorganic phosphorus compound-ashless dispersant mixture so as to provide a molar amount (atomic proportion) of basic nitrogen up to that equal to the molar amount of basic nitrogen contributed by the ashless dispersant. Preferred auxiliary nitrogen compounds are long chain primary, secondary and tertiary alkyl amines containing from 12 to 24 carbon atoms, including their hydroxyalkyl and aminoalkyl derivatives. The long chain alkyl group may optionally contain one or more ether groups. Examples of suitable compounds are oleyl amine, N-oleyltrimethylene diamine, N-tallow diethanolamine, N,N-dimethyl oleylamine, and myristyloxapropyl amine.

Other materials normally used in lubricant additives which do not interfere with the process may also be added, for example, a benzotriazole, including lower (C_1-C_4) alkyl-substituted benzotriazoles, which function to protect copper surfaces.

The heating step is conducted at temperatures sufficient to produce a liquid composition which contains phosphorus. The heating can be carried out in the absence of a solvent by heating a mixture of the ashless dispersant and one or more suitable inorganic phosphorus compounds. The temperatures used will vary somewhat depending upon the nature of the ashless dispersant and the inorganic phosphorus reagent being utilized. Generally speaking however, the temperature will usually fall within the range of 40 to 200°C. The duration of the heating is likewise susceptible to variation, but ordinarily will fall in the range of 1 to 3 hours. When conducting the heating in bulk, it is important to thoroughly agitate the components to insure intimate contact therebetween. When utilizing the preferred phosphorus reagent (solid phosphorous acid), it is convenient to apply heat to the mixture until a clear liquid composition is formed. Alternatively, the phosphorous acid may be utilized in the form of an aqueous solution. Water formed in the process and any added water is preferably removed from the heated mixture by vacuum distillation at temperatures of from 100 to 140°C. The heating may be conducted in more than one stage if desired. Preferably the heating step or steps will be conducted in a diluent oil or other inert liquid medium such as light mineral oils, and the like.

The amount of inorganic phosphorus acid employed in the heating process preferably ranges from 0.001 mole to 0.999 mole per mole of basic nitrogen and free hydroxyl in the mixture being heated, up to one half of which may be contributed by an auxiliary nitrogen compound. It is possible however to use the inorganic phosphorus acid(s) in excess of the amount of basic nitrogen and/or hydroxyl groups in the dispersant being heated.

When used, the amount of diluent usually ranges from 10 to 50% by weight of the mixture being subjected to heating. Water can be added to the mixture, before and/or during the heating, if desired.

Usually the phosphorylated dispersants utilized as component a-2) in the compositions of this invention when in their undiluted state will have on a weight basis a phosphorus content of at least 5,000 parts per million (ppm) (preferably at least 6,000 ppm and more preferably at least 7,000 ppm). When forming component a-2) in part by use of one or more organic phosphorus compounds such as one or more organic phosphates (e.g., trihydrocarbyl phosphates, dihydrocarbyl monoacid phosphates, monohydrocarbyl diacid phosphates, or mixtures thereof), phosphites (e.g., trihydrocarbyl phosphites, dihydrocarbyl hydrogen phosphites, hydrocarbyl diacid phosphites, or mixtures thereof), phosphonates (e.g., hydrocarbyl phosphonic acids, mono- and/or dihydrocarbyl esters of phosphonic acids, or mixtures thereof), phosphonites (e.g., hydrocarbyl phosphinic acids, mono- and/or dihydrocarbyl esters of phosphinic acids, or mixtures thereof), etc., or the partial or total sulfur analogs thereof, and in part by use of one or more inorganic phosphorus acids, the latter should be used in an amount sufficient to provide at least 25% (preferably at least 50% and more preferably at least 75%) of the total content of phosphorus in the phosphorylated dispersant.

The preparation of phosphorylated ashless dispersants suitable for use as component a-2) in the compositions of this invention is illustrated by the following Examples 51-96 in which all parts and percentages are by weight unless otherwise clearly specified.

EXAMPLE 51

A mixture is formed from 260 parts of a polyisobutenyl succinimide ashless dispersant (derived from polybutene having a number average molecular weight of 950 and a mixture of a polyethylene polyamines having an average overall composition approximating that of tetraethylene pentamine), 100 parts of a 100 Solvent Neutral refined mineral oil diluent, 8 parts of solid phosphorous acid, and 3.5 parts of tolutriazole. The mixture is heated at 110°C for two hours. A vacuum of 40 mm Hg is gradually drawn on the product to remove traces of water while the temperature is maintained at 110°C. A clear solution or composition is obtained which is soluble in oil and suitable for use as component a-2).

EXAMPLE 52

The procedure of Example 51 is repeated except that the succinimide ashless dispersant used is derived from polybutene having a number average molecular weight of 1,150. The average number of succinic groups per alkenyl group in the succinimide is approximately 1.2.

EXAMPLE 53

The procedure of Example 51 is repeated except that the succinimide ashless dispersant used is derived from polybutene having a number average molecular weight of 2,100.

EXAMPLE 54

The procedure of Example 51 is repeated except that the succinimide ashless dispersant is replaced by an equal amount of a boron-free Mannich polyamine dispersant made from tetraethylene pentamine, polyisobutenyl phenol (made from polyisobutene having a number average molecular weight of about 1710 and formalin) having a nitrogen content of 1.1%.

EXAMPLE 55

The procedure of Example 51 is repeated except that the succinimide ashless dispersant is replaced by an equal amount of an ashless dispersant of the pentaerythritol succinic ester type.

EXAMPLE 56

The procedure of Example 51 is repeated except that 9.6 parts of orthophosphoric acid is used in place of the phosphorous acid, and the mixture is heated for three hours at 110°C to provide a clear, oil-soluble composition suitable for use as component a-2).

EXAMPLE 57

The procedure of Example 51 is repeated except that the phosphorous acid is replaced by 6.4 parts of hypophosphorous acid.

EXAMPLE 58

The procedures of Examples 51 through 57 are repeated except that the tolutriazole is omitted from the initial mixtures subjected to the thermal processes.

EXAMPLE 59

To 2,500 parts of a polyisobutenyl succinimide (derived from polyisobutene having a number average molecular weight of 950 and a mixture of polyethylene polyamines having an overall average composition approximating that of tetraethylene pentamine) warmed to 28°C are added 54.31 parts of phosphorous acid, 20.27

parts of tolutriazole and 23.91 parts of water. This mixture is heated at 110°C for 1.5 hours. Then the reflux condenser is replaced by a distillation column and water is removed under vacuum for 2.25 hours at 110°C to form a homogeneous liquid composition suitable for use as component a-2).

EXAMPLE 60

A mixture of 7300 parts of a polyisobutenyl succinimide (derived from polybutene having a number average molecular weight of about 1,300 and a mixture of polyethylene polyamines having an average overall composition approximating that of tetraethylene pentamine), and 2500 parts of 100 Solvent Neutral mineral oil is heated to 90-100°C. To this mixture is added 200 parts of phosphorous acid and the resultant mixture is heated at 90-100°C for 2 hours. The resultant homogeneous liquid composition is suitable for use as component a-2).

EXAMPLE 61

A mixture of 58,415.5 parts of a polyisobutenyl succinimide (derived from polyisobutene having a number average molecular weight of 1300 and a mixture of polyethylene polyamines having an overall average composition approximating that of tetraethylene pentamine), and 12,661.6 parts of 100 Solvent Neutral mineral oil is heated to 80°C. To this mixture is added 1942.28 parts of phosphorous acid and the resultant mixture is heated at 110°C for 2 hours. The resultant homogeneous liquid composition is suitable for use as component a-2).

EXAMPLE 62

The procedure of Example 61 is repeated using 45,600 parts of the ashless dispersant, 8983.2 parts of the mineral oil diluent, and 2416.8 parts of the phosphorous acid.

EXAMPLE 63

A mixture of 14,400 parts of a polyisobutenyl succinimide (derived from polyisobutene having a number average molecular weight of 950 and a mixture of polyethylene polyamines having an overall average composition approximating that of tetraethylene pentamine), and 3121.2 parts of 100 Solvent Neutral mineral oil is heated to 80°C. To this mixture is added 478.8 parts of phosphorous acid and the resultant mixture is heated at 110°C for 2 hours. The resultant homogeneous liquid composition contains about 1.04% of phosphorus and is suitable for use as component a-2).

EXAMPLE 64

A mixture of 7300 parts of ashless dispersant as used in Example 60, 2500 parts of 100 Solvent Neutral mineral oil, and 200 parts of phosphorous acid is formed at room temperature and heated to 110°C for two hours. The resultant homogeneous liquid composition is suitable for use as component a-2).

EXAMPLE 65

A mixture of 4680 parts of phosphorylated dispersant formed as in Example 64 and 2340 parts of a commercial boronated succinimide ashless dispersant (HiTEC® 648 dispersant) is formed. The resultant homogeneous liquid composition is suitable for use in the practice of this invention. A portion of the resultant mixture can be heated to 110°C for two hours, and this resultant homogeneous liquid composition is also suitable for use as component a-2).

EXAMPLE 66

(a) A mixture of 1,000 parts (0.495 mole) of polyisobutene ($\overline{M}n$ = 2020; $\overline{M}w$ = 6049, both determined using the methodology of U.S. Pat. No. 4,234,435) and 115 parts (1.17 moles) of maleic anhydride is heated to 110°C. This mixture is heated to 184°C in 6 hours during which 85 parts (1.2 moles) of gaseous chlorine is added beneath the surface. At 184-189°C, an additional 59 parts (0.83 mole) of chlorine is added over 4 hours. The reaction mixture is stripped by heating at 186-190°C with nitrogen purged for 26 hours. The residue is predominately polyisobutenyl succinic anhydride acylating agent.

(b) A mixture is prepared by the addition of 57 parts (1.38 equivalents) of a commercial mixture of ethylene polyamines having the approximate overall composition of tetraethylene pentamine to 1,067 parts of mineral oil and 893 parts (1.38 equivalents) of substituted succinic acylating agent prepared as in (a) while maintaining the temperature at 140-145°C. The reaction mixture is then heated to 155°C over a three hour period and stripped by blowing with nitrogen. The reaction mixture is filtered to yield the filtrate as an oil solution of the desired product composed predominately of polyisobutenyl succinimides.

(c) A mixture is formed from 250 parts of the polyisobutenyl succinimide product solution formed as in (b), 8 parts of phosphorous acid, and 3.5 parts of tolutriazole. The mixture is heated at 100°C for two hours. A clear solution or composition is obtained which is soluble in oil and suitable for use as component a-2).

EXAMPLE 67

The procedure of Example 66 is repeated except that the tolutriazole is eliminated from the reaction mixture of (c).

EXAMPLE 68

The procedure of Example 67 is repeated except that the phosphorous acid is replaced by 11.1 parts of phosphoromonothioic acid (H_3PO_3S).

EXAMPLE 69

(a) A mixture of 1.000 parts (0.495 mole) of polyisobutene ($\overline{M}n$ = 2020; $\overline{M}w$ = 6049, both determined using the methodology of U.S. Pat. No. 4,234,435) and 115 parts (1.17 moles) of maleic anhydride is heated to 110°C. This mixture is heated to 184°C in 6 hours during which 85 parts (1.2 moles) of gaseous chlorine is added teneath the surface. At 184-189°C, an additional 59 parts (0.83 mole) of chlorine is added over 4 hours. The reaction mixture is stripped by heating at 186-190°C with nitrogen purged for 26 hours. The residue is predominately polyisobutenyl succinic anhydride acylating agent.

(b) A mixture is prepared by the addition of 18.2 parts (0.433 equivalents) of a commercial mixture of ethylene polyamines having the approximate overall composition of tetraethylene pentamine to 392 parts of mineral oil and 348 parts (0.52 equivalent) of substituted succinic acylating agent prepared as in (a) while maintaining the temperature at 140°C. The reaction mixture is then heated to 150°C in 1.8 hours and stripped by blowing with nitrogen. The reaction mixture is filtered to yield the filtrate as an oil solution of the desired product composed predominately of polyisobutenyl succinimides.

(c) A mixture is formed from 250 parts of the polyisobutenyl succinimide product solution formed as in (b), 8 parts of phosphorous acid, and 3.5 parts of tolutriazole. The mixture is heated at 100°C for two hours. A clear solution or composition is obtained which is soluble in oil and suitable for use as component a-2).

EXAMPLE 70

The procedure of Example 69 is repeated except that the tolutriazole is eliminated from the reaction mixture of (c).

EXAMPLE 71

The procedure of Example 70 is repeated except that the phosphorous acid is replaced by 13.7 parts of phosphoramidic acid, $(HO)_2PONH_2$.

EXAMPLE 72

(a) A mixture of 1,000 parts (0.495 mole) of polyisobutene ($\overline{M}n$ = 2020; $\overline{M}w$ = 6049, both determined using the methodology of U.S. Pat. No. 4,234,435) and 115 parts (1.17 moles) of maleic anhydride is heated to 110°C. This mixture is heated to 184°C in 6 hours during which 85 parts (1.2 moles) of gaseous chlorine is added beneath the surface. At 184-189°C, an additional 59 parts (0.83 mole) of chlorine is added over 4 hours. The reaction mixture is stripped by heating at 186-190°C with nitrogen purged for 26 hours. The residue is predominately polyisobutenyl succinic anhydride acylating agent.

(b) A mixture of 334 parts (0.52 equivalents) of the polyisobutene substituted succinic acylating agent prepared as in (a), 548 parts of mineral oil, 30 parts (0.88 equivalent) of pentaerythritol and 8.6 parts (0.0057 equivalent) of Polyglycol 112-2 demulsifier is heated at 150°C for 2.5 hours. The reaction mixture is then heated to 210°C over a period of 5 hours and then held at 210°C for an additional 3.2 hours. The reaction mixture is cooled to 190°C and 8.5 parts (0.2 equivalent) of a commercial mixture of ethylene polyamines having an overall composition approximating that of tetraethylene pentamine is added. The reaction mixture is stripped by heating at 205°C with nitrogen blowing for 3 hours, and then filtered to yield the filtrate as an oil solution of the desired ashless dispersant product.

(c) A mixture is formed from 300 parts of the ashless dispersant product solution formed as in (b), 8 parts of phosphorous acid, and 3.5 parts of tolutriazole. The mixture is heated at 100°C for two hours. A clear solution or composition is obtained which is soluble in oil and suitable for use as component a-2).

EXAMPLE 73

The procedure of Example 72 is repeated except that the tolutriazole is eliminated from the reaction mixture of (c).

EXAMPLE 74

The procedure of Example 73 is repeated except that the phosphorous acid is replaced by 9.6 parts of orthophosphoric acid.

EXAMPLE 75

(a) A mixture of 1,000 parts (0.495 mole) of polyisobutene ($\overline{M}n$ = 2020; $\overline{M}w$ = 6049, both determined using the methodology of U.S. Pat. No. 4,234,435) and 115 parts (1.17 moles) of maleic anhydride is heated to 110°C. This mixture is heated to 184°C in 6 hours during which 85 parts (1.2 moles) of gaseous chlorine is added beneath the surface. At 184-189°C, an additional 59 parts (0.83 mole) of chlorine is added over 4 hours. The reaction mixture is stripped by heating at 186-190°C with nitrogen purged for 26 hours. The residue is predominately polyisobutenyl succinic anhydride acylating agent.

(b) A mixture of 3225 parts (5.0 equivalents) of the polyisobutene-substituted succinic acylating agent prepared as in (a), 289 parts (8.5 equivalents) of pentaerythritol and 5204 parts of mineral oil is heated at 225-235°C for 5.5 hours. The reaction mixture is filtered at 130°C to yield an oil solution of the desired ashless dispersant product.

(c) A mixture is formed from 300 parts of the ashless dispersant product solution formed as in (b), 8 parts of phosphorous acid, and 3.5 parts of tolutriazole. The mixture is heated at 100°C for two hours. A clear solution or composition is obtained which is soluble in oil and suitable for use as component a-2).

EXAMPLE 76

The procedure of Example 75 is repeated except that the tolutriazole is eliminated from the reaction mixture of (c).

EXAMPLE 77

The procedure of Example 76 is repeated except that 11 parts of phosphoric acid is used in place of the phosphorous acid to provide a clear, oil-soluble composition suitable for use as component a-2).

EXAMPLE 78

The procedure of Example 77 is repeated except that 10 parts of an equimolar mixture of phosphoric acid and phosphorous acid is used.

EXAMPLE 79

(a) A mixture of 1,000 parts (0.495 mole) of polyisobutene ($\overline{M}n$ = 2020; $\overline{M}w$ = 6049, both determined using the methodology of U.S. Pat. No. 4,234,435) and 115 parts (1.17 moles) of maleic anhydride is heated to 110°C. This mixture is heated to 184°C in 6 hours during which 85 parts (1.2 moles) of gaseous chlorine is added beneath the surface. At 184-189°C, an additional 59 parts (0.83 mole) of chlorine is added over 4 hours. The reaction mixture is stripped by heating at 186-190°C with nitrogen purged for 26 hours. The residue is predominately polyisobutenyl succinic anhydride acylating agent.

(b) A mixture of 322 parts (0.5 equivalent) of the polyisobutene-substituted succinic acylating agent prepared as in (a), 68 parts (2.0 equivalents) of pentaerythritol and 508 parts of mineral oil is heated at 204-227°C for 5 hours. The reaction mixture is cooled to 162°C and 5.3 parts (0.13 equivalent) of a commercial ethylene polyamine mixture having an overall composition approximating that of tetraethylene pentamine is added. The reaction mixture is heated at 162-163°C for 1 hour, then cooled to 130°C and filtered. The filtrate is an oil solution of the desired ashless dispersant product.

(c) A mixture is formed from 350 parts of the ashless dispersant product solution formed as in (b), 8 parts of phosphorous acid, and 3.5 parts of tolutriazole. The mixture is heated at 100°C for two hours. A clear solution or composition is obtained which is soluble in oil and suitable for use as component a-2).

EXAMPLE 80

The procedure of Example 79 is repeated except that the tolutriazole is eliminated from the reaction mixture of (c).

EXAMPLE 81

The procedure of Example 80 is repeated except that 15.8 parts of phosphorotetrathioic acid (H_3PS_4) is used in place of the phosphorous acid.

EXAMPLE 82

(a) A mixture of 510 parts (0.28 mole) of polysobutene ($\overline{M}n$ = 1845; $\overline{M}w$ = 5325, both determined using the methodology of U.S. Pat. No. 4,234,435) and 59 parts (0.59 mole) of maleic anhydride is heated to 110°C. This mixture is heated to 190°C in 7 hours during which 43 parts (0.6 mole) of gaseous chlorine is added beneath the surface. At 190-192°C, an additional 11 parts (0.16 mole) of chlorine is added over 3.5 hours. The reaction mixture is stripped by heating at 190-193 °C with nitrogen blowing for 10 hours. The residue is predominately polyisobutenyl succinic anhydride acylating agent.

(b) A mixture of 334 parts (0.52 equivalents) of the polyisobutene substituted succinic acylating agent prepared as in (a), 548 parts of mineral oil, 30 parts (0.88 equivalent) of pentaerythritol and 8.6 parts (0.0057 equivalent) of Polyglycol 112-2 demulsifier is heated at 150°C for 2.5 hours. The reaction mixture is then heated to 210°C over a period of 5 hours and then held at 210°C for an additional 3.2 hours. The reaction mixture is cooled to 190°C and 8.5 parts (0.2 equivalent) of a commercial mixture of ethylene polyamines having an overall composition approximating that of tetraethylene pentamine is added. The reaction mixture is stripped by heating at 205°C with nitrogen blowing for 3 hours, and then filtered to yield the filtrate as an oil solution of the desired ashless dispersant product.

(c) A mixture is formed from 260 parts of the ashless dispersant product solution formed as in (b), 8 parts of phosphorous acid, and 3.5 parts of tolutriazole. The mixture is heated at 100°C for two hours. A clear solution or composition is obtained which is soluble in oil and suitable for use as component a-2).

EXAMPLE 83

The procedure of Example 82 is repeated except that the tolutriazole is eliminated from the reaction mixture of (c).

EXAMPLE 84

The procedure of Example 83 is repeated except that 6.4 parts of hypophosphorous acid (H_3PO_2) is used in place of the phosphorous acid.

EXAMPLE 85

(a) A mixture of 510 parts (0.28 mole) of polyisobutene ($\overline{M}n$ = 1845; $\overline{M}w$ = 5325, both determined using the methodology of U.S. Pat. No. 4,234,435) and 59 parts (0.59 mole) of maleic anhydride is heated to 110°C. This mixture is heated to 190°C in 7 hours during which 43 parts (0.6 mole) of gaseous chlorine is added beneath the surface. At 190-192°C, an additional 11 parts (0.16 mole) of chlorine is added over 3.5 hours. The reaction mixture is stripped by heating at 190-193°C with nitrogen blowing for 10 hours. The residue is predominately polyisobutenyl succinic anhydride acylating agent.

(b) A mixture is prepared by the addition of 10.2 parts (0.25 equivalent) of a commercial mixture of ethylene polyamines having the approximate overall composition of tetraethylene pentamine to 113 parts of mineral oil and 161 parts (0.25 equivalent) of the substituted succinic acylating agent prepared as in (a) while maintaining the temperature at 138°C. The reaction mixture is heated to 150°C over a 2 hour period and stripped by blowing with nitrogen. The reaction mixture is filtered to yield the filtrate as an oil solution of the desired ashless dispersant product.

(c) A mixture is formed from 125 parts of the polyisobutenyl succinimide product solution formed as in (b), 8 parts of phosphorous acid, and 3.5 parts of tolutriazole. The mixture is heated at 100°C. to form a composition which is soluble in oil and suitable for use as component a-2).

EXAMPLE 86

The procedure of Example 85 is repeated except that the tolutriazole is eliminated from the reaction mixture of (c).

EXAMPLE 87

The procedure of Example 86 is repeated except that 9.6 parts of orthophosphoric acid is used instead of the phosphorous acid.

EXAMPLE 88

To a reactor are charged under a nitrogen atmosphere 67.98 parts of a commercially-available polyisobutenyl succinimide of a mixture of polyethylene polyamines having the approximate overall composition of tetraethylene pentamine (the polyisobutenyl group derived from polyisobutene having a number average molecular weight of about 950; the succinimide product having a ratio of about 1.15 succinic groups per alkenyl group) and 26.14 parts of a 100 Solvent Neutral refined mineral oil. After raising the temperature of the resulting solution to 100-105°C, 2.09 parts of phosphorous acid are introduced into the reactor, followed by 0.92 part of tolutriazole (Cobratec TT-100). The resultant mixture is heated at 100-105°C for two hours. Then the temperature is gradually raised to 115°C with the application of a vacuum to 40 mm Hg. Stripping is continued for 90 minutes and until 120°C/40 mm Hg has been reached. A flow of dry nitrogen is then applied to the system and the product mixture is allowed to cool. The product mixture is suitable for use as component a-2).

EXAMPLE 89

The procedure of Example 88 is repeated except that the tolutriazole is omitted from the reaction mixture.

EXAMPLE 90

The procedure of Example 63 is repeated except that 763.2 parts of phosphorous acid (H_3PO_3) and 2,836.8 parts of 100 Solvent Neutral mineral oil are used. The phosphorus content of the final product is about 1.66%.

EXAMPLE 91

(a) A mixture of 322 parts of the polyisobutene-substituted succinic acylating agent prepared as in Example 85(a), 68 parts of pentaerythritol and 508 parts of mineral oil is heated at 204-227°C for 5 hours. The reaction mixture is cooled to 162°C and 5.3 parts of a commercial ethylene polyamine mixture having the approximate overall composition corresponding to tetraethylene pentamine is added. The reaction mixture is heated at 162-163°C for 1 hour, then cooled to 130°C and filtered. The filtrate is an oil solution of the desired product.

(b) A mixture is formed from 275 parts of the product solution formed as in (a), 8 parts of phosphorous acid, and 3.5 parts of tolutriazole. The mixture is heated at 100°C for two hours. A clear solution or composition is obtained which is soluble in oil and suitable for use as component a-2).

EXAMPLE 92

The procedures of Examples 51 through 55 and 59 through 64 are repeated except that in each case the phosphorylating agent consists of a chemically equivalent amount of a mixture consisting of an equimolar mixture of phosphorous acid and dibutyl hydrogen phosphite.

EXAMPLE 93

(a) To 120 parts of chlorinated polyisobutylene having a number average molecular weight of about 1,300 and containing about 2.8 weight percent chlorine are added 21.7 parts of pentaethylene hexamine and 5.6 parts of sodium carbonate. The reaction mixture is heated to about 205°C and maintained at this temperature for about 5 hours. A stream of nitrogen is passed through the reaction mixture to remove the water of reaction. The reaction mixture is diluted with 60 parts of light mineral oil and hexane, filtered and extracted with methanol to remove excess pentaethylene hexamine. The hexane is stripped from the product by heating the mixture to 120°C under a suitable vacuum. The product should have a nitrogen content of approximately 1.0 to 1.5 weight percent.

(b) A mixture is formed from 80 parts of a diluted reaction product formed as in (a), 20 parts of a 100 Solvent Neutral refined mineral oil diluent, and 2.1 parts of phosphorous acid. The resultant mixture is heated at 100-105°C for 2 hours and then the temperature is gradually raised to 115°C with the application of a vacuum to 40 mm Hg. Stripping is continued for 90 minutes and until 120°C/40 mm Hg has been reached. A flow of dry nitrogen is then applied to the system and the product mixture is allowed to cool. The product mixture is suitable for use as component a-2).

EXAMPLE 94

(a) Into a reactor are placed 220 parts of p-nonylphenol and 465 parts of diethylenetriamine. The mixture is heated to 80°C and 152 parts of 37% formalin is added dropwise over a period of about 30 minutes. The mixture is then heated to 125°C for several hours until the evolution of water has ceased. The resultant product should contain approximately 16-20% nitrogen.

(b) Into a reactor are placed 202 parts of styrene-maleic anhydride resin (having a number average molecular weight in the range of 600-700 and a mole ratio of styrene to maleic anhydride of 1:1), 202.5 parts of octadecyl amine and 472 parts of a 95 VI lubricating oil having a viscosity at 100°F of 150 SUS. The mixture is heated to 225°C for several hours. To this mixture is added dropwise over a period of about 30 minutes, 85 parts of the product formed as in (a). The resulting mixture is heated for 6 hours at 210-230°C while collecting the water formed during reaction. The polymeric product so formed should have a nitrogen content of about 2.1 weight percent.

(c) To a reactor are charged 200 parts of the basic nitrogen polymer produced as in (b) and 50 parts of a 100 Solvent Neutral refined mineral oil. After raising the temperature of the resulting mixture to 100-105°C, 4.0 parts of phosphorous acid is added. The resultant mixture is heated at 100-105°C for two hours and then the temperature is gradually raised to 115°C with the application of a vacuum to 40 mm Hg. Stripping is continued for 90 minutes and until 120°C/40 mm Hg has been reached. A flow of dry nitrogen is then applied to the system and the product mixture is allowed to cool. The product mixture is suitable for use as component a-2).

EXAMPLE 95

The procedure of Example 63 is repeated except that the proportions of the reaction components are 14,400 parts of the succinimide, 3409.2 parts of the mineral oil, and 190.8 parts of phosphorous acid (H_3PO_3). This product contains approximately 0.40% of phosphorus.

EXAMPLE 96

The procedure of Example 61 is repeated except that the proportions of the reaction components are 45,600 parts of the succinimide, 10,795.8 parts of the process oil, and 604.2 parts of phosphorous acid (H_3PO_3). This product contains approximately 0.41 % of phosphorus.

Production of Component a-3):

Typical procedures for producing component a-3) phosphorylated and boronated ashless dispersants involve concurrently or sequentially heating one or more ashless dispersants of the types described above with (i) water and at least one water-hydrolyzable organic phosphorus compound and (ii) at least one boron compound under conditions yielding a liquid phosphorus- and boron-containing composition. Examples of organic phosphorus compounds which are useful in forming such products include mono-, di-, and triesters of phosphoric acid (e.g., trihydrocarbyl phosphates, dihydrocarbyl monoacid phosphates monohydrocarbyl diacid phosphates, and mixtures thereof), mono-, di-, and triesters of phosphorous acid (e.g., trihydrocarbyl phosphites, dihydrocarbyl hydrogen phosphites, hydrocarbyl diacid phosphites, and mixtures thereof), esters of phosphonic acids (both "primary", $RP(O)(OR)_2$, and "secondary", $R_2P(O)(OR)$), esters of phosphinic acids, phosphonyl halides (e.g., $RP(O)Cl_2$ and $R_2P(O)Cl$), halophosphites (e.g., $(RO)PCl_2$ and $(RO)_2PCl$), halophosphates (e.g., $ROP(O)Cl_2$ and $(RO)_2P(O)Cl$), tertiary pyrophosphate esters (e.g., $(RO)_2P(O)\text{-}O\text{-}P(O)(OR)_2$), and the total or partial sulfur analogs of any of the foregoing organic phosphorus compounds, and the like. Also usable, although less preferred, are the halophosphine halides (e.g., hydrocarbyl phosphorus tetrahalides, dihydrocarbyl phosphorus trihalides, and trihydrocarbyl phosphorus dihalides), and the halophosphines (monohalophosphines and dihalophosphines). By "water-hydrolyzable" is meant that the organic phosphorus compound when boiled at atmospheric pressure for a period of 5 hours with either (a) distilled water, or (a) water adjusted to at least one pH between 1 and 7 by use of H_2SO_4, or (c) water adjusted to at least one pH between 7 and 13 with KOH, is hydrolyzed to the extent of at least 50 mole %. In some cases, hydrolysis of certain types of organophosphorus compounds results in concomitant oxidation, and compounds which undergo both hydrolysis and oxidation under the foregoing conditions are usable in forming the phosphorylated dispersants for use in this invention. Likewise, certain sulfur-containing organophosphorus compounds undergo loss of sulfur under hydrolysis conditions. Here again compounds of this type are suitable for use in forming the phosphorylated dispersants used in the practice of this invention. Considerable information exists in the literature concerning hydrolysis of organophosphorus compounds -- see for example Kosolapoff, <u>Organophosphorus Compounds</u>, John Willey & Sons, Inc., 1950 (and pertinent references cited therein), Van Wazer, <u>Phosphorus</u> and its Compounds, Interscience Publishers, Inc., Vol. I: Chemistry, 1958 (and pertinent references cited therein), and Vojvodic, et al, <u>Arch. Belg. Med. Soc., Hyg., Med. Trav. Med. Leg., Suppl.</u> (Proc.-World Congr. "New Compd. Biol. Chem. Warf.: Tox Eval.", 1st, 1984), pp. 49-52. The preferred water-hydrolyzable organic phosphorus compounds are the water-hydrolyzable phosphate esters, and the water-hydrolyzable phosphite esters, especially the dihydrocarbyl hydrogen phosphites.

Suitable compounds of boron useful in forming the phosphorylated and boronated ashless dispersants for use as component a-3) include, for example, boron acids, boron oxides, boron esters, and amine or ammonium salts of boron acids. Illustrative compounds include boric acid (sometimes referred to as orthoboric acid), boronic acid, tetraboric acid, metaboric acid, pyroboric acid, esters of such acids, such as mono-, di-, and tri-organic esters with alcohols or polyols having up to 20 or more carbon atoms (e.g., methanol, ethanol, 2-propanol, propanol, butanols, pentanols, hexanols, ethylene glycol, propylene glycol, trimethylol propane, diethanol amine, etc.), boron oxides such as boric oxide and boron oxide hydrate, and ammonium salts such as ammonium borate, ammonium pyroborate, etc. While usable, boron halides such as boron trifluoride, boron trichloride, and the like, are undesirable as they tend to introduce halogen atoms into the boronated dispersant, a feature which is detrimental from the environmental, toxicological and conservational standpoints. Amine borane addition compounds and hydrocarbyl boranes can also be used, although they tend to be relatively expensive. The preferred boron reagent is boric acid, H_3BO_3.

Optionally, additional sources of basic nitrogen can be included in the organic phosphorus compound-ashless dispersant-boron compound-water mixture so as to provide a molar amount (atomic proportion) of basic nitrogen up to that equal to the molar amount of basic nitrogen contributed by the ashless dispersant. Preferred auxiliary nitrogen compounds are long chain primary, secondary and tertiary alkyl amines containing from 12 to 24 carbon atoms, including their hydroxyalkyl and aminoalkyl derivatives. The long chain alkyl group may optionally contain one or more ether groups. Examples of suitable compounds are oleyl amine, N-oleyltrimethylene diamine, N-tallow diethanolamine, N,N-dimethyl oleylamine, and myristyloxapropyl amine.

Other materials normally used in lubricant additives which do not interfere with the process may also be added, for example, a benzotriazole, including lower (C_1-C_4) alkyl-substituted benzotriazoles, which function to protect copper surfaces.

The concurrent heating step or the combination of sequential heating steps is conducted at temperatures sufficient to produce a final liquid composition which contains both phosphorus and boron. The heating can be carried out in the absence of a solvent by heating a mixture of the ashless dispersant, water and one or more suitable organic phosphorus compounds, or one or more suitable boron compounds, or, preferably, a combination of water, one or more suitable organic phosphorus compounds and one or more suitable boron compounds. The temperatures used will vary somewhat depending upon the nature of the ashless dispersant and the organic phosphorus and/or boron reagent being utilized. Generally speaking however, the temperature will usually fall within the range of 40 to 200°C. The duration of the heating is likewise susceptible to variation, but ordinarily will fall in the range of 1 to 3 hours. When conducting the heating in bulk, it is important to thoroughly agitate the components to insure intimate contact therebetween. When utilizing the preferred boron reagent (boric acid) in a boronation conducted separately from the phosphorylation, it is preferable to add water with the boric acid to facilitate initial dissolution of the boric acid.

Water and relatively volatile alcohols formed in the hydrolysis process and the added water are preferably removed from the heated mixture by vacuum distillation at temperatures of from 100 to 140°C. Preferably the heating step or steps will be conducted in a diluent oil or other inert liquid medium such as light mineral oils, and the like.

The amount of phosphorus compound employed in the heating process ranges from 0.001 mole to 0.999 mole per mole of basic nitrogen and free hydroxyl in the mixture being heated, up to one half of which may be contributed by an auxiliary nitrogen compound. The amount of boron compound employed ranges from 0.001 mole to 1 mole per mole of basic nitrogen and/or hydroxyl in the mixture which is in excess of the molar amount of inorganic phosphorus compound. When conducting the phosphorylation and boronation on a sequential basis (or when conducting one of these operations on a dispersant which has previously been subjected to the other such operation), the last-to-be-used reagent(s) -- water and organic phosphorus compound(s) or boron compound(s), as the case may be -- can be used in an amount equivalent to (or even in excess of) the amount of basic nitrogen and/or hydroxyl groups in the dispersant being heated with such last-to-be-used reagent(s).

As noted above, insofar as the phosphorylation is concerned, it is preferable to heat the ashless dispersant with one or more water-hydrolyzable organic phosphorus compounds in the presence of water. In this case the water can be added before and/or during the heating step, and before, after, or at the same time one or more phosphorus compounds are introduced into the vessel in which the heating is taking place or is to take place. It is also possible to heat the ashless dispersant with the organic phosphorus compound and then subsequently heat the resultant composition with water, although this procedure is less preferred.

The amount of added water is not particularly critical as long as a sufficient amount is present to effect hydrolysis of the water-hydrolyzable organic phosphorus compound. Water present in the system can be removed by distillation (preferably at reduced pressure) during the course of, and preferably is removed at the end of, the heating step. Amounts of water up to 15% by weight of the mixture being heated are preferred, and amounts of water of up to 5% by weight are particularly preferred. When used, the amount of diluent usually ranges from 10 to 50% by weight of the mixture being subjected to heating.

The hydrolysis of the water-hydrolyzable organic phosphorus compound(s) employed in the phosphorylation operation can be effected in any of a variety of ways. For example, the dispersant to be phosphorylated, one or more water-hydrolyzable organic phosphorus compounds, and water may be mixed together and heated either in an open system at atmospheric pressure or in a closed system at superatmospheric pressure. If conducted with an open system, the temperature may be kept below the boiling point of water and the mixture subjected to stirring of sufficient intensity to cause and maintain intimate contact among the components within the hydrolysis reaction mixture. It is also feasible to raise the temperature of the mixture in an open system to the boiling point of water and allow the water vapor either to escape from the system or to be condensed in a suitable condensing system and returned to the refluxing hydrolysis reaction mixture. If the water is allowed to escape, sufficiently large amounts of water should be used to insure that a substantial amount of hydrolysis occurs before the supply of water in the hydrolysis mixture has been depleted. In all such cases, water can be fed to the system as an initial complete charge or it can be fed intermittently or continuously into the hydrolysis mixture.

When conducting the hydrolysis in a closed system, the system may be kept at one or more selected autogenous pressures by suitable adjustment and regulation of the temperature. And, still higher pressures may be imposed upon the system, as for example by injecting high pressure steam into a sealed autoclave containing the hydrolysis reaction mixture.

The water itself may be charged to the system in any suitable form, such as in the form of liquid water, steam, or even ice. Similarly, the water may be introduced in the form of hydrated solids so that the water is released by the application of heat during the course of the hydrolysis operation. Injection of wet steam into a well-agitated hydrolysis system is one preferred way of conducting the operation.

The hydrolysis operation should be conducted under any given set or sequence of hydrolysis conditions for a period of time long enough that at least 10%, preferably at least 50%, and most preferably at least 75%, of the organic phosphorus compound(s) present in the hydrolysis mixture has been hydrolyzed. The nature of the hydrolysis products can be expected to vary in relation to the type of phosphorus compound(s) used and the severity of the hydrolysis conditions imposed upon the hydrolysis system. Thus inorganic and organic hydrolysis products can be formed in the system, and these in turn can be expected to be taken up by the ashless dispersant(s) present in the system substantially as they are formed. Accordingly, although the chemical structure(s) of the phosphorylated dispersant(s) are not known with absolute certainty, it is reasonable to conclude that at least some interaction occurs between the dispersant(s) and organic and/or inorganic phosphorus-containing species formed in the hydrolysis reactions taking place in the system. It is also conceivable that such interacted components may undergo displacements and/or other forms of interactions with components present in the hydrolysis system as the hydrolysis operation proceeds.

As pointed out above, the phosphorylation may be conducted apart from the boronation, or it may be conducted concurrently with the boronation. When performing the phosphorylation and boronation operations concurrently, any of the foregoing hydrolysis procedures can be utilized, the principal difference being that one or more boron compounds are used in combination with one or more water-hydrolyzable organic phosphorus compounds.

If desired, small amounts of one or more acids (e.g., sulfuric acid, phosphoric acid, phosphorous acid, etc.) or bases (e.g., NaOH, KOH, ammonium hydroxide, etc.) may be added to the hydrolysis mixture to facilitate hydrolysis of the organic phosphorus compound(s) being used.

For further details concerning procedures for conducting the boronation operation apart from the phosphorylation operation, reference may be had, for example, to the disclosures of U.S. Pat. Nos. 3,087,936; 3,254,025; 3,281,428; 3,282,955; 3,284,410; 3,338,832; 3,344,069; 3,533,945; 3,718,663; 4,097,389; 4,554,086; and 4,634,543.

The phosphorylated and boronated dispersants utilized as component a-3) in the compositions of this invention when in their undiluted state should have on a weight basis a phosphorus content of at least 100 parts per million (ppm) (preferably at least 500 ppm and more preferably at least 1000 ppm) and a boron content of at least 100 ppm (preferably at least 500 ppm and more preferably at least 1000 ppm). When forming component a-3) in part by use of one or more inorganic phosphorus compounds such as phosphorous acid (H_3PO_3, sometimes depicted as $H_2(HPO_3)$, and sometimes called ortho-phosphorous acid or phosphonic acid), phosphoric acid (H_3PO_4, sometimes called orthophosphoric acid), hypophosphorous acid (H_3PO_2, sometimes called phosphinic acid), hypophosphoric acid ($H_4P_2O_6$), metaphosphoric acid (HPO_3), pyrophosphoric acid ($H_4P_2O_7$), pyrophosphorous acid ($H_4P_2O_5$, sometimes called pyrophosphonic acid), phosphinous acid (H_3PO), tripolyphosphoric acid ($H_5P_3O_{10}$), tetrapolyphosphoric acid ($H_6P_4O_{13}$), trimetaphosphoric acid ($H_3P_3O_9$), phosphorus trioxide, phosphorus tetraoxide, phosphorus pentoxide, and/or partial or total sulfur analogs of the foregoing such as phosphorotetrathioic acid (H_3PS_4), phosphoromonothioic acid (H_3PO_3S), phosphorodithioic acid ($H_3PO_2S_2$), phosphorotrithioic acid (H_3POS_3), phosphorus sesquisulfide, phosphorus heptasulfide, and phosphorus pentasulfide (P_2S_5, sometimes referred to as P_4S_{10}), or the like, and in part by use of one or more water-hydrolyzable organic phosphorus compounds, the latter should be used in an amount sufficient to provide at least 10% (preferably at least 50% and more preferably at least 75%) of the total phosphorus content of the phosphorylated and boronated dispersant. For crankcase lubricant usage, component a-3) when in the undiluted state preferably contains at least 3000 ppm (more preferably at least 5000 ppm and most preferably at least 7000 ppm) of phosphorus and at least 1500 ppm (more preferably at least 2500 ppm and most preferably at least 3500 ppm) of boron.

The preparation of phosphorylated and boronated ashless dispersants suitable for use as component a-3) in the compositions of this invention is illustrated by the following Examples 97-148 in which all parts and percentages are by weight unless otherwise clearly specified.

EXAMPLE 97

A mixture is formed from 260 parts of a commercial succinimide ashless dispersant (HiTEC® 644 dispersant), 100 parts of a 100 Solvent Neutral refined mineral oil diluent, 26 parts of dibutyl hydrogen phosphite, 3.5 parts of tolutriazole, 10 parts of boric acid, and 8 parts of water. The mixture is heated at 100°C for two hours until all of the solid materials are dissolved. A vacuum of 40 mm Hg is gradually drawn on the product to remove the water and butanol while the temperature is slowly raised to 100°C. A clear solution or composition is obtained which is soluble in oil and suitable for use as component a-3).

EXAMPLE 98

The procedure of Example 97 is repeated except that the succinimide ashless dispersant used is derived from polybutene having a number average molecular weight of 1,100. The average number of succinic groups per alkenyl group in the succinimide is approximately 1.2.

EXAMPLE 99

The procedure of Example 97 is repeated except that the succinimide ashless dispersant used is derived from polybutene having a number average molecular weight of 2,100.

EXAMPLE 100

The procedure of Example 97 is repeated except that the succinimide ashless dispersant is replaced by an equal amount of a Mannich polyamine dispersant (AMOCO® 9250 dispersant). The Amoco 9250 dispersant as supplied by the manufacturer is believed to be a boronated dispersant and in such case, another material suitable for use as component a-3) can be formed by eliminating the boric acid from the procedure used in this example and thereby conducting phosphorylation on an already boronated dispersant.

EXAMPLE 101

The procedure of Example 97 is repeated except that the succinimide ashless dispersant is replaced by an equal amount of a commercial ashless dispersant of the pentaerythritol succinic ester type (Lubrizol® 936 dispersant). As in the case of Example 100, the initial dispersant as supplied by the manufacturer is believed to be a boronated dispersant. In such cases, the dispersant can, if desired, be subjected just to phosphorylation to thereby form still another product suitable for use as component a-3).

EXAMPLE 102

The procedure of Example 97 is repeated except that 16 parts of trimethyl phosphite is used in place of the dibutyl hydrogen phosphite, to provide a clear, oil-soluble composition suitable for use as component a-3).

EXAMPLE 103

The procedure of Example 97 is repeated except that the dibutyl hydrogen phosphite is replaced by 16.3 parts of O-ethyl-O,O- 1,2-ethanediyl phosphite.

EXAMPLE 104

The procedures of Examples 97 through 103 are repeated except that the tolutriazole is omitted from the initial mixtures subjected to the thermal processes.

EXAMPLE 105

A mixture of 12,000 parts of a commercial boronated succinimide (HiTEC® 648 dispersant), 90 parts of water, and 584 parts of triphenylmethane phosphonyl dichloride is heated to 100-110°C for 6 hours while sweeping the reaction mixture with nitrogen. A vacuum of 40 mm Hg is then gradually applied to remove water and thereby form a homogeneous liquid composition suitable for use as component a-3). For convenience in handling, 100 Solvent Neutral mineral oil can be added to form an 80% solution of the additive in the oil.

EXAMPLE 106

A mixture of 260 parts of a commercial succinimide (HiTEC® 644 dispersant), 3 parts of water, 13 parts of tributyl phosphate, and 4 parts of phosphorous acid is heated to 100°C for 2 hours. To this product is added 8 parts of orthoboric acid and 4 parts of water, and the resultant mixture is heated at 100°C for another 2 hours. A vacuum of 40 mm of Hg is applied to the system and the temperature is gradually raised to 110°C. The resultant homogeneous liquid composition is suitable for use as component a-3).

EXAMPLE 107

A mixture of 260 parts of a commercial succinimide (HiTEC® 644 dispersant), 8 parts of orthoboric acid and 4 parts of water is heated to 100°C for 2 hours. Then 16 parts of diethyl hydrogen phosphite and 6 parts of aqueous ammonium hydroxide (3N) are added to the reaction mixture and the temperature of the mixture is held at 100°C for another 2 hours. A vacuum of 40 mm of Hg is applied to the system and the temperature is gradually raised to 110°C. The resultant homogeneous liquid composition is suitable for use as component a-3).

EXAMPLE 108

A mixture of 260 parts of a commercial succinic pentaerythritol ester ashless dispersant (Lubrizol® 936 dispersant), 6 parts of water, and 16 parts of methyl dichlorophosphate is heated to 100°C for 2 hours. To this product are added 8 parts of orthoboric acid and 4 parts of water, and the resultant mixture is heated at 100°C for another 2 hours. The mixture is then swept with nitrogen for one hour at 100°C. A vacuum of 40 mm of Hg is applied to the system and the temperature is gradually raised to 110°C. The resultant homogeneous liquid composition is suitable for use as component a-3).

EXAMPLE 109

A mixture of 260 parts of a commercial succinic pentaerythritol ester ashless dispersant (Lubrizol® 936 dispersant), 8 parts of orthoboric acid and 6 parts of water is heated to 100°C for 2 hours. Then 19 parts of methyl bis(phenyl) phosphate, 5 parts of phosphoric acid, and 0.4 part of additional water are added to the reaction mixture and the temperature of the mixture is held at 100°C for another 2 hours. A vacuum of 40 mm of Hg is applied to the system and the temperature is gradually raised to 130°C. The resultant homogeneous liquid composition is suitable for use as component a-3).

EXAMPLE 110

A mixture of 260 parts of a commercial Mannich polyamine dispersant (AMOCO® 9250 dispersant), 8 parts of water, and 35 parts of dibenzyl methyl phosphate is heated to 100°C for 2 hours. To this product is added 8 parts of orthoboric acid and 4 parts of water, and the resultant mixture is heated at 100°C for another 2 hours. A vacuum of 40 mm of Hg is applied to the system and the temperature is gradually raised to 130°C. The resultant homogeneous liquid composition is suitable for use as component a-3).

EXAMPLE 111

A mixture of 260 parts of a commercial Mannich polyamine dispersant (AMOCO® 9250 dispersant), 8 parts of orthoboric acid and 4 parts of water is heated to 100°C for 2 hours. Then 9 parts of monophenyl phosphate, 4 parts of phosphorous acid, and an additional 3 parts of water are added to the reaction mixture and the temperature of the mixture is held at 100°C for another 2 hours. A vacuum of 40 mm of Hg is applied to the system and the temperature is gradually raised to 130°C. The resultant homogeneous liquid composition is suitable for use as component a-3).

EXAMPLE 112

(a) A mixture of 1,000 parts (0.495 mole) of polyisobutene ($\overline{M}n$ = 2020; $\overline{M}w$ = 6049, both determined using the methodology of U.S. Pat. No. 4,234,435) and 115 parts (1.17 moles) of maleic anhydride is heated to 110°C. This mixture is heated to 184°C in 6 hours during which 85 parts (1.2 moles) of gaseous chlorine is added beneath the surface. At 184-189°C, an additional 59 parts (0.83 mole) of chlorine is added over 4 hours. The reaction mixture is stripped by heating at 186-190°C with nitrogen purged for 26 hours. The residue is predominantly polyisobutenyl succinic anhydride acylating agent.

(b) A mixture is prepared by the addition of 57 parts (1.38 equivalents) of a commercial mixture of ethylene polyamines having the approximate overall composition of tetraethylene pentamine to 1,067 parts of mineral oil and 893 parts (1.38 equivalents) of substituted succinic acylating agent prepared as in (a) while maintaining the temperature at 140-145°C. The reaction mixture is then heated to 155°C over a three hour period and stripped by blowing with nitrogen. The reaction mixture is filtered to yield the filtrate as an oil solution of the desired product composed predominantly of polyisobutenyl succinimides.

(c) A mixture is formed from 250 parts of the polyisobutenyl succinimide product solution formed as in (b), 11 parts of dibutyl chlorophosphate, 5 parts of phosphoric acid, 3.5 parts of tolutriazole, 8 parts of boric acid, and 8 parts of water. The mixture is heated at 100°C for four hours until all of the solid materials are dissolved. A vacuum of 40 mm Hg is gradually drawn on the product to remove the water while the temperature is slowly raised to 100°C. A clear solution or composition is obtained which is soluble in oil and suitable for use as component a-3).

EXAMPLE 113

The procedure of Example 112 is repeated except that the tolutriazole is eliminated from the reaction mixture of (c).

EXAMPLE 114

The procedure of Example 112 is repeated except that 9 parts of an equimolar mixture of dibutyl hydrogen phosphite and monobutyl dihydrogen phosphite is used in place of the dibutyl chlorophosphate to provide a clear, oil-soluble composition suitable for use as component a-3).

EXAMPLE 115

The procedure of Example 112 is repeated except that the dibutyl chlorophosphate is replaced by 11 parts of mono-2-naphthyl orthophosphate.

EXAMPLE 116

(a) A mixture of 1,000 parts (0.495 mole) of polyisobutene ($\overline{M}n$ = 2020; $\overline{M}w$ = 6049, both determined using the methodology of U.S. Pat. No. 4,234,435) and 115 parts (1.17 moles) of maleic anhydride is heated to 110°C. This mixture is heated to 184°C in 6 hours during which 85 parts (1.2 moles) of gaseous chlorine is added beneath the surface. At 184-189°C, an additional 59 parts (0.83 mole) of chlorine is added over 4 hours. The reaction mixture is stripped by heating at 186-190°C with nitrogen purged for 26 hours. The residue is predominantly polyisobutenyl succinic anhydride acylating agent.
(b) A mixture is prepared by the addition of 18.2 parts (0.433 equivalents) of a commercial mixture of ethylene polyamines having the approximate overall composition of tetraethylene pen-tamine to 392 parts of mineral oil and 348 parts (0.52 equivalent) of substituted succinic acylating agent prepared as in (a) while maintaining the temperature at 140°C. The reaction mixture is then heated to 150°C in 1.8 hours and stripped by blowing with nitrogen. The reaction mixture is filtered to yield the filtrate as an oil solution of the desired product composed predominantly of polyisobutenyl succinimides.
(c) A mixture is formed from 250 parts of the polyisobutenyl succinimide product solution formed as in (b), 18 parts of phenyl dimethyl phosphate, 3.5 parts of tolutriazole, 8 parts of boric acid, and 8 parts of water. The mixture is heated at 100°C for three hours. A vacuum of 40 mm Hg is gradually drawn on the product to remove the water while the temperature is slowly raised to 130°C. A clear solution or composition is obtained which is soluble in oil and suitable for use as component a-3).

EXAMPLE 117

The procedure of Example 116 is repeated except that the tolutriazole is eliminated from the reaction mixture of (c).

EXAMPLE 118

The procedure of Example 116 is repeated except that 15 parts of trimethyl phosphite is used in place of the phenyl dimethyl phosphate to provide a clear, oil-soluble composition suitable for use as component a-3).

EXAMPLE 119

The procedure of Example 116 is repeated except that the phenyl dimethyl phosphate is replaced by 36 parts of 4-dimethyl-aminophenyl phosphorus tetrachloride and the heated mixture in (c) is swept with nitrogen during the three-hour period.

EXAMPLE 120

(a) A mixture of 1,000 parts (0.495 mole) of polyisobutene ($\overline{M}n$ = 2020; $\overline{M}w$ = 6049, both determined using the methodology of U.S. Pat. No. 4,234,435) and 115 parts (1.17 moles) of maleic anhydride is heated to 110°C. This mixture is heated to 184°C in 6 hours during which 85 parts (1.2 moles) of gaseous chlorine is added beneath the surface. At 184-189°C, an additional 59 parts (0.83 mole) of chlorine is added over

4 hours. The reaction mixture is stripped by heating at 186-190°C with nitrogen purged for 26 hours. The residue is predominantly polyisobutenyl succinic anhydride acylating agent.

(b) A mixture of 334 parts (0.52 equivalents) of the polyisobutene substituted succinic acylating agent prepared as in (a), 548 parts of mineral oil, 30 parts (0.88 equivalent) of pentaerythritol and 8.6 parts (0.0057 equivalent) of Polyglycol 112-2 demulsifier is heated at 150°C for 2.5 hours. The reaction mixture is then heated to 210°C over a period of 5 hours and then held at 210°C for an additional 3.2 hours. The reaction mixture is cooled to 190°C and 8.5 parts (0.2 equivalent) of a commercial mixture of ethylene polyamines having an overall composition approximating that of tetraethylene pentamine is added. The reaction mixture is stripped by heating at 205°C with nitrogen blowing for 3 hours, and then filtered to yield the filtrate as an oil solution of the desired ashless dispersant product.

(c) A mixture is formed from 300 parts of the ashless dispersant product solution formed as in (b), 37 parts of bis(2-ethylhexyl) hydrogen phosphite, 3.5 parts of tolutriazole, 8 parts of boric acid, and 8 parts of water. The mixture is heated at 100°C for two hours until all of the solid materials are dissolved. A vacuum of 40 mm Hg is gradually drawn on the product to remove the water while the temperature is slowly raised to 130°C. A clear solution or composition is obtained which is soluble in oil and suitable for use as component a-3).

EXAMPLE 121

The procedure of Example 120 is repeated except that the tolutriazole is eliminated from the reaction mixture of (c).

EXAMPLE 122

The procedure of Example 120 is repeated except that 26 parts of dibutyl hydrogen phosphite is used in place of the bis(2-ethylhexyl) hydrogen phosphite to provide a clear, oil-soluble composition suitable for use as component a-3).

EXAMPLE 123

The procedure of Example 120 is repeated except that the bis(2-ethylhexyl) hydrogen phosphite is replaced by 15 parts of trimethyl phosphite.

EXAMPLE 124

(a) A mixture of 1,000 parts (0.495 mole) of polyisobutene ($\overline{M}n$ = 2020; $\overline{M}w$ = 6049, both determined using the methodology of U.S. Pat. No. 4,234,435) and 115 parts (1.17 moles) of maleic anhydride is heated to 110°C. This mixture is heated to 184°C in 6 hours during which 85 parts (1.2 moles) of gaseous chlorine is added beneath the surface. At 184-189°C, an additional 59 parts (0.83 mole) of chlorine is added over 4 hours. The reaction mixture is stripped by heating at 186-190°C with nitrogen purged for 26 hours. The residue is predominantly polyisobutenyl succinic anhydride acylating agent.

(b) A mixture of 3225 parts (5.0 equivalents) of the polyisobutene-substituted succinic acylating agent prepared as in (a), 289 parts (8,5 equivalents) of pentaerythritol and 5204 parts of mineral oil is heated at 225-235°C for 5.5 hours. The reaction mixture is filtered at 130°C to yield an oil solution of the desired ashless dispersant product.

(c) A mixture is formed from 300 parts of the ashless dispersant product solution formed as in (b), 27 parts of dibutyl chlorophosphate, 3.5 parts of tolutriazole, 8 parts of boric acid, and 8 parts of water. The mixture is heated at 100°C for two hours until all of the solid materials are dissolved. A vacuum of 40 mm Hg is gradually drawn on the product to remove the water while the temperature is slowly raised to 100°C. A clear solution or com-position is obtained which is soluble in oil and suitable for use as component a-3).

EXAMPLE 125

The procedure of Example 124 is repeated except that the tolutriazole is eliminated from the reaction mixture of (c).

EXAMPLE 126

The procedure of Example 124 is repeated except that 8 parts of ethyl dichlorophosphate and 4 parts of phosphorous acid are used in place of the dibutyl chlorophosphate to provide a clear, oil-soluble composition suitable for use as component a-3).

EXAMPLE 127

The procedure of Example 124 is repeated except that the dibutyl chlorophosphate is replaced by 10 parts of dibutyl hydrogen phosphite and 5 parts of phosphoric acid.

EXAMPLE 128

(a) A mixture of 1,000 parts (0.495 mole) of polyisobutene ($\overline{M}n$ = 2020; $\overline{M}w$ = 6049, both determined using the methodology of U.S. Pat. No. 4,234,435) and 115 parts (1.17 moles) of maleic anhydride is heated to 110°C. This mixture is heated to 184°C in 6 hours during which 85 parts (1.2 moles) of gaseous chlorine is added beneath the surface. At 184-189°C, an additional 59 parts (0.83 mole) of chlorine is added over 4 hours. The reaction mixture is stripped by heating at 186-190°C with nitrogen purged for 26 hours. The residue is predominantly polyisobutenyl succinic anhydride acylating agent.

(b) A mixture of 322 parts (0.5 equivalent) of the polyisobutene-substituted succinic acylating agent prepared as in (a), 68 parts (2.0 equivalents) of pentaerythritol and 508 parts of mineral oil is heated at 204-227°C for 5 hours. The reaction mixture is cooled to 162°C and 5.3 parts (0.13 equivalent) of a commercial ethylene polyamine mixture having an overall composition approximating that of tetraethylene pentamine is added. The reaction mixture is heated at 162-163°C for 1 hour, then cooled to 130°C and filtered. The fitrate is an oil solution of the desired ashless dispersant product.

(c) A mixture is formed from 350 parts of the ashless dispersant product solution formed as in (b), 16 parts of diethyl hydrogen phosphite, 3.5 parts of tolutriazole, 8 parts of boric acid, and 6 parts of water. The mixture is heated at 100°C for two hours until all of the solid materials are dissolved. A vacuum of 40 mm Hg is gradually drawn on the product to remove the water while the temperature is slowly raised to 100°C. A clear solution or composition is obtained which is soluble in oil and suitable for use as component a-3).

EXAMPLE 129

The procedure of Example 128 is repeated except that the tolutriazole is eliminated from the reaction mixture of (c).

EXAMPLE 130

The procedure of Example 128 is repeated except that 20 parts of diethyl chlorophosphate is used in place of the diethyl hydrogen phosphite to provide a clear, oil-soluble composition suitable for use as component a-3).

EXAMPLE 131

The procedure of Example 128 is repeated except that the diethyl hydrogen phosphite is replaced by 12 parts of ethyl dibutyl phosphate and 4 parts of phosphorous acid.

EXAMPLE 132

(a) A mixture of 510 parts (0.28 mole) of polyisobutene ($\overline{M}n$ = 1845; $\overline{M}w$ = 5325, both determined using the methodology of U.S. Pat No. 4,234,435) and 59 parts (0.59 mole) of maleic anhydride is heated to 110°C. This mixture is heated to 190°C in 7 hours during which 43 parts (0.6 mole) of gaseous chlorine is added beneath the surface. At 190-192°C, an additional 11 parts (0.16 mole) of chlorine is added over 3.5 hours. The reaction mixture is stripped by heating at 190-193 °C with nitrogen blowing for 10 hours. The residue is predominantly polyisobutenyl succinic anhydride acylating agent.

(b) A mixture of 334 parts (0.52 equivalents) of the polyisobutene substituted succinic acylating agent prepared as in (a), 548 parts of mineral oil, 30 parts (0.88 equivalent) of pentaerythritol and 8.6 parts (0.0057 equivalent) of Polyglycol 112-2 demulsifier is heated at 150°C for 2.5 hours. The reaction mixture is then heated to 210°C over a period of 5 hours and then held at 210°C for an additional 3.2 hours. The reaction mixture is cooled to 190°C and 8.5 parts (0.2 equivalent) of a commercial mixture of ethylene polyamines having an overall composition approximating that of tetraethylene pentamine is added. The reaction mixture is stripped by heating at 205°C with nitrogen blowing for 3 hours, and then filtered to yield the filtrate as an oil solution of the desired ashless dispersant product.

(c) A mixture is formed from 260 parts of the ashless dispersant product solution formed as in (b), 20 parts of ethyl dichloro phosphate, 3.5 parts of tolutriazole, 8 parts of boric acid, and 8 parts of water. The mixture is heated at 100°C for two hours until all of the solid materials are dissolved. A vacuum of 40 mm Hg is gradually drawn on the product to remove the water while the temperature is slowly raised to 100°C. A clear solution or composition is obtained which is soluble in oil and suitable for use as component a-3).

EXAMPLE 133

The procedure of Example 132 is repeated except that the tolutriazole is eliminated from the reaction mixture of (c).

EXAMPLE 134

The procedure of Example 132 is repeated except that 23 parts of butyl dichloro phosphate is used in place of the ethyl dichloro phosphate to provide a clear, oil-soluble composition suitable for use as component a-3).

EXAMPLE 135

The procedure of Example 132 is repeated except that the ethyl dichloro phosphate is replaced by 30 parts of monobutyl-mono-2-ethylhexyl hydrogen phosphite.

EXAMPLE 136

(a) A mixture of 510 parts (0.28 mole) of polyisobutene ($\overline{M}n$ = 1845; $\overline{M}w$ = 5325, both determined using the methodology of U.S. Pat. No. 4,234,435) and 59 parts (0.59 mole) of maleic anhydride is heated to 110°C. This mixture is heated to 190°C in 7 hours during which 43 parts (0.6 mole) of gaseous chlorine is added beneath the surface. At 190-192°C, an additional 11 parts (0.16 mole) of chlorine is added over 3.5 hours. The reaction mixture is stripped by heating at 190-193°C with nitrogen blowing for 10 hours. The residue is predominantly polyisobutenyl succinic anhydride acylating agent.

(b) A mixture is prepared by the addition of 10.2 parts (0.25 equivalent) of a commercial mixture of ethylene polyamines having the approximate overall composition of tetraethylene pentamine to 113 parts of mineral oil and 161 parts (0.25 equivalent) of the substituted succinic acylating agent prepared as in (a) while maintaining the temperature at 138°C. The reaction mixture is heated to 150°C over a 2 hour period and stripped by blowing with nitrogen. The reaction mixture is filtered to yield the filtrate as an oil solution of the desired ashless dispersant product.

(c) A mixture is formed from 125 parts of the polyisobutenyl succinimide product solution formed as in (b), 9 parts of monobenzyl phosphate and 4 parts of phosphorous acid, 3.5 parts of tolutriazole, 8 parts of boric acid, and 6 parts of water. The mixture is heated at 100°C for two hours until all of the solid materials are dissolved. A vacuum of 40 mm Hg is gradually drawn on the product to remove the water while the temperature is slowly raised to 100°C. A clear solution or composition is obtained which is soluble in oil and suitable for use as component a-3).

EXAMPLE 137

The procedure of Example 136 is repeated except that the tolutriazole is eliminated from the reaction mixture of (c).

EXAMPLE 138

The procedure of Example 136 is repeated except that 14 parts of dibenzyl phosphate is used in place of the monobenzyl phosphate to provide a clear, oil-soluble composition suitable for use as component a-3).

EXAMPLE 139

The procedure of Example 136 is repeated except that the monobenzyl phosphate is replaced by 17 parts of monophenyl dibenzyl phosphate.

EXAMPLE 140

To a reactor are charged under a nitrogen atmosphere 67.98 parts of a commercially-available polyisobutenyl succinimide of a mixture of polyethylene polyamines having the approximate overall composition of tetraethylene pentamine (the polyisobutenyl group derived from polyisobutene having a number average molecular weight of about 900; the succinimide product having a ratio of about 1.15 succinic groups per alkenyl group) and 26.14 parts of a 100 Solvent neutral refined mineral oil. After raising the temperature of the resulting solution to 100-105°C, 2.09 parts of boric acid and 4.6 parts of dibutyl hydrogen phosphite are introduced into the reactor, followed by 0.92 part of tolutriazole (Cobratec TT-100) and then 3 parts of water. The resultant mixture is heated at 100-105°C for two hours and then the temperature is gradually raised to 115°C with the application of a vacuum to 40 mm Hg. Stripping is continued for 90 minutes and until 120°C/40 mm Hg has been reached. A flow of dry nitrogen is then applied to the system and the product mixture is allowed to cool. The product mixture is suitable for use as component a-3).

EXAMPLE 141

The procedure of Example 140 is repeated except that the tolutriazole is omitted from the reaction mixture.

EXAMPLE 142

(a) A mixture of 322 parts of the polyisobutene-substituted succinic acylating agent prepared as in Example 136(a), 68 parts of pentaerythritol and 508 parts of mineral oil is heated at 204-227°C for 5 hours. The reaction mixture is cooled to 162°C and 5.3 parts of a commercial ethylene polyamine mixture having the approximate overall composition corresponding to tetraethylene pentamine is added. The reaction mixture is heated at 162-163°C for 1 hour, then cooled to 130°C and filtered. The filtrate is an oil solution of the desired product.

(b) A mixture is formed from 275 parts of the product solution formed as in (a), 20 parts of diisopropyl hydrogen phosphite, 3.5 parts of tolutriazole, 8 parts of boric acid, and 8 parts of water. The mixture is heated at 100°C for two hours until all of the solid materials are dissolved. A vacuum of 40 mm Hg is gradually drawn on the product to remove the water while the temperature is slowly raised to 100°C. A clear solution or composition is obtained which is soluble in oil and suitable for use as component a-3).

EXAMPLE 143

The procedures of Examples 97 through 104 are repeated except that in each case a chemically equivalent amount of trimethyl borate is substituted for the boric acid.

EXAMPLE 144

The procedures of Examples 97 through 101, and 106 through 111 are repeated except that in each case the boronating agent consists of a chemically equivalent amount of trimethyl borate in lieu of boric acid, and the phosphorylating agent consists of a chemically equivalent amount of a mixture consisting of an equimolar mixture of phosphorous acid and dibutyl hydrogen phosphite.

EXAMPLE 145

(a) To 120 parts of chlorinated polyisobutylene having a number average molecular weight of about 1,300 and containing about 2.8 weight percent chlorine are added 21.7 parts of pentaethylene hexamine and 5.6 parts of sodium carbonate. The reaction mixture is heated to about 205°C and maintained at this temperature for about 5 hours. A stream of nitrogen is passed through the reaction mixture to remove the water of reaction. The reaction mixture is diluted with 60 parts of light mineral oil and hexane, filtered and extracted with methanol to remove excess pentaethylene hexamine. The hexane is stripped from the product by heating the mixture to 120°C under a suitable vacuum. The product should have a nitrogen content of approximately 1.0 to 1.5 weight percent.

(b) A mixture is formed from 80 parts of a diluted reaction product formed as in (a), 20 parts of a 100 Solvent Neutral refined mineral oil diluent, 5.0 parts of dibutyl hydrogen phosphite, 4.6 parts of boric acid, and 3.0 parts of water. The resultant mixture is heated at 100-105°C for 2 hours and then the temperature is gradually raised to 115°C with the application of a vacuum to 40 mm Hg. Stripping is continued for 90 minutes and until 120°C/40 mm Hg has been reached. A flow of dry nitrogen is then applied to the system and the product mixture is allowed to cool. The product mixture is suitable for use as component a-3) in the compositions of this invention.

(c) 2 Parts of powdered anhydrous boric acid is added with stirring to 80 parts of a 50 weight percent mineral oil solution of a reaction product formed as in (a) heated to 90°C. The temperature of the mixture is then increased to 150°C and maintained at this temperature for 4 hours while collecting the water of reaction overhead. The mixture is then filtered and mixed with 10 parts of a 100 Solvent Neutral refined mineral oil diluent, 3.6 parts of dibutyl hydrogen phosphite and 3.0 parts of water. The resultant mixture is heated at 100-105°C for 2 hours and then the temperature is gradually raised to 115°C with the application of a vacuum to 40 mm Hg. Stripping is continued for 90 minutes and until 120°C/40 mm Hg has been reached. A flow of dry nitrogen is then applied to the system and the product mixture is allowed to cool. The product mixture is suitable for use as component a-3).

EXAMPLE 146

(a) Into a reactor are placed 220 parts of p-nonylphenol and 465 parts of diethylenetriamine. The mixture is heated to 80°C and 152 parts of 37% formalin is added dropwise over a period of about 30 minutes. The mixture is then heated to 125°C for several hours until the evolution of water has ceased. The resultant product should contain approximately 16-20% nitrogen.

(b) Into a reactor are placed 202 parts of styrene-maleic anhydride resin (having a number average molecular weight in the range of 600-700 and a mole ratio of styrene to maleic anhydride of 1:1), 202.5 parts of octadecyl amine and 472 parts of a 95 VI lubricating oil having a viscosity at 100°F of 150 SUS. The mixture is heated to 225°C for several hours. To this mixture is added dropwise over a period of about 30 minutes, 85 parts of the product formed as in (a). The resulting mixture is heated for 6 hours at 210-230°C while collecting the water formed during reaction. The polymeric product so formed should have a nitrogen content of about 2.1 weight percent.

(c) To a reactor are charged 250 parts of the basic nitrogen polymer produced as in (b) and 50 parts of a 100 Solvent Neutral refined mineral oil. After raising the temperature of the resulting mixture to 100-105°C, 5.7 parts of boric acid, 35 parts of dibutyl hydrogen phosphite, and 8 parts of water are added. The resultant mixture is heated at 100-105°C for two hours and then the temperature is gradually raised to 115°C with the application of a vacuum to 40 mm Hg. Stripping is continued for 90 minutes and until 120°C/40 mm Hg has been reached. A flow of dry nitrogen is then applied to the system and the product mixture is allowed to cool. The product mixture is suitable for use as component a-3).

EXAMPLE 147

The procedure of Example 128 is repeated except that the diethyl hydrogen phosphite is replaced by 10 parts of dimethyl hydrogen phosphite.

EXAMPLE 148

The procedure of Example 128 is repeated except that the diethyl hydrogen phosphite is replaced by 5 parts of dimethyl hydrogen phosphite and 4 parts of phosphorous acid.

Production of Component a-4):

Typical procedures for producing component a-4) phosphorylated ashless dispersants involve heating one or more ashless dispersants of the types described above with at least one water-hydrolyzable organic phosphorus compound and water under conditions yielding a liquid phosphorus-containing composition.
The water-hydrolyzable organic phosphorus compounds used and the conditions under which they are used are the same as described above in connection with production of component a-3), except of course no boron compound is employed in the process.

Usually the phosphorylated dispersants utilized as component a-4) in the compositions of this invention when in their undiluted state will have on a weight basis a phosphorus content of at least 5,000 parts per million (ppm) (preferably at least 6,000 ppm and more preferably at least 7,000 ppm).

The preparation of phosphorylated ashless dispersants suitable for use as component a-4) in the compositions of this invention is illustrated by the Examples 149-198 in which all parts and percentages are by weight unless otherwise clearly specified.

EXAMPLE 149

A mixture is formed from 260 parts of a polyisobutenyl succinimide ashless dispersant (derived from polybutene having a number average molecular weight of about 950 and a mixture of a polyethylene polyamines having an average overall composition approximating that of tetraethylene pentamine), 100 parts of a 100 Solvent Neutral refined mineral oil diluent, 26 parts of dibutyl hydrogen phosphite, 3.5 parts of tolutriazole and 8 parts of water. The mixture is heated at 110°C for two hours. A vacuum of 40 mm Hg is gradually drawn on the product to remove water and butanol while the temperature is maintained at 110°C. A clear solution or composition is obtained which is soluble in oil and suitable for use as component a-4).

EXAMPLE 150

The procedure of Example 149 is repeated except that the succinimide ashless dispersant used is derived from polybutene having a number average molecular weight of 1,100. The average number of succinic groups per alkenyl group in the succinimide is approximately 1.2.

EXAMPLE 151

The procedure of Example 149 is repeated except that the succinimide ashless dispersant used is derived from polybutene having a number average molecular weight of 2,100.

EXAMPLE 152

The procedure of Example 149 is repeated except that the succinimide ashless dispersant is replaced by an equal amount of a boron-free Mannich polyamine dispersant made from tetraethylene pentamine, polyisobutenyl phenol (made from polyisobutene having a number average molecular weight of about 1710 and formalin) having a nitrogen content of 1.1%.

EXAMPLE 153

The procedure of Example 149 is repeated except that the succinimide ashless dispersant is replaced by an equal amount of an ashless dispersant of the pentaerythritol succinic ester type.

EXAMPLE 154

The procedure of Example 149 is repeated except that 16 parts of trimethyl phosphite is used in place of the dibutyl hydrogen phosphite to provide a clear, oil-soluble composition suitable for use as component a-4).

EXAMPLE 155

The procedure of Example 149 is repeated except that the dibutyl hydrogen phosphite is replaced by 16.3 parts of O-ethyl-O,O-1,2-ethanediyl phosphite.

EXAMPLE 156

The procedures of Examples 149 through 155 are repeated except that the tolutriazole is omitted from the initial mixtures subjected to the thermal processes.

EXAMPLE 157

A mixture of 12,000 parts of a commercial boron-free succinimide (HiTEC® 644 dispersant), 90 parts of water, and 584 parts of triphenylmethane phosphonyl dichloride is heated to 100-110°C for 6 hours while sweeping the reaction mixture with nitrogen. A vacuum of 40 mm Hg is then gradually applied to remove water and thereby form a homogeneous liquid composition suitable for use as component a-4). For convenience in handling 100 Solvent Neutral mineral oil can be added to form an 80% solution of the additive in the oil.

EXAMPLE 158

A mixture of 260 parts of a commercial succinimide (HiTEC® 644 dispersant), 3 parts of water, 13 parts of tributyl phosphate, and 4 parts of phosphorous acid is heated to 100°C for 2 hours. Then a vacuum of 40 mm of Hg is applied to the system and the temperature is gradually raised to 110°C. The resultant homogeneous liquid composition is suitable for use as component a-4).

EXAMPLE 159

A mixture of 260 parts of polyisobutenyl succinimide (derived from polybutene having a number average molecular weight of about 1,100 and a mixture of polyethylene polyamines having an average overall composition approximating that of tetraethylene pentamine), 4 parts of water, 16 parts of diethyl hydrogen phosphite and 6 parts of aqueous ammonium hydroxide (3N) is heated at 100°C for 2 hours. A vacuum of 40 mm of Hg is applied to the system and the temperature is gradually raised to 110°C. The resultant homogeneous liquid composition is suitable for use as component a-4).

EXAMPLE 160

A mixture of 260 parts of a polyisobutenylsuccinic pentaerythritol ester ashless dispersant, 6 parts of water, and 16 parts of methyl dichlorophosphate is heated to 100°C for 2 hours. The mixture is then swept with nitrogen for one hour at 100°C. A vacuum of 40 mm of Hg is applied to the system and the temperature is gradually raised to 110°C. The resultant homogeneous liquid composition is suitable for use as component a-4).

EXAMPLE 161

A mixture of 260 parts of a succinic pentaerythritol ester ashless dispersant, 6.5 parts of water, 19 parts of methyl bis(phenyl) phosphate, and 5 parts of phosphoric acid is heated at a temperature 100°C for 2 hours. A vacuum of 40 mm of Hg is applied to the system and the temperature is gradually raised to 130°C. The resultant homogeneous liquid composition is suitable for use as component a-4).

EXAMPLE 162

A mixture of 260 parts of a Mannich polyamine dispersant, 8 parts of water, and 35 parts of dibenzyl methyl phosphate is heated to 100°C for 2 hours. A vacuum of 40 mm of Hg is applied to the system and the temperature is gradually raised to 130°C. The resultant homogeneous liquid composition is suitable for use as component a-4).

EXAMPLE 163

A mixture of 260 parts of a Mannich polyamine dispersant, 9 parts of monophenyl phosphate, 4 parts of phosphorous acid, and 7 parts of water is heated to 100°C for 2 hours. A vacuum of 40 mm of Hg is applied to the system and the temperature is gradually raised to 130°C. The resultant homogeneous liquid composition is suitable for use as component a-4).

EXAMPLE 164

A mixture of 46.8 parts of phosphorylated dispersant formed as in Example 158 and 23.4 parts of a commercial boronated succinimide ashless dispersant (HiTEC® 648 dispersant) is formed. The resultant homogeneous liquid composition is suitable for use in the practice of this invention. A portion of the resultant mixture can be heated to 110°C for two hours, and this resultant homogeneous liquid composition is also suitable for use as component a-4) in the practice of this invention.

EXAMPLE 165

(a) A mixture of 1,000 parts (0.495 mole) of polyisobutene ($\overline{M}n$ = 2020; $\overline{M}w$ = 6049, both determined using the methodology of U.S. Pat. No. 4,234,435) and 115 parts (1.17 moles) of maleic anhydride is heated to 110°C. This mixture is heated to 184°C in 6 hours during which 85 parts (1.2 moles) of gaseous chlorine is added beneath the surface. At 184-189°C, an additional 59 parts (0.83 mole) of chlorine is added over 4 hours. The reaction mixture is stripped by heating at 186-190°C with nitrogen purged for 26 hours. The residue is predominately polyisobutenyl succinic anhydride acylating agent.

(b) A mixture is prepared by the addition of 57 parts (1.38 equivalents) of a commercial mixture of ethylene polyamines having the approximate overall composition of tetraethylene pentamine to 1,067 parts of mineral oil and 893 parts (1.38 equivalents) of substituted succinic acylating agent prepared as in (a) while maintaining the temperature at 140-145°C. The reaction mixture is then heated to 155°C over a three hour period and stripped by blowing with nitrogen. The reaction mixture is filtered to yield the filtrate as an oil solution of the desired product composed predominately of polyisobutenyl succinimides.

(c) A mixture is formed from 250 parts of the polyisobutenyl succinimide product solution formed as in (b), 11 parts of dibutyl chlorophosphate, 5 parts of phosphoric acid, 3.5 parts of tolutriazole, and 8 parts of water. The mixture is heated at 100°C for four hours until all of the solid materials are dissolved. A vacuum of 40 mm Hg is gradually drawn on the product to remove the water while the temperature is slowly raised to 100°C. A clear solution or composition is obtained which is soluble in oil and suitable for use as component a-4).

EXAMPLE 166

The procedure of Example 165 is repeated except that the tolutriazole is eliminated from the reaction mixture of (c).

EXAMPLE 167

The procedure of Example 165 is repeated except that 9 parts of an equimolar mixture of dibutyl hydrogen phosphite and monobutyl dihydrogen phosphite is used in place of the dibutyl chlorophosphate to provide a clear, oil-soluble composition suitable for use as component a-4).

EXAMPLE 168

The procedure of Example 165 is repeated except that the dibutyl chlorophosphate is replaced by 11 parts of mono-2-naphthyl orthophosphate.

EXAMPLE 169

(a) A mixture of 1,000 parts (0.495 mole) of polyisobutene ($\overline{M}n$ = 2020; $\overline{M}w$ = 6049, both determined using the methodology of U.S. Pat. No. 4,234,435) and 115 parts (1.17 moles) of maleic anhydride is heated to 110°C. This mixture is heated to 184°C in 6 hours during which 85 parts (1.2 moles) of gaseous chlorine is added beneath the surface. At 184-189°C, an additional 59 parts (0.83 mole) of chlorine is added over 4 hours. The reaction mixture is stripped by heating at 186-190°C with nitrogen purged for 26 hours. The residue is predominately polyisobutenyl succinic anhydride acylating agent.

(b) A mixture is prepared by the addition of 18.2 parts (0.433 equivalents) of a commercial mixture of ethylene polyamines having the approximate overall composition of tetraethylene pentamine to 392 parts of mineral oil and 348 parts (0.52 equivalent) of substituted succinic acylating agent prepared as in (a) while maintaining the temperature at 140°C. The reaction mixture is then heated to 150°C in 1.8 hours and stripped by blowing with nitrogen. The reaction mixture is filtered to yield the filtrate as an oil solution of the desired product composed predominately of polyisobutenyl succinimides.

(c) A mixture is formed from 250 parts of the polyisobutenyl succinimide product solution formed as in (b), 18 parts of phenyl dimethyl phosphate, 3.5 parts of tolutriazole, and 8 parts of water. The mixture is heated at 100°C for three hours. A vacuum of 40 mm Hg is gradually drawn on the product to remove the water while the temperature is slowly raised to 130°C. A clear solution or composition is obtained which is soluble in oil and suitable for use as component a-4).

EXAMPLE 170

The procedure of Example 169 is repeated except that 15 parts of trimethyl phosphite is used in place of the phenyl dimethyl phosphate to provide a clear, oil-soluble composition suitable for use as component a-4).

EXAMPLE 171

The procedure of Example 169 is repeated except that the phenyl dimethyl phosphate is replaced by 36 parts of 4-dimethyl-aminophenyl phosphorus tetrachloride and the heated mixture in (c) is swept with nitrogen during the three-hour period.

EXAMPLE 172

(a) A mixture of 1,000 parts (0.495 mole) of polyisobutene ($\overline{M}n$ = 2020; $\overline{M}w$ = 6049, both determined using the methodology of U.S. Pat. No. 4,234,435) and 115 parts (1.17 moles) of maleic anhydride is heated to 110°C. This mixture is heated to 184°C in 6 hours during which 85 parts (1.2 moles) of gaseous chlorine is added beneath the surface. At 184-189°C, an additional 59 parts (0.83 mole) of chlorine is added over 4 hours. The reaction mixture is stripped by heating at 186-190°C with nitrogen purged for 26 hours. The residue is predominately polyisobutenyl succinic anhydride acylating agent.

(b) A mixture of 334 parts (0.52 equivalents) of the polyisobutene substituted succinic acylating agent prepared as in (a), 548 parts of mineral oil, 30 parts (0.88 equivalent) of pentaerythritol and 8.6 parts (0.0057 equivalent) of Polyglycol 112-2 demulsifier is heated at 150°C for 2.5 hours. The reaction mixture is then heated to 210°C over a period of 5 hours and then held at 210°C for an additional 3.2 hours. The reaction mixture is cooled to 190°C and 8.5 parts (0.2 equivalent) of a commercial mixture of ethylene polyamines having an overall composition approximating that of tetraethylene pentamine is added. The reaction mixture is stripped by heating at 205°C with nitrogen blowing for 3 hours, and then filtered to yield the filtrate as an oil solution of the desired ashless dispersant product.

(c) A mixture is formed from 300 parts of the ashless dispersant product solution formed as in (b), 37 parts of bis(2-ethylhexyl) hydrogen phosphite, 3.5 parts of tolutriazole, and 8 parts of water. The mixture is heated at 100°C for two hours until all of the solid materials are dissolved. A vacuum of 40 mm Hg is gradually drawn on the product to remove the water while the temperature is slowly raised to 130°C. A clear solution or composition is obtained which is soluble in oil and suitable for use as component a-4).

EXAMPLE 173

The procedure of Example 172 is repeated except that the tolutriazole is eliminated from the reaction mixture of (c).

EXAMPLE 174

The procedure of Example 172 is repeated except that 26 parts of dibutyl hydrogen phosphite is used in place of the bis(2-ethylhexyl) hydrogen phosphite to provide a clear, oil-soluble composition suitable for use as component a-4).

EXAMPLE 175

The procedure of Example 172 is repeated except that the bis(2-ethylhexyl) hydrogen phosphite is replaced by 15 parts of trimethyl phosphite.

EXAMPLE 176

(a) A mixture of 1,000 parts (0.495 mole) of polyisobutene ($\overline{M}n$ = 2020; $\overline{M}w$ = 6049, both determined using the methodology of U.S. Pat. No. 4,234,435) and 115 parts (1.17 moles) of maleic anhydride is heated to 110°C. This mixture is heated to 184°C in 6 hours during which 85 parts (1.2 moles) of gaseous chlorine is added beneath the surface. At 184-189°C, an additional 59 parts (0.83 mole) of chlorine is added over 4 hours. The reaction mixture is stripped by heating at 186-190°C with nitrogen purged for 26 hours. The residue is predominately polyisobutenyl succinic anhydride acylating agent.

(b) A mixture of 3225 parts (5.0 equivalents) of the polyisobutene-substituted succinic acylating agent prepared as in (a), 289 parts (8.5 equivalents) of pentaerythritol and 5204 parts of mineral oil is heated at 225-235°C for 5.5 hours. The reaction mixture is filtered at 130°C to yield an oil solution of the desired ashless dispersant product.

(c) A mixture is formed from 300 parts of the ashless dispersant product solution formed as in (b), 27 parts of dibutyl chlorophosphate, 3.5 parts of tolutriazole, and 8 parts of water. The mixture is heated at 100°C for two hours until all of the solid materials are dissolved. A vacuum of 40 mm Hg is gradually drawn on the product to remove the water while the temperature is slowly raised to 100°C. A clear solution or composition is obtained which is soluble in oil and suitable for use as component a-4).

EXAMPLE 177

The procedure of Example 176 is repeated except that the tolutriazole is eliminated from the reaction mixture of (c).

EXAMPLE 178

The procedure of Example 176 is repeated except that 8 parts of ethyl dichlorophosphate and 4 parts of phosphorous acid are used in place of the dibutyl chlorophosphate to provide a clear, oil-soluble composition suitable for use as component a-4).

EXAMPLE 179

The procedure of Example 176 is repeated except that the dibutyl chlorophosphate is replaced by 10 parts of dibutyl hydrogen phosphite and 5 parts of phosphoric acid.

EXAMPLE 180

(a) A mixture of 1,000 parts (0.495 mole) of polyisobutene ($\overline{M}n$ = 2020; $\overline{M}w$ = 6049, both determined using the methodology of U.S. Pat. No. 4,234,435) and 115 parts (1.17 moles) of maleic anhydride is heated to 110°C. This mixture is heated to 184°C in 6 hours during which 85 parts (1.2 moles) of gaseous chlorine is added beneath the surface. At 184-189°C, an additional 59 parts (0.83 mole) of chlorine is added over 4 hours. The reaction mixture is stripped by heating at 186-190°C with nitrogen purged for 26 hours. The residue is predominately polyisobutenyl succinic anhydride acylating agent.

(b) A mixture of 322 parts (0.5 equivalent) of the polyisobutene-substituted succinic acylating agent prepared as in (a), 68 parts (2.0 equivalents) of pentaerythritol and 508 parts of mineral oil is heated at 204-227°C for 5 hours. The reaction mixture is cooled to 162°C and 5.3 parts (0. 13 equivalent) of a commercial ethylene polyamine mixture having an overall composition approximating that of tetraethylene pentamine is added. The reaction mixture is heated at 162-163°C for 1 hour, then cooled to 130°C and filtered. The filtrate is an oil solution of the desired ashless dispersant product.

(c) A mixture is formed from 350 parts of the ashless dispersant product solution formed as in (b), 16 parts of diethyl hydrogen phosphite, 3.5 parts of tolutriazole, and 6 parts of water. The mixture is heated at 100°C for two hours until all of the solid materials are dissolved. A vacuum of 40 mm Hg is gradually drawn on the product to remove the water while the temperature is slowly raised to 100°C. A clear solution or composition is obtained which is soluble in oil and suitable for use as component a-4).

EXAMPLE 181

The procedure of Example 180 is repeated except that the tolutriazole is eliminated from the reaction mixture of (c).

EXAMPLE 182

The procedure of Example 180 is repeated except that 20 parts of diethyl chlorophosphate is used in place of the diethyl hydrogen phosphite to provide a clear, oil-soluble composition suitable for use as component a-4).

EXAMPLE 183

The procedure of Example 180 is repeated except that the diethyl hydrogen phosphite is replaced by 12 parts of ethyl dibutyl phosphate and 4 parts of phosphorous acid.

EXAMPLE 184

(a) A mixture of 510 parts (0.28 mole) of polysobutene ($\overline{M}n$ = 1845; $\overline{M}w$ = 5325, both determined using the methodology of U.S. Pat. No. 4,234,435) and 59 parts (0.59 mole) of maleic anhydride is heated to 110°C. This mixture is heated to 190°C in 7 hours during which 43 parts (0.6 mole) of gaseous chlorine is added beneath the surface. At 190-192°C, an additional 11 parts (0.16 mole) of chlorine is added over 3.5 hours. The reaction mixture is stripped by heating at 190-193°C with nitrogen blowing for 10 hours. The residue is predominately polyisobutenyl succinic anhydride acylating agent.

(b) A mixture of 334 parts (0.52 equivalents) of the polyisobutene substituted succinic acylating agent prepared as in (a), 548 parts of mineral oil, 30 parts (0.88 equivalent) of pentaerythritol and 8.6 parts (0.0057 equivalent) of Polyglycol 112-2 demulsifier is heated at 150°C for 2.5 hours. The reaction mixture is then heated to 210°C over a period of 5 hours and then held at 210°C for an additional 3.2 hours. The reaction mixture is cooled to 190°C and 8.5 parts (0.2 equivalent) of a commercial mixture of ethylene polyamines having an overall composition approximating that of tetraethylene pentamine is added. The reaction mixture is stripped by heating at 205°C with nitrogen blowing for 3 hours, and then filtered to yield the filtrate as an oil solution of the desired ashless dispersant product.

(c) A mixture is formed from 260 parts of the ashless dispersant product solution formed as in (b), 20 parts of ethyl dichloro phosphate, 3.5 parts of tolutriazole, and 8 parts of water. The mixture is heated at 100°C for two hours until all of the solid materials are dissolved. A vacuum of 40 mm Hg is gradually drawn on the product to remove the water while the temperature is slowly raised to 100°C. A clear solution or composition is obtained which is soluble in oil and suitable for use as component a-4).

EXAMPLE 185

The procedure of Example 184 is repeated except that the tolutriazole is eliminated from the reaction mixture of (c).

EXAMPLE 186

The procedure of Example 184 is repeated except that 23 parts of butyl dichloro phosphate is used in place of the ethyl dichloro phosphate to provide a clear, oil-soluble composition suitable for use as component a-4).

EXAMPLE 187

The procedure of Example 184 is repeated except that the ethyl dichloro phosphate is replaced by 30 parts of monobutyl-mono-2-ethylhexyl hydrogen phosphite.

EXAMPLE 188

(a) A mixture of 510 parts (0.28 mole) of polyisobutene ($\overline{M}n$ = 1845; $\overline{M}w$ = 5325, both determined using the methodology of U.S. Pat. No. 4,234,435) and 59 parts (0.59 mole) of maleic anhydride is heated to 110°C. This mixture is heated to 190°C in 7 hours during which 43 parts (0.6 mole) of gaseous chlorine is added beneath the surface. At 190-192°C, an additional 11 parts (0.16 mole) of chlorine is added over 3.5 hours. The reaction mixture is stripped by heating at 190-193°C with nitrogen blowing for 10 hours. The residue is predominately polyisobutenyl succinic anhydride acylating agent.

(b) A mixture is prepared by the addition of 10.2 parts (0.25 equivalent) of a commercial mixture of ethylene polyamines having the approximate overall composition of tetraethylene pentamine to 113 parts of mineral oil and 161 parts (0.25 equivalent) of the substituted succinic acylating agent prepared as in (a) while maintaining the temperature at 138°C. The reaction mixture is heated to 150°C over a 2 hour period and stripped by blowing with nitrogen The reaction mixture is filtered to yield the filtrate as an oil solution of the desired ashless dispersant product.

(c) A mixture is formed from 125 parts of the polyisobutenyl succinimide product solution formed as in (b), 9 parts of monobenzyl phosphate and 4 parts of phosphorous acid, 3.5 parts of tolutriazole, and 6 parts of water. The mixture is heated at 100°C for two hours until all of the solid materials are dissolved. A vacuum of 40 mm Hg is gradually drawn on the product to remove the water while the temperature is slowly raised to 100°C. A clear solution or composition is obtained which is soluble in oil and suitable for use as component a-4).

EXAMPLE 189

The procedure of Example 188 is repeated except that the tolutriazole is eliminated from the reaction mixture of (c).

EXAMPLE 190

The procedure of Example 188 is repeated except that 14 parts of dibenzyl phosphate is used in place of the monobenzyl phosphate to provide a clear, oil-soluble composition suitable for use as component a-4).

EXAMPLE 191

The procedure of Example 188 is repeated except that the monobenzyl phosphate is replaced by 17 parts of monophenyl dibenzyl phosphate.

EXAMPLE 192

To a reactor are charged under a nitrogen atmosphere 67.98 parts of a commercially-available polyisobutenyl succinimide of a mixture of polyethylene polyamines having the approximate overall composition of tetraethylene pentamine (the polyisobutenyl group derived from polyisobutene having a number average molecular weight of about 900; the succinimide product having a ratio of about 1.15 succinic groups per alkenyl group) and 26.14 parts of a 100 Solvent Neutral refined mineral oil. After raising the temperature of the resulting solution to 100-105°C, 4.6 parts of dibutyl hydrogen phosphite is introduced into the reactor, followed by 0.92 part of tolutriazole (Cobratec TT-100), and then 3 parts of water. The resultant mixture is heated at 100-105 °C for two hours and then the temperature is gradually raised to 115°C with the application of a vacuum to 40 mm Hg. Stripping is continued for 90 minutes and until 120°C/40 mm Hg has been reached. A flow of dry nitrogen is then applied to the system and the product mixture is allowed to cool. The product mixture is suitable for use as component a-4).

EXAMPLE 193

The procedure of Example 192 is repeated except that the tolutriazole is omitted from the reaction mixture.

EXAMPLE 194

(a) A mixture of 322 parts of the polyisobutene-substituted succinic acylating agent prepared as in Example 188(a), 68 parts of pentaerythritol and 508 parts of mineral oil is heated at 204-227°C for 5 hours. The reaction mixture is cooled to 162°C and 5.3 parts of a commercial ethylene polyamine mixture having the approximate overall composition corresponding to tetraethylene pentamine is added. The reaction mixture is heated at 162-163°C for 1 hour, then cooled to 130°C and filtered. The filtrate is an oil solution of the desired product.

(b) A mixture is formed from 275 parts of the product solution formed as in (a), 20 parts of diisopropyl hydrogen phosphite, 3.5 parts of tolutriazole, and 8 parts of water. The mixture is heated at 100°C for two hours until all of the solid materials are dissolved. A vacuum of 40 mm Hg is gradually drawn on the product to remove the water while the temperature is slowly raised to 100°C. A clear solution or composition is obtained which is soluble in oil and suitable for use as component a-4).

EXAMPLE 195

(a) To 120 parts of chlorinated polyisobutylene having a number average molecular weight of about 1,300 and containing about 2.8 weight percent chlorine are added 21.7 parts of pentaethylene hexamine and 5.6 parts of sodium carbonate. The reaction mixture is heated to about 205°C and maintained at this temperature for about 5 hours. A stream of nitrogen is passed through the reaction mixture to remove the water of reaction. The reaction mixture is diluted with 60 parts of light mineral oil and hexane, filtered and extracted with methanol to remove excess pentaethylene hexamine. The hexane is stripped from the product by heating the mixture to 120°C under a suitable vacuum. The product should have a nitrogen content of approximately 1.0 to 1.5 weight percent.

(b) A mixture is formed from 80 parts of a diluted reaction product formed as in (a), 20 parts of a 100 Solvent Neutral refined mineral oil diluent, 5.0 parts of dibutyl hydrogen phosphite, and 3.0 parts of water. The resultant mixture is heated at 100-105°C for 2 hours and then the temperature is gradually raised to 115°C with the application of a vacuum to 40 mm Hg. Stripping is continued for 90 minutes and until 120°C/40 mm Hg has been reached. A flow of dry nitrogen is then applied to the system and the product mixture is allowed to cool. The product mixture is suitable for use as component a-4).

EXAMPLE 196

(a) Into a reactor are placed 220 parts of p-nonylphenol and 465 parts of diethylenetriamine. The mixture is heated to 80°C and 152 parts of 37% formalin is added dropwise over a period of about 30 minutes. The mixture is then heated to 125°C for several hours until the evolution of water has ceased. The resultant product should contain approximately 16-20% nitrogen.

(b) Into a reactor are placed 202 parts of styrene-maleic anhydride resin (having a number average molecular weight in the range of 600-700 and a mole ratio of styrene to maleic anhydride of 1:1), 202.5 parts of octadecyl amine and 472 parts of a 95 VI lubricating oil having a viscosity at 100°F of 150 SUS. The mixture is heated to 225°C for several hours. To this mixture is added dropwise over a period of about 30 minutes, 85 parts of the product formed as in (a). The resulting mixture is heated for 6 hours at 210-230°C while collecting the water formed during reaction. The polymeric product so formed should have a nitrogen content of about 2.1 weight percent.

(c) To a reactor are charged 250 parts of the basic nitrogen polymer produced as in (b) and 50 parts of a 100 Solvent Neutral refined mineral oil. After raising the temperature of the resulting mixture to 100-105°C, 35 parts of dibutyl hydrogen phosphite and 8 parts of water are added. The resultant mixture is heated at 100-105°C for two hours and then the temperature is gradually raised to 115°C with the application of a vacuum to 40 mm Hg. Stripping is continued for 90 minutes and until 120°C/40 mm Hg has been reached. A flow of dry nitrogen is then applied to the system and the product mixture is allowed to cool. The product mixture is suitable for use as component a-4) in the compositions of this invention.

EXAMPLE 197

The procedure of Example 196 is repeated except that the dibutyl hydrogen phosphite is replaced by 10 parts of dimethyl hydrogen phosphite.

EXAMPLE 198

The procedure of Example 196 is repeated except that the dibutyl hydrogen phosphite is replaced by 5 parts of dimethyl hydrogen phosphite and 4 parts of phosphorous acid.

A particularly preferred embodiment of this invention involves using as component a-1) and a-3) a phosphorylated and boronated alkenyl succinimide of a polyethylene polyamine or mixture of polyethylene polyamines, wherein the succinimide is formed from (i) an alkenyl succinic acylating agent having a succination ratio (i.e., the ratio of the average number of chemically bound succinic groups per alkenyl group in the molecular structure of the succinic acylating agent) in the range of 1 to 1.3, the alkenyl group being derived from a polyolefin (most preferably a polyisobutene) having a number average molecular weight in the range of 600 to 1,300 (more preferably in the range of 700 to 1,250 and most preferably in the range of 800 to 1,200).

Another particularly preferred embodiment of this invention involves using as component a-2) and a-4) a phosphorylated alkenyl succinimide of a polyethylene polyamine or mixture of polyethylene polyamines, wherein the succinimide is formed from (i) an alkenyl succinic acylating agent having a succination ratio (i.e., the ratio of the average number of chemically bound succinic groups per alkenyl group in the molecular structure of the succinic acylating agent) in the range of 1 to 1.3, the alkenyl group being derived from a polyolefin (most preferably a polyisobutene) having a number average molecular weight in the range of 600 to 1,300 (more preferably in the range of 700 to 1,205 and most preferably in the range of 800 to 1,200).

To determine the succination ratio of the alkenyl succinic acylating agents utilized in forming such particularly preferred ashless dispersants:

A. The number average molecular weight ($\overline{M}n$) of the polyalkene from which the substituent is derived is determined by use of either of two methods, namely, vapor pressure osmometry (VPO) or gel permeation chromatography (GPC). The VPO determination should be conducted in accordance with ASTM D-2503-82 using high purity toluene as the measuring solvent. Alternatively, a GPC procedure can be employed. As is well known, the GPC technique involves separating molecules according to their size in solution. For this purpose liquid chromatographic columns are packed with a styrene-divinyl benzene copolymer of controlled particle and pore sizes. When the polyalkene molecules from which the substituent is derived are transported through the GPC columns by a solvent (tetrahydrofuran), the polyalkene molecules small enough to penetrate into the pores of the column packing are retarded in their progress through the columns. On the other hand, the polyalkene molecules which are larger either penetrate the pores only slighly or are totally excluded from the pores. As a consequence, these larger polyalkene molecules are retarded in their progress through the columns to a lesser extent. Thus a velocity separation occurs according to the size of the respective polyalkene molecules. In order to define the relationship between polyalkene molecular weight and elution time, the GPC system to be used is calibrated using known molecular weight polyalkene standards and an internal standard method. Details concerning such GPC procedures and methods for column calibration are extensively reported in the literature. See for example, W. W. Yau, J. J. Kirkland, and D. D. Bly, Modern Size-Exclusion Liquid Chromatography, John Wiley & Sons, 1979, Chapter 9 (pages 285-341), and references cited therein.

B. The total weight of the substituent groups present in the substituted succinic acylating agent is determined by conventional methods for determination of the number of carbonyl functions. The preferred procedure for use involves nonaqueous titration of the substituted acylating agent with standardized sodium isopropoxide. In this procedure the titration is conducted in a 1:1 mineral spirits:1-butanol solvent system. An alternative, albeit less preferred, procedure is the ASTM D-94 procedure.

The results from procedures A and B above are used in calculating the weight of substituent groups per unit weight of total sample.

C. In determining the succination ratio of the alkenyl succinic acylating agents, the determination is to be based on the active portion of the sample. That is to say, alkenyl succinic acylating agents are often produced as a mixture with an inactive diluent. Thus for the purpose of succination ratio determination, such diluent should not be considered a part of the succinic acylating agent, and accordingly a separation as between the diluent and the alkenyl succinic acylating agent should be accomplished. Such separation can be effected before determination of total weight of the subtituent groups present in the substituted succinic acylating agent. However, it is preferable to effect such separation after such determination using a mathematical correction of the result The separation itself can be achieved using a silica gel column separation technique. A low molecular weight non-polar hydrocarbon solvent, such as hexane and more preferably pentane, is used as the solvent whereby the unreactive diluent is readily eluted from the column. The substituted succinic acylating agent entrained in the column can then be recovered by use of a more polar elution solvent, preferably methanol/methylene dichloride.

Component b) - Metal-Free Sulfur-Containing Antiwear and/or Extreme Pressure Agent

A variety of oil-soluble metal-free sulfur-containing antiwear and/or extreme pressure additives can be used as the other indispensable component in the practice of this invention, provided they have the requisite minimum sulfur content of at least 20 wt %. Examples are included within the categories of dihydrocarbyl polysulfides; sulfurized olefins; trithiones; sulfurized thienyl derivatives; sulfurized terpenes; sulfurized oligomers of C_2-C_8 monoolefins; xanthates; hydrocarbyl trithiocarbonates; and sulfurized Diels-Alder adducts such as those disclosed in U.S. reissue patent Re 27,331. Specific examples include sulfurized polyisobutene of $\overline{M}n$ 1,100, sulfurized isobutylene, sulfurized diisobutylene, sulfurized triisobutylene, dicyclohexyl polysulfide, diphenyl polysulfide, dibenzyl polysulfide, dinonyl polysulfide, and mixtures of di-tert-butyl polysulfide such as mixtures of di-tert-butyl trisulfide, di-tert-butyl tetrasulfide and di-tert-butyl pentasulfide, among others. Combinations of such categories of sulfur-containing antiwear and/or extreme pressure agents can also be used, such as a combination of sulfurized isobutylene and di-tert-butyl trisulfide, a combination of sulfurized isobutylene and dinonyl trisulfide, a combination of sulfurized triisobutylene and dibenzyl polysulfide.

The preferred sulfur-containing antiwear and/or extreme pressure agents are the oil-soluble active sulfur-containing antiwear and/or extreme pressure agents. Generally speaking, these are substances which possess a linkage of two or more sulfur atoms (e.g., -S-S-, -S-S-S-, -S-S-S-S-, -S-S-S-S-S-, etc.).

To determine for the purpose of this invention whether a sulfur-containing material is an active sulfur-containing material, use can be made of a copper coupon corrosion test conducted as follows: A copper coupon approximately 70 x 15 mm and about 1.25 mm in thickness is cleaned by use of steel wool (0000 grade), washed with heptane, and then with acetone, dried, and weighed to the nearest 0.1 mg. The cleaned coupon is placed in a test tube and covered completely with the composition to be tested, and the system is heated to 125°C by means of an oil bath. After holding the system at 125°C for three hours, the copper coupon is removed from the test tube, rinsed with heptane, and then with acetone. The dried coupon is then rubbed with a paper towel moistened with acetone to remove any surface flakes formed by copper corrosion. The coupon is then air-dried and weighed to the nearest 0.1 mg. The difference in weight between the initial copper coupon and the coupon after the test represents the extent to which the copper was corroded under the test conditions. Therefore the larger the weight difference, the greater the copper corrosion, and thus the more active the sulfur compound. For the purposes of this invention, if the coupon weight loss is 30 milligrams or more, the sulfur-containing agent is considered "active". Oil-soluble sulfur-containing antiwear and/or extreme pressure agents yielding a weight loss of above 50 mg in the above test are more preferred.

Another test which can be used for determining the activity of a sulfur-containing additive for use as component b) is the 4-Ball EP test, listed as ASTM D 2783-88, (Measurement of Extreme Pressure Properties of Lubricating Fluids). In general, the higher the weld point in the test, the more active is the sulfur-containing additive. Thus a sulfur additive at 1% (wt) concentration achieving or exceeding 250 kilograms weld point is deemed active for the purposes of this invention.

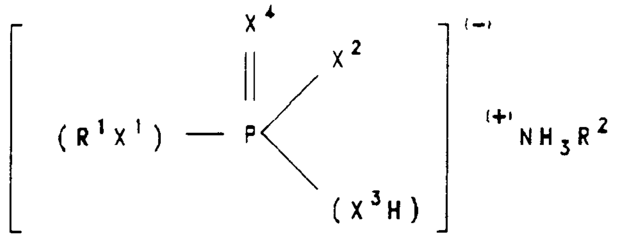
Because of the toxicity of hydrogen sulfide, it is important to utilize in the practice of this invention oil-soluble sulfur-containing antiwear and/or extreme pressure agents, and more preferably oil-soluble active sulfur-containing antiwear and/or extreme pressure agents, that yield less than 25 ppm, and more preferably less than 10 ppm, and most preferably no detectable amounts, of vapor space H_2S when heated in the concentrated state for one week at 65°C. HiTEC® 309 and 312 sulfurized isobutylene additives (Ethyl Petroleum Additives, Inc.; Ethyl Petroleum Additives, Ltd.; Ethyl S.A.; Ethyl Canada Ltd.) are especially desirable in this respect.

The most preferred oil-soluble metal-free sulfur-containing antiwear and/or extreme pressure agents from the cost-effectiveness standpoint are the sulfurized olefins containing at least 30% by weight of sulfur, the dihydrocarbyl polysulfides containing at least 25% by weight of sulfur, and mixtures of such sulfurized olefins and polysulfides. Of these materials, di-tert-alkyl polysulfides having a sulfur content of at least 35% by weight are particularly desirable. Sulfurized isobutylene having a sulfur content of at least 40% and as much as 50% by weight or more and a chlorine content of less than 1% by weight is the most especially preferred material.

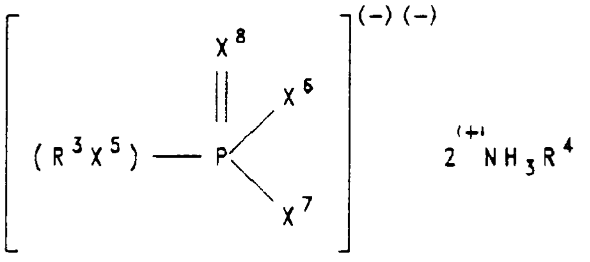
Methods of preparing sulfurized olefins are described in U.S. Pat. Nos. 2,995,569; 3,673,090; 3,703,504; 3,703,505; 3,796,661; 3,873,454; 4,795,576; 4,954,274; and 4,966,720. Also useful are the sulfurized olefin derivatives described in U.S. Pat. No. 4,654,156.

<u>Component c) - Amine Salt of Mono- and/or Dihydrocarbyl Ester of a Monomeric Pentavalent Acid of Phosphorus</u>

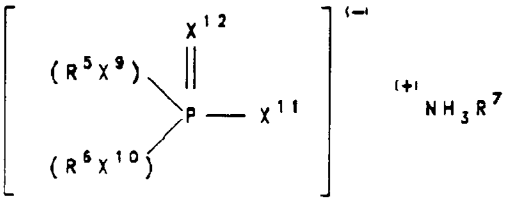
This optional but preferred component is composed of one or more oil-soluble amine salts of one or more partial esters of one or more phosphoric acids and/or thiophosphoric acids. Such compounds may be collectively represented by the formulas



$$\left[(R^1X^1) - \overset{\overset{X^4}{\|}}{P}\begin{matrix} X^2 \\ (X^3H) \end{matrix} \right]^{(-)} {}^{(+)}NH_3R^2 \qquad (I)$$



(II)



(III)

or mixtures thereof. In Formulas I, II and III, each of R^1, R^2, R^3, R^4, R^5, R^6,and R^7 is, independently, a hydrocarbyl group and each of X^1, X^2, X^3, X^4, X^5, X^6, X^7, X^8, X^9, X^{10}, X^{11}, and X^{12} is, independently, an oxygen atom or a sulfur atom.

In one preferred sub-category the amine salts are formed with one or more partially esterified monothiophosphoric acids. These are compounds of Formulas (I), (II), and (III) above wherein only one of X^1, X^2, X^3, and X^4, only one of X^5, X^6, X^7, and X^8, and only one of X^9, X^{10}, X^{11}, and X^{12} is a sulfur atom.

In another preferred sub-category the amine salts are formed with one or more partially esterified phosphoric acids. These are compounds of Formulas (I), (II), and (III) above wherein all of X^1, X^2, X^3, X^4, X^5, X^6, X^7, X^8, X^9, X^{10}, X^{11}, and X^{12} are oxygen atoms.

Another preferred sub-category of amine salts are those formed with one or more partially esterified dithiophosphoric acids. These are compounds of Formulas (I), (II), and (III) above wherein two of X^1, X^2, X^3, and X^4, two of X^5, X^6, X^7, and X^8, and two of X^9, X^{10}, X^{11}, and X^{12} are sulfur atoms.

Also useful are amine salts of Formulas (I), (II), and (III) above wherein three or four of X^1, X^2, X^3, and X^4, three or four of X^5, X^6, X^7, and X^8, and three or four of X^9, X^{10}, X^{11}, and X^{12} are sulfur atoms.

While all of the above oil-soluble amine salts are useful as components in the compositions of this invention, it is most preferred to include at least one oil-soluble amine salt of a dihydrocarbyl monothiophosphoric acid (one sulfur atom per molecule), either alone or in combination with at least one oil-soluble amine salt of a dihydrocarbyl phosphoric acid (no sulfur atom in the molecule).

Use can be made of the octylamine, nonylamine, decylamine, undecylamine, dodecylamine, tridecylamine, tetradecylamine, pentadecylamine, hexadecylamine, heptadecylamine, octadecylamine, cyclohexylamine, phenylamine, mesitylamine, oleylamine, cocoamine, soyamine, C_{12-14} tertiary alkyl primary amine, C_{22-24} tertiary alkyl primary amine, and phenethylamine salts or adducts of the above and similar partially esterified acids of monothiophosphoric acid, including mixtures of any such compounds. Generally speaking, the preferred amine salts are salts of aliphatic amines, especially the saturated or olefinically unsaturated aliphatic primary amines, such as n-octylamine, 2-ethylhexylamine, tert-octylamine, n-decylamine, the C_{10}, C_{12}, C_{14} and C_{16} tertiary alkyl primary amines (either singly or in any combinations thereof, such as a mixture of the C_{12} and C_{14} tertiary alkyl primary amines), n-undecylamine, lauryl amine, hexadecylamine, heptadecylamine, octadecylamine, the C_{22} and C_{24} tertiary alkyl primary amines (either singly or in combination), decenylamine, dodecenylamine, palmitoleylamine, oleylamine, linoleylamine, eicosenylamine, etc. Secondary hydrocarbyl amines and tertiary hydrocarbyl amines can also be used either alone or in combination with each other or in combination with primary amines. Thus any combination of primary, secondary and/or tertiary amines, whether monoamine or polyamine, can be used in forming the salts or adducts. Use of primary amines is preferred.

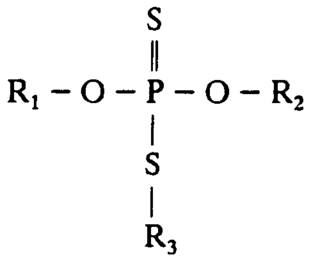
Especially preferred amines are alkyl monoamines and alkenyl monoamines having from 8 to 24 carbon atoms in the molecule.

Methods for the preparation of such amine salts are well known and reported in the literature. See for example, U.S. Pat. Nos. 2,063,629; 2,224,695; 2,447,288; 2,616,905; 3,984,448; 4,431,552; Pesin et al, Zhurnal Obshchei Khimii,Vol. 31, No. 8, pp. 2508-2515 (1961); and International Application Publication No. WO 87/07638.

Amine salts of partially esterified monothiophosphoric acids are usually made by reacting a mono- and/or dihydrocarbyl phosphite with sulfur or an arrive sulfur-containing compound such as are referred to above under the caption "Sulfur-Containing Antiwear and/or Extreme Pressure Agents" and one or more primary or secondary amines. Such reactions tend to be highly exothermic reactions which can become uncontrollable, if not conducted properly. One preferred method of forming these amine salts involves a process which comprises (i) introducing, at a rate such that the temperature does not exceed about 60°C, one or more dihydrocarbyl hydrogen phosphites, such as a dialkyl hydrogen phosphite, into an excess quantity of one or more active sulfur-containing materials, such as sulfurized branched-chain olefin (e.g., isobutylene, diisobutylene, triisobutylene, etc.), while agitating the mixture so formed, (ii) introducing into this mixture, at a rate such that the temperature does not exceed about 60°C, one or more aliphatic primary or secondary amines, preferably one or more aliphatic primary monoamines having in the range of 8 to 24 carbon atoms per molecule while agitating the mixture so formed, and (iii) maintaining the temperature of the resultant agitated reaction mixture at between 55 and 60°C until reaction is substantially complete. Another suitable way of producing these amine salts is to concurrently introduce all three of the reactants into the reaction zone at suitable rates and under temperature control such that the temperature does not exceed about 60°C.

Component d) - Trihydrocarbyl Ester of a Dithiophosphoric Acid

This group of optional but preferred compounds is composed of O,O-dihydrocarbyl-S-hydrocarbyl thiothionophosphates (also known as O,O-dihydrocarbyl-S-hydrocarbyl phosphorothiothionates) which can be represented by the general formula:



$$\begin{array}{c} S \\ \| \\ R_1-O-P-O-R_2 \\ | \\ S \\ | \\ R_3 \end{array}$$

wherein each of R_1, R_2, and R_3 is independently a hydrocarbyl group, especially where R_3 is an alicyclic hydrocarbyl group. Particularly preferred are the O,O-dialkyl-S-hydrocarbyl phosphorothiothionates wherein R_3 is an alicyclic group an R_1 and R_2 are alkyl groups each having up to 18 carbon atoms and most preferably up to 12 carbon atoms.

These compounds can be made by various known methods. Probably the most efficacious method involves reacting phosphorus pentasulfide (P_2S_5, often regarded as P_4S_{10}) with the appropriate alcohols or mixture of alcohols. Compounds in which one of the hydrocarbyl groups differs from the other two are preferably made by first reacting the phosphorus pentasulfide with an appropriate alcohol to form an intermediate product, viz. $(RO)_2PSSH$, which in turn is reacted with a compound containing at least one reactive olefinic double bond. See in this connection U.S. Pat. Nos. 2,528,732, 2,561,773, 2,665,295, 2,767,206, 2,802,856, 3,023,209, and J. Org. Chem., 1963, 28, 1262-8.

Exemplary compounds suitable for use in the compositions of this invention include such compounds as trioctylphosphorothiothionate, tridecylphosphorothiothionate, trilaurylphosphorothiothionate, O,O-diethyl bicyclo(2.2.1)-hepten-2-yl phosphorothiothionate, O,O-diethyl 7,7-dimethyl-bicyclo(2.2.1)-5-hepten-2-yl phosphorothiothionate, the product formed by reaction of dithiophosphoric acid-O,O-dimethyl ester with cis-endomethylene-tetrahydrophthalic acid dimethyl ester, the product formed by reaction of dithiophosphoric acid-O,O-dimethyl ester with cis-endomethylene-tetrahydrophthalic acid dibutyl ester, the product formed by reaction of dithiophosphoric acid-O,O-dibutyl ester with cis-endomethylene-tetrahydrophthalic acid dilauryl ester, the product formed by reaction of dithiophosphoric acid-O,O-dimethyl ester with 2,5-endomethylene-1-methyl-tetrahydrobenzoic acid butyl ester, the product formed by reaction of dithiophosphoric acid-O,O-dimethyl ester with 2,5-endomethylene-1-methyl-tetrahydrobenzoic acid decyl ester, the product formed by reaction of dithiophosphoric acid-O,O- dimethyl ester with 2,5-endomethylene-6-methyl-tetrahydrobenzoin acid ethyl ester, the product formed by reaction of dithiophosphoric acid-O,O-diethyl ester with 2,5-endomethylene-tetrahydrobenzyl alcohol, the product formed by reaction of dithiophosphoric acid- O,O-dimethyl ester with the Diels-Alder adduct of cyclopentadiene and allyl alcohol (2 mols : 1 mol), the product formed by reaction of dithiophosphoric acid-O,O-dimethyl ester with 2,5-endomethylenetetrahydrophenyl acetate, the product formed by reaction of dithiophosphoric acid-O,O-dibutyl ester with the Diels-Alder adduct of cyclopentadiene and vinyl acetate (2 mols : 1 mol), the product formed by reaction of dithiophosphoric acid-O,O-dimethyl ester with the bis-cyclopentadiene adduct of p-benzoquinone, the product formed by reaction of dithiophosphoric acid-O,O-dimethyl ester with the azodicarboxylic acid diethyl ester, the product formed by reaction of dithiophosphoric acid-O,O- dimethyl ester with dicyclopentadiene, the product formed by reaction of dithiophosphoric acid-O,O-dibutyl ester with dicyclopentadiene, the product formed by reaction of dithiophosphoric acid-O,O-dioctyl ester with dicyclopentadiene, the product formed by reaction of dithiophosphoric acid- O,O-dilauryl ester with dicyclopentadiene, the product formed by reaction of dithiophosphoric acid-O,O-di-2-ethylhexyl ester with wax olefin, the product formed by reaction of dithiophosphoric acid-O,O-di-2-ethylhexyl ester with oleyl alcohol, the product formed by reaction of dithiophosphoric acid-O,O-di-2-ethylhexyl ester with linseed oil, the product formed by reaction of dithiophosphoric acid-O,O-diamyl ester with alpha pinene, the product formed by reaction of dithiophosphoric acid-O,O-diphenyl ester with alpha pinene, the product formed by reaction of dithiophosphoric acid-O,O-diamyl ester with allo-ocimene, and the product formed by reaction of dithiophosphoric acid-O,O-dioctyl ester with dipentene.

Component e) - Amine Salt of a Carboxylic Acid

Another component which can be and preferably is used in the compositions of this invention is one or more amine salts of one or more long chain carboxylic acids. The acids can be monocarboxylic acids or polycarboxylic acids. Generally speaking, these acids contain from 8 to 50 carbon atoms in the molecule and thus the salts are oil-soluble. A variety of amines can be used in forming such salts, including primary, secondary and tertiary amines, and the amines can be monoamines, or polyamines. Further, the amines may be cyclic or acyclic aliphatic amines, aromatic amines, heterocyclic amines, or amines containing various mixtures of acyclic and cyclic groups.

Preferred amine salts include the alkyl amine salts of alkanoic acid and the alkyl amines salts of alkanedioic acids.

The amine salts are formed by classical chemical reactions, namely, the reaction of an amine or mixture of amines, with the appropriate acid or mixture of acids. Accordingly, further discussion concerning methods for the preparation of such materials would be redundant.

Among the amine salts of long-chain acids that may be used are the following: lauryl ammonium laurate (i.e., the lauryl amine salt of lauric acid), stearyl ammonium laurate, cyclohexyl ammonium laurate, octyl ammonium laurate, pyridine laurate, aniline laurate, lauryl ammonium stearate, stearyl ammonium stearate, cyclohexyl ammonium stearate, octylammonium stearate, pyridine stearate, aniline stearate, lauryl ammonium octanoate, stearyl ammonium octanoate, cyclohexyl ammonium octanoate, octyl ammonium octanoate, pyridine octanoate, aniline octanoate, nonyl ammonium laurate, nonyl ammonium stearate, nonyl ammonium octanoate, lauryl ammonium nonanoate, stearyl ammonium nonanoate, cyclohexyl ammonium nonanoate, octyl ammonium nonanoate, pyridine nonanoate, aniline nonanoate, nonyl ammonium nonanoate, lauryl ammonium decanoate, stearyl ammonium decanoate, cyclohexyl ammonium decanoate, octyl ammonium decanoate, pyridine decanoate, aniline decanoate, decyl ammonium laurate, decyl ammonium stearate, decyl ammonium octanoate, decyl ammonium nonanoate, decyl ammonium decanoate, bis octyl amine salt of suberic acid, bis cyclohexyl amine salt of suberic acid, bis lauryl amine salt of suberic acid, bis stearyl amine salt of suberic acid, bis octyl amine salt of sebacic acid, bis cyclohexyl amine salt of sebacic acid, bis lauryl amine salt of sebacic acid, bis stearyl amine salt of sebacic acid, the tert-dodecyl and tert-tetradecyl primary amine salts of octanoic acid, the tert-decyl and tert-dodecyl primary amine salts of octanoic acid, the tert-dodecyl and tert-tetradecyl primary amine salts of lauric acid, the tert-decyl and tert-dodecyl primary amine salts of lauric acid, the tert-dodecyl and tert-tetradecyl primary salts of stearic acid, the tert-decyl and tert-dodecyl primary amine salts of stearic acid, the hexyl amine salt of C_{24}-dicarboxylic acid, the octyl amine salt of C_{28}-dicarboxylic acid, the octyl amine salt of C_{30}-dicarboxylic acid, the decyl amine salt of C_{30}-dicarboxylic acid, the octyl amine salt of C_{32}-dicarboxylic acid, the bis lauryldimethyl amine salt of traumatic acid, diethyl ammonium laurate, dioctyl ammonium laurate, dicyclohexyl ammonium laurate, diethyl ammonium octanoate, dioctyl ammonium octanoate, dicyclohexyl ammonium octanoate, diethyl ammonium stearate, dioctyl ammonium stearate, diethyl ammonium stearate, dibutyl ammonium stearate, dicyclopentyl ammonium stearate, dipropyl ammonium benzoate, didecyl ammonium benzoate, dimethylcyclohexyl ammonium benzoate, triethyl ammonium laurate, triethyl ammonium octanoate, triethyl ammonium stearate, triethyl ammonium benzoate, trioctyl ammonium laurate, trioctyl ammonium octanoate, trioctyl ammonium stearate, and trioctyl ammonium benzoate. It will be understood of course that the amine salt of the monocarboxylic and/or polycarboxylic acid used should be sufficiently soluble in the base oil used as to provide homogeneous solution at the concentration employed.

Among the preferred amine salts are the primary amine salts of long chain monocarboxylic acids in which the amine thereof is a monoalkyl monoamine, RNH_2; the secondary amine salts of long chain monocarboxylic acids in which the amine thereof is a dialkyl monoamine, R_2NH; the tertiary amine salts of long chain monocarboxylic acids in which the amine thereof is a trialkyl monoamine, R_3N; the bis primary amine salts of long chain dicarboxylic acids in which the amine thereof is a monoalkyl monoamine, RNH_2; the bis secondary amine salts of long chain dicarboxylic acids in which the amine thereof is a dialkyl monoamine, R_2NH; the bis tertiary amine salts of long chain dicarboxylic acids in which the amine thereof is a trialkyl monoamine, R_3N; and mixtures thereof. In the foregoing formulae, R is an alkyl group which contains up to 30 or more carbon atoms, and preferably from 6 to 24 carbon atoms.

Component f) - Demulsifier

Typical additives which may be employed as demulsifiers include alkyl benzene sulfonates, polyethylene oxides, polypropylene oxides, block copolymers of ethylene oxide and propylene oxide, and salts and esters or oil soluble acids.

Component g) - Copper Corrosion Inhibitor

One type of copper corrosion inhibitor additives is comprised of thiazoles, triazoles and thiadiazoles. Examples of such compounds include benzotriazole, tolyltriazole, octyltriazole, decyltriazole, dodecyltriazole, 2-mercaptobenzothiazole, 2,5-dimercapto-1,3,4-thiadiazole, 2-mercapto-5-hydrocarbylthio-1,3,4-thiadiazoles, 2-mercapto-5-hydrocarbyldithio-1,3,4- thiadiazoles, 2,5-bis(hydrocarbylthio)-1,3,4-thiadiazoles, and 2,5-(bis)hydrocarbyldithio)-1,3,4-thiadiazoles. The preferred compounds are the 1,3,4-thiadiazoles, especially the 2-hydrocarbyldithio-5-mercapto-1,3,4-thiadiazoles and the 2,5-bis(hydrocarbylthio)- 1,3,4-thiadiazoles, a number of which are available as articles of commerce. Such compounds are generally synthesized from hydrazine and carbon disulfide by known procedures. See for example U.S. Pat. Nos. 2,749,311; 2,760,933; 2,765,289; 2,850,453; 2,910,439; 3,663,561; 3,862,798; 3,840,549; and 4,097,387.

Other suitable inhibitors of copper corrosion include ether amines; polyethoxylated compounds such as ethoxylated amines, ethoxylated phenols, and ethoxylated alcohols; and imidazolines. Materials of these types are well known to those skilled in the art and a number of such materials are available as articles of commerce.

Component h) - Boron-Containing Additive

The boron-containing additive components are preferably oil-soluble additive components, but effective use can be made of boron-containing components which are sufficiently finely divided as to form stable dispersions in the base oil. Examples of the latter type of boron-containing components include the finely-divided inorganic orthoborate salts such as lithium borate, sodium borate, potassium borate, magnesium borate, calcium borate, ammonium borate and the like.

The oil-soluble boron-containing components include boronated ashless dispersants (often referred to as borated ashless dispersants) and esters of acids of boron. Examples of boronated ashless dispersants and descriptions of methods by which they can be prepared are well-documented in the literature. See for example the disclosures of U.S. Pat. Nos. 3,087,936; 3,254,025; 3,281,428; 3,282,955; 3,533,945; 3,539,633; 3,658,836; 3,697,574; 3,703,536; 3,704,308; 4,025,445; and 4,857,214. Likewise the literature is replete with examples of oil-soluble esters of boron acids and methods for their production. See for example the disclosures of U.S. Pat. Nos. 2,866,811; 2,931,774; 3,009,797; 3,009,798; 3,009,799; 3,014,061; and 3,092,586.

Other Optional Additive Components

The oleaginous fluids and additive concentrates of this invention can and preferably will contain additional components in order to partake of the properties which can be conferred to the overall composition by such additional components. The nature of such components will, to a large extent, be governed by the particular use to which the ultimate oleaginous composition (lubricant or functional fluid) is to be subjected. Some of these other additives are referred to below.

A) Supplemental phosphorus-containing antiwear and/or extreme pressure agents.

Supplemental metal-free phosphorus-containing antiwear and/or extreme pressure agents can be used in the compositions of this invention. Such compounds are for the most part partially or fully esterified acids of phosphorus, and include for example phosphates, phosphites, phosphonates, phosphonites, and their various sulfur analogs. Examples include monohydrocarbyl phosphites; monohydrocarbyl phosphates; monohydrocarbyl mono-, di-, tri-, and tetrathiophosphites; monohydrocarbyl mono-, di-, tri-, and tetrathiophosphates; dihydrocarbyl phosphites; dihydrocarbyl phosphates; dihydrocarbyl mono-, di-, tri-, and tetrathiophosphites; dihydrocarbyl mono-, di-, tri-, and tetrathiophosphates; trihydrocarbyl phosphites; trihydrocarbylphosphates; trihydrocarbyl mono-, di-, tri-, and tetrathiophosphites; trihydrocarbyl mono-, di-, tri-, and tetrathiophosphates; the various hydrocarbyl phosphonates and thiophosphonates; the various hydrocarbyl phosphonites and thiophosphonites, and analogous oil-soluble derivatives of polyphosphoric and polythiophosphoric acids; and many others. A few specific specific examples of such compounds are tricresyl phosphate, tributyl phosphite, triphenyl phosphite, tri-(2-ethylhexyl) phosphate, dihexyl thiophosphite, diisooctyl butylphosphonate, tricyclohexyl phosphate, cresyl diphenyl phosphate, tris(2-butoxyethyl) phosphite, diisopropyl dithiophosphate, tris(tridecyl)tetrathiophosphate, tris(2-chloroethyl) phosphate, and like compounds.

B) Supplemental ashless dispersants.

Any of a variety of additional ashless dispersants can be utilized in the compositions of this invention. These include carboxylic ashless dispersants, polymeric polyamine dispersants, and post-treated dispersants of these types. All such materials which have been described hereinabove.

C) Antioxidants.

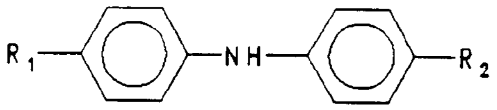
Most oleaginous compositions will contain a conventional quantity of one or more antioxidants in order to protect the composition from premature degradation in the presence of air, especially at elevated temperatures. Typical antioxidants include hindered phenolic antioxidants, secondary aromatic amine antioxidants, sulfurized phenolic antioxidants, oil-soluble copper compounds, and phosphorus-containing antioxidants.

Illustrative sterically hindered phenolic antioxidants include orthoalkylated phenolic compounds such as 2,6-di-tert-butylphenol, 4-methyl-2,6-di-tert-butylphenol, 2,4,6-tri-tert-butylphenol, 2- tert-butylphenol, 2,6-diisopropylphenol, 2-methyl-6- tert-butylphenol, 2,4-dimethyl-6-tert-butylphenol, 4-(N,N-dimethylaminomethyl)-2,6-di-tert-butylphenol, 4-ethyl-2,6-di-tert-butylphenol, 2-methyl- 6-styrylphenol, 2,6-di-styryl-4-nonylphenol, and their analogs and homologs. Mixtures of two or more such mononuclear phenolic compounds are also suitable.

Also useful are methylene-bridged alkylphenols, and these can be used singly or in combinations with each other, or in combinations with sterically-hindered unbridged phenolic compounds. Illustrative methylene bridged compounds include 4,4′-methylenebis(6-tert-butyl-o-cresol), 4,4′-methylenebis(2-tert-amyl-o-cresol), 2,2′-methylene-bis(4-methyl-6-tert-butylphenol), 4,4′-methylene-bis(2,6-di-tert-butylphenol), and similar compounds. Preferred are mixtures of methylene-bridged alkylphenols such as are described in U.S. Pat. No. 3,211,652.

Amine antioxidants, especially oil-soluble aromatic secondary amines can also be used. Although aromatic secondary monoamines are preferred, aromatic secondary polyamines are also suitable. Illustrative aromatic secondary monoamines include diphenylamine, alkyl diphenylamines containing 1 or 2 alkyl substituents each having up to about 16 carbon atoms, phenyl-α-naphthylamine, phenyl-β-naphthylamine, alkyl- or aralkyl-substituted phenyl-α-naphthylamine containing one or two alkyl or aralkyl groups each having up to about 16 carbon atoms, alkyl- or aralkyl-substituted phenyl-βnaphthylamine containing one or two alkyl or aralkyl groups each having up to about 16 carbon atoms, and similar compounds.

A preferred type of aromatic amine antioxidant is an alkylated diphenylamine of the general formula



wherein R_1 is an alkyl group (preferably a branched alkyl group) having 8 to 12 carbon atoms, (more preferably 8 or 9 carbon atoms) and R_2 is a hydrogen atom or an alkyl group (preferably a branched alkyl group) having

8 to 12 carbon atoms, (more preferably 8 or 9 carbon atoms). Most preferably, R_1 and R_2 are the same. One such preferred compound is available commercially as Naugalube 438L, a material which is understood to be predominately a 4,4′-di-nonyldiphenylamine (i.e., bis(4-nonylphenyl)amine) wherein the nonyl groups are branched.

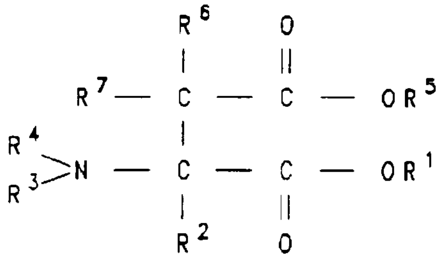
Another useful type of antioxidant for inclusion in the compositions of this invention is comprised to one or more liquid, partially sulfurized phenolic compounds such as are prepared by reacting sulfur monochloride with a liquid mixture of phenols -- at least about 50 weight percent of which mixture of phenols is composed of one or more reactive, hindered phenols -- in proportions to provide from 0.3 to 0.7 gram atoms of sulfur monochloride per mole of reactive, hindered phenol so as to produce a liquid product. Typical phenol mixtures useful in making such liquid product compositions include a mixture containing by weight about 75% of 2,6-di-tert-butylphenol, about 10% of 2-tert-butylphenol, about 13% of 2,4,6-tri-tert-butylphenol, and about 2% of 2,4-di-tert-butylphenol. The reaction is exothermic and thus is preferably kept within the range of 15°C to 70°C, most preferably between 40°C to 60°C.

Mixtures of different antioxidants can also be used. One suitable mixture is comprised of a combination of (i) an oil-soluble mixture of at least three different sterically-hindered tertiary butylated monohydric phenols which is in the liquid state at 25°C, (ii) an oil-soluble mixture of at least three different sterically-hindered tertiary butylated methylene-bridged polyphenols, and (iii) at least one bis(4-alkylphenyl)amine wherein the alkyl group is a branched alkyl group having 8 to 12 carbon atoms, the proportions of (i), (ii) and (iii) on a weight basis falling in the range of 3.5 to 5.0 parts of component (i) and 0.9 to 1.2 parts of component (ii) per part by weight of component (iii).

D) Rust inhibitors.

The compositions of this invention may also contain a suitable quantity of a rust inhibitor. This may be a single compound or a mixture of compounds having the property of inhibiting corrosion of ferrous metal surfaces. Such materials include include oil-soluble monocarboxylic acids such as 2-ethylhexanoic acid, lauric acid, myristic acid, palmitic acid, oleic acid, linoleic acid, linolenic acid, behenic acid, cerotic acid, etc., and oil-soluble polycarboxylic acids including dimer and trimer acids, such as are produced from tall oil fatty acids, oleic acid, or linoleic acid. Other suitable corrosion inhibitors include alkenylsuccinic acids in which the alkenyl group contains 10 or more carbon atoms such as, for example, tetrapropenylsuccinic acid, tetradecenylsuccinic acid, and hexadecenylsuccinic acid; long-chain α,ω-icarboxylic acids in the molecular weight range of 600 to 3000; and other similar materials. Products of this type are currently available from various commercial sources, such as, for example, the dimer and trimer acids sold under the HYSTRENE trademark by the Humco Chemical Division of Witco Chemical Corporation and under the EMPOL trademark by Emery Chemicals. Another useful type of acidic corrosion inhibitors are the half esters of alkenyl succinic acids having 8 to 24 carbon atoms in the alkenyl group with alcohols such as the polyglycols. The corresponding half amides of such alkenyl succinic acids are also useful. Although added in acidic form, some or all of the carboxylic groups of these carboxylic acid type corrosion inhibitors may be neutralized by excess amine present in the compositions. Other suitable corrosion inhibitors include ether amines; acid phosphates; amines; polyethoxylated compounds such as ethoxylated amines, ethoxylated phenols, and ethoxylated alcohols; and imidazolines. Materials of these types are well known to those skilled in the art and a number of such materials are available as articles of commerce.

Other useful corrosion inhibitors are aminosuccinic acids or derivatives thereof represented by the formula:



$$\begin{array}{ccccccc} & & R^6 & & O & & \\ & & | & & \| & & \\ & R^7 - & C & - & C & - & OR^5 \\ & & | & & & & \\ R^4R^3{>}N & - & C & - & C & - & OR^1 \\ & & | & & \| & & \\ & & R^2 & & O & & \end{array}$$

wherein each of R^1, R^2, R^5, R^6 and R^7 is, independently, a hydrogen atom or a hydrocarbyl group containing 1 to 30 carbon atoms, and wherein each of R^3 and R^4 is, independently, a hydrogen atom, a hydrocarbyl group containing 1 to 30 carbon atoms, or an acyl group containing from 1 to 30 carbon atoms. The groups R^1, R^2,

R^3, R^4, R^5, R^6 and R^7, when in the form of hydrocarbyl groups, can be, for example, alkyl, cycloalkyl or aromatic containing groups. Preferably R^1 and R^5 are the same or different straight-chain or branched-chain hydrocarbon radicals containing 1-20 carbon atoms. Most preferably, R^1 and R^5 are saturated hydrocarbon radicals containing 3-6 carbon atoms. R^2, either R^3 or R^4, R^6 and R^7, when in the form of hydrocarbyl groups, are preferably the same or different straight-chain or branched-chain saturated hydrocarbon radicals. Preferably a dialkyl ester of an aminosuccinic acid is used in which R^1 and R^5 are the same or different alkyl groups containing 3-6 carbon atoms, R^2 is a hydrogen atom, and either R^3 or R^4 is an alkyl group containing 15-20 carbon atoms or an acyl group which is derived from a saturated or unsaturated carboxylic acid containing 2-10 carbon atoms.

Most preferred of the aminosuccinic acid derivatives is a dialkylester of an aminosuccinic acid of the above formula wherein R^1 and R^5 are isobutyl, R^2 is a hydrogen atom, R^3 is octadecyl and/or octadecenyl and R^4 is 3-carboxy-1-oxo-2-propenyl. In such ester R^6 and R^7 are most preferably hydrogen atoms.

E) Antifoam agents.

Suitable antifoam agents include silicones and organic polymers such as acrylate polymers. Various antifoam agents are described in Foam Control Agents by H.T. Kerner (Noyes Data Corporation, 1976, pages 125-176). Mixtures of silicone-type antifoam agents such as the liquid dialkyl silicone polymers with various other substances are also effective. Typical of such mixtures are silicones mixed with an acrylate polymer, silicones mixed with one or more amines, and silicones mixed with one or more amine carboxylates.

F) Friction modifiers.

These materials include such substances as the alkyl phosphonates as disclosed in U.S. Pat. No. 4,356,097, aliphatic hydrocarbyl-substituted succinimides derived from ammonia or alkyl monoamines as disclosed in European Patent Publication No. 20037, dimer acid esters as disclosed in U.S. Pat. 4,105,571, and oleamide. Such additives, when used are generally present in amounts of 0.1 to 3 weight percent. Glycerol oleates are another example of fuel economy additives and these are usually present in very small amounts, such as 0.05 to 1 weight percent based on the weight of the formulated oil.

Other suitable friction modifiers include aliphatic amines or ethoxylated aliphatic amines, aliphatic fatty acid amides, aliphatic carboxylic acids, aliphatic carboxylic esters, aliphatic carboxylic ester-amides, aliphatic phosphates, aliphatic thiophosphonates, aliphatic thiophosphates, etc., wherein the aliphatic group usually contains above about eight carbon atoms so as to render the compound suitably oil soluble.

A desirable friction modifier additive combination which may be used in the practice of this invention is described in European Patent Publication No. 389,237. This combination involves use of a long chain succinimide derivative and a long chain amide.

G) Seal swell agents.

Additives may be introduced into the compositions of this invention in order to improve the seal performance (elastomer compatibility) of the compositions. Known materials of this type include dialkyl diesters such as dioctyl sebacate, aromatic hydrocarbons of suitable viscosity such as Panasol AN-3N, products such as Lubrizol 730, polyol esters such as Emery 2935, 2936, and 2939 esters from the Emery Group of Henkel Corp. and Hatcol 2352, 2962, 2925, 2938, 2939, 2970, 3178, and 4322 polyol esters from Hatco Corp. Generally speaking the most suitable diesters include the adipates, azelates, and sebacates of C_8-C_{13} alkanols (or mixtures thereof), and the phthalates of C_4-C_{13} alkanols (or mixtures thereof). Mixtures of two or more different types of diesters (e.g., dialkyl adipates and dialkyl azelates, etc.) can also be used. Examples of such materials include the n-octyl, 2-ethylhexyl, isodecyl, and tridecyl diesters of adipic acid, azelaic acid, and sebacic acid, and the n-butyl, isobutyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, and tridecyl diesters of phthalic acid.

H) Viscosity index improvers.

Depending upon the viscosity grade required, the lubricant compositions can contain one or more viscosity index improvers (polymeric materials which are often supplied in the form of a solution in a solvent or carrier fluid). Among the numerous types of materials known for such use are hydrocarbon polymers grafted with, for example, nitrogen-containing polymers, olefin polymers such as polybutene, ethylene-propylene copolymers, hydrogenated polymers and copolymers and terpolymers of styrene with isoprene and/or butadiene, polymers of alkyl acrylates or alkyl methacrylates, copolymers of alkyl methacrylates with N-vinyl pyrrolidone or dimethylaminoalkyl methacrylate; post-grafted polymers of ethylene-propylene with an active monomer such as maleic anhydride which may be further reacted with an alcohol or an alkylene polyamine; and styrene/maleic anhydride polymers post-treated with alcohols and/or amines.

Dispersant viscosity index improvers, which combine the activity of dispersants and viscosity index improvers, suitable for use in the compositions of this invention are described, for example, in U.S. Pat. Nos. 3,702,300; 4,068,056; 4,068,058; 4,089,794; 4,137,185; 4,146,489; 4,149,984; 4,160,739; and 4,519,929.

I) Pour point depressants.

Another useful type of additive which can be included in compositions of this invention is one or more pour point depressants. The use of pour point depressants in oil-base compositions to improve the low temperature properties of the compositions is well known to the art. See, for example, the books Lubricant Additives by C. V. Smalheer and R. Kennedy Smith (Lezius-Hiles Co. Publishers, Cleveland, Ohio, 1967); Gear and Transmission Lubricants by C. T. Boner (Reinhold Publishing Corp., New York, 1964); and Lubricant Additives by M. W. Ranney (Noyes Data Corporation, New Jersey, 1973). Among the types of compounds which function satisfactorily as pour point depressants in the compositions of this invention are polymethacrylates, polyacrylates, condensation products of haloparaffin waxes and aromatic compounds, and vinyl carboxylate polymers. Also useful as pour point depressants are terpolymers made by polymerizing a dialkyl fumarate, vinyl ester of a fatty acid and a vinyl alkyl ether. Techniques for preparing such polymers and their uses are disclosed in U.S. Pat. No. 3,250,715.

J) Other metal corrosion inhibitors.

In order to protect such metallic as lead, cadmium, aluminum, magnesium, silver, zinc and alloys thereof etc., special corrosion inhibitors can be used. These include such substances as gallic acid esters, and phthalic acid esters.

The above description of other additives which can be used in the compositions of this invention is not to be construed as limitive, as many other types of additives can be used in such compositions. The only requirements are that such other additives not excessively interfere with the performance of the compositions of this invention and that they exhibit suitable compatibility with the additives otherwise being employed therein.

K) Free Amine.

The free amines which can be employed in the compositions of this invention can be any of the amines referred to above in connection with the amine salts of partial esters of phosphoric acid or thiophosphoric acids or in connection with the amine salts of carboxylic acids, provided that the amines are oil-soluble. Of the various amines, the preferred type is composed of alkyl primary monoamines, and alkenyl primary monoamines, especially those containing from 6 to 24 carbon atoms. Examples of such amines include hexylamine, octylamine, nonylamine, decylamine, undecylamine, dodecylamine, tridecylamine, tetradecylamine, pentadecylamine, hexadecylamine, heptadecylamine, octadecylamine, eicosylamine, docosylamine, tetracosylamine, oleylamine, cocoamine, soyamine, C_{12-14} tertiary alkyl primary amine, and C_{22-24} tertiary alkyl primary amine.

Generally speaking, the free amine used in the compositions will correspond to the amine used in forming either the amine salt of the phosphorus acid or the amine salt of the carboxylic acid, or both.

The term "free amine" refers to the form of the amine as it is charged into the blender or mixing vessel in which the additive concentrate or the lubricating oil or functional fluid composition is being formed. Some or all of the free amine may complex with or react with other components being used in the product being formed, such as acidic additive components. Thus the term "free amine" does not signify or imply that the amine must remain free -- all or part of it may remain uncomplexed and unreacted, but this is not a requirement.

Base oils

The additive combinations of this invention can be incorporated in a wide variety of lubricants and functional fluids in effective amounts to provide suitable active ingredient concentrations. The base oils not only can be hydrocarbon oils of lubricating viscosity derived from petroleum (or tar sands, coal, shale, etc.), but also can be natural oils of suitable viscosities such as rapeseed oil, etc., and synthetic oils such as hydrogenated polyolefin oils; poly-α-olefins (e.g., hydrogenated or unhydrogenated α-olefin oligomers such as hydrogenated poly-1-decene); alkyl esters of dicarboxylic acids; complex esters of dicarboxylic acid, polyglycol and alcohol;

alkyl esters of carbonic or phosphoric acids; polysilicones; fluorohydrocarbon oils; and mixtures of mineral, natural and/or synthetic oils in any proportion, etc. The term "base oil" for this disclosure includes all the foregoing.

The additive combinations of this invention can thus be used in lubricating oil and functional fluid compositions, such as automotive crankcase lubricating oils, automatic transmission fluids, gear oils, hydraulic oils, cutting oils, etc., in which the base oil of lubricating viscosity is a mineral oil, a synthetic oil, a natural oil such as a vegetable oil, or a mixture thereof, e.g., a mixture of a mineral oil and a synthetic oil.

Suitable mineral oils include those of appropriate viscosity refined from crude oil of any source including Gulf Coast, Midcontinent, Pennsylvania, California, Alaska, Middle East, North Sea, etc. Standard refinery operations may be used in processing the mineral oil. Among the general types of petroleum oils useful in the compositions of this invention are solvent neutrals, bright stocks, cylinder stocks, residual oils, hydrocracked base stocks, paraffin oils including pale oils, and solvent extracted naphthenic oils. Such oils and blends of them are produced by a number of conventional techniques which are widely known by those skilled in the art.

As is noted above, the base oil can consist essentially of or comprise a portion of one or more synthetic oils. Among the suitable synthetic oils are homo- and inter-polymers of C_2-C_{12} olefins, carboxylic acid esters of both monoalcohols and polyols, polyethers, silicones, polyglycols, silicates, alkylated aromatics, carbonates, thiocarbonates, orthoformates, phosphates and phosphites, borates and halogenated hydrocarbons. Representative of such oils are homo- and interpolymers of C_2-C_{12} monoolefinic hydrocarbons, alkylated benzenes (e.g., dodecyl benzenes, didodecyl benzenes, tetradecyl benzenes, dinonyl benzenes, di-(2-ethylhexyl)benzenes, wax-alkylated naphthalenes); and polyphenyls (e.g., biphenyls, terphenyls).

Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc., constitute another class of synthetic oils. These are exemplified by the oils prepared through polymerization of alkylene oxides such as ethylene oxide or propylene oxide, and the alkyl and aryl ethers of these polyoxyalkylene polymers (e.g., methyl polyisopropylene glycol ether having an average molecular weight of 1000, diphenyl ether of polyethylene glycol having a molecular weight of 500-1000, diethyl ether of polypropylene glycol having a molecular weight of 1000-1500) or mono- and poly-carboxylic esters thereof, for example, the acetic acid ester, mixed C_3-C_6 fatty acid esters, or the C_{13} Oxo acid diester of tetraethylene glycol.

Another suitable class of synthetic oils comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol). Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl) adipate, didodecyl adipate, di(tridecyl) adipate, di(2-ethylhexyl) sebacate, dilauryl sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, di(eicosyl) sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid.

Other esters which may be used include those made from C_3-C_{18} monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylolpropane, pentaerythritol and dipentaerythritol. Trimethylol propane tripelargonate, pentaerythritol tetracaproate, the ester formed from trimethylolpropane, caprylic acid and sebacic acid, and the polyesters derived from a C_4-C_{14} dicarboxylic acid and one or more aliphatic dihydric C_3-C_{12} alcohols such as derived from azelaic acid or sebacic acid and 2,2,4-trimethyl-1,6-hexanediol serve as examples.

Silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy-, or polyaryloxy-siloxane oils and silicate oils comprise another class of synthetic lubricants (e.g., tetraethyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl) silicate, tetra-(p-tert-butylphenyl) silicate, poly(methyl)siloxanes, and poly(methylphenyl)siloxanes. Other synthetic lubricating oils include liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, triphenyl phosphite, and diethyl ester of decane phosphonic acid.

Also useful as base oils or as components of base oils are hydrogenated or unhydrogenated liquid oligomers of C_6-C_{16} α-olefins, such as hydrogenated or unhydrogenated oligomers formed from 1-decene. Methods for the production of such liquid oligomeric 1-alkene hydrocarbons are known and reported in the literature. See for example U. S. Pat. Nos. 3,749,560; 3,763,244; 3,780,128; 4,172,855; 4,218,330; 4,902,846; 4,906,798; 4,910,355; 4,911,758; 4,935,570; 4,950,822; 4,956,513; and 4,981,578. Additionally, hydrogenated 1-alkene oligomers of this type are available as articles of commerce, e.g., under the trade designations ETHYLFLO 162, ETHYLFLO 164, ETHYLFLO 166, ETHYLFLO 168, ETHYLFLO 170, ETHYLFLO 174, and ETHYLFLO 180 poly-α-olefin oils (Ethyl Corporation; Ethyl Canada Limited; Ethyl S.A.). Blends of such materials can also be used in order to adjust the viscometrics of the given base oil. Suitable 1-alkene oligomers are also available from other suppliers. As is well known, hydrogenated oligomers of this type contain little, if any, residual ethylenic unsaturation.

Preferred oligomers are formed by use of a Friedel-Crafts catalyst (especially boron trifluoride promoted with water or a C_{1-20} alkanol) followed by catalgic hydrogenation of the oligomer so formed using procedures such as are described in the foregoing U.S. patents.

Other catalyst systems which can be used to form oligomers of 1-alkene hydrocarbons, which, on hydrogenation, provide suitable oleaginous liquids include Ziegler catalysts such as ethyl aluminum sesquichloride with titanium tetrachloride, aluminum alkyl catalysts, chromium oxide catalysts on silica or alumina supports and a system in which a boron trifluoride catalyst oligomerization is followed by treatment with an organic peroxide.

It is also possible in accordance with this invention to utilize blends of one or more liquid hydrogenated 1-alkene oligomers in combination with other oleaginous materials having suitable viscosities, provided that the resultant blend has suitable compatibility and possesses the physical properties desired.

Typical natural oils that may be used as base oils or as components of the base oils include castor oil, olive oil, peanut oil, rapeseed oil, corn oil, sesame oil, cottonseed oil, soybean oil, sunflower oil, safflower oil, hemp oil, linseed oil, tung oil, oiticica oil, jojoba oil, and meadowfoam oil. Such oils may be partially or fully hydrogenated, if desired.

The fact that the base oils used in the compositions of this invention may be composed of (i) one or more mineral oils, (ii) one or more synthetic oils, (iii) one or more natural oils, or (iv) a blend of (i) and (ii), or (i) and (iii), or (ii) and (iii), or (i), (ii) and (iii) does not mean that these various types of oils are necessarily equivalents of each other. Certain types of base oils may be used in certain compositions for the specific properties they possess such as high temperature stability, non-flammability or lack of corrosivity towards specific metals (e.g., silver or cadmium). In other compositions, other types of base oils may be preferred for reasons of availability or low cost. Thus, the skilled artisan will recognize that while the various types of base oils discussed above may be used in the compositions of this invention, they are not necessarily functional equivalents of each other in every instance.

Proportions and Concentrations

In general, the components of the additive compositions of this invention are employed in the oleaginous liquids (e.g., lubricating oils and functional fluids) in minor amounts sufficient to improve the performance characteristics and properties of the base oil or fluid. When employing free amine, the amount employed is most preferably the amount sufficient to render the pH (determined as described hereinafter) of the finished additive concentrate as formed within the range of 4 to 9. The amounts of the other components will vary in accordance with such factors as the viscosity characteristics of the base oil or fluid employed, the viscosity characteristics desired in the finished product, the service conditions for which the finished product is intended, and the performance characteristics desired in the finished product. However, generally speaking, when using component a-1) or a-3), the following concentrations (weight percent) of the components (active ingredients) in the base oils or fluids are illustrative:

	Typical Range	Preferred Range
P- & B-contg dispersant	1 - 7	2 - 5
S-contg antiwear/E.P. agent	2 - 6	3 - 4
Amine salt of P-contg acid-ester	0 - 3	0 - 2
Trihydrocarbyl dithiophosphate	0 - 3	0 - 2
Amine salt of carboxylic acid	0 - 1	0.01 - 2
Demulsifier	0 - 1	0 - 0.2
Cu corrosion inhibitor	0 - 0.5	0.01 - 0.2
Supplemental P-antiwear/E.P. agent	0 - 0.7	0.05 - 0.4
Supplemental ashless dispersant	0 - 3	0 - 2
Antioxidant	0 - 2	0 - 1
Rust inhibitor	0 - 2	0.02 - 1
Antifoam agent	0 - 0.3	0.0002 - 0.1
Friction modifier	0 - 3	0 - 1
Seal swell agent	0 - 20	0 -10
Viscosity index improver	0 - 20	0 - 15
Pour point depressant	0 - 2	0 - 1
Other metal corrosion inhibitors	0 - 1	0 - 0.5
Free amine	0 - 2	0.3 - 1

Likewise, generally speaking, when using component a-2) or a-4), the following concentrations (weight percent) of the components (active ingredients) in the base oils or fluids are illustrative:

	Typical Range	Preferred Range
P-contg dispersant	1 - 7	2 - 5
S-contg antiwear/E.P. agent	2 - 6	3 - 4
Amine salt of P-contg acid-ester	0 - 3	0 - 2
Trihydrocarbyl dithiophosphate	0 - 3	0 - 2
Amine salt of carboxylic acid	0 - 1	0.01 - 2
Demulsifier	0 - 1	0 - 0.2
Cu corrosion inhibitor	0 - 0.5	0.01 - 0.2
B-contg additive	0 - 5	0 - 2
Supplemental P-antiwear/E.P. agent	0 - 0.7	0.05 - 0.4
Supplemental ashless dispersant	0 - 3	0 - 2
Antioxidant	0 - 2	0 - 1
Rust inhibitor	0 - 2	0.02 - 1
Antifoam agent	0 - 0.3	0.0002 - 0.1
Friction modifier	0 - 3	0 - 1
Seal swell agent	0 - 20	0 - 10
Viscosity index improver	0 - 20	0 - 15
Pour point depressant	0 - 2	0 - 1
Other metal corrosion inhibitors	0 - 1	0 - 0.5
Free amine	0 - 2	0.3 - 1

The individual components can be separately blended into the base oil or fluid or can be blended therein in various subcombinations, if desired. Moreover, such components can be blended in the form of separate solutions in a diluent. Except for viscosity index improvers and/or pour point depressants (which in many instances are blended apart from other components), it is preferable to blend the other selected components into the base oil by use of an additive concentrate of this invention, as this simplifies the blending operations, reduces the likelihood of blending errors, and takes advantage of the compatibility and solubility characteristics afforded by the overall concentrate.

The additive concentrates of this invention will contain the individual components in amounts proportioned to yield finished oil or fluid blends consistent with the concentrations tabulated above. In most cases, the additive concentrate will contain one or more diluents such as light mineral oils, to facilitate handling and blending of the concentrate. Thus concentrates containing up to 50% by weight of one or more diluents or solvents can be used.

The oleaginous liquids provided by this invention can be used in a variety of applications. For example, they can be employed as crankcase lubricants, gear oils, hydraulic fluids, manual transmission fluids, automatic transmission fluids, cutting and machining fluids, brake fluids, shock absorber fluids, heat transfer fluids, quenching oils, and transformer oils. The compositions are particularly suitable for use as automotive and industrial gear oils.

Blending

The formulation or blending operations are relatively simple and involve mixing together in a suitable container or vessel, using a dry, inert atmosphere where necessary or desirable, appropriate proportions of the selected ingredients. Those skilled in the art are cognizant of and familiar with the procedures suitable for formulating and blending additive concentrates and lubricant compositions. Usually the order of addition of components to the blending tank or vessel is not critical provided of course, that the components being blended at any given time are not incompatible or excessively reactive with each other. Agitation such as with mechanical stirring equipment is desirable to facilitate the blending operation. Frequently it is helpful to apply sufficient heat to the blending vessel during or after the introduction of the ingredients thereto, so as to maintain the temperature at, say, 40-60°C, and preferably no higher than about 60°C. Similarly, it is sometimes helpful to preheat highly viscous components to a suitable temperature even before they are introduced into the blending vessel in order to render them more fluid and thereby facilitate their introduction into the blending vessel and render the resultant mixture easier to stir or blend. Naturally the temperatures used during the blending operations should be controlled so as not to cause any significant amount of thermal degradation or unwanted chemical interactions.

When forming the lubricant compositions of this invention, it is usually desirable to introduce the additive ingredients into the base oil with stirring and application of mildly elevated temperatures, as this facilitates the dissolution of the components in the oil and achievement of product uniformity.

The following examples illustrate preferred additive concentrates and oleaginous compositions containing such concentrates. These examples are not intended to limit, and should not be construed as limiting, this invention.

EXAMPLE I

To a reaction vessel are charged 38.0 parts of sulfurized isobutylene, 14.0 parts of a product formed by reaction of dicyclopentadiene with dithiophosphoric acid-0,0-dialkyl ester in which on a molar basis 40% of the alkyl groups are isopropyl, 40% are isobutyl and 20% are 2-ethylhexyl, 4.76 parts of dibutyl hydrogen phosphite, and 1.75 parts of 2-ethylhexyl acid phosphate. Throughout this addition, the components of the reaction vessel are agitated and maintained at 30°C for 10 minutes. To this mixture is added 6.0 parts of a product composed of C_{12} and C_{14} tertiary alkyl monoamines (Primene® 81R amine; Rohm & Haas), and the mixture is stirred for 20 minutes without application of heat. Then another 4.9 parts of this tertiary alkyl monoamine product is added and the contents of the reaction vessel are maintained at 50°C for 1 hour with continuous stirring. While cooling the vessel contents to 40°C, 4.31 parts of oleic acid and 0.58 part of antifoam agent (M530; Monsanto Company) are added. Then, without application of heat, 1.8 parts of 2-tert-dodecyldithio-5-mercapto-1,3,4-thiadiazole, 12.3 parts of a phosphorylated and boronated composition formed as in Example 44 hereinabove, 0.77 parts of an ethylene oxide-propylene oxide block copolymer (Pluronic L-121 demulsifier; BASF Corporation) and 11.53 parts of process oil are added to the contents of the reaction vessel. The resulting additive concentrate of this invention is stirred for 60 minutes to insure homogeneity.

EXAMPLE II

To a reaction vessel are charged 38.3 parts of sulfurized isobutylene, 14.3 parts of di-tert-nonyl polysulfide, 5.7 parts of dibutyl hydrogen phosphite, 0.1 part of tolyltriazole, and 2.9 parts of amyl acid phosphate. Throughout this addition, the components of the reaction vessel are agitated and maintained at 30°C for 10 minutes. To this mixture are added 3.7 parts of C_{12} and C_{14} tertiary alkyl monoamines (Primene® 81R amine), 3.7 parts of C_{16} and C_{18} primary amines, 1.0 part of octyl amine, and 3.2 parts of process oil, and the mixture is stirred for 20 minutes while maintaining the contents of the reaction vessel at 50°C for 1 hour with continuous stirring. Then, while cooling the contents to 40°C, 0.6 part of C_{36} dimer acid, 0.6 part of caprylic acid, 1.0 part of antifoam agent (M530), and 3.2 parts of process oil are added. Thereafter, without application of heat, 2.7 parts of 2-tert-dodecyldithio-5-mercapto-1,3,4-thiadiazole, 12.2 parts of a phosphorylated and boronated ashless dispersant formed as in Example 44 hereinabove, 0.5 part of ethylene oxide-propylene oxide block copolymer (Pluronic L-101 demulsifier; BASF Corporation), 2.9 parts of phenolic antioxidant (ETHYL® antioxidant 733) and 3.4 parts of process oil are added to the contents of the reaction vessel. The resulting additive concentrate of this invention is stirred for 60 minutes.

EXAMPLE III

To a reaction vessel are charged 35.8 parts of sulfurized isobutylene, 3.6 parts of dibutyl hydrogen phosphite, 18.9 parts of a product formed by reaction of dicyclopentadiene with dithiophosphoric acid-0,0-dialkyl ester in which on a molar basis 40% of the alkyl groups are isopropyl, 40% are isobutyl and 20% are 2-ethylhexyl, and 1.7 parts of 2-ethylhexyl acid phosphate. Throughout this addition, the components of the reaction vessel are agitated and maintained at 30°C for 10 minutes. To this mixture are added 3.9 parts of C_{16} and C_{18} primary amines, 0.7 part of octyl amine, and 9.1 parts of process oil, and the mixture is stirred for 20 minutes while maintaining the contents of the reaction vessel at 50°C for 1 hour with continuous stirring. Then, while cooling the contents to 40°C, 0.7 part of caprylic acid, 0.7 part of acrylate copolymer (M544 defoamer), and 5.8 parts of process oil are added. Thereafter, without application of heat, 12.0 parts of a phosphorylated and boronated ashless dispersant formed as in Example 44 hereinabove, 1.5 parts of 2-tert-dodecyldithio-5-

mercapto-1,3,4-thiadiazole, 0.8 part of hydrogenated castor oil ethoxylate (Chemax HCO-5; Chemax, Inc.), and 4.8 parts of process oil are added to the contents of the reaction vessel. The resulting additive concentrate of this invention is stirred for 60 minutes.

EXAMPLE IV

To a reaction vessel are charged 35.1 parts of sulfurized isobutylene, 3.8 parts of dibutyl hydrogen phosphite, 16.6 parts of a product formed by reaction of dicyclopentadiene with dithiophosphoric acid-0,0-dialkyl ester in which on a molar basis 40% of the alkyl groups are isopropyl, 40% are isobutyl and 20% are 2-ethylhexyl, and 1.0 part of 2-ethylhexyl acid phosphate. Throughout this addition, the components of the reaction vessel are agitated and maintained at 30°C for 10 minutes. To this mixture are added 3.3 parts of C_{16} and C_{18} primary amines, and 8.3 parts of process oil, and the mixture is stirred for 20 minutes while maintaining the contents of the reaction vessel at 50°C for 1 hour with continuous stirring. Then, while cooling the contents to 40°C, 0.6 part of caprylic acid, 0.6 part of acrylate copolymer (M544 defoamer), and 8.3 parts of process oil are added. Thereafter, without application of heat, 12.8 parts of a phosphorylated and boronated ashless dispersant formed as in Example 44 hereinabove, 1.3 parts of 2-tert-dodecyldithio-5-mercapto-1,3,4-thiadiazole, and 8.3 parts of process oil are added to the contents of the reaction vessel. The resulting additive concentrate of this invention is stirred for 60 minutes.

EXAMPLE V

To a reaction vessel are charged 38.0 parts of sulfurized isobutylene, 14.0 parts of a product formed by reaction of dicyclopentadiene with dithiophosphoric acid-0,0-dialkyl ester in which on a molar basis 40% of the alkyl groups are isopropyl, 40% are isobutyl and 20% are 2-ethylhexyl, 4.76 parts of dibutyl hydrogen phosphite, and 1.75 parts of 2-ethylhexyl acid phosphate. Throughout this addition, the components of the reaction vessel are agitated and maintained at 30°C for 10 minutes. To this mixture is added 6.0 parts of a product composed of C_{12} and C_{14} tertiary alkyl monoamines (Primene® 81R amine), and the mixture is stirred for 20 minutes without application of heat. Then another 4.9 parts of this tertiary alkyl monoamine product is added and the contents of the reaction vessel are maintained at 50°C for 1 hour with continuous stirring. While cooling the vessel contents to 40°C, 4.31 parts of oleic acid and 0.58 part of antifoam agent (M530) are added. Then, without application of heat, 1.8 parts of 2-tert-dodecyldithio-5-mercapto-1,3,4-thiadiazole, 12.3 parts of a phosphorylated composition formed as in Example 51 hereinabove, 0.77 parts of an ethylene oxidepropylene oxide block copolymer (Pluronic L-121 demulsifer) and 11.53 parts of process oil are added to the contents of the reaction vessel. The resulting additive concentrate of this invention is stirred for 60 minutes to insure homogeneity.

EXAMPLE VI

To a reaction vessel are charged 38.3 parts of sulfurized isobutylene, 14.3 parts of di-tert-nonyl polysulfide, 5.7 parts of dibutyl hydrogen phosphite, 0.1 part of tolyltriazole, and 2.9 parts of amyl acid phosphate. Throughout this addition, the components of the reaction vessel are agitated and maintained at 30°C for 10 minutes. To this mixture are added 3.7 parts of C_{12} and C_{14} tertiary alkyl monoamines (Primene® 81R amine), 3.7 parts of C_{16} and C_{18} primary amines, 1.0 part of octyl amine, and 3.2 parts of process oil, and the mixture is stirred for 20 minutes while maintaining the contents of the reaction vessel at 50°C for 1 hour with continuous stirring. Then, while cooling the contents to 40°C, 0.6 part of C_{36} dimer acid, 0.6 part of caprylic acid, 1.0 part of antifoam agent (M530), and 3.2 parts of process oil are added. Thereafter, without application of heat, 2.7 parts of 2-tert-dodecyldithio-5-mercapto-1,3,4-thiadiazole, 12.2 parts of a phosphorylated ashless dispersant formed as in Example 51 hereinabove, 0.5 part of ethylene oxide-propylene oxide block copolymer (Pluronic L-101 demulsifier), 2.9 parts of phenolic antioxidant (ETHYL® antioxidant 733) and 3.4 parts of process oil are added to the contents of the reaction vessel. The resulting additive concentrate of this invention is stirred for 60 minutes.

EXAMPLE VII

To a reaction vessel are charged 35.8 parts of sulfurized isobutylene, 3.6 parts of dibutyl hydrogen phosphite, 18.9 parts of a product formed by reaction of dicyclopentadiene with dithiophosphoric acid-0,0-dialkyl ester in which on a molar basis 40% of the alkyl groups are isopropyl, 40% are isobutyl and 20% are 2-ethylhexyl, and 1.7 parts of 2-ethylhexyl acid phosphate. Throughout this addition, the components of the reaction vessel are agitated and maintained at 30°C for 10 minutes. To this mixture are added 3.9 parts of C_{16} and C_{18} primary amines, 0.7 part of octyl amine, and 9.1 parts of process oil, and the mixture is stirred for 20 minutes while maintaining the contents of the reaction vessel at 50°C for 1 hour with continuous stirring. Then, while cooling the contents to 40°C, 0.7 part of caprylic acid, 0.7 part of acrylate copolymer (M544 defoamer), and 5.8 parts of process oil are added. Thereafter, without application of heat, 12.0 parts of a phosphorylated ashless dispersant formed as in Example 51 hereinabove, 1.5 parts of 2-tert-dodecyldithio-5-mercapto-1,3,4-thiadiazole, 0.8 part of hydrogenated castor oil ethoxylate (Chemax HCO-5), and 4.8 parts of process oil are added to the contents of the reaction vessel. The resulting additive concentrate of this invention is stirred for 60 minutes.

EXAMPLE VIII

To a reaction vessel are charged 35.1 parts of sulfurized isobutylene, 3.8 parts of dibutyl hydrogen phosphite, 16.6 parts of a product formed by reaction of dicyclopentadiene with dithiophosphoric acid-0,0-dialkyl ester in which on a molar basis 40% of the alkyl groups are isopropyl, 40% are isobutyl and 20% are 2-ethylhexyl, and 1.0 part of 2-ethylhexyl acid phosphate. Throughout this addition, the components of the reaction vessel are agitated and maintained at 30°C for 10 minutes. To this mixture are added 3.3 parts of C_{16} and C_{18} primary amines, and 8.3 parts of process oil, and the mixture is stirred for 20 minutes while maintaining the contents of the reaction vessel at 50°C for 1 hour with continuous stirring. Then, while cooling the contents to 40°C, 0.6 part of caprylic acid, 0.6 part of acrylate copolymer (M544 defoamer), and 8.3 parts of process oil are added. Thereafter, without application of heat, 12.8 parts of a phosphorylated ashless dispersant formed as in Example 51 hereinabove, 1.3 parts of 2-tert-dodecyldithio-5-mercapto-1,3,4-thiadiazole, and 8.3 parts of process oil are added to the contents of the reaction vessel. The resulting additive concentrate of this invention is stirred for 60 minutes.

EXAMPLE IX

To a reaction vessel are charged 38.0 parts of sulfurized isobutylene, 14.0 parts of a product formed by reaction of dicyclopentadiene with dithiophosphoric acid-0,0-dialkyl ester in which on a molar basis 40% of the alkyl groups are isopropyl, 40% are isobutyl and 20% are 2-ethylhexyl, 4.76 parts of dibutyl hydrogen phosphite, and 1.75 parts of 2-ethylhexyl acid phosphate. Throughout this addition, the components of the reaction vessel are agitated and maintained at 30°C for 10 minutes. To this mixture is added 6.0 parts of a product composed of C_{12} and C_{14} tertiary alkyl monoamines (Primene® 81R amine), and the mixture is stirred for 20 minutes without application of heat. Then another 4.9 parts of this tertiary alkyl monoamine product is added and the contents of the reaction vessel are maintained at 50°C for 1 hour with continuous stirring. While cooling the vessel contents to 40°C, 4.31 parts of oleic acid and 0.58 part of antifoam agent (M530) are added. Then, without application of heat, 1.8 parts of 2-tert-dodecyldithio-5-mercapto-1,3,4-thiadiazole, 12.3 parts of a phosphorylated and boronated composition formed as in Example 140 hereinabove, 0.77 parts of an ethylene oxide-propylene oxide block copolymer (Pluronic L-121 demulsifier) and 11.53 parts of process oil are added to the contents of the reaction vessel. The resulting additive concentrate of this invention is stirred for 60 minutes to insure homogeneity.

EXAMPLE X

To a reaction vessel are charged 38.3 parts of sulfurized isobutylene, 14.3 parts of di-tert-nonyl polysulfrde, 5.7 parts of dibutyl hydrogen phosphite, 0.1 part of tolyltriazole, and 2.9 parts of amyl acid phosphate. Throughout this addition, the components of the reaction vessel are agitated and maintained at 30°C for 10 minutes. To this mixture are added 3.7 parts of C_{12} and C_{14} tertiary alkyl monoamines (Primene® 81R amine), 3.7 parts of C_{16} and C_{18} primary amines, 1.0 part of octyl amine, and 3.2 parts of process oil, and the mixture is stirred for 20 minutes while maintaining the contents of the reaction vessel at 50°C for 1 hour with continuous stirring. Then, while cooling the contents to 40°C, 0.6 part of C_{36} dimer acid, 0.6 part of caprylic acid, 1.0 part of antifoam agent (M530), and 3.2 parts of process oil are added. Thereafter, without application of heat, 2.7 parts of 2-tert-dodecyldithio-5-mercapto-1,3,4-thiadiazole, 12.2 parts of a phosphorylated and boronated ashless dispersant formed as in Example 140 hereinabove, 0.5 part of ethylene oxide-propylene oxide block copolymer (Pluronic L-101 demulsifier), 2.9 parts of phenolic antioxidant (ETHYL® antioxidant 733) and 3.4 parts of process oil are added to the contents of the reaction vessel. The resulting additive concentrate of this invention is stirred for 60 minutes.

EXAMPLE XI

To a reaction vessel are charged 35.8 parts of sulfurized isobutylene, 3.6 parts of dibutyl hydrogen phosphite, 18.9 parts of a product formed by reaction of dicyclopentadiene with dithiophosphoric acid-0,0-dialkyl ester in which on a molar basis 40% of the alkyl groups are isopropyl, 40% are isobutyl and 20% are 2-ethylhexyl, and 1.7 parts of 2-ethylhexyl acid phosphate. Throughout this addition, the components of the reaction vessel are agitated and maintained at 30°C for 10 minutes. To this mixture are added 3.9 parts of C_{16} and C_{18} primary amines, 0.7 part of octyl amine, and 9.1 parts of process oil, and the mixture is stirred for 20 minutes while maintaining the contents of the reaction vessel at 50°C for 1 hour with continuous stirring. Then, while cooling the contents to 40°C, 0.7 part of caprylic acid, 0.7 part of acrylate copolymer (M544 defoamer), and 5.8 parts of process oil are added. Thereafter, without application of heat, 12.0 parts of a phosphorylated and boronated ashless dispersant formed as in Example 140 hereinabove, 1.5 parts of 2-tert-dodecyldithio-5-mercapto-1,3,4-thiadiazole, 0.8 part of hydrogenated castor oil ethoxylate (Chemax HCO-5), and 4.8 parts of process oil are added to the contents of the reaction vessel. The resulting additive concentrate of this invention is stirred for 60 minutes.

EXAMPLE XII

To a reaction vessel are charged 35.1 parts of sulfurized isobutylene, 3.8 parts of dibutyl hydrogen phosphite, 16.6 parts of a product formed by reaction of dicyclopentadiene with dithiophosphoric acid-0,0-dialkyl ester in which on a molar basis 40% of the alkyl groups are isopropyl, 40% are isobutyl and 20% are 2-ethylhexyl, and 1.0 part of 2-ethylhexyl acid phosphate. Throughout this addition the components of the reaction vessel are agitated and maintained at 30°C for 10 minutes. To this mixture are added 3.3 parts of C_{16} and C_{18} primary amines, and 8.3 parts of process oil, and the mixture is stirred for 20 minutes while maintaining the contents of the reaction vessel at 50°C for 1 hour with continuous stirring. Then, while cooling the contents to 40°C, 0.6 part of caprylic acid, 0.6 part of acrylate copolymer (M544 defoamer), and 8.3 parts of process oil are added. Thereafter, without application of heat, 12.8 parts of a phosphorylated and boronated ashless dispersant formed as in Example 140 hereinabove, 1.3 parts of 2-tert-dodecyldithio-5-mercapto-1,3,4-thiadiazole, and 8.3 parts of process oil are added to the contents of the reaction vessel. The resulting additive concentrate of this invention is stirred for 60 minutes.

EXAMPLE XIII

To a reaction vessel are charged 38.0 parts of sulfurized isobutylene, 14.0 parts of a product formed by reaction of dicyclopentadiene with dithiophosphoric acid-0,0-dialkyl ester in which on a molar basis 40% of the alkyl groups are isopropyl, 40% are isobutyl and 20% are 2-ethylhexyl, 4.76 parts of dibutyl hydrogen phosphite, and 1.75 parts of 2-ethylhexyl acid phosphate. Throughout this addition, the components of the reaction vessel are agitated and maintained at 30°C for 10 minutes. To this mixture is added 6.0 parts of a product composed of C_{12} and C_{14} tertiary alkyl monoamines (Primene® 81R amine), and the mixture is stirred for 20 minutes without application of heat. Then another 4.9 parts of this tertiary alkyl monoamine product is added and the contents of the reaction vessel are maintained at 50°C for 1 hour with continuous stirring. While cooling the vessel contents to 40°C, 4.31 parts of oleic acid and 0.58 part of antifoam agent (M530) are added. Then, without application of heat, 1.8 parts of 2-tert-dodecyldithio-5-mercapto-1,3,4-thiadiazole, 12.3 parts of a phosphorylated and boronated composition formed as in Example 192 hereinabove, 0.77 parts of an ethylene oxide-propylene oxide block copolymer (Pluronic L-121 demulsifier) and 11.53 parts of process oil are added to the contents of the reaction vessel. The resulting additive concentrate of this invention is stirred for 60 minutes to insure homogeneity.

EXAMPLE XIV

To a reaction vessel are charged 38.3 parts of sulfurized isobutylene, 14.3 parts of di-tert-nonyl polysulfide, 5.7 parts of dibutyl hydrogen phosphite, 0.1 part of tolyltriazole, and 2.9 parts of amyl acid phosphate. Throughout this addition, the components of the reaction vessel are agitated and maintained at 30°C for 10 minutes. To this mixture are added 3.7 parts of C_{12} and C_{14} tertiary alkyl monoamines (Primene® 81R amine), 3.7 parts of C_{16} and C_{18} primary amines, 1.0 part of octyl amine, and 3.2 parts of process oil, and the mixture is stirred for 20 minutes while maintaining the contents of the reaction vessel at 50°C for 1 hour with continuous stirring. Then, while cooling the contents to 40°C, 0.6 part of C_{36} dimer acid, 0.6 part of caprylic acid, 1.0 part of antifoam agent (M530), and 3.2 parts of process oil are added. Thereafter, without application of heat, 2.7 parts of 2-

tert-dodecyldithio-5-mercapto-1,3,4-thiadiazole, 12.2 parts of a phosphorylated and boronated ashless dispersant formed as in Example 192 hereinabove, 0.5 part of ethylene oxide-propylene oxide block copolymer (Pluronic L-101 demulsifier), 2.9 parts of phenolic antioxidant (ETHYL® antioxidant 733) and 3.4 parts of process oil are added to the contents of the reaction vessel. The resulting additive concentrate of this invention is stirred for 60 minutes.

EXAMPLE XV

To a reaction vessel are charged 35.8 parts of sulfurized isobutylene, 3.6 parts of dibutyl hydrogen phosphite, 18.9 parts of a product formed by reaction of dicyclopentadiene with dithiophosphoric acid-0,0-dialkyl ester in which on a molar basis 40% of the alkyl groups are isopropyl, 40% are isobutyl and 20% are 2-ethylhexyl, and 1.7 parts of 2-ethylhexyl acid phosphate. Throughout this addition, the components of the reaction vessel are agitated and maintained at 30°C for 10 minutes. To this mixture are added 3.9 parts of C_{16} and C_{18} primary amines, 0.7 part of octyl amine, and 9.1 parts of process oil, and the mixture is stirred for 20 minutes while maintaining the contents of the reaction vessel at 50°C for 1 hour with continuous stirring. Then, while cooling the contents to 40°C, 0.7 part of caprylic acid, 0.7 part of acrylate copolymer (M544 defoamer), and 5.8 parts of process oil are added. Thereafter, without application of heat, 12.0 parts of a phosphorylated and boronated ashless dispersant formed as in Example 192 hereinabove, 1.5 parts of 2-tert-dodecyldithio-5-mercapto-1,3,4-thiadiazole, 0.8 part of hydrogenated castor oil ethoxylate (Chemax HCO-5), and 4.8 parts of process oil are added to the contents of the reaction vessel. The resulting additive concentrate of this invention is stirred for 60 minutes.

EXAMPLE XVI

To a reaction vessel are charged 35.1 parts of sulfurized isobutylene, 3.8 parts of dibutyl hydrogen phosphite, 16.6 parts of a product formed by reaction of dicyclopentadiene with dithiophosphoric acid-0,0-dialkyl ester in which on a molar basis 40% of the alkyl groups are isopropyl, 40% are isobutyl and 20% are 2-ethylhexyl, and 1.0 part of 2-ethylhexyl acid phosphate. Throughout this addition, the components of the reaction vessel are agitated and maintained at 30°C for 10 minutes. To this mixture are added 3.3 parts of C_{16} and C_{18} primary amines, and 8.3 parts of process oil, and the mixture is stirred for 20 minutes while maintaining the contents of the reaction vessel at 50°C for 1 hour with continuous stirring. Then, while cooling the contents to 40°C, 0.6 part of caprylic acid, 0.6 part of acrylate copolymer (M544 defoamer), and 8.3 parts of process oil are added. Thereafter, without application of heat, 12.8 parts of a phosphorylated and boronated ashless dispersant formed as in Example 192 hereinabove, 1.3 parts of 2-tert-dodecyldithio-5-mercapto-1,3,4-thiadiazole, and 8.3 parts of process oil are added to the contents of the reaction vessel. The resulting additive concentrate of this invention is stirred for 60 minutes.

EXAMPLE XVII

The effectiveness of the compositions of this invention was illustrated in several standard L-37 and L-42 tests. In one set of L-37 and L-42 tests, the composition was prepared by blending together the following components in which the proportions are by weight:

Phosphorylated ashless dispersant	4.00%
Sulfurized isobutylene	3.50%
Exxon 1365 mineral oil	28.68%
Exxon 2507 mineral oil (Bright Stock)	63.82%

The phosphorylated ashless dispersant was formed from a polyisobutenyl succinimide, viz., HiTEC® 646 additive (Ethyl Petroleum Additives, Inc.; Ethyl Petroleum Additives, Ltd.; Ethyl S.A.; Ethyl Canada Ltd.). Phosphorylation was accomplished in the manner of Example 51 using 2.7 parts by weight of HiTEC® 646 additive, 0.3 parts by weight of solid phosphorous acid (H_3PO_3), and 1 part by weight of process oil diluent. The slfurized isobutylene was HiTEC® 309 sulfurized isobutylene additive; (Ethyl Petroleum Additives, Inc.; Ethyl Petroleum Additives, Ltd.; Ethyl S.A.; Ethyl Canada Ltd.). This oil blend had kinematic viscosity at of 153.98 cSt at 40°C, and 16.63 cSt at 100°C.

The results in terms of numerical ratings of the L-37 test were as follows:

Description	Ring	Pinion
Ridging	0.00	0.00
Rippling	0.00	0.01
Spalling	0.00	0.00
Wear	0.01	0.01
Pitting	0.01	0.01
Scoring	0.00	0.00

The above numerical scale is as follows:

None = 0.00
Trace = 0.01
Light = 0.50
Medium = 5.00
Heavy = 10.00

The Ring-Gear Drive Side Inspection after completion of a High-Speed, Low Torque 100-minute run, was rated Satisfactory. The Pinion-Drive Side and Ring-Gear Drive Side Inspection after the complete test resulted in the following Gear-tooth surface condition ratings:

Description	Pinion	Ring Gear
Burnish	Heavy	Light
Wear	Trace	Trace
Surface fatigue		
a) Rippling	Trace	None
b) Ridging	None	None
c) Pitting	Trace	Trace
d) Spalling	None	None
Scoring	None	None
Discoloration	Light	Light
Corrosion	Trace	Trace
Deposits	None	None

Inspection before and after the complete test resulted in the following Backlash measurements:

Initial	0.004 cm
After test	0.005 cm

After the test the axle shafts, axle housing, carrier housing, pinion assembly, ring-gear assembly and differential assembly were rated in Good condition, the bearings (races) and differential pins showed Light discoloration and the bearings (rollers) showed Light discoloration with a Trace of corrosion.

In the L-42 test, the Sequence 3 inspection showed no scoring on either the drive side or the coast side of the ring gear. The end of test inpection gave the following results:

Ring Gear, Drive Side	4% scored
Ring Gear, Coast Side	6% scored
Pinion Gear, Drive Side	5% scored
Pinion Gear, Coast Side	8% scored

Another L-42 test was conducted using the same oil composition as above except that the sulfurized isobutylene was replaced by an equal amount of a di-tert-butyl polysufide composed mainly of the trisulfide. In this L-42 test, the Sequence 3 inspection showed no scoring on either the drive side or the coast side of the ring gear, and the end of test inpection showed the following:

Ring Gear, Drive Side	No Scoring
Ring Gear, Coast Side	10% scored
Pinion Gear, Drive Side	No Scoring
Pinion Gear, Coast Side	13% scored

These results are considered a pass, and actually are better than the results achieved with a passing reference oil.

The procedure used in determining pH of preferred additive concentrates of this invention involves diluting the sample of the composition in a mixture of methanol and toluene and then assaying "non-aqueous" pH with a conventional pH probe as used in aqueous systems.

Copper corrosion ratings for the purposes of this invention are conducted using the standard ASTM D-130 procedure modified to the extent that the additive concentrate to be tested is first stored in an oven for 120 hours at 65°C. Then the concentrate is blended into the test oil to the selected test concentration and the test is conducted at 121°C.

As used in the foregoing description, the term "oil-soluble" is used in the sense that the component in question has sufficient solubility in the selected base oil in order to dissolve therein at ordinary temperatures to a concentration at least equivalent to the minimum concentration specified herein for use of such component. Preferably, however, the solubility of such component in the selected base oil will be in excess of such minimum concentration, although there is no requirement that the component be soluble in the base oil in all proportions. As is well known to those skilled in the art, certain useful additives do not completely dissolve in base oils but rather are used in the form of stable suspensions or dispersions. Additives of this type can be employed in the compositions of this invention, provided they do not significantly interfere with the performance or usefulness of the composition in which they are employed.

Claims

1. An additive concentrate which comprises a minor proportion of diluent oil and a major proportion of additive components, said additive components comprising:

   a-1) at least one oil-soluble additive composition formed by heating concurrently or in any sequence at least one ashless dispersant which contains basic nitrogen and/or at least one hydroxyl group with (i) at least one inorganic phosphorus acid or anhydride, or at least one partial or total sulfur analog thereof, or any combination of the foregoing, and (ii) at least one boron compound; suck that a liquid composition is formed; or

   a-2) at least one oil-soluble boron-free additive composition formed by heating (i) at least one boron-free oil-soluble ashless dispersant containing basic nitrogen and/or at least one hydroxyl group, with (ii) at least one inorganic phosphorus acid such that a liquid boron-free phosphorus-containing composition is formed; or

   a-3) one or more oil-soluble additive compositions formed by heating concurrently or in any sequence at least one ashless dispersant which contains basic nitrogen and/or at least one hydroxyl group with (i) at least one water-hydrolyzable organic phosphorus compound and water; and (ii) at least one boron compound; such that a liquid phosphorus- and boron-containing composition is formed; or

   a-4) one or more oil-soluble boron-free additive compositions formed by heating concurrently or in any sequence (i) at least one boron-free oil-soluble ashless dispersant which contains basic nitrogen and/or at least one hydroxyl group, with (ii) -at least one water-hydrolyzable organic phosphorus compound and water; such that a liquid boron-free phosphorus-containing composition is formed; and

b) at least one oil-soluble metal-free sulfur-containing antiwear and/or extreme pressure agent having a sulfur content of at least 20% by weight;

components a-1), a-2), a-3), or a-4) and b) being proportioned such that the mass ratio (wt:wt) of sulfur in component b) to phosphorus in component a-1), a-2), a-3), or a-4)) is in the range of 8:1 to 30:1.

2. A composition according to Claim 1 wherein said mass ratio is in the range of 10:1 to 20:1.

3. A composition according to Claim 1 wherein said mass ratio is in the range of 14:1 to 20:1.

4. A composition according to any of Claims 1-3 wherein component a-1) is utilized.

5. A composition according to any one of Claims 1-3 wherein component a-2) is utilized.

6. A composition according to any one of Claims 1-3 wherein component a-3) is utilized.

7. A composition according to any one of Claims 1-3 wherein component a-4) is utilized.

8. A composition according to any one of Claims 1-7 wherein said additive components of said additive concentrate further comprise the following additive components:

c) at least one oil-soluble amine salt of a mono- or dihydrocarbyl ester of monomeric pentavalent acid of phosphorus;
d) at least one oil-soluble trihydrocarbyl ester of a dithiophosphoric acid;
e) at least one oil-soluble amine salt of a carboxylic acid;
f) at least one oil-soluble demulsifying agent; or
g) at least one oil-soluble copper corrosion inhibitor;

or a combination of any two, or any three, or any four, or all five of c), d), e), f), and g).

9. A composition according to Claim 5 or 7 wherein said additive components of said additive concentrate further comprise
the following additive components:

c) at least one oil-soluble amine salt of a mono- or dihydrocarbyl ester of a monomeric pentavalent acid of phosphorus;
d) at least one oil-soluble trihydrocarbyl ester of a dithiophosphoric acid;
e) at least one oil-soluble amine salt of a carboxylic acid;
f) at least one oil-soluble demulsifying agent;
g) at least one oil-soluble copper corrosion inhibitor; or
h) at least one oil-soluble or oil-dispersible boron-containing compound;

or a combination of any two, or any three, or any four, or any five or all six of c), d), e), f), g) and h).

10. An oleaginous composition which comprises a major proportion of at least one base oil of lubricating viscosity and a minor amount of additive components according to any of one Claims 1-9.

11. A composition according to Claim 10 wherein component b) is present in amount sufficient to provide a sulfur content in said base oil of at least about 1.0 weight percent based on the total weight of the oleaginous composition.

12. A method of lubricating relatively moving metallic surfaces in close proximity to each other which comprises providing for use or using as the lubricant for such surfaces an oleaginous composition in accordance with Claim 10 or 11.

13. The method of Claim 12 wherein said relatively moving metallic surfaces are comprised of mechanical energy transferring surfaces in close proximity to each other.

14. A mechanical apparatus which includes relatively moving metallic surfaces in close proximity to each other requiring lubrication and a lubricant therefor, wherein said lubricant is an oleaginous composition in accordance with Claim 10 or 11.

European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 92 30 7448

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
P,X	EP-A-0 492 934 (ETHYL) * page 43, line 14; claims 1,4,10,19 * * page 43, line 37 - line 38 * * page 36 - page 37 * ---	1,4,6, 8-14	C10M141/08 C10M141/10 C10M161/00 C10M163/00 C10M167/00 //(C10M129:95, 133:52,133:56, 135:02,135:04, 153:04,159:12B, 159:16) (C10N30:04,30:06 40:04,60:12, 60:14,70:00)
P,Y	EP-A-0 459 656 (ETHYL) * page 13, line 3; claims 1-10 * * page 13, line 16 * * page 13, line 36 - line 54 * * page 16, line 25 - line 40 * ---	1,4-14	
D,Y	EP-A-0 359 522 (ETHYL) * the whole document * ---	1,4,6, 8-14	
Y	EP-A-0 399 764 (ETHYL) * page 5, line 10 * ---	1,4,6, 8-14	
Y	EP-A-0 384 639 (ETHYL) * the whole document * ---	1,4-14	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
Y	EP-A-0 430 624 (ETHYL) * page 3, line 1 - line 5 * ---	1,4-14	C10M
A	EP-A-0 428 393 (ETHYL) * the whole document * ---	1-14	
A	US-A-4 058 468 (MALEC) * the whole document * -----	1	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	20 NOVEMBER 1992	DE LA MORINERIE

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document