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(54) **A low-phosphorus lubricating oil composition for extended drain intervals**

(57) The present invention is directed to a lubricating oil composition comprising a major amount of a base oil of lubricating viscosity and a minor amount of each of the following:

- a) from about 3.0 to about 7.0 weight percent of an ethylene carbonated-treated ashless dispersant;
- b) from about 2.0 to about 5.0 weight percent of a borated-treated ashless dispersant;

wherein the weight ratio of a) to b) is about 0.3 to about 0.5;

- c) from about 1.0 to about 3.0 weight percent of a

high overbased metal-containing detergent;
d) from about 0.1 to about 2.0 weight percent of a phosphorus-containing compound;

wherein the weight percent of total phosphorus in the lubricating oil composition is no more than 0.08 weight percent based on the total weight of the lubricating oil composition.

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Description

[0001] The present invention relates to lubricating oil compositions having improved wear, extreme pressure, and oxidation performance in internal combustion engines. In particular, the present invention relates to lubricating oil compositions for reducing wear and controlling oxidation in internal combustion engines lubricated with a low phosphorus content lubricating oil intended for extended drain interval applications and to methods employing such.

BACKGROUND OF THE INVENTION

[0002] Current passenger car motor oils meeting the American Petroleum Institute (API) "SL" or International Lubricant Standardization and Approval Committee (ILSAC) GF-3 specifications are designed for approximately 5,000 mile (8,000 kilometer) drain intervals or less depending on driving severity per Original Equipment Manufacturer (OEM) owner's manuals. These oils pass a rigorous series of industry-standard engine and bench tests documented within the Society of Automotive Engineers (SAE) Surface Vehicle Standard J183 (June 2001) and American Society For Testing and Materials (ASTM) D 4485-01 a (February 2002) to demonstrate, for example, oxidation stability, wear, sludge and varnish deposit control, among other requirements. However, significant increases in performance specifications are evolving. Next generation engine oils may soon meet the proposed ILSAC GF-4 specification.

[0003] With the increasing emphasis on oil conservation and the desire for more maintenance-free vehicles, there is a trend toward extending engine oil drain intervals. Current API SL quality engine oils provide good engine cleanliness and wear protection at normal drain intervals of 3,000 to 10,000 miles. However, problems with excessive oil thickening, increased engine sludge and /or varnish deposits, and engine wear become apparent for many SL products as recommended drain intervals are extended.

[0004] Extended oil drains are currently under consideration throughout the automotive lubrication industry and were part of early discussions regarding future engine oil specification requirements (ILSAC GF-4). Extension of oil change interval recommendations beyond 15,000 miles is now being discussed. OEMs are interested in extending the drain intervals on engine oils without compromising the deposit and wear performance of a lubricating oil composition. Of great importance to one OEM is protection of the engine during severe operating service, in rental fleets, or during lease periods where the operator has little incentive to maintain the vehicle properly. For example, one OEM would like engine oil in factory fill and service fill applications that can go at least 30,000 miles before the next engine oil change. This is particularly desirable in leased vehicles that sometimes go for extended intervals without an engine oil change at the proper recommended service interval. To provide a lubricating oil composition that meets this requirement and the ILSAC GF-4 specifications is an extreme challenge.

[0005] The problem of providing an extended service motor oil formulation is a serious one. In essence, an oil must be capable of providing satisfactory lubrication for a period of from three to six times as long as had been required in the past. At the same time it must maintain the crankcase as well as other parts of the engine free of harmful sludge deposits, and must afford protection against rust and corrosion as well as wear protection for engine parts such as valve lifters which are in extreme contact pressure. Moreover, long service motor oils must retain the characteristics of suitability for spark-ignition engines such as oxidation stability, viscosity maintenance, cold starting characteristics, certain combustion chamber control features, and oil mileage and fuel economy which consumers have come to expect from all premium grade oils. While additives are known which are capable of increasing one or perhaps two of these characteristics, there are many sources of specific interactions with other lubricant additives that careful and extensive experimentation leads to truly useful motor oil formulations suitable for the more severe extended service.

[0006] A key requirement in the proposed ILSAC GF-4 specification is that the phosphorus content be reduced from the currently allowable limit of 0.10 weight percent specified in the ILSAC GF-3 specification, to as low as 0.05 weight percent, because phosphorus and its derivatives poison catalyst components of catalytic converters. This is a major concern, because effective catalytic converters are needed to reduce pollution and to meet governmental regulations designed to reduce toxic gases, such as hydrocarbons, carbon monoxide, and nitrogen oxides, in internal combustion engine exhaust emissions. Such catalytic converters generally use a combination of catalytic metals such as platinum or its variations and metal oxides and are installed in the exhaust streams to convert the toxic gases to non-toxic gases. When the phosphorus content in the emission is excessive, the components of the catalytic converter become ineffective and may ultimately lose their intended function.

[0007] One additive class impacted by the new specification is the phosphorus-containing additives used in lubricating oil composition for internal combustion engines. Zinc dialkyldithiophosphates are, for example, contained in most of the commercially available internal combustion engine oils, especially those used for automobiles, because of their favorable characteristics as an anti-wear agent and performance as an oxidation inhibitor. It is generally employed in lubricating oils at phosphorus levels about 0.1 weight percent when used for wear control. A problem arises when the level of phosphorus is reduced containing the phosphorus-containing compound in that there is a significant reduction in anti-wear and oxidation control performance arising from this diminution in phosphorus content. Therefore, it is

necessary to find a way to reduce phosphorus content while still retaining the anti-wear and oxidation properties of higher phosphorus content engine oils.

[0008] To get more fuel efficiency from engines, even lower viscosity lubricants will be required. The only practical way to meet the combined requirements for an SAE 0W-20 engine oil is to use synthetic base fluids. Until recently, polyalphaolefin (PAO) base oils combination with ester fluids such as C₇-C₉ tetramethanolpropane esters were one way to meet SAE 0W-20 requirements while maintaining acceptable oil consumption and oxidation stability. The SAE 0W-20 viscosity grade represents the lowest viscosity grade that will likely be utilized by OEM in factory fill and service fill applications. This grade of engine oil will typically be formulated with polyalphaolefin (PAO) base oils because base oils derived from crude oil cannot meet the combination of volatility and low temperature requirements for this viscosity grade.

[0009] The present invention is directed to a lubricating oil composition having extended drain properties as evidenced by improved wear, extreme pressure, and oxidation performance.

SUMMARY OF THE INVENTION

[0010] The present invention provides a lubricating oil composition having improved wear, extreme pressure, and oxidation performance in internal combustion engines. More particularly, the present invention relates to lubricating oil compositions for reducing wear and controlling oxidation in internal combustion engines lubricated with a low phosphorus content lubricating oil intended for extended drain interval applications and to methods employing such.

[0011] Accordingly, in one of its composition aspects, the present invention is directed to a lubricating oil composition comprising a major amount of a base oil of lubricating viscosity and a minor amount of each of the following: -

- a) from about 3.0 to about 7.0 weight percent of an ethylene carbonated-treated ashless dispersant;
- b) from about 2.0 to about 5.0 weight percent of a borated-treated ashless dispersant;
- wherein the weight ratio of a) to b) is about 0.3 to about 0.5;
- c) from about 1.0 to about 3.0 weight percent of a high overbased metal-containing detergent;
- d) from about 0.1 to about 2.0 weight percent of a phosphorus-containing compound;

wherein the weight percent of total phosphorus in the lubricating oil composition is no more than 0.08 weight percent based on the total weight of the lubricating oil composition.

[0012] The lubricating oil composition of the present may further comprise a low overbased metal-containing detergent, a nitrogen-containing ashless antioxidant, an alkylthiocarbamoyl compound, a molybdenum-succinimide complex or mixtures thereof.

[0013] In a preferred embodiment, the total phosphorus in the composition is no more than 0.05 weight percent based on the total weight of the composition.

[0014] Preferably, the base oil of lubricating viscosity is selected from the group consisting of a Group III base stock, Group IV base stock, Group V base stock and any mixture thereof.

[0015] Preferably, the ashless dispersant is selected from the group consisting of an alkenyl succinimide, an alkenyl succinic anhydride, an alkenyl succinate ester, benzylamine or mixtures thereof. More preferably, the ashless dispersant is an alkenyl succinimide.

[0016] Preferably, the metal-containing detergent is a metal phenate or metal sulfonate. The metal sulfonate is more preferred.

[0017] Preferably, the oil-soluble, phosphorus-containing, anti-wear compound is selected from the group consisting of metal dithiophosphates, phosphorus esters (including phosphates, phosphonates, phosphinates, phosphine oxides, phosphites, phosphonites, phosphinites, phosphines and the like), amine phosphates and amine phosphinates, sulfur-containing phosphorus esters including phosphoro monothionate and phosphoro dithionates, phosphoramides, phosphonamides and the like. More preferably, the phosphorus-containing compound is a metal dithiophosphate and, even more preferably, a zinc dithiophosphate.

[0018] Preferably, the nitrogen-containing ashless antioxidant is an alkylated diphenylamine.

[0019] Preferably, the alkylthiocarbamoyl compound is an alkylene bis(dialkylthiocarbamate).

[0020] The complex of a molybdenum/nitrogen-containing compound is preferably a molybdenum succinimide. The complex includes both sulfurized and non-sulfurized forms and, preferably, the complex is sulfurized.

[0021] A particularly preferred complex of a molybdenum/nitrogen containing compound is disclosed in commonly assigned U.S. Patent Application Serial No. 10/159,446 filed on May 31, 2002 and entitled "REDUCED COLOR MOLYBDENUM-CONTAINING COMPOSITION AND A METHOD OF MAKING SAME" which application is incorporated herein by reference in its entirety.

[0022] The present invention is directed to a method of enhancing the life of a lubricating oil composition as evidenced by an improvement in wear, extreme pressure, and oxidation performance, the method comprising operating an internal

combustion engine with a lubricating oil composition comprising a major amount of a base oil of lubricating viscosity and a minor amount of each of the following:

- a) from about 3.0 to about 7.0 weight percent of an ethylene carbonated-treated ashless dispersant;
- b) from about 2.0 to about 5.0 weight percent of a borated-treated ashless dispersant;
- wherein the weight ratio of a) to b) is about 0.3 to about 0.5;
- c) from about 1.0 to about 3.0 weight percent of a high overbased metal-containing detergent;
- d) from about 0.1 to about 2.0 weight percent of a phosphorus-containing compound;

wherein the weight percent of total phosphorus in the lubricating oil composition is no more than 0.08 weight percent based on the total weight of the lubricating oil composition.

[0023] Among other factors, the present invention is based on the surprising discovery that the lubricating oil composition has extended drain properties as evidenced by improved wear, extreme pressure, and oxidation performance. The lubricating oil composition of the present invention have a low phosphorus content while maintaining excellent wear and oxidation performance that is critical in an extended drain lubricating oil.

DETAILED DESCRIPTION OF THE INVENTION

[0024] The present invention provides for a low phosphorus lubricating oil composition having no more than 0.08 weight percent total phosphorus based on the total weight of the composition. The combination of additive components in the lubricating oil composition of the present invention provides improved wear, extreme pressure and oxidation performance and are hereinbelow described in detail.

Base Oil of Lubricating Viscosity

[0025] The lubricant compositions of the present invention include a major amount of base oil of lubricating viscosity. Base oil as used herein is defined as a base stock or blend of base stocks which is a lubricant component that is produced by a single manufacturer to the same specifications (independent of feed source or manufacturer's location); that meets the same manufacturer's specification; and that is identified by a unique formula, product identification number, or both. Base stocks may be manufactured using a variety of different processes including but not limited to distillation, solvent refining, hydrogen processing, oligomerization, esterification, and rerefining. Rerefined stock shall be substantially free from materials introduced through manufacturing, contamination, or previous use. The base oil of this invention may be any natural or synthetic lubricating base oil fraction particularly those having a kinematic viscosity at 100 degrees Centigrade (C) and about 4 centistokes (cSt) to about 20 cSt. Hydrocarbon synthetic oils may include, for example, oils prepared from the polymerization of ethylene, i.e., polyalphaolefin or PAO, or from hydrocarbon synthesis procedures using carbon monoxide and hydrogen gases such as in a Fisher-Tropsch process. A preferred base oil is one that comprises little, if any, heavy fraction; e.g., little, if any, lube oil fraction of viscosity about 20 cSt or higher at about 100 degrees C.

[0026] The base oil may be derived from natural lubricating oils, synthetic lubricating oils or mixtures thereof. Suitable base oil includes base stocks obtained by isomerization of synthetic wax and slack wax, as well as hydrocrackate base stocks produced by hydrocracking (rather than solvent extracting) the aromatic and polar components of the crude. Suitable base oils include those in all API categories I, II, III, IV and V as defined in API Publication 1509, 14th Edition, Addendum I, December 1998. Saturates levels and viscosity indices for Group I, II and III base oils are listed in Table 1. Group IV base oils are polyalphaolefins (PAO). Group V base oils include all other base oils not included in Group I, II, III, or IV. Although Group II, III and IV base oils are preferred for use in this invention, these preferred base oils may be prepared by combining one or more of Group I, II, III, IV and V base stocks or base oils.

TABLE 1

SATURATES, SULFUR AND VISCOSITY INDEX OF GROUP I, II AND III BASE STOCKS		
Group	Saturates (As determined by ASTM D 2007) Sulfur (As determined by ASTM D 2270)	Viscosity Index (As determined by ASTM D 4294, ASTM D 4297 or ASTM D 3120)
I	Less than 90 % saturates and/or Greater than to 0.03 % sulfur	Greater than or equal to 80 and less than 120
II	Greater than or equal to 90 % saturates and less than or equal to 0.03 % sulfur	Greater than or equal to 80 and less than 120
III	Greater than or equal to 90 % saturates and less than or equal to 0.03% sulfur	Greater than or equal to 120

[0027] Natural lubricating oils may include animal oils, vegetable oils (e.g., rapeseed oils, castor oils and lard oil), petroleum oils, mineral oils, and oils derived from coal or shale.

[0028] Synthetic oils may include hydrocarbon oils and halo-substituted hydrocarbon oils such as polymerized and inter-polymerized olefins, alkylbenzenes, polyphenyls, alkylated diphenyl ethers, alkylated diphenyl sulfides, as well as their derivatives, analogues and homologues thereof, and the like. Synthetic lubricating oils also include alkylene oxide polymers, interpolymers, copolymers and derivatives thereof wherein the terminal hydroxyl groups have been modified by esterification, etherification, etc. Another suitable class of synthetic lubricating oils comprises the esters of dicarboxylic acids with a variety of alcohols. Esters useful as synthetic oils also include those made from C₅ to C₁₂ monocarboxylic acids and polyols and polyol ethers. Tri-alkyl phosphate ester oils such as those exemplified by tri-n-butyl phosphate and tri-iso-butyl phosphate are also suitable for use as base oils.

[0029] Silicon-based oils (such as the polyalkyl-, polyaryl-, polyalkoxy or polyaryloxy-siloxane oils and silicate oils) comprise another useful class of synthetic lubricating oils. Other synthetic lubricating oils include liquid esters of phosphorus-containing acids, polymeric tetrahydrofurans, polyalphaolefins, and the like.

[0030] The base oil may be derived from unrefined, refined, rerefined oils, or mixtures thereof. Unrefined oils are obtained directly from a natural source or synthetic source (e.g., coal, shale, or tar sand bitumen) without further purification or treatment. Examples of unrefined oils include a shale oil obtained directly from a retorting operation, a petroleum oil obtained directly from distillation, or an ester oil obtained directly from an esterification process, each of which may then be used without further treatment. Refined oils are similar to the unrefined oils except that refined oils have been treated in one or more purification steps to improve one or more properties. Suitable purification techniques include distillation, hydrocracking, hydrotreating, dewaxing, solvent extraction, acid or base extraction, filtration, and percolation, all of which are known to those skilled in the art. Rerefined oils are obtained by treating used oils in processes similar to those used to obtain the refined oils. These rerefined oils are also known as reclaimed or reprocessed oils and often are additionally processed by techniques for removal of spent additives and oil breakdown products.

[0031] Base oil derived from the hydroisomerization of wax may also be used, either alone or in combination with the aforesaid natural and/or synthetic base oil. Such wax isomerate oil is produced by the hydroisomerization of natural or synthetic waxes or mixtures thereof over a hydroisomerization catalyst.

[0032] It is preferred to use a major amount of base oil in the lubricating oil of the present invention. A major amount of base oil as defined herein comprises 40 weight percent or more. Preferred amounts of base oil comprise about 40 weight percent to about 97 weight percent of at least one of Group III, IV and V base oil or preferably greater than about 50 weight percent to about 97 weight percent of at least one of Group III, IV and V base oil or more preferably about 60 weight percent to about 97 weight percent of at least one of Group III, IV and V base oil. (When weight percent is used herein, it is referring to weight percent of the lubricating oil unless otherwise specified.) A more preferred embodiment of this invention may comprise an amount of base oil that comprises about 80 weight percent to about 95 weight percent of the lubricating oil.

[0034] Ashless dispersants are broadly divided into several groups. One such group is directed to copolymers which contain a carboxylate ester with one or more additional polar function, including amine, amide, imine, imide, hydroxyl carboxyl, and the like. These products can be prepared by copolymerization of long chain alkyl acrylates or methacrylates with monomers of the above function. Such groups include alkyl methacrylate-vinyl pyrrolidinone copolymers, alkyl methacrylate-dialkylaminoethyl methacrylate copolymers and the like. Additionally, high molecular weight amides and polyamides or esters and polyesters such as tetraethylene pentamine, polyvinyl polysterarates and other polys-tearamides may be employed. Preferred dispersants are N-substituted long chain alkenyl succinimides.

$$\begin{array}{c} \text{R}^1 \\ \diagup \\ \text{C}=\text{O} \\ | \\ \text{N}-\text{Alk}-(\text{N}-\text{Alk})_a-\text{NR}^3\text{R}^4 \\ | \\ \text{R}^2 \\ \diagdown \\ \text{C}=\text{O} \end{array}$$

[0036] These N-substituted alkenyl succinimides can be prepared by reacting maleic anhydride with an olefinic hydrocarbon followed by reacting the resulting alkenyl succinic anhydride with the alkylene polyamine. The R¹ radical of the above formula, that is, the alkenyl radical, is preferably derived from a polymer prepared from an olefin monomer containing from about 2 to about 5 carbon atoms. Thus, the alkenyl radical is obtained by polymerizing an olefin containing from about 2 to about 5 carbon atoms to form a hydrocarbon having a molecular weight ranging from about 400 to about 3,000. Such olefin monomers are exemplified by ethylene, propylene, 1-butene, 2-butene, isobutene, and mixtures thereof.

$$\text{H}_2\text{N}-\text{Alk}-\left(\text{N}-\text{Alk}\right)_b\text{NR}^3\text{R}^4$$

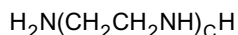
$$\quad \quad \quad |$$

$$\quad \quad \quad \text{R}^2$$

[0038] The alkylene amines include principally methylene amines, ethylene amines, butylene amines, propylene amines, pentylene amines, hexylene amines, heptylene amines, octylene amines, other polymethylene amines and also the cyclic and the higher homologs of such amines as piperazine and amino alkylsubstituted piperazines. They are exemplified specifically by ethylene diamine, triethylene tetraamine, propylene diamine, decamethyl diamine, octamethylene diamine, diheptamethylene triamine, tripropylene tetraamine, tetraethylene pentamine, trimethylene diamine, pentaethylene hexamine, ditrimethylene triamine, 2-heptyl-3-(2-aminopropyl)-imidazoline, 4-methyl imidazoline, N,N-dimethyl-1,3-propane diamine, 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 such as are obtained by condensing two or more of the above-illustrated alkylene amines likewise are useful.

[0039] The ethylene amines are especially useful. They are described in some detail under the heading "Ethylene Amines" in Encyclopedia of Chemical Technology, Kirk-Othmer, Vol. 5, pp. 898-905 (Interscience Publishers, New York, 1950).

[0040] The term "ethylene amine" is used in a generic sense to denote a class of polyamines conforming for the most part to the structure:



wherein c is an integer from 1 to about 10.

[0041] Thus, it includes, for example, ethylene diamine, diethylene triamine, triethylene tetraamine, tetraethylene pentamine, pentaethylene hexamine, and the like.

[0042] Also included within the term "alkenyl succinimides" are post-treated succinimides such as post-treatment processes involving ethylene carbonate and boric acid disclosed by Wollenberg, et al., U.S. Patent No. 4,612,132; Wollenberg, et al., U.S. Patent No. 4,746,446; and the like as well as other post-treatment processes each of which are incorporated herein by reference in its entirety.

[0043] In the lubricating oil composition of the present invention both the ethylene carbonate-treated and boric acid-treated succinimides are preferably employed in a weight ratio of about 0.3 to about 0.5. The ethylene carbonate-treated ashless dispersant and the borated ashless dispersant are preferably contained in the lubricating oil composition in a total amount of from about 4.0 to about 10 weight percent, based on the total weight of the lubricating oil composition.

[0044] Preferably, the weight range of the ethylene carbonated-treated ashless dispersant will be from about 3.0 to about 7.0 weight percent, preferably from about 4.0 to about 6.0 weight percent, more preferably from about 4.5 to about 5.5 weight percent.

[0045] Preferably, the weight range of the boric acid-treated ashless dispersant will be from about 2.0 to about 5.0 weight percent, preferably from about 2.5 to about 3.5 weight percent.

[0046] The combination of the two succinimides produces superior detergency and soot dispersancy to either the carbonated-treated or borated-treated succinimides when used alone.

Metal-Containing Detergent

[0047] The detergent employed in the lubricating oil composition of the present invention is a metal-containing detergent. There are a number of materials that are suitable as detergents for the purpose of this invention. These materials include phenates (high overbased or low overbased), high overbased phenate stearates, phenolates, salicylates, phosphonates, thiophosphonates and sulfonates and mixtures thereof. Preferably, sulfonates are used, such as high overbased sulfonates, low overbased sulfonates, or phenoxy sulfonates. In addition the sulfonic acids themselves can also be used.

[0048] The sulfonate detergent is preferably an alkali or alkaline earth metal salt of a hydrocarbyl sulfonic acid having from about 15 to about 200 carbons. Preferably the term "sulfonate" encompasses the salts of sulfonic acid derived from petroleum products. Such acids are well known in the art. They can be obtained by treating petroleum products with sulfuric acid or sulfur trioxide. The acids thus obtained are known as petroleum sulfonic acids and the salts as petroleum sulfonates. Most of the petroleum products which become sulfonated contain an oil-solubilizing hydrocarbon group. Also included within the meaning of "sulfonate" are the salts of sulfonic acids of synthetic alkyl aryl compounds. These acids also are prepared by treating an alkyl aryl compound with sulfuric acid or sulfur trioxide. At least one alkyl substituent of the aryl ring is an oil-solubilizing group, as discussed above. The acids thus obtained are known as alkyl aryl sulfonic acids and the salts as alkyl aryl sulfonates. The sulfonates where the alkyl is straight-chain are the well-known linear alkylaryl sulfonates.

[0049] The acids obtained by sulfonation are converted to the metal salts by neutralizing with a basic reacting alkali or alkaline earth metal compound to yield the Group I or Group II metal sulfonates. Generally, the acids are neutralized with an alkali metal base. Alkaline earth metal salts are obtained from the alkali metal salt by metathesis. Alternatively, the sulfonic acids can be neutralized directly with an alkaline earth metal base. The sulfonates can then be overbased. For purposes of the present invention, overbasing is preferred. Overbased materials and methods of preparing such materials are well known to those skilled in the art. See, for example, LeSuer U.S. Patent No. 3,496,105, issued Feb. 17, 1970, particularly columns 3 and 4.

[0050] The sulfonates are present in the oil dispersion in the form of alkali and/or alkaline earth metal salts, or mixtures thereof. The alkali metals include lithium, sodium and potassium. The alkaline earth metals include barium magnesium and calcium, of which the latter two are preferred.

[0051] Particularly preferred, however, because of their wide availability, are salts of the petroleum sulfonic acids, particularly the petroleum sulfonic acids which are obtained by sulfonating various hydrocarbon fractions such as lu-

bricating oil fractions and extracts rich in aromatics which are obtained by extracting a hydrocarbon oil with a selective solvent, which extracts may, if desired, be alkylated before sulfonation by reacting them with olefins or alkyl chlorides by means of an alkylation catalyst; organic polysulfonic acids such as benzene disulfonic acid which may or may not be alkylated; and the like.

[0052] The preferred salts for use in the present invention are those of alkylated aromatic sulfonic acids in which the alkyl radical or radicals contain at least about 8 carbon atoms, for example from about 8 to about 22 carbon atoms. Another preferred group of sulfonate starting materials are the aliphatic-substituted cyclic sulfonic acids in which the aliphatic substituents or substituents contain a total of at least about 12 carbon atoms, such as the alkyl aryl sulfonic acids, alkyl cycloaliphatic sulfonic acids, the alkyl heterocyclic sulfonic acids and aliphatic sulfonic acids in which the aliphatic radical or radicals contain a total of at least about 12 carbon atoms. Specific examples of these oil-soluble sulfonic acids include petroleum sulfonic acids, mono- and poly-wax-substituted naphthalene sulfonic acids, substituted sulfonic acids, such as cetyl benzene sulfonic acids, cetyl phenyl sulfonic acids, and the like, aliphatic sulfonic acid, such as paraffin wax sulfonic acids, hydroxy-substituted paraffin wax sulfonic acids, etc., cycloaliphatic sulfonic acids, petroleum naphthalene sulfonic acids, cetyl cyclopentyl sulfonic acid, mono- and poly-wax-substituted cyclohexyl sulfonic acids, and the like. The term "petroleum sulfonic acids" is intended to cover all sulfonic acids that are derived directly from petroleum products.

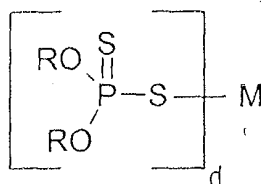
[0053] Typical Group II metal sulfonates suitable for use in the present invention include the metal sulfonates exemplified as follows: calcium white oil benzene sulfonate, barium white oil benzene sulfonate, magnesium white oil benzene sulfonate, calcium dipolypropene benzene sulfonate, barium dipolypropene benzene sulfonate, magnesium dipolypropene benzene sulfonate, calcium mahogany petroleum sulfonate, barium mahogany petroleum sulfonate, magnesium mahogany petroleum sulfonate, calcium triacontyl sulfonate, magnesium triacontyl sulfonate, calcium lauryl sulfonate, barium lauryl sulfonate, magnesium lauryl sulfonate, etc.

[0054] The lubricating oil composition of the present invention may employ a high overbased and low overbased metal-containing detergent, i.e., metal sulfonate. The high overbased metal-containing detergent will generally range from about 1.0 to about 3.0 weight percent and preferably from about 1.4 to about 1.8 weight percent, based on the total weight of the lubricating oil composition and has a Total Base Number (TBN) from about 5.7 to about 7.4. The low overbased metal-containing detergent will generally range from about 0.2 to about 6.0 weight percent and preferably from about 0.3 to about 0.5 weight percent, based on the total weight of the lubricating oil composition and has a TBN from about 0.5 to about 0.9.

Phosphorus-Containing Compound

[0055] The phosphorus-containing compound employed in the lubricating oil compositions of the present invention is selected from the group consisting of metal dithiophosphates, phosphorus esters (including phosphates, phosphonates, phosphinates, phosphine oxides, phosphites, phosphonites, phosphinites, phosphines and the like), amine phosphates and amine phosphinates, sulfur-containing phosphorus esters including phosphoro monothionate and phosphoro dithionates, phosphoramides, phosphonamides and the like; all of which are well known in the art. More preferably, the phosphorus-containing compound is a metal dithiophosphate and, even more preferably, a zinc dithiophosphate. Most preferably, the phosphorous containing compound is a zinc dialkyl dithiophosphate wherein the alkyl groups are independently selected from C_3 to C_{13} , branched or straight chain carbon groups including mixtures thereof. Even more preferable, the phosphorous containing compound is a zinc dialkyldithiophosphate made from a mixture of secondary alcohols where the average carbon chain length is between about 3 and about 6 carbon atoms.

[0056] The metal dithiophosphates are characterized by formula I:



wherein each R^5 is independently a hydrocarbyl group containing from about 3 to about 13 carbon atoms, M is a metal, and d is an integer equal to the valence of M.

[0057] The hydrocarbyl groups, R^5 , in the dithiophosphate (or as described elsewhere in this application) can be a C_3 to C_{13} alkyl, C_3 to C_{13} cycloalkyl, C_7 to C_{13} aralkyl or C_7 to C_{13} alkaryl groups, or a substantially hydrocarbon group of similar structure. By "substantially hydrocarbon" is meant hydrocarbons that contain substituent groups such as ether, ester, nitro, or halogen which do not materially affect the hydrocarbon character of the group.

[0058] Illustrative alkyl groups include isopropyl, isobutyl, n-butyl, sec-butyl, the various amyl groups, n-hexyl, methylisobutyl carbonyl, heptyl, 2-ethylhexyl, diisobutyl, isooctyl, nonyl, behenyl, decyl, dodecyl, tridecyl, etc. Illustrative lower alkylphenyl groups include butylphenyl, amylphenyl, heptylphenyl, etc. Cycloalkyl groups likewise are useful and these include chiefly cyclohexyl and the lower alkyl-cyclohexyl radicals. Many substituted hydrocarbon groups may

also be used, e.g., chlorophenyl, dichlorophenyl, and dichlorodecyl. In another embodiment, at least one R⁵ group is an isopropyl or secondary butyl group. In yet another embodiment, both R⁵ groups are secondary alkyl groups.

[0059] The phosphorodithioic acids from which the metal salts useful in the present invention are prepared are well known. Examples of dihydrocarbyl phosphorodithioic acids and metal salts, and processes for preparing such acids and salts are found in, for example, U.S. Patent Nos. 4,263,150; 4,289,635; 4,308,154; and 4,417,990. These patents are hereby incorporated by reference for such disclosures.

[0060] The phosphorodithioic acids are typically prepared by the reaction of phosphorus pentasulfide with an alcohol or phenol or mixtures of alcohols and/or phenols. The reaction involves four moles of the alcohol or phenol per mole of phosphorus pentasulfide, and may be carried out within the temperature range from about 50°C to about 200°C. Thus, the preparation of O,O-di-n-hexyl phosphorodithioic acid involves the reaction of phosphorus pentasulfide with four moles of n-hexyl alcohol at about 100°C for about two hours. Hydrogen sulfide is liberated and the residue is the defined acid. The preparation of the metal salt of this acid may be effected by reaction with metal oxide. Simply mixing and heating these two reactants is sufficient to cause the reaction to take place and the resulting product is sufficiently pure for the purposes of this invention.

[0061] The metal dihydrocarbyl dithiophosphates that are useful in this invention include those salts containing Group I metals, Group II metals, zinc, aluminum, lead, tin, molybdenum, manganese, cobalt, and nickel or mixtures thereof. The Group II metals, zinc, aluminum, tin, iron, cobalt, lead, molybdenum, manganese, nickel and copper are among the preferred metals. Zinc and copper either alone or in combination are especially useful metals. Especially preferred is zinc. In one embodiment, the lubricant compositions of the invention contain examples of metal compounds which may be reacted with the acid include lithium oxide, lithium hydroxide, sodium hydroxide, sodium carbonate, potassium hydroxide, potassium carbonate, silver oxide, magnesium oxide, magnesium hydroxide, calcium oxide, zinc hydroxide, zinc oxide, strontium hydroxide, cadmium oxide, cadmium hydroxide, barium oxide, aluminum oxide, iron carbonate, copper hydroxide, lead hydroxide, tin borylate, cobalt hydroxide, nickel hydroxide, nickel carbonate, etc.

[0062] In some instances, the incorporation of certain ingredients such as small amounts of the metal acetate or acetic acid (glacial) in conjunction with the metal reactant will facilitate the reaction and result in an improved product. For example, the use of up to about 5% of zinc acetate in combination with the required amount of zinc oxide facilitates the formation of a zinc phosphorodithioate.

[0063] In one preferred embodiment, the alkyl groups, R⁵, are derived from secondary alcohols such as isopropyl alcohol, secondary butyl alcohol, 2-pentanol, 4-methyl-2-pentanol, 2-hexanol, 3-hexanol, etc. Preferably R⁵ is derived from a mixture of secondary alcohols such as 2-butanol and 4-methyl-2-pentanol. Particularly preferred R⁵ is derived from the above mixture containing from about 65 to about 75 weight percent 2-butanol with the remainder 4-methyl-2-pentanol.

[0064] Especially useful metal phosphorodithioates can be prepared from phosphorodithioic acids that, in turn, are prepared by the reaction of phosphorus pentasulfide with mixtures of alcohols. In addition, the use of such mixtures enables the utilization of cheaper alcohols which in themselves may not yield oil-soluble phosphorodithioic acids.

[0065] Useful mixtures of metal salts of dihydrocarbyl dithiophosphoric acid are obtained by reacting phosphorus pentasulfide with a mixture of (a) isopropyl or secondary butyl alcohol, and (b) an alcohol containing at least about 5 carbon atoms wherein at least about 10 mole percent, preferably about 20 or about 25 mole percent, of the alcohol in the mixture is isopropyl alcohol, secondary butyl alcohol or a mixture thereof.

[0066] Thus, a mixture of isopropyl and hexyl alcohols can be used to produce a very effective, oil-soluble metal phosphorodithioate. For the same reason, mixtures of phosphorodithioic acids can be reacted with the metal compounds to form less expensive, oil-soluble salts.

[0067] The mixtures of alcohols may be mixtures of different primary alcohols, mixtures of different secondary alcohols or mixtures of primary and secondary alcohols. Examples of useful mixtures include: n-butanol and n-octanol; n-pentanol and 2-ethyl-1-hexanol; isobutanol and n-hexanol; isobutanol and isoamyl alcohol; isopropanol and 4-methyl-2-pentanol; isopropanol and sec-butyl alcohol; isopropanol and isooctyl alcohol; sec-butyl alcohol and 4-methyl-2-pentanol, etc. Particularly useful alcohol mixtures are mixtures of secondary alcohols containing at least about 20 mole percent and preferably at least about 40 mole percent of isopropyl alcohol. In a preferred embodiment, at least about 75 mole percent of sec-butyl alcohol is used and preferably combined with 4-methyl-2-pentanol, and most preferably further combined with a zinc metal.

[0068] Particularly preferred metal dihydrocarbyl phosphorodithioates include the zinc dithiophosphates. Patents describing the synthesis of such zinc dithiophosphates include U.S. Patent Nos. 2,680,123; 3,000,822; 3,151,075; 3,385,791; 4,377,527; 4,495,075 and 4,778,906. Each of these patents is incorporated herein by reference in their

entirety.

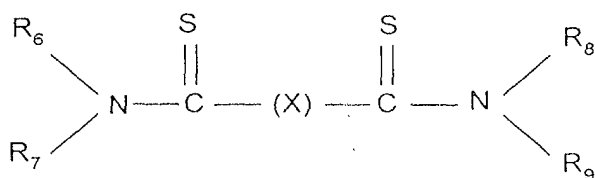
[0069] The amount of the phosphorus-containing compound in the lubricating oil composition of the present invention will range from about 0.1 to about 4 weight percent, preferably about 0.1 to about 2.0 weight percent, most preferably, about 0.4 to about 0.8 weight percent, based on the total weight of the lubricating oil composition.

Nitrogen-Containing Ashless Antioxidant

[0070] The nitrogen-containing ashless antioxidants of the present invention are the diphenylamine type. Examples of diphenylamine-type antioxidants include, but are not limited to, alkylated diphenylamine, phenyl- α -naphthylamine, and alkylated- α -naphthylamine. Preferably, the nitrogen-containing ashless antioxidant is an alkylated diphenylamine such as, for example, dialkylated diphenylamine. The nitrogen-containing ashless antioxidant is generally incorporated into the lubricating oil composition in an amount of about 0.5 to about 3.0 weight percent, preferably about 1.0 to about 2.0 weight percent, based on the total weight of the lubricating oil composition.

Alkylthiocarbamoyl Compound

[0071] The alkylthiocarbamoyl compound of the lubricating oil in the present invention may be represented by the formula:



wherein R^6 , R^7 , R^8 and R^9 are the same or different and each represents an alkyl group of 1 to about 18 carbon atoms, and (X) represents S, S-S, S-CH₂-S, S-CH₂-CH₂-S, S-CH₂-CH₂-CH₂-S or S-CH₂-CH(CH₃)-CH₂-S. Preferably, R^6 , R^7 , R^8 , and R^9 are independently selected from alkyl groups having 1 to about 6 carbon atoms. More preferably, the dithiocarbamate compound is methylene bis(dibutylthiocarbamate).

[0072] The lubricating oil composition of the present invention will generally have from about 0.3 to about 1.0 weight percent, preferably about 0.3 to about 0.7 weight percent, most preferably about 0.4 to about 0.6 weight percent, of the alkylthiocarbamoyl compound, based on the total weight of the lubricating oil composition.

Molybdenum-Succinimide Complex

[0073] The molybdenum-succinimide complex employed in the present invention may be generally characterized as a molybdenum complex of a basic nitrogen compound. Such molybdenum/sulfur complexes are known in the art and are described, for example, in U.S. Patent No. 4,263,152 to King et al., the disclosure of which is hereby incorporated by reference.

[0074] The structure of the molybdenum compositions employed in the present invention are not known with certainty; however, they are believed to be compounds in which molybdenum, whose valences are satisfied with atoms of oxygen or sulfur, is either complexed by, or the salt of, one or more nitrogen atoms of the basic nitrogen containing compound used in the preparation of these compositions.

[0075] The molybdenum compounds used to prepare the molybdenum and molybdenum/sulfur complexes employed in this invention are acidic molybdenum compounds. By acidic is meant that the molybdenum compounds will react with a basic nitrogen compound as measured by ASTM test D-664 or D-2896 titration procedure. Typically these molybdenum compounds are hexavalent and are represented by the following compositions: molybdic acid, ammonium molybdate, sodium molybdate, potassium molybdate and other alkaline metal molybdates and other molybdenum salts such as hydrogen salts, e.g., hydrogen sodium molybdate, MoOCl_4 , MoO_2Br_2 , $\text{Mo}_2\text{O}_3\text{Cl}_6$, molybdenum trioxide or similar acidic molybdenum compounds. Preferred acidic molybdenum compounds are molybdic acid, ammonium molybdate, and alkali metal molybdates. Particularly preferred are molybdic acid and ammonium molybdate.

[0076] The basic nitrogen compound used to prepare the molybdenum complexes have at least one basic nitrogen and are preferably oil-soluble. Typical examples of such compositions are succinimides, carboxylic acid amides, hydrocarbyl monoamines, hydrocarbon polyamines, Mannich bases, phosphoramides, thiophosphoramides, phosphonamides, dispersant viscosity index improvers, and mixtures thereof. Any of the nitrogen-containing compositions may be after-treated with, e.g., boron, using procedures well known in the art so long as the compositions continue to contain

basic nitrogen. These after-treatments are particularly applicable to succinimides and Mannich base compositions.

[0077] The mono and polysuccinimides that can be used to prepare the molybdenum complexes described herein are disclosed in numerous references and are well known in the art. Certain fundamental types of succinimides and the related materials encompassed by the term of art "succinimide" are taught in U.S. Patent No's. 3,219,666; 3,172,892; and 3,272,746, the disclosures of which are hereby incorporated by reference. The term "succinimide" is understood in the art to include many of the amide, imide, and amidine species which may also be formed. The predominant product however is a succinimide and this term has been generally accepted as meaning the product of a reaction of an alkenyl substituted succinic acid or anhydride with a nitrogen-containing compound. Preferred succinimides, because of their commercial availability, are those succinimides prepared from a hydrocarbyl succinic anhydride, wherein the hydrocarbyl group contains from about 24 to about 350 carbon atoms, and an ethylene amine, said ethylene amines being especially characterized by ethylene diamine, diethylene triamine, triethylene tetramine, and tetraethylene pentamine. Particularly preferred are those succinimides prepared from polyisobutenyl succinic anhydride of about 70 to about 128 carbon atoms and tetraethylene pentamine or triethylene tetramine or mixtures thereof.

[0078] Also included within the term "succinimide" are the cooligomers of a hydrocarbyl succinic acid or anhydride and a poly secondary amine containing at least one tertiary amino nitrogen in addition to two or more secondary amino groups. Ordinarily this composition has between about 1,500 and about 50,000 average molecular weight. A typical compound would be that prepared by reacting polyisobutenyl succinic anhydride and ethylene dipiperazine.

[0079] Carboxylic acid amide compositions are also suitable starting materials for preparing the molybdenum complexes employed in the present invention. Typical of such compounds are those disclosed in U.S. Patent No. 3,405,064, the disclosure of which is hereby incorporated by reference. These compositions are ordinarily prepared by reacting a carboxylic acid or anhydride or ester thereof, having at least about 12 to about 350 aliphatic carbon atoms in the principal aliphatic chain and, if desired, having sufficient pendant aliphatic groups to render the molecule oil soluble with an amine or a hydrocarbyl polyamine, such as an ethylene amine, to give a mono or polycarboxylic acid amide. Preferred are those amides prepared from (1) a carboxylic acid of the formula $R^{10}COOH$, where R^{10} is C_{12} to C_{20} alkyl or a mixture of this acid with a polyisobutenyl carboxylic acid in which the polyisobutenyl group contains from about 72 to about 128 carbon atoms and (2) an ethylene amine, especially triethylene tetramine or tetraethylene pentamine or mixtures thereof.

[0080] Another class of compounds which are useful in the present invention are hydrocarbyl monoamines and hydrocarbyl polyamines, preferably of the type disclosed in U.S. Patent No. 3,574,576, the disclosure of which is hereby incorporated by reference. The hydrocarbyl group, which is preferably alkyl, or olefinic having one or two sites of unsaturation, usually contains from about 9 to about 350, preferably from about 20 to about 200 carbon atoms. Particularly preferred hydrocarbyl polyamines are those which are derived, e.g., by reacting polyisobutenyl chloride and a polyalkylene polyamine, such as an ethylene amine, e.g., ethylene diamine, diethylene triamine, tetraethylene pentamine, 2-aminoethylpiperazine, 1,3-propylene diamine, 1,2-propylenediamine, and the like.

[0081] Another class of compounds useful for supplying basic nitrogen are the Mannich base compositions. These compositions are prepared from a phenol or C_9 to C_{200} alkylphenol, an aldehyde, such as formaldehyde or formaldehyde precursor such as paraformaldehyde, and an amine compound. The amine may be a mono or polyamine and typical compositions are prepared from an alkylamine, such as methylamine or an ethylene amine, such as, diethylene triamine, or tetraethylene pentamine, and the like. The phenolic material may be sulfurized and preferably is dodecylphenol or a C_{80} to C_{100} alkylphenol. Typical Mannich bases which can be used in this invention are disclosed in U.S. Pat. Nos. 4,157,309 and 3,649,229; 3,368,972; and 3,539,663, the disclosures of which are hereby incorporated by reference. The last referenced patent discloses Mannich bases prepared by reacting an alkylphenol having at least about 50 carbon atoms, preferably about 50 to about 200 carbon atoms with formaldehyde and an alkylene polyamine $HN(ANH)_eH$ where A is a saturated divalent alkyl hydrocarbon of about 2 to about 6 carbon atoms and e is 1 to about 10 and where the condensation product of said alkylene polyamine may be further reacted with urea or thiourea. The utility of these Mannich bases as starting materials for preparing lubricating oil additives can often be significantly improved by treating the Mannich base using conventional techniques to introduce boron into the composition.

[0082] Another class of composition useful for preparing the molybdenum complexes employed in the present invention are the phosphoramides and phosphonamides such as those disclosed in U.S. Patent Nos. 3,909,430 and 3,968,157, the disclosures of which are hereby incorporated by reference. These compositions may be prepared by forming a phosphorus compound having at least one P-N bond. They can be prepared, for example, by reacting phosphorus oxychloride with a hydrocarbyl diol in the presence of a monoamine or by reacting phosphorus oxychloride with a difunctional secondary amine and a mono-functional amine. Thiophosphoramides can be prepared by reacting an unsaturated hydrocarbon compound containing from about 2 to about 450 or more carbon atoms, such as polyethylene, polyisobutylene, polypropylene, ethylene, 1-hexene, 1,3-hexadiene, isobutylene, 4-methyl-1-pentene, and the like, with phosphorus pentasulfide and a nitrogen-containing compound as defined above, particularly an alkylamine, alkyl-diamine, alkylpolyamine, or an alkyleneamine, such as ethylene diamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, and the like.

[0083] Another class of nitrogen-containing compositions useful in preparing the molybdenum complexes employed in the present invention includes the so-called dispersant viscosity index improvers (VI improvers). These VI improvers are commonly prepared by functionalizing a hydrocarbon polymer, especially a polymer derived from ethylene and/or propylene, optionally containing additional units derived from one or more co-monomers such as alicyclic or aliphatic olefins or diolefins. The functionalization may be carried out by a variety of processes which introduce a reactive site or sites which usually has at least one oxygen atom on the polymer. The polymer is then contacted with a nitrogen-containing source to introduce nitrogen-containing functional groups on the polymer backbone. Commonly used nitrogen sources include any basic nitrogen compound especially those nitrogen-containing compounds and compositions described herein. Preferred nitrogen sources are alkylene amines, such as ethylene amines, alkyl amines, and Mannich bases.

[0084] Preferred basic nitrogen compounds for use in the present invention are succinimides, carboxylic acid amides, and Mannich bases. More preferred are succinimides having an average molecular weight of about 1,000 or about 1,300 or about 2,300 and mixtures thereof. Such succinimides can be post treated with boron or ethylene carbonate as known in the art.

[0085] Preferably, the molybdenum complexes of the present invention are sulfurized. Representative sulfur sources for preparing the molybdenum/sulfur complexes used in this invention are sulfur, hydrogen sulfide, sulfur monochloride, sulfur dichloride, phosphorus pentasulfide, $R^{11}S_f$ where R^{11} is hydrocarbyl, preferably C_1 to C_{40} alkyl, and f is at least 2, inorganic sulfides and polysulfides such as $(NH_4)_2S_g$, where g is at least 1, thioacetamide, thiourea, and mercaptans of the formula $R^{11}SH$ where R^{11} is as defined above. Also useful as sulfurizing agents are traditional sulfur-containing antioxidants such as wax sulfides and polysulfides, sulfurized olefins, sulfurized carboxylic and esters and sulfurized ester-olefins, and sulfurized alkylphenols and the metal salts thereof.

[0086] The sulfurized fatty acid esters are prepared by reacting sulfur, sulfur monochloride, and/or sulfur dichloride with an unsaturated fatty ester under elevated temperatures. Typical esters include C_1 to C_{20} alkyl esters of C_8 to C_{24} unsaturated fatty acids, such as palmitoleic, oleic, ricinoleic, petroselinic, vaccenic, linoleic, linolenic, oleostearic, licanic, paranaric, tariric, gadoleic, arachidonic, cetoleic, etc. Particularly good results have been obtained with mixed unsaturated fatty acid esters, such as are obtained from animal fats and vegetable oils, such as tall oil, linseed oil, olive oil, castor oil, peanut oil, rape oil, fish oil, sperm oil, and so forth.

[0087] Exemplary fatty esters include lauryl tallate, methyl oleate, ethyl oleate, lauryl oleate, cetyl oleate, cetyl linoleate, lauryl ricinoleate, oleyl linoleate, oleyl stearate, and alkyl glycerides.

[0088] Cross-sulfurized ester olefins, such as a sulfurized mixture of C_{10} to C_{25} olefins with fatty acid esters of C_{10} to C_{25} fatty acids and C_{10} to C_{25} alkyl or alkenyl alcohols, wherein the fatty acid and/or the alcohol is unsaturated may also be used.

[0089] Sulfurized olefins are prepared by the reaction of the C_3 to C_6 olefin or a low-molecular-weight polyolefin derived therefrom with a sulfur-containing compound such as sulfur, sulfur monochloride, and/or sulfur dichloride.

[0090] Also useful are the aromatic and alkyl sulfides, such as dibenzyl sulfide, dityl sulfide, dicetyl sulfide, diparaffin wax sulfide and polysulfide, cracked wax-olefin sulfides and so forth. They can be prepared by treating the starting material, e.g., olefinically unsaturated compounds, with sulfur, sulfur monochloride, and sulfur dichloride. Particularly preferred are the paraffin wax thiomers described in U.S. Patent No. 2,346,156.

[0091] Sulfurized alkyl phenols and the metal salts thereof include compositions such as sulfurized dodecylphenol and the calcium salts thereof. The alkyl group ordinarily contains from about 9 to about 300 carbon atoms. The metal salt may be preferably, a Group I or Group II salt, especially sodium, calcium, magnesium, or barium.

[0092] Preferred sulfur sources are sulfur, hydrogen sulfide, phosphorus pentasulfide, $R^{12}S_h$ where R^{12} is hydrocarbyl, preferably C_1 to C_{10} alkyl, and h is at least about 3, mercaptans wherein R^{12} is C_1 to C_{10} alkyl, inorganic sulfides and polysulfides, thioacetamide, and thiourea. Most preferred sulfur sources are sulfur, hydrogen sulfide, phosphorus pentasulfide, and inorganic sulfides and polysulfides.

[0093] The polar promoter used in the preparation of the molybdenum complexes employed in this invention is one which facilitates the interaction between the acidic molybdenum compound and the basic nitrogen compound. A wide variety of such promoters are well known to those skilled in the art. Typical promoters are 1,3-propanediol, 1,4-butanediol, diethylene glycol, butyl cellosolve, propylene glycol, 1,4-butyleneglycol, methyl carbitol, ethanolamine, diethanolamine, N-methyl-diethanol-amine, dimethyl formamide, N-methyl acetamide, dimethyl acetamide, methanol, ethylene glycol, dimethyl sulfoxide, hexamethyl phosphoramide, tetrahydrofuran and water. Preferred are water and ethylene glycol. Particularly preferred is water.

[0094] While ordinarily the polar promoter is separately added to the reaction mixture, it may also be present, particularly in the case of water, as a component of non-anhydrous starting materials or as waters of hydration in the acidic molybdenum compound, such as $(NH_4)_6Mo_7O_{24}H_2O$. Water may also be added as ammonium hydroxide.

[0095] A method for preparing the molybdenum complexes used in the present invention is to prepare a solution of the acidic molybdenum precursor and a polar promoter with a basic nitrogen-containing compound with or without diluent. The diluent is used, if necessary, to provide a suitable viscosity for easy stirring. Typical diluents are lubricating

oil and liquid compounds containing only carbon and hydrogen. If desired, ammonium hydroxide may also be added to the reaction mixture to provide a solution of ammonium molybdate. This reaction is carried out at a variety of temperatures, typically at or below the melting point of the mixture to reflux temperature. It is ordinarily carried out at atmospheric pressure although higher or lower pressures may be used if desired. This reaction mixture may optionally be treated with a sulfur source as defined above at a suitable pressure and temperature for the sulfur source to react with the acidic molybdenum and basic nitrogen compounds. In some cases, removal of water from the reaction mixture may be desirable prior to completion of reaction with the sulfur source.

[0096] In a preferred and improved method for preparing the molybdenum complexes, the reactor is agitated and heated at a temperature less than or equal to about 120 degrees Celsius, preferably from about 70 degrees Celsius to about 90 degrees Celsius. Molybdic oxide or other suitable molybdenum source is then charged to the reactor and the temperature is maintained at a temperature less than or equal to about 120 degrees Celsius, preferably at about 70 degrees Celsius to about 90 degrees Celsius, until the molybdenum is sufficiently reacted. Excess water is removed from the reaction mixture. Removal methods include but are not limited to vacuum distillation or nitrogen stripping while maintaining the temperature of the reactor at a temperature less than or equal to about 120 degrees Celsius, preferably between about 70 degrees Celsius to about 90 degrees Celsius. The temperature during the stripping process is held at a temperature less than or equal to about 120 degrees Celsius to maintain the low color intensity of the molybdenum-containing composition. It is ordinarily carried out at atmospheric pressure although higher or lower pressures may be used. The stripping step is typically carried out for a period of about 0.5 to about 5 hours.

[0097] If desired, this product can be sulfurized by treating this reaction mixture with a sulfur source as defined above at a suitable pressure and temperature, not to exceed about 120 degrees Celsius for the sulfur source to react with the acidic molybdenum and basic nitrogen compounds. The sulfurization step is typically carried out for a period of from about 0.5 to about 5 hours and preferably from about 0.5 to about 2 hours. In some cases, removal of the polar promoter (water) from the reaction mixture may be desirable prior to completion of reaction with the sulfur source. The molybdenum complex and molybdenum/sulfur complex produced by such method is lighter in color (when compared to complexes prepared at higher temperatures) while maintaining good fuel economy, excellent oxidation inhibition, and anti-wear performance qualities. Color in this instance can be more visibly or more quantifiably using a UV spectrophotometer such as a Perkin-Elmer Lambda 18 UV-Visible Double-Beam Spectrophotometer. As used herein, this test recorded the visible spectra of molybdenum compositions at a constant concentration in an isooctane solvent. The spectra represent the absorbance intensity plotted versus the wavelength in nanometers. The spectra extend from the visible region into the near infrared region of the electromagnetic radiation (350 nanometers to 900 nanometers). In this test, the highly colored samples showed increasingly higher absorbance at increasingly higher wavelengths at a constant molybdenum concentration. The preparation of the sample for color measurement comprises diluting the molybdenum-containing composition with isooctane to achieve a constant molybdenum concentration of 0.00025 g molybdenum per gram of the molybdenum-containing composition/isooctane mixture. Prior to sample measurement the spectrophotometer is referenced by scanning air versus air. The UV visible spectrum from about 350 nanometers to about 900 nanometers is obtained using a one centimeter path-length quartz cell versus an air reference. The spectra are offset corrected by setting the about 867 nanometer absorbance to zero. Then the absorbance of the sample is determined at about 350 nanometers wavelength.

[0098] Characteristics of these new molybdenum/sulfur complexes are disclosed in U.S. Patent Application Serial No. 10/159,446 filed May 31, 2002, entitled REDUCED COLOR MOLYBDENUM-CONTAINING COMPOSITION AND A METHOD OF MAKING SAME, incorporated herein by reference in its entirety.

[0099] In the reaction mixture, the ratio of molybdenum compound to basic nitrogen compound is not critical; however, as the amount of molybdenum with respect to basic nitrogen increases, the filtration of the product becomes more difficult. Since the molybdenum component probably oligomerizes, it is advantageous to add as much molybdenum as can easily be maintained in the composition.

[0100] Usually, the reaction mixture will have charged to it from about 0.01 to about 2.00 atoms of molybdenum per basic nitrogen atom. Preferably from about 0.3 to about 1.0, and most preferably from about 0.4 to about 0.7, atoms of molybdenum per atom of basic nitrogen is added to the reaction mixture.

[0101] When optionally sulfurized, the sulfurized molybdenum containing compositions may be generally characterized as a sulfur/molybdenum complex of a basic nitrogen dispersant compound preferably with a sulfur to molybdenum weight ratio of about (0.01 to 1.0) to 1 and more preferably from about (0.05 to 0.5) to 1 and a nitrogen to molybdenum weight ratio of about (1 to 10) to 1 and more preferably from about (2 to 5) to 1. For extremely low sulfur incorporation the sulfur to molybdenum weight ratio can be from about (0.01 to 0.08) to 1.

[0102] The sulfurized and unsulfurized molybdenum-succinimide complexes of this invention are typically employed in the lubricating oil composition of the present invention in an amount of about 0.1 to about 1.5 weight percent, more preferably from about 0.5 to about 1.0 weight percent.

Other Additives

[0103] The following additive components are examples of some of the components that can be favorably employed in the present invention. These examples of additives are provided to illustrate the present invention, but they are not intended to limit it:

1. Metal detergents: sulfurized or unsulfurized alkyl or alkenyl phenates, alkyl or alkenyl aromatic sulfonates, sulfurized or unsulfurized metal salts of multi-hydroxy alkyl or alkenyl aromatic compounds, alkyl or alkenyl hydroxy aromatic sulfonates, sulfurized or unsulfurized alkyl or alkenyl naphthenates, metal salts of alkanolic acids, metal salts of an alkyl or alkenyl multiacid, and chemical and physical mixtures thereof.

2. Anti-oxidants: Anti-oxidants reduce the tendency of mineral oils to deteriorate in service which deterioration is evidenced by the products of oxidation such as sludge and varnish-like deposits on the metal surfaces and by an increase in viscosity. Examples of anti-oxidants useful in the present invention include, but are not limited to, phenol type (phenolic) oxidation inhibitors, such as 4,4'-methylene-bis(2,6-di-tert-butylphenol), 4,4'-bis(2,6-di-tert-butylphenol), 4,4'-bis(2-methyl-6-tert-butylphenol), 2,2'-methylene-bis(4-methyl-6-tert-butylphenol), 4,4'-butylidene-bis(3-methyl-6-tert-butylphenol), 4,4'-isopropylidene-bis(2,6-di-tert-butylphenol), 2,2'-methylene-bis(4-methyl-6-nonylphenol), 2,2'-isobutylidene-bis(4,6-dimethylphenol), 2,2'-methylene-bis(4-methyl-6-cyclohexylphenol), 2,6-di-tert-butyl-4-methylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,4-dimethyl-6-tert-butylphenol, 2,6-di-tert-butyl-4-dimethylamino-p-cresol, 2,6-di-tert-butyl-4-(N,N'-dimethylaminomethylphenol), 4,4'-thiobis(2-methyl-6-tert-butylphenol), 2,2'-thiobis(4-methyl-6-tert-butylphenol), bis(3-methyl-4-hydroxy-5-tert-butylbenzyl)-sulfide, and bis(3,5-di-tert-butyl-4-hydroxybenzyl). Other types of oxidation inhibitors include metal dithiocarbamate (e.g., zinc dithiocarbamate), and methylenebis(dibutylthiocarbamate).

3. Anti-wear agents: As their name implies, these agents reduce wear of moving metallic parts. Examples of such agents include, but are not limited to, phosphates, phosphites, carbamates, esters, sulfur containing compounds, and molybdenum complexes.

4. Rust inhibitors (Anti-rust agents)

a) Nonionic polyoxyethylene surface active agents: polyoxyethylene lauryl ether, polyoxyethylene higher alcohol ether, polyoxyethylene nonyl phenyl ether, polyoxyethylene octyl phenyl ether, polyoxyethylene octyl stearyl ether, polyoxyethylene oleyl ether, polyoxyethylene sorbitol monostearate, polyoxyethylene sorbitol mono-oleate, and polyethylene glycol mono-oleate.

b) Other compounds: stearic acid and other fatty acids, dicarboxylic acids, metal soaps, fatty acid amine salts, metal salts of heavy sulfonic acid, partial carboxylic acid ester of polyhydric alcohol, and phosphoric ester.

5. Demulsifiers: addition product of alkylphenol and ethylene oxide, polyoxyethylene alkyl ether, and polyoxyethylene sorbitan ester.

6. Extreme pressure agents (EP agents): zinc dialkyldithiophosphate (primary alkyl, secondary alkyl, and aryl type), sulfurized oils, diphenyl sulfide, methyl trichlorostearate, chlorinated naphthalene, fluoroalkylpolysiloxane, and lead naphthenate.

7. Friction modifiers: fatty alcohol, fatty acid, amine, borated ester, and other esters.

8. Multifunctional additives: sulfurized oxymolybdenum dithiocarbamate, sulfurized oxymolybdenum organo phosphorodithioate, oxymolybdenum monoglyceride, oxymolybdenum diethylate amide, amine-molybdenum complex compound, and sulfur-containing molybdenum complex compound.

9. Viscosity index improvers: polymethacrylate type polymers, ethylenepropylene copolymers, styrene-isoprene copolymers, hydrated styrene-isoprene copolymers, polyisobutylene, and dispersant type viscosity index improvers.

10. Pour point depressants: polymethyl methacrylate.

11. Foam inhibitors: alkyl methacrylate polymers and dimethyl silicone polymers.

EXAMPLES

[0104] The invention will be further illustrated by the following examples, which set forth particularly advantageous method embodiments. While the Examples are provided to illustrate the present invention, they are not intended to limit it. This application is intended to cover those various changes and substitutions that may be made by those skilled in the art without departing from the spirit and scope of the appended claims.

Example 1

[0105] The low phosphorus lubricating oil compositions of the present invention were prepared by blending together at room temperature the following components to obtain a SAE 0W-20 viscosity grade formulation.

Table 1.

Lubricating Oil Compositions						
Additive Component	Weight Percent of Additive Component					
	Oil 1	Oil 2	Oil 3	Oil 4	Oil 5	Oil 6
EC-Treated Ashless Dispersant	5.2	5.2	5.2	5.2	5.2	5.2
Borated-Treated ashless Dispersant	3.2	3.2	3.2	3.2	3.2	3.2
LOB Detergent	0.3	0.3	0.3	0.3	0.3	0.3
HOB Detergent	1.6	1.6	1.6	1.6	1.6	1.6
Phosphorus-containing compound	0.7	0.7	0.7	0.7	0.7	0.7
Nitrogen-containing Ashless antioxidant	1.5	1.5	1.5	1.5	1.5	1.5
Alkylthiocarbamoyl compound	0	0	0	0.5	0.5	0.5
Molybdenum-Succinimide Complex	0.7	0.7	0.7	0.7	0.7	0.7
Base Oil:						
Group III	0	100	0	0	100	0
PAO (Group IV)	100	0	90	100	0	90
Ester (Group V)	0	0	10	0	0	10

Other additives comprise the balance of the lubricating oil composition.

Comparative Example A

[0106] The low phosphorus lubricating oil compositions were compared with a commercially recognized long drain lubricating oil (Mobil 1®). This reference oil is a fully-formulated synthetic passenger car engine oil formulated to SAE 5W-30 viscometrics and meeting the API SJ/CF specifications. The competitive commercial formulation was the minimum acceptable performance target for the extended drain interval oils described. Duplicate reference oils were run in the below described bench tests and average results compared with the low phosphorus lubricating oils of the present invention.

Example 2Rotary Bomb Oxidation Test

[0107] The Rotary Bomb Oxidation test (RBOT) was conducted according to the standard test method specified by ASTM D 2272.

[0108] Test oil, water, and copper catalyst coil, contained in a covered glass container, were placed in a vessel equipped with a pressure gauge. The vessel was charged with oxygen to a gauge pressure of 620 kPa (90 psi, 6.2 bar), placed in a constant-temperature oil bath set at 150°C, and rotated axially at 100 rpm at an angle of 30° from the horizontal. The number of minutes required to reach a specific drop in gauge pressure (25 psi) was the oil oxidation stability of the test sample. The longer times indicates better oxidative stability.

[0109] The precision and bias statement was generated from the research report (95% confidence). The data range of results in RR:D02-1409 was from 30 to 1,000 minutes.

[0110] Repeatability - "The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

0.22X

where X denotes mean value."

[0111] Results of this are presented in Table 2. The time to 25 psi pressure drop was 100 minutes for the Reference Oil. However, the low phosphorus lubricating oils of the present invention lasted noticeably longer than the Reference Oil, indicating improved oxidative stability.

Example 3

Thin Film Oxygen Uptake Test

[0112] The Thin Film Oxygen Uptake test (TFOUT) was conducted according to the standard test method specified in ASTM D 4742.

[0113] "The test oil was mixed in a glass container with three other liquids that were used to simulate engine conditions: (1) an oxidized/nitrated fuel component, (2) a mixture of soluble metal naphthenates (lead, copper, iron, manganese, and tin naphthenates), and (3) distilled water.

[0114] The glass container holding the oil mixture was placed in a high pressure reactor equipped with a pressure gage. The high pressure reactor was sealed, charged with oxygen to a pressure of 620 kPa (90 psig), and placed in an oil bath at 160 °C at an angle of 30° from the horizontal. The high pressure reactor was rotated axially at a speed of 100 rpm forming a thin film of oil within the glass container resulting in a relatively large oil-oxygen contact area.

[0115] The pressure of the high pressure reactor was recorded continuously from the beginning of the test and the test was terminated when a rapid decrease of the high pressure reactor pressure was observed. The period of time that elapses between the time when the high pressure reactor was placed in the oil bath and the time at which the pressure began to decrease rapidly was called the oxidation induction time and was used as a measure of the relative oil oxidation stability. The longer times indicates better oxidative stability."

[0116] The precision of this test method, as determined from statistical examination of interlaboratory results on oxidation point time, was as follows;

[0117] "The difference between successive results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

$$0.10(x + 5 \text{ min})$$

where x is the mean of replicate runs in min."

[0118] Results of this are presented in Table 2. The Reference Oil lasts about 534 minutes prior to rapid pressure drop. Although Oil 3 performs somewhat worse, Oil 1, 2, and 4-6 performs better. In particular, Oil 4-6 with the supplemental antiwear/antioxidant, the preferred formulations, performed better.

Example 4

Komatsu Hot Tube Test

[0119] The Komatsu Hot Tube Test (KHTT) is used for screening and quality control of deposit formation performance for engine oils and other oils subjected to high temperatures.

[0120] A glass tube was placed inside an aluminum block and a small air hose was attached to a holder at the bottom of the glass tube. A 5-mL syringe and 12-inch flexible tubing were filled with the oil sample. The tubing was attached to the holder above the air hose and oil was steadily introduced into the glass tube. Air forces the oil up the glass tube through the heating block for the duration of the test. After 16 hours, the glass tubes were removed, rinsed and rated against a standard. The rating, between 0 and 10, was reported. The test was often run at several temperatures to determine the deposit performance over a temperature range. Temperatures frequently tested were between 230°C and 330°C.

[0121] Note: high numbers are desirable, a ten being a perfectly clean tube.

[0122] Results of this are presented in Table 2. The Reference Oil gave an 8.5 rating versus 6.5 to 7.0 for Oils 1-6. While these results were lower relative to the Reference Oil, Oils 1-6 nevertheless yielded outstanding deposit control.

Example 5

Four-Ball Weld Test

[0123] The Four-Ball Weld Test (FBWT) was conducted according to the standard test method specified in ASTM D 2783.

[0124] "The test was operated with one steel ball under load rotating against three steel balls held stationary in the form of a cradle. Test lubricant covered the lower three balls. The rotating speed was 1760 rpm. The machine and test lubricant were brought to 18.33° to 35.0 °C (65° to 95 °F) and then a series of tests of 10-second duration were made at increasing loads until welding occurred. Ten tests were made below the welding point. If ten loads have not been run when welding occurs and the scars at loads below seizure were within 5% of the compensation line no further runs were necessary."

[0125] Results of this are presented in Table 2. The Reference Oil gave a load wear index of 29.0. The low phosphorus lubricating oils of the present invention (Oil 1-6) were at least comparable and, for the oils (Oils 4-6) with the supplemental antiwear/antioxidant, at least 13 % better wear.

[0126] The last non-seizure load showed much the same results. That is, the lubricating oil composition of the present invention are at least comparable and usually superior in wear performance to the Reference Oil.

[0127] These results demonstrate the wear improvement provided by the lubricating oil composition of the present invention.

Table 2.

Bench Test Results					
Oil	RBOT Min. to 25 PSI Drop	TFOUT	KHTT	FBWT	
				Load Wear Index, KGF	Last Non-Seizure Load, KGF
1	190	796	6.5	34.4	80
2	223	683	6.5	28.6	63
3	179	388	7.0	28.8	63
4	180	649	6.5	32.9	63
5	177	1026	6.5	35.3	80
6	159	712	7.0	35.3	80
Reference	100	534	8.5	29.0	63

[0128] It will be understood that this invention is not based on the discovery of any one of the disclosed components as new compositions of matter or their individual usefulness as additive agents in lubricant oil compositions. Rather this invention is based on the discovery of a lubricant oil composition useful for the severe service function imposed by long drain life which composition comprises a major amount of a base oil of lubricating viscosity and a minor amount of an ethylene carbonated-treated ashless dispersant, a borated-treated ashless dispersant, and a high overbased metal-containing detergent.

Claims

1. A lubricating oil composition comprising a major amount of a base oil of lubricating viscosity and a minor amount of each of the following:
 - a) from about 3.0 to about 7.0 weight percent of an ethylene carbonated-treated ashless dispersant;
 - b) from about 2.0 to about 5.0 weight percent of a borated-treated ashless dispersant;
 - wherein the weight ratio of a) to b) is about 0.3 to about 0.5;
 - c) from about 1.0 to about 3.0 weight percent of a high overbased metal-containing detergent;
 - d) from about 0.1 to about 2.0 weight percent of a phosphorus-containing compound;

wherein the weight percent of total phosphorus in the lubricating oil composition is no more than 0.08 weight percent based on the total weight of the lubricating oil composition.

2. A lubricating oil composition according to Claim 1, further comprising from about 0.2 to about 6.0 weight percent of a low overbased metal containing detergent.
3. A lubricating oil composition according to Claim 1, further comprising from about 0.5 to about 3.0 weight percent of a nitrogen-containing ashless antioxidant.
4. A lubricating oil composition according to Claim 1, further comprising from about 0.3 to about 1.0 weight percent of an alkylthiocarbamoyl compound.
5. A lubricating oil composition according to Claim 1, further comprising from about 0.1 to about 1.5 weight percent of a molybdenum-succinimide complex.
6. A lubricating oil composition according to Claim 1 wherein the total phosphorus in the composition is no more than 0.05 weight percent based on the total weight of the composition.
7. A lubricating oil composition according to Claim 1 wherein the base oil of lubricating viscosity is selected from the group consisting of a Group III base stock, Group IV base stock, Group V base stock and any mixture thereof.
8. A lubricating oil composition according to Claim 1 wherein the ashless dispersant is selected from the group consisting of an alkenyl succinimide, an alkenyl succinic anhydride, an alkenyl succinate ester, benzylamine or mixtures thereof.
9. A lubricating oil composition according to Claim 8 wherein the ashless dispersant is an alkenyl succinimide.
10. A lubricating oil composition according to Claim 9 wherein the alkenyl succinimide is a polyalkylene succinimide.
11. A lubricating oil composition according to Claim 10 wherein the polyalkylene succinimide is a polyisobutylene succinimide.
12. A lubricating oil composition according to Claim 1 wherein the metal -containing detergent is a metal phenate or metal sulfonate.
13. A lubricating oil composition according to Claim 12 wherein the metal -containing detergent is a metal sulfonate.
14. A lubricating oil composition according to Claim 1 wherein the phosphorus-containing compound is selected from the group consisting of metal dithiophosphates, phosphorus esters, amine phosphates and amine phosphinates, sulfur-containing phosphorus esters, phosphoramides and phosphonamides.
15. The lubricating oil composition of Claim 14 wherein the phosphorus esters are selected from the group consisting of phosphates, phosphonates, phosphinates, phosphine oxides, phosphites, phosphonites, phosphinites, and phosphines.
16. The lubricating oil composition of Claim 14 wherein the sulfur-containing phosphorus esters are selected from the group consisting of phosphoro monothionate and phosphoro dithionates.
17. The lubricating oil composition of Claim 14 wherein the phosphorus-containing compound is a metal dithiophosphate.
18. The lubricating oil composition of Claim 17 wherein the metal dithiophosphate is a zinc dialkyldithiophosphate.
19. The lubricating oil composition of Claim 1, wherein the nitrogen-containing ashless antioxidant is a diphenylamine.
20. The lubricating oil composition of Claim 19, wherein the diphenylamine is an alkylated diphenyl amine.
21. The lubricating oil composition of Claim 1 wherein the alkylthiocarbamoyl compound is an alkylene, bis(dialkyldithi-

ocarbamate).

22. The lubricating oil composition of Claim 21 wherein the alkylene bis(dialkyldithiocarbamate) is methylene bis(dialkyldithiocarbamate).

23. The lubricating oil composition of Claim 22 wherein the methylene bis(dialkyldithiocarbamate) is methylene bis(dibutyldithiocarbamate).

24. The lubricating oil composition of Claim 1 wherein the nitrogen-containing compound employed in the molybdenum/nitrogen-containing complex is selected from the group consisting of succinimides, carboxylic acid amides, hydrocarbyl monoamines, hydrocarbon polyamines, Mannich bases, phosphoramides, thiophosphoramides, phosphonamides, dispersant viscosity index improvers, and mixtures thereof.

25. The lubricating oil composition of Claim 24 wherein the nitrogen-containing compound is a succinimide and the molybdenum/nitrogen-containing complex is a molybdenum succinimide.

26. The lubricating oil composition of Claim 25 wherein the molybdenum succinimide is a sulfurized molybdenum succinimide.

27. The lubricating oil composition of Claim 25 wherein the molybdenum succinimide is a non-sulfurized molybdenum succinimide.

28. The lubricating oil composition of Claim 25 wherein the molybdenum succinimide is employed in an amount sufficient to provide from about 10 to about 5,000 parts per million of atomic molybdenum in the lubricant composition.

29. A method of enhancing the life of a lubricating oil composition as evidenced by an improvement in wear, extreme pressure, oxidation, and deposit control performance, the method comprising operating an internal combustion engine with a lubricating oil composition comprising a major amount of a base oil of lubricating viscosity and a minor amount of each of the following:

- a) from about 3.0 to about 7.0 weight percent of an ethylene carbonated-treated ashless dispersant;
- b) from about 2.0 to about 5.0 weight percent of a borated-treated ashless dispersant;
- wherein the weight ratio of a) to b) is about 0.3 to about 0.5;
- c) from about 1.0 to about 3.0 weight percent of a high overbased metal-containing detergent;
- d) from about 0.1 to about 2.0 weight percent of a phosphorus-containing compound;

wherein the weight percent of total phosphorus in the lubricating oil composition is no more than 0.08 weight percent based on the total weight of the lubricating oil composition.

30. A method according to Claim 29, further comprising from about 0.2 to about 0.6 weight percent of a low overbased metal-containing detergent.

31. A method according to Claim 29, further comprising from about 0.5 to about 3.0 weight percent of a nitrogen-containing ashless antioxidant.

32. A method according to Claim 1, further comprising from about 0.3 to about 1.0 weight percent of an alkylthiocarbamoyl compound.

33. A method according to Claim 1, further comprising from about 0.3 to about 1.5 weight percent of a molybdenum-succinimide complex.

34. A method according to Claim 1 wherein the total phosphorus in the composition is no more than 0.05 weight percent based on the total weight of the composition.