

## LUBRICATING OIL COMPOSITION

BACKGROUND OF THE INVENTION1. Technical Field

[0001] The present invention generally relates to lubricating oil compositions for reducing wear in engines.

2. Description of the Related Art

[0002] Automobile spark ignition and diesel engines have valve train systems including, for example, valves, cams and rocker arms, which present special lubrication concerns. It is extremely important that the lubricant, i.e., the engine oil, protects these parts from wear. It is also important for the engine oils to suppress the production of deposits in the engines. Such deposits are produced from non-combustibles and incomplete combustion of hydrocarbon fuels (e.g., gasoline and diesel fuel oil) and by the deterioration of the engine oil employed.

[0003] Engine oils typically use a mineral oil or a synthetic oil as a base oil. However, simple base oils alone do not provide the necessary properties to provide the necessary wear protection, deposit control, etc., required to protect internal combustion engines. Thus, base oils are formulated with various additives, for imparting auxiliary functions, such as ashless dispersants, metallic detergents (i.e., metal-containing detergents), antiwear agents, antioxidants (i.e., oxidation inhibitors), viscosity index improvers and the like to give a formulated oil (i.e., a lubricating oil composition).

[0004] A number of such engine oil additives are known and employed in practice. For example, zinc dialkyldithiophosphates are usually contained in the commercially available internal composition engine oils, especially those used for automobiles, because of their favorable characteristics as an antiwear agent and performance as an oxidation inhibitor.

[0005] However, a problem associated with the use of zinc dialkyldithiophosphate is that their phosphorus and sulfur derivatives poison the catalyst components of the catalytic converters. This is a major concern as effective catalytic converters are needed to reduce pollution and to meet governmental regulation designed to reduce toxic gases such as, for example, hydrocarbons, carbon monoxide and nitrogen oxides, in internal combustion engine exhaust emissions. Such catalytic converters generally use a combination of catalytic metals,

e.g., platinum and metal oxides, and are installed in the exhaust streams, e.g., the exhaust pipes of automobiles, to convert the toxic gases to nontoxic gases. As previously mentioned, these catalyst components are poisoned by the phosphorus and sulfur components, or the phosphorus and sulfur decomposition product of the zinc dialkyldithiophosphate; and accordingly, the use of engine oils containing phosphorus and sulfur additives may substantially reduce the life and effectiveness of catalytic converters.

[0006] There is also governmental and automotive industry pressure towards reducing the phosphorus and sulfur content. For example, current GF-4 motor oil specifications require a finished oil to contain less than 0.08 wt % and 0.7 wt % phosphorus and sulfur, respectively, and CJ-4 motor oil specifications, the most current generation heavy duty diesel engine oil, require an oil to contain less than 0.12 wt % and 0.4 wt % phosphorus and sulfur, respectively, and 1.0 wt % sulfated ash. It is widely believed that lowering these limits may have a serious impact on engine performance, engine wear, and oxidation of engine oils. This is because historically a major contributor to the phosphorus content in engine oils has been zinc dialkyldithiophosphates. Accordingly, it would be desirable to eliminate the amount of zinc dialkyldithiophosphate in lubricating oils, thus reducing catalyst deactivation and hence increasing the life and effectiveness of catalytic converters while also meeting future industry standard proposed phosphorus and sulfur contents in the engine oil. However, simply decreasing the amount of zinc dialkyldithiophosphate presents problems because this necessarily lowers the antiwear properties and oxidation inhibition properties of the lubricating oil. Therefore, it is necessary to find a way to reduce or eliminate phosphorus and sulfur content while still retaining the antiwear properties of the higher phosphorus and sulfur content engine oils.

[0007] Accordingly, as demand for further decrease of the phosphorus content and a limit on the sulfur content of lubricating oils is very high, this reduction cannot be satisfied by the present measures in practice and still meet the severe antiwear properties required of today's engine oils. Thus, it would be desirable to develop lubricating oil compositions having relatively low levels of phosphorus and sulfur but which still provide the needed wear protection now provided by lubricating oils containing zinc dialkyl dithiophosphate. It would therefore be desirable to develop improved lubricating oil compositions which exhibit improved wear when used in an internal combustion engine while containing no zinc therein and relatively low levels or free of any phosphorus and/or sulfur content.

## SUMMARY OF THE DISCLOSURE

[0008] In accordance with one embodiment of the present disclosure, a lubricating oil composition is provided comprising (a) a major amount of an oil of lubricating viscosity, (b) an ashless dispersant, (c) at least one metal-containing detergent, (d) an antioxidant, and (e) an anti-wear agent, wherein the lubricating oil composition is free of any zinc dialkyl dithiophosphate compound and further wherein the lubricating oil composition is substantially free of any phosphorus content.

[0008a] In one aspect, there is provided the use of a lubricating oil composition comprising (a) a major amount of an oil of lubricating viscosity, (b) an ashless dispersant, (c) at least one metal-containing detergent, (d) an antioxidant, and (e) an anti-wear agent, wherein the lubricating oil composition is free of any zinc dialkyl dithiophosphate compound and is substantially free of any phosphorus content, for the purpose of wear inhibition in an internal combustion engine.

[0009] In accordance with a second embodiment of the present disclosure, a lubricating oil composition is provided comprising (a) a major amount of an oil of lubricating viscosity, (b) an ashless dispersant, (c) at least one metal-containing detergent, (d) an antioxidant, and (e) an anti-wear agent, wherein the lubricating oil composition is free of any zinc dialkyl dithiophosphate compound and is substantially free of any phosphorus content, and further wherein the lubricating oil composition has a wear reducing property greater than that of a corresponding lubricating oil composition in which a zinc dialkyl dithiophosphate compound is present therein.

[0010] In accordance with a third embodiment of the present disclosure, a method for improving the wear reducing properties of a lubricating oil composition is provided comprising the step of forming a lubricating oil composition comprising (a) a major amount of an oil of lubricating viscosity, (b) an ashless dispersant, (c) at least one metal-containing detergent, (d) an antioxidant, and (e) an anti-wear agent, wherein the lubricating oil composition is free of any zinc dialkyl dithiophosphate compound and is substantially free of any phosphorus content.

[0011] In accordance with a fourth embodiment of the present disclosure, there is provided a method of reducing wear in an internal combustion engine which comprises operating the internal combustion engine with a lubricating oil composition comprising (a) a major amount of an oil of lubricating viscosity, (b) an ashless dispersant, (c) at least one metal-containing detergent, (d) an antioxidant, and (e) an anti-wear agent, wherein the lubricating oil composition is free of any zinc dialkyl dithiophosphate compound and is substantially free of any phosphorus content.

[0012] In accordance with a fifth embodiment of the present disclosure, there is provided an internal combustion engine lubricated with a lubricating oil composition

comprising (a) a major amount of an oil of lubricating viscosity, (b) an ashless dispersant, (c) at least one metal-containing detergent, (d) an antioxidant, and (e) an anti-wear agent, wherein the lubricating oil composition is free of any zinc dialkyl dithiophosphate compound and is substantially free of any phosphorus content.

[0013] The lubricating oil composition of the present disclosure advantageously possesses improved wear reducing properties while containing no zinc dialkyl dithiophosphate compound as compared to a corresponding lubricating oil composition in which a zinc dialkyl dithiophosphate compound is present therein. This is unexpected as zinc dialkyl dithiophosphate is a known antiwear agent typically used in lubricating oil compositions. In addition, the improved wear reducing properties can be achieved with the lubricating oil compositions of the present disclosure while also employing relatively low levels or free of any phosphorus content and relatively low levels of sulfur.

#### BRIEF DESCRIPTION OF THE DRAWING

[0014] Figure 1 is a bar graph comparing the wear performance of the lubricating oil composition of Example 1 versus the lubricating oil compositions of Comparative Examples A and B.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0015] The present invention is directed to a lubricating oil composition containing at least (a) a major amount of an oil of lubricating viscosity; (b) an ashless dispersant; (c) at least one metal-containing detergent; (d) an antioxidant; and (e) an anti-wear agent other than a zinc dialkyl dithiophosphate compound, wherein the lubricating oil composition is free of any zinc dialkyl dithiophosphate compound and is substantially free of any phosphorus content, e.g., a phosphorus content not exceeding 0.08 wt. %, more preferably not exceeding 0.05 wt. % and most preferably 0 wt. %, based on the total weight of the lubricating oil composition. In another embodiment, the lubricating oil composition of the present invention contains relatively low levels of sulfur, i.e., not exceeding 0.7 wt. % and preferably not exceeding 0.2 wt. %. The amount of phosphorus and sulfur in the lubricating oil composition of the present invention is measured according to ASTM D4951.

[0016] The oil of lubricating viscosity for use in the lubricating oil compositions of this invention, also referred to as a base oil, is typically present in a major amount, e.g., an

amount of greater than 50 wt. %, preferably greater than about 70 wt. %, more preferably from about 80 to about 99.5 wt. % and most preferably from about 85 to about 98 wt. %, based on the total weight of the composition. The expression "base oil" as used herein shall be understood to mean 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. The base oil for use herein can be any presently known or later-discovered base oil of lubricating viscosity used in formulating lubricating oil compositions for any and all such applications, e.g., engine oils, marine cylinder oils, functional fluids such as hydraulic oils, gear oils, transmission fluids, etc. Additionally, the base oils for use herein can optionally contain viscosity index improvers, e.g., polymeric alkylmethacrylates; olefinic copolymers, e.g., an ethylene-propylene copolymer or a styrene-butadiene copolymer; and the like and mixtures thereof.

[0017] As one skilled in the art would readily appreciate, the viscosity of the base oil is dependent upon the application. Accordingly, the viscosity of a base oil for use herein will ordinarily range from about 2 to about 2000 centistokes (cSt) at 100° Centigrade (C). Generally, individually the base oils used as engine oils will have a kinematic viscosity range at 100°C of about 2 cSt to about 30 cSt, preferably about 3 cSt to about 16 cSt, and most preferably about 4 cSt to about 12 cSt and will be selected or blended depending on the desired end use and the additives in the finished oil to give the desired grade of engine oil, e.g., a lubricating oil composition having an SAE Viscosity Grade of 0W, 0W-20, 0W-30, 0W-40, 0W-50, 0W-60, 5W, 5W-20, 5W-30, 5W-40, 5W-50, 5W-60, 10W, 10W-20, 10W-30, 10W-40, 10W-50, 15W, 15W-20, 15W-30 or 15W-40. Oils used as gear oils can have viscosities ranging from about 2 cSt to about 2000 cSt at 100°C.

[0018] 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 the lubricating oil compositions of this invention may be any natural or synthetic lubricating base oil. Suitable hydrocarbon synthetic oils include, but are not limited to, oils prepared from the polymerization of ethylene or from the polymerization of 1-olefins to provide polymers such as polyalphaolefin or PAO oils, or from hydrocarbon synthesis

procedures using carbon monoxide and hydrogen gases such as in a Fischer-Tropsch process. For example, a suitable base oil is one that comprises little, if any, heavy fraction; e.g., little, if any, lube oil fraction of viscosity 20 cSt or higher at 100°C.

[0019] 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 hydrocracked 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, Dec. 1998. 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 base oils may be prepared by combining one or more of Group I, II, III, IV and V base stocks or base oils.

[0020] Useful natural oils include mineral lubricating oils such as, for example, liquid petroleum oils, solvent-treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic or mixed paraffinic-naphthenic types, oils derived from coal or shale, animal oils, vegetable oils (e.g., rapeseed oils, castor oils and lard oil), and the like.

[0021] Useful synthetic lubricating oils include, but are not limited to, hydrocarbon oils and halo-substituted hydrocarbon oils such as polymerized and interpolymers of olefins, e.g., polybutylenes, polypropylenes, propylene-isobutylene copolymers, chlorinated polybutylenes, poly(1-hexenes), poly(1-octenes), poly(1-decenes), and the like and mixtures thereof; alkylbenzenes such as dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di(2-ethylhexyl)-benzenes, and the like; polyphenyls such as biphenyls, terphenyls, alkylated polyphenyls, and the like; alkylated diphenyl ethers and alkylated diphenyl sulfides and the derivative, analogs and homologs thereof and the like.

[0022] Other useful synthetic lubricating oils include, but are not limited to, oils made by polymerizing olefins of less than 5 carbon atoms such as ethylene, propylene, butylenes, isobutene, pentene, and mixtures thereof. Methods of preparing such polymer oils are well known to those skilled in the art.

[0023] Additional useful synthetic hydrocarbon oils include liquid polymers of alpha olefins having the proper viscosity. Especially useful synthetic hydrocarbon oils are the hydrogenated liquid oligomers of C<sub>6</sub> to C<sub>12</sub> alpha olefins such as, for example, 1-decene trimer.

[0024] Another class of useful synthetic lubricating oils include, but are not limited to, alkylene oxide polymers, i.e., homopolymers, interpolymers, and derivatives thereof where the terminal hydroxyl groups have been modified by, for example, esterification or etherification. These oils are exemplified by the oils prepared through polymerization of ethylene oxide or propylene oxide, the alkyl and phenyl ethers of these polyoxyalkylene polymers (e.g., methyl poly propylene glycol ether having an average molecular weight of 1,000, diphenyl ether of polyethylene glycol having a molecular weight of 500 to 1000, diethyl ether of polypropylene glycol having a molecular weight of 1,000 to 1,500, etc.) or mono- and polycarboxylic esters thereof such as, for example, the acetic esters, mixed C<sub>3</sub> to C<sub>8</sub> fatty acid esters, or the C<sub>13</sub> oxo acid diester of tetraethylene glycol.

[0025] Yet another class of useful synthetic lubricating oils include, but are not limited to, the esters of dicarboxylic acids e.g., phthalic acid, succinic acid, alkyl succinic acids, alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acids, alkyl malonic acids, alkenyl malonic acids, etc., with a variety of alcohols, e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol, etc. Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl)sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid and the like.

[0026] Esters useful as synthetic oils also include, but are not limited to, those made from carboxylic acids having from about 5 to about 12 carbon atoms with alcohols, e.g., methanol, ethanol, etc., polyols and polyol ethers such as neopentyl glycol, trimethylol propane, pentaerythritol, dipentaerythritol, tripentaerythritol, and the like.

[0027] Silicon-based oils such as, for example, polyalkyl-, polyaryl-, polyalkoxy- or polyaryloxy-siloxane oils and silicate oils, comprise another useful class of synthetic lubricating oils. Specific examples of these include, but are not limited to, tetraethyl silicate, tetra-isopropyl silicate, tetra-(2-ethylhexyl) silicate, tetra-(4-methyl-hexyl)silicate, tetra-(p-tert-butylphenyl)silicate, hexyl-(4-methyl-2-pentoxo)disiloxane, poly(methyl)siloxanes, poly(methylphenyl)siloxanes, and the like.

[0028] The lubricating oil may be derived from unrefined, refined and rerefined oils, either natural, synthetic or mixtures of two or more of any of these of the type disclosed hereinabove. Unrefined oils are those obtained directly from a natural or synthetic source (e.g., coal, shale, or tar sands bitumen) without further purification or treatment. Examples of unrefined oils include, but are not limited to, a shale oil obtained directly from retorting operations, a petroleum oil obtained directly from distillation or an ester oil obtained directly from an esterification process, each of which is then used without further treatment. Refined oils are similar to the unrefined oils except they have been further treated in one or more purification steps to improve one or more properties. These purification techniques are known to those of skill in the art and include, for example, solvent extractions, secondary distillation, acid or base extraction, filtration, percolation, hydrotreating, dewaxing, etc. Rerefined oils are obtained by treating used oils in processes similar to those used to obtain refined oils. Such rerefined oils are also known as reclaimed or reprocessed oils and often are additionally processed by techniques directed to removal of spent additives and oil breakdown products.

[0029] Lubricating oil base stocks derived from the hydroisomerization of wax may also be used, either alone or in combination with the aforesaid natural and/or synthetic base stocks. Such wax isomerate oil is produced by the hydroisomerization of natural or synthetic waxes or mixtures thereof over a hydroisomerization catalyst.

[0030] Natural waxes are typically the slack waxes recovered by the solvent dewaxing of mineral oils; synthetic waxes are typically the wax produced by the Fischer-Tropsch process.

[0031] The ashless dispersant compounds employed in the lubricating oil composition of the present invention are generally used to maintain in suspension insoluble materials resulting from oxidation during use, thus preventing sludge flocculation and precipitation or deposition on metal parts. The lubricating oil composition of the present invention may contain one or more ashless dispersants. Nitrogen-containing ashless (metal-free) dispersants are basic, and contribute to the total base number or TBN (as can be measured by ASTM D2896) of a lubricating oil composition to which they are added, without introducing additional sulfated ash. The term "Total Base Number" or "TBN" as used herein refers to the amount of base equivalent to milligrams of KOH in one gram of sample. Thus, higher TBN numbers reflect more alkaline products, and therefore a greater alkalinity. TBN was

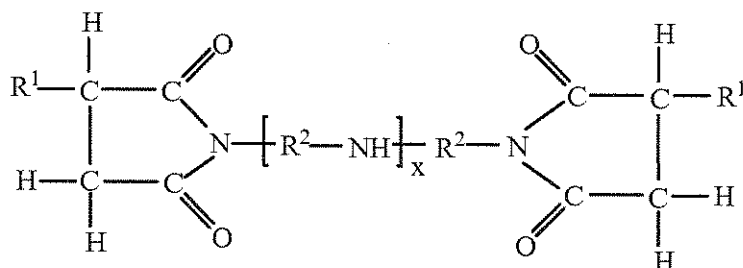
determined using ASTM D 2896 test. An ashless dispersant generally comprises an oil soluble polymeric hydrocarbon backbone having functional groups that are capable of associating with particles to be dispersed. Many types of ashless dispersants are known in the art.

[0032] Representative examples of ashless dispersants include, but are not limited to, amines, alcohols, amides, or ester polar moieties attached to the polymer backbones via bridging groups. An ashless dispersant of the present invention may be, for example, selected from oil soluble salts, esters, amino-esters, amides, imides, and oxazolines of long chain hydrocarbon substituted mono and dicarboxylic acids or their anhydrides; thiocarboxylate derivatives of long chain hydrocarbons, long chain aliphatic hydrocarbons having a polyamine attached directly thereto; and Mannich condensation products formed by condensing a long chain substituted phenol with formaldehyde and polyalkylene polyamine.

[0033] Carboxylic dispersants are reaction products of carboxylic acylating agents (acids, anhydrides, esters, etc.) comprising at least about 34 and preferably at least about 54 carbon atoms with nitrogen containing compounds (such as amines), organic hydroxy compounds (such as aliphatic compounds including monohydric and polyhydric alcohols, or aromatic compounds including phenols and naphthols), and/or basic inorganic materials. These reaction products include imides, amides, and esters.

[0034] Succinimide dispersants are a type of carboxylic dispersants. They are produced by reacting hydrocarbyl-substituted succinic acylating agent with organic hydroxy compounds, or with amines comprising at least one hydrogen atom attached to a nitrogen atom, or with a mixture of the hydroxy compounds and amines. The term "succinic acylating agent" refers to a hydrocarbon-substituted succinic acid or a succinic acid-producing compound, the latter encompasses the acid itself. Such materials typically include hydrocarbyl-substituted succinic acids, anhydrides, esters (including half esters) and halides.

[0035] Succinic-based dispersants have a wide variety of chemical structures. One class of succinic-based dispersants may be represented by the formula:



wherein each  $R^1$  is independently a hydrocarbyl group, such as a polyolefin-derived group. Typically the hydrocarbyl group is an alkyl group, such as a polyisobutyl group. Alternatively expressed, the  $R^1$  groups can contain about 40 to about 500 carbon atoms, and these atoms may be present in aliphatic forms.  $R^2$  is an alkylene group, commonly an ethylene ( $C_2H_4$ ) group. Examples of succinimide dispersants include those described in, for example, U.S. Patent Nos. 3,172,892, 4,234,435 and 6,165,235.

[0036] The polyalkenes from which the substituent groups are derived are typically homopolymers and interpolymers of polymerizable olefin monomers of 2 to about 16 carbon atoms, and usually 2 to 6 carbon atoms. The amines which are reacted with the succinic acylating agents to form the carboxylic dispersant composition can be monoamines or polyamines.

[0037] Succinimide dispersants are referred to as such since they normally contain nitrogen largely in the form of imide functionality, although the amide functionality may be in the form of amine salts, amides, imidazolines as well as mixtures thereof. To prepare a succinimide dispersant, one or more succinic acid-producing compounds and one or more amines are heated and typically water is removed, optionally in the presence of a substantially inert organic liquid solvent/diluent. The reaction temperature can range from about 80°C up to the decomposition temperature of the mixture or the product, which typically falls between about 100°C to about 300°C. Additional details and examples of procedures for preparing the succinimide dispersants of the present invention include those described in, for example, U.S. Patent Nos. 3,172,892, 3,219,666, 3,272,746, 4,234,435, 6,165,235 and 6,440,905.

[0038] Suitable ashless dispersants may also include amine dispersants, which are reaction products of relatively high molecular weight aliphatic halides and amines, preferably polyalkylene polyamines. Examples of such amine dispersants include those described in, for example, U.S. Patent Nos. 3,275,554, 3,438,757, 3,454,555 and 3,565,804.

[0039] Suitable ashless dispersants may further include "Mannich dispersants," which are reaction products of alkyl phenols in which the alkyl group contains at least about 30 carbon atoms with aldehydes (especially formaldehyde) and amines (especially polyalkylene polyamines). Examples of such dispersants include those described in, for example, U.S. Patent Nos. 3,036,003, 3,586,629, 3,591,598 and 3,980,569.

[0040] Suitable ashless dispersants may also be post-treated ashless dispersants such as post-treated succinimides, e.g., post-treatment processes involving borate or ethylene carbonate as disclosed in, for example, U.S. Patent Nos. 4,612,132 and 4,746,446; and the like as well as other post-treatment processes. The carbonate-treated alkenyl succinimide is a polybutene succinimide derived from polybutenes having a molecular weight of about 450 to about 3000, preferably from about 900 to about 2500, more preferably from about 1300 to about 2300, and most preferably from about 2000 to about 2400, as well as mixtures of these molecular weights. Preferably, it is prepared by reacting, under reactive conditions, a mixture of a polybutene succinic acid derivative, an unsaturated acidic reagent copolymer of an unsaturated acidic reagent and an olefin, and a polyamine, such as disclosed in U.S. Patent No. 5,716,912, the contents of which are incorporated herein by reference.

[0041] Suitable ashless dispersants may also be polymeric, which are interpolymers of oil-solubilizing monomers such as decyl methacrylate, vinyl decyl ether and high molecular weight olefins with monomers containing polar substitutes. Examples of polymeric dispersants include those described in, for example, U.S. Patent Nos. 3,329,658; 3,449,250 and 3,666,730.

[0042] In a preferred embodiment of the present invention, an ashless dispersant for use in the lubricating oil composition is an ethylene, carbonate-treated bissuccinimide derived from a polyisobutenyl group having a number average molecular weight of about 2300. The dispersant(s) for use in the lubricating oil compositions of the present invention are preferably non-polymeric (e.g., are mono- or bissuccinimides).

[0043] Generally, the ashless dispersant is present in the lubricating oil composition in an amount ranging from about 3 to about 10 wt. %, and preferably from about 4 to about 8 wt. %, based on the total weight of the lubricating oil composition.

[0044] The at least one metal-containing detergent compound employed in the lubricating oil composition of the present invention functions both as a detergent to reduce or remove deposits and as an acid neutralizer or rust inhibitor, thereby reducing wear and corrosion and extending engine life. Detergents generally comprise a polar head with long hydrophobic tail, with the polar head comprising a metal salt of an acid organic compound.

[0045] The lubricating oil composition of the present invention may contain one or more detergents, which are normally salts, and especially overbased salts. Overbased salts, or overbased materials, are single phase, homogeneous Newtonian systems characterized by a

metal content in excess of that which would be present according to the stoichiometry of the metal and the particular acidic organic compound reacted with the metal. The overbased materials are prepared by reacting an acidic material (typically an inorganic acid or lower carboxylic acid such as carbon dioxide) with a mixture comprising an acidic organic compound, in a reaction medium comprising at least one inert, organic solvent (such as mineral oil, naphtha, toluene, xylene) in the presence of a stoichiometric excess of a metal base and a promoter.

[0046] Useful acidic organic compounds for making the overbased compositions include carboxylic acids, sulfonic acids, phosphorus-containing acids, phenols and mixtures thereof. Preferably, the acidic organic compounds are carboxylic acids or sulfonic acids with sulfonic or thiousulfonic groups (such as hydrocarbyl-substituted benzenesulfonic acids), and hydrocarbyl-substituted salicylic acids.

[0047] Carboxylate detergents, e.g., salicylates, can be prepared by reacting an aromatic carboxylic acid with an appropriate metal compound such as an oxide or hydroxide. Neutral or overbased products may then be obtained by methods well known in the art. The aromatic moiety of the aromatic carboxylic acid can contain one or more heteroatoms such as nitrogen and oxygen. Preferably, the moiety contains only carbon atoms. More preferably, the moiety contains six or more carbon atoms, such as a benzene moiety. The aromatic carboxylic acid may contain one or more aromatic moieties, such as one or more benzene rings, optionally fused together or otherwise connected via alkylene bridges. Representative examples of aromatic carboxylic acids include salicylic acids and sulfurized derivatives thereof such as hydrocarbyl substituted salicylic acid and derivatives thereof. Processes for sulfurizing, for example, a hydrocarbyl-substituted salicylic acid, are known to those skilled in the art. Salicylic acids are typically prepared by carboxylation, for example, by the Kolbe-Schmitt process, of phenoxides. In that case, salicylic acids are generally obtained in a diluent in admixture with an uncarboxylated phenol.

[0048] Metal salts of phenols and sulfurized phenols are prepared by reaction with an appropriate metal compound such as an oxide or hydroxide. Neutral or overbased products may be obtained by methods well known in the art. For example, sulfurized phenols may be prepared by reacting a phenol with sulfur or a sulfur-containing compound such as hydrogen sulfide, sulfur monohalide or sulfur dihalide, to form products that are mixtures of compounds in which 2 or more phenols are bridged by sulfur-containing bridges.

[0049] The metal compounds useful in making the overbased salts are generally any Group I or Group II metal compounds in the Periodic Table of the Elements. Group I metals of the metal base include Group 1a alkali metals (e.g., sodium, potassium, lithium) as well as Group 1b metals such as copper. Group I metals are preferably sodium, potassium, lithium and copper, more preferably sodium or potassium, and particularly preferably sodium. Group II metals of the metal base include Group IIa alkaline earth metals (e.g., magnesium, calcium, strontium, barium) as well as Group IIb metals such as zinc or cadmium. Preferably, the Group II metals are magnesium, calcium, barium, or zinc, more preferably magnesium or calcium, and most preferably calcium.

[0050] Examples of the overbased detergents include, but are not limited to, calcium sulfonates, calcium phenates, calcium salicylates, calcium stearates and mixtures thereof. Overbased detergents suitable for use in the lubricating oil compositions of the present invention may be low overbased (e.g., an overbased detergent having a TBN below about 100). The TBN of such a low-overbased detergent may be from about 5 to about 50, or from about 10 to about 30, or from about 15 to about 20. Alternatively, the overbased detergents suitable for use in the lubricating oil compositions of the present invention may be high overbased (e.g., an overbased detergent having a TBN above about 100). The TBN of such a high-overbased detergent may be from about 150 to about 450, or from about 200 to about 350, or from about 250 to about 280. A low-overbased calcium sulfonate detergent with a TBN of about 17 and a high-overbased sulfurized calcium phenate with a TBN of about 400 are two exemplary overbased detergents for use in the lubricating oil compositions of the present invention. The lubricating oil compositions of the present invention may contain more than one overbased detergent, which may be all low-TBN detergents, all high-TBN detergents, or a mixture thereof. For example, the lubricating oil compositions of the present invention may contain a first metal-containing detergent which is an overbased alkaline earth metal sulfonate detergent having a TBN of about 150 to about 450 and a second metal-containing detergent which is an overbased alkaline earth metal sulfonate detergent having a TBN of about 10 to about 50.

[0051] Suitable detergents for the lubricating oil compositions of the present invention also include "hybrid" detergents such as, for example, phenate/salicylates, sulfonate/phenates, sulfonate/salicylates, sulfonates/phenates/salicylates, and the like.

Examples of hybrid detergents include those described in, for example, U.S. Patent Nos, 6,153,565, 6,281,179, 6,429,178, and 6,429,179.

[0052] Generally, the metal-containing detergent is present in the lubricating oil composition in an amount ranging from about 0.25 to about 3 wt. %, and preferably from about 0.5 to about 2 wt. %, based on the total weight of the lubricating oil composition.

[0053] The antioxidant compounds employed in the lubricating oil composition of the present invention reduce the tendency of base stocks to deteriorate in service, which deterioration can be evidenced by the products of oxidation such as sludge and varnish-like deposits on the metal surfaces and by viscosity growth. Such oxidation inhibitors include hindered phenols, ashless oil soluble phenates and sulfurized phenates, alkyl-substituted diphenylamine, alkyl-substituted phenyl and naphthylamines and the like and mixtures thereof. Suitable diphenylamine antioxidants include, but are not limited to, monoalkylated diphenylamine, dialkylated diphenylamine, trialkylated diphenylamine, and the like and mixtures thereof. Representative examples of diphenylamine antioxidants include butyldiphenylamine, di-butyldiphenylamine, octyldiphenylamine, di-octyldiphenylamine, nonyldiphenylamine, di-nonyldiphenylamine, t-butyl-t-octyldiphenylamine, and the like and mixtures thereof.

[0054] Generally, the antioxidant compound is present in the lubricating oil composition in an amount ranging from about 0.2 to about 4 wt. %, and preferably from about 0.3 to about 1 wt. %, based on the total weight of the lubricating oil composition.

[0055] The anti-wear agent compounds other than a zinc dialkyl dithiophosphate compound employed in the lubricating oil composition of the present invention include molybdenum-containing complexes such as, for example, a molybdenum/nitrogen-containing complex. Such complexes are known in the art and are described, for example, in U.S. Patent No. 4,263,152, the content of which is incorporated by reference herein.

[0056] The structure of the molybdenum/nitrogen complexes is not known with certainty. However, the molybdenum/nitrogen complexes 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. The molybdenum compounds used to prepare the molybdenum and molybdenum/nitrogen complexes 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. Suitable molybdenum compounds include 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,  $\text{MoOCl}_4$ ,  $\text{MoO}_2\text{Br}_2$ ,  $\text{Mo}_2\text{O}_3\text{Cl}_6$ , molybdenum trioxide and the like and mixtures thereof. Preferred acidic molybdenum compounds are molybdic acid, ammonium molybdate, and alkali metal molybdates. Particularly preferred are molybdic acid and ammonium molybdate.

[0057] The basic nitrogen-containing compound used to prepare the molybdenum/nitrogen complexes have at least one basic nitrogen and are preferably oil-soluble. Representative examples of basic nitrogen-containing compounds include succinimides, carboxylic acid amides, hydrocarbyl monoamines, hydrocarbon polyamines, Mannich bases, phosphoramides, thiophosphoramides, phosphonamides, dispersant viscosity index improvers, and the like and mixtures thereof. Any of the nitrogen-containing compounds may be post-treated with, e.g., boron, using procedures well known in the art so long as the compositions continue to contain basic nitrogen. The post-treatments are particularly applicable to succinimides and Mannich base compositions.

[0058] The succinimides 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 Nos. 3,172,892; 3,219,666 and 3,272,746, the content of which is incorporated by reference herein. 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. Examples of ethylene amines include ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine and the like. Particularly preferred are those succinimides prepared from polyisobutenyl succinic anhydride of about 70 to about 128 carbon atoms and tetraethylene pentamine or triethylene tetramine and mixtures thereof.

[0059] 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.

[0060] Carboxylic acid amide compounds are also suitable starting materials for preparing the molybdenum complexes. Examples of such compounds include those disclosed in, for example, U.S. Patent No. 3,405,064, the content of which is incorporated by reference herein. These compounds 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  $R^1\text{COOH}$ , wherein  $R^1$  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.

[0061] Another class of basic nitrogen-compounds which are useful in preparing the molybdenum/nitrogen complex is hydrocarbyl monoamines and hydrocarbyl polyamines, e.g., as disclosed in U.S. Pat. No. 3,574,576, the content of which is incorporated by reference herein. The hydrocarbyl group, e.g., an alkyl group or olefinic group having one or two sites of unsaturation, usually contains from about 9 to about 350 carbon atoms, and 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.

[0062] Another class of basic nitrogen-compounds useful for supplying basic nitrogen is the Mannich base compound. These compounds 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, e.g., diethylene triamine or tetraethylene pentamine, and the like. The phenolic material may be sulfurized and preferably is dodecylphenol or a C<sub>80</sub> to C<sub>100</sub> alkylphenol. Typical Mannich bases are disclosed in U.S. Patent Nos. and 3,368,972; 3,539,663; 3,649,229 and 4,157,309, the content of which is incorporated by reference herein. The Mannich base can be 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 H<sub>2</sub>N(ANH)<sub>e</sub>H 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 the 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 compound.

[0063] The molybdenum-containing complexes can be sulfurized or non-sulfurized. Representative sulfur sources for preparing the molybdenum/sulfur complexes include sulfur, hydrogen sulfide, sulfur monochloride, sulfur dichloride, phosphorus pentasulfide, R<sup>2</sup>S<sub>f</sub> wherein R<sup>2</sup> is a hydrocarbyl such as a C<sub>1</sub> to C<sub>40</sub> alkyl, and f is at least 2, inorganic sulfides and polysulfides such as (NH<sub>4</sub>)<sub>2</sub>S<sub>g</sub>, where g is at least 1, thioacetamide, thiourea, and mercaptans of the formula R<sup>2</sup>SH wherein R<sup>2</sup> 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.

[0064] Generally, the molybdenum/nitrogen-containing complex can be made with an organic solvent comprising a polar promoter during a complexation step and procedures for preparing such complexes are described, for example, e.g., in U.S. Pat. Nos. 4,259,194; 4,259,195; 4,261,843; 4,263,152; 4,265,773; 4,283,295; 4,285,822; 4,369,119; 4,370,246; 4,394,279; 4,402,840; and 6,962,896 and U.S. Patent Application Publication No. 2005/0209111, the contents of which are incorporated by reference herein. As shown in these references, the molybdenum/nitrogen-containing complex can further be sulfurized.

[0065] In one embodiment, the anti-wear agent compounds for use herein are substantially free of any phosphorus and/or sulfur content. In another embodiment, the anti-wear agent compounds for use herein are free of any phosphorus and/or sulfur content.

[0066] Generally, the anti-wear agent compounds other than a zinc dialkyl dithiophosphate compound are present in the lubricating oil composition in an amount ranging from about 0.25 to about 5 wt. %, and preferably from about 0.3 to about 2 wt. %, based on the total weight of the lubricating oil composition.

[0067] The lubricating oil compositions of the present invention can be conveniently prepared by simply blending or mixing the ashless dispersant, at least one metal-containing detergent, antioxidant and anti-wear agent other than a zinc dialkyl dithiophosphate compound, optionally with other additives, with the oil of lubricating viscosity. The ashless dispersant, metal-containing detergent, antioxidant and anti-wear agent other than a zinc dialkyl dithiophosphate compound may also be preblended as a concentrate or package with various other additives, if desired, in the appropriate ratios to facilitate blending of a lubricating composition containing the desired concentration of additives. The ashless dispersant, at least one metal-containing detergent, antioxidant and anti-wear agent other than a zinc dialkyl dithiophosphate compound are blended with the base oil using a concentration at which they provide improved antiwear effect and are both soluble in the oil and compatible with other additives in the desired finished lubricating oil. Compatibility in this instance generally means that the present compounds as well as being oil soluble in the applicable treat rate also do not cause other additives to precipitate under normal conditions. Suitable oil solubility/compatibility ranges for a given compound of lubricating oil formulation can be determined by those having ordinary skill in the art using routine solubility testing procedures. For example, precipitation from a formulated lubricating oil composition at ambient conditions (about 20°C to 25°C) can be measured by either actual precipitation from the oil composition or the formulation of a "cloudy" solution which evidences formation of insoluble wax particles.

[0068] The lubricating oil compositions of the present invention may also contain other conventional additives for imparting auxiliary functions to give a finished lubricating oil composition in which these additives are dispersed or dissolved. For example, the lubricating oil compositions can be blended with friction modifiers, rust inhibitors, dehazing agents, demulsifying agents, metal deactivating agents, pour point depressants, antifoaming agents, co-solvents, package compatibilisers, corrosion-inhibitors, dyes, extreme pressure agents and the like and mixtures thereof. A variety of the additives are known and commercially available. These additives, or their analogous compounds, can be employed

for the preparation of the lubricating oil compositions of the invention by the usual blending procedures.

[0069] Examples of friction modifiers include, but are not limited to, alkoxylated fatty amines; borated fatty epoxides; fatty phosphites, fatty epoxides, fatty amines, borated alkoxylated fatty amines, metal salts of fatty acids, fatty acid amides, glycerol esters, borated glycerol esters; and fatty imidazolines as disclosed in U.S. Patent No. 6,372,696, the contents of which are incorporated by reference herein; friction modifiers obtained from a reaction product of a C<sub>4</sub> to C<sub>75</sub>, preferably a C<sub>6</sub> to C<sub>24</sub>, and most preferably a C<sub>6</sub> to C<sub>20</sub>, fatty acid ester and a nitrogen-containing compound selected from the group consisting of ammonia, and an alkanolamine and the like and mixtures thereof. The friction modifier can be incorporated in the lubricating oil composition in an amount ranging of from about 0.02 to about 2.0 wt. % of the lubricating oil composition, preferably from about 0.05 to about 1.0 wt. %, and more preferably from about 0.1 to about 0.5 wt. %.

[0070] Examples of rust inhibitors include, but are not limited to, nonionic polyoxyalkylene agents, e.g., polyoxyethylene lauryl ether, polyoxyethylene higher alcohol ether, polyoxyethylene nonylphenyl ether, polyoxyethylene octylphenyl ether, polyoxyethylene octyl stearyl ether, polyoxyethylene oleyl ether, polyoxyethylene sorbitol monostearate, polyoxyethylene sorbitol monooleate, and polyethylene glycol monooleate; 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; phosphoric esters; (short-chain) alkenyl succinic acids; partial esters thereof and nitrogen-containing derivatives thereof; synthetic alkarylsulfonates, e.g., metal dinonylnaphthalene sulfonates; and the like and mixtures thereof.

[0071] Examples of antifoaming agents include, but are not limited to, polymers of alkyl methacrylate; polymers of dimethylsilicone and the like and mixtures thereof.

[0072] The lubricating composition of the present invention may also contain a viscosity index improver. Examples of the viscosity index improvers include poly-(alkyl methacrylate), ethylene-propylene copolymer, styrene-butadiene copolymer, and polyisoprene. Viscosity index improvers of the dispersant type (having increased dispersancy) or multifunction type are also employed. These viscosity index improvers can be used singly or in combination. The amount of viscosity index improver to be incorporated

into an engine oil varies with desired viscosity of the compounded engine oil, and generally in the range of about 0.5 to about 20 wt. % per total amount of the engine oil.

[0073] The lubricating oil composition of the present invention possesses a wear reducing property greater than that of a corresponding lubricating oil composition in which a zinc dihydrocarbyl dithiophosphate such as a zinc dialkyl dithiophosphate compound is present therein. In one embodiment of the present invention, the lubricating oil composition of the present invention possesses a wear reducing property at least about 20% greater than that of a corresponding lubricating oil composition in which a zinc dihydrocarbyl dithiophosphate such as a zinc dialkyl dithiophosphate compound is present therein. In another embodiment of the present invention, the lubricating oil composition of the present invention possesses a wear reducing property at least about 25% greater than that of a corresponding lubricating oil composition in which a zinc dialkyl dithiophosphate compound is present therein.

[0074] The final application of the lubricating oil compositions of this invention may be, for example, in marine cylinder lubricants in crosshead diesel engines, crankcase lubricants in automobiles and railroads and the like, lubricants for heavy machinery such as steel mills and the like, or as greases for bearings and the like. In one embodiment, the lubricating oil compositions of this invention are used to lubricate an internal combustion engine such as a spark ignition engine, a compression ignition diesel engine, e.g., a heavy duty diesel engine or a compression ignition diesel engine equipped with at least one of an exhaust gas recirculation (EGR) system; a catalytic converter; and a particulate trap.

[0075] Whether the lubricating oil composition is fluid or solid will ordinarily depend on whether a thickening agent is present. Typical thickening agents include polyurea acetates, lithium stearate and the like.

[0076] The following non-limiting examples are illustrative of the present invention.

#### EXAMPLE 1

[0077] A lubricating oil composition was formed containing 3.858 wt. % of an ethylene carbonate post-treated bis-succinimide prepared from a 2300 average molecular weight polyisobutenyl succinic anhydride with a heavy polyamine, 0.286 wt. % borated glycerol monooleate friction modifier, 0.487 wt. % molybdenum succinimide dispersant/wear inhibitor, 0.490 wt. % diphenylamine antioxidant, 0.593 wt. % 17 TBN calcium sulfonate

detergent, 1.141 wt. % 410 TBN calcium sulfonate detergent, 0.050 wt. % silicone-based foam inhibitor, 0.537 wt. % Exxon 100 N diluent oil and 4.800 wt. % ethylene-propylene copolymer viscosity index improver, in 87.46 wt. % Group II base oil. The resulting lubricating oil composition had a phosphorus content of 0 wt. % and a sulfur content of 0.051 wt. %.

#### COMPARATIVE EXAMPLE A

[0078] To the lubricating oil composition of Example 1 was added 0.64 wt. % of zinc dihydrocarbyl dithiophosphate. The resulting lubricating oil composition had a phosphorus content of 0.048 wt. % and a sulfur content of 0.151 wt. %.

#### COMPARATIVE EXAMPLE B

[0079] A lubricating oil composition was formed containing 2.35 wt. % succinimide dispersant, 6 wt. % borated succinimide dispersant, 2.84 wt. % 260 TBN sulfurized calcium phenate detergent, 1.02 wt. % 17 TBN calcium sulfonate detergent, 0.22 wt. % 410 TBN calcium sulfonate detergent, 0.3 wt. % diphenyl amine antioxidant, 0.6 wt. % hindered phenol antioxidant, 0.4 wt. % terephthalic acid salt of a bis-succinimide (derived from 1300 MW PIBSA and heavy polyamine) dispersant, 0.5 wt. % molybdenum succinimide complex dispersant/wear inhibitor, 10 ppm foam inhibitor, 5.75 wt. % functionalized viscosity index improver, 0.3 wt. % pour point depressant, 0.75 wt. % non-functionalized viscosity index improver, and 1.89 wt. % zinc dihydrocarbyl dithiophosphate in 76.17 wt. % base oil consisting of 24.5 wt. % base oil consisting of 24.5% Group II base oil having a kinematic viscosity (kv) at 100°C of 4.7 to 4.9 cSt and 75.5 wt. % Group II base oil having a kv at 100°C of 7.8 to 7.9 cSt. The resulting lubricating oil composition had a phosphorus content of 0.150 wt. % and a sulfur content of 0.445 wt. %.

[0080] Testing

[0081] Mini-traction Machine Evaluation

[0082] The lubricating oil composition of Example 1 and the lubricating oil compositions of Comparative Examples A and B were evaluated using a PCS Instruments Ltd., London UK, Mini-Traction Machine (MTM) bench test. The PCS MTM instrument

was modified so that a 1/4-in. diameter Falex 52100 steel test ball (with special holder) was substituted for the pin holder that came with the instrument (see, e.g., Yamaguchi, E. S., "Friction and Wear Measurements Using a Modified MTM Tribometer," IP.com Journal 7, Vol. 2, 9, pp 57-58 (August 2002), No. IPCOM000009117D; and Yamaguchi, E. S., "Soot Wear in Diesel Engines", Journal of Engineering Tribology, Proceedings of the Institution of Mechanical Engineers Part J, Vol. 220, No. J5, pp. 463-469 (2006)). The instrument was used in the pin-on-disk mode and run under sliding conditions. It is achieved by fixing the ball rigidly in the special holder, such that the ball stays still while the disk slides under it. The conditions are shown in Table 1.

TABLE 1

| Test Conditions for MTM  |              |      |
|--------------------------|--------------|------|
| Load                     | 14 N         |      |
| Initial Contact Pressure | 1.53 GPa     |      |
| Temperature              | 116°C        |      |
| Tribocouple              | 52100/52100  |      |
| Speed                    | mm/Sec.      | Min. |
|                          | 3800         | 10   |
|                          | 2000         | 10   |
|                          | 1000         | 10   |
|                          | 100          | 10   |
|                          | 20           | 10   |
|                          | 10           | 10   |
|                          | 5            | 10   |
| Length of Timer          | 70 Min. Test |      |
| Diesel Engine Soot       | 9%           |      |

[0083] Engine soot obtained from the overhead recovery system of an engine testing facility was used for this test. Mineral oil was added to the soot before it was shipped. Therefore, the soot has to be washed prior to the test. It was made into a thin slurry with pentane. The slurry was stirred for a few minutes before it was filtered through a Whatman Number 2 filter paper over a Buchner funnel. The precipitate was made into a thin slurry

again and filtered through a Whatman Number 2 filter paper again. The precipitate was then dried in a vacuum oven at 20 inch vacuum and 90°C for more than 16 hours. The dried soot was then sieved through a 50 mesh (300  $\mu\text{m}$  maximum) before use. The objective of this operation was to remove the oil and other impurities so that reproducible particles are made and they would give rise to abrasive wear as seen in modern exhaust gas recirculation (EGR) engines.

[0084] To prepare the test specimens, the anti-corrosion coating of the PCS Instruments 52100 smooth (0.02 micron  $R_a$ ), steel discs was removed using heptane, hexane, and isooctane. Then, the discs were wiped clean with a soft tissue and submersed in a beaker of the cleaning solvent until the film on the disc track had been removed, and the track of the disc appeared shiny. The discs and test balls were placed in individual containers and submerged in Chevron 450 thinner. Lastly, the test specimens were ultrasonically cleaned by placing them in a sonicator for 30 minutes.

[0085] The results of this evaluation are set forth in Figure 1, which show the wear scar diameter (WSD) and standard deviation (STD) of the lubricating oil compositions of Example 1 and Comparative Examples A and B. As the data show, the lubricating oil composition of Example 1 containing no zinc dihydrocarbyl dithiophosphate provided a significantly improved MTM wear result as compared to the same lubricating oil composition of Comparative Example A treated with a zinc dihydrocarbyl dithiophosphate. This was unexpected as zinc dihydrocarbyl dithiophosphate is a known antiwear agent and would be expected to improve the wear result of the lubricating oil composition. In fact, the MTM wear result of the lubricating oil composition of Example 1 is lower than the lubricating oil composition of Comparative Example B, which is a standard lubricant containing a relatively high amount of zinc dihydrocarbyl dithiophosphate.

[0086] It will be understood that various modifications may be made to the embodiments disclosed herein. Therefore the above description should not be construed as limiting, but merely as exemplifications of preferred embodiments. For example, the functions described above and implemented as the best mode for operating the present invention are for illustration purposes only. Other arrangements and methods may be implemented by those skilled in the art without departing from the scope and spirit of this invention. Moreover, those skilled in the art will envision other modifications within the scope and spirit of the claims appended hereto.

WHAT IS CLAIMED IS:

1. A lubricating oil composition comprising (a) a major amount of an oil of lubricating viscosity, (b) an ashless dispersant, (c) at least one metal-containing detergent, (d) an antioxidant, and (e) an anti-wear agent, wherein the lubricating oil composition is free of any zinc dialkyl dithiophosphate compound and is substantially free of any phosphorus content.

2. The lubricating oil composition of Claim 1, wherein the ashless dispersant is a bissuccinimide derived from one or more polyalkylene succinic anhydrides.

3. The lubricating oil composition of Claim 2, wherein the polyalkylene group is a polyisobutenyl group having an average molecular weight of from 900 to 2300.

4. The lubricating oil composition of Claim 3, wherein the bissuccinimide is post-treated with ethylene carbonate.

5. The lubricating oil composition of Claim 1, wherein the at least one metal-containing detergent is an overbased alkaline earth metal sulfonate detergent having a total base number (TBN) of 10 to 450.

6. The lubricating oil composition of Claim 1, wherein the at least one metal-containing detergent comprises two metal-containing detergents.

7. The lubricating oil composition of Claim 6, wherein the two metal-containing detergents comprise a first metal-containing detergent which is an overbased alkaline earth metal sulfonate detergent having a TBN of 150 to 450 and a second metal-containing detergent which is an overbased alkaline earth metal sulfonate detergent having a TBN of 10 to 50.

8. The lubricating oil composition of Claim 1, wherein the antioxidant is a diphenylamine compound.

9. The lubricating oil composition of Claim 1, wherein the anti-wear agent comprises a molybdenum-containing complex.

10. The lubricating oil composition of Claim 9, wherein the molybdenum-containing complex comprises a molybdenum/nitrogen complex.

11. The lubricating oil composition of Claim 1, comprising  
3 wt. % to 10 wt. %, based on the total weight of the lubricating oil composition, of the ashless dispersant;

0.5 wt. % to 2 wt. %, based on the total weight of the lubricating oil composition, of the at least one metal-containing detergent;

0.2 wt. % to 1 wt. %, based on the total weight of the lubricating oil composition; of the antioxidant; and

0.1 wt. % to 2 wt. %, based on the total weight of the lubricating oil composition; of the anti-wear agent.

12. The lubricating oil composition of Claim 1, further comprising at least one additive selected from the group consisting of a friction modifier, extreme pressure agent, viscosity index improver, pour point depressant and mixtures thereof.

13. The lubricating oil composition of Claim 1, which possesses a wear reducing property of at least 20% greater than that of a corresponding lubricating oil composition in which a zinc dihydrocarbyl dithiophosphate compound is present therein.

14. The lubricating oil composition of Claim 1, which possesses a wear reducing property of at least 25% greater than that of a corresponding lubricating oil composition in which a zinc dihydrocarbyl dithiophosphate compound is present therein.

15. A method for reducing wear in an internal combustion engine, the method comprising operating the engine with the lubricating oil composition according to Claims 1-14.

16. Use of a lubricating oil composition comprising (a) a major amount of an oil of lubricating viscosity, (b) an ashless dispersant, (c) at least one metal-containing detergent, (d) an antioxidant, and (e) an anti-wear agent, wherein the lubricating oil composition is free of any zinc dialkyl dithiophosphate compound and is substantially free of any phosphorus content, for the purpose of wear inhibition in an internal combustion engine.