

LUBRICATING OIL COMPOSITIONS COMPRISING A MOLYBDENUM COMPOUND AND A ZINC DIALKYLDITHIOPHOSPHATE

FIELD

[0001] Provided herein are lubricating oil compositions comprising a base oil, an oil soluble molybdenum compound and a zinc dithiophosphate compound. Methods of making and using the lubricating oil compositions are also described.

BACKGROUND

[0002] Lubricating oil compositions used to lubricate internal combustion engines contain base oil of lubricating viscosity, or a mixture of such oils, and additives used to improve the performance characteristics of the oil. For example, additives are used to improve detergency, to reduce engine wear, to provide stability against heat and oxidation, to reduce oil consumption, to inhibit corrosion, to act as a dispersant, and to reduce friction loss. Some additives provide multiple benefits, such as dispersant-viscosity modifiers. Other additives, while improving one characteristic of the lubricating oil, have an adverse effect on other characteristics. Thus, to provide lubricating oil having optimal overall performance, it is necessary to characterize and understand all the effects of the various additives available, and carefully balance the additive content of the lubricant.

[0003] It has been proposed in many patents and articles (for example, U.S. Pat. Nos. 4,164,473; 4,176,073; 4,176,074; 4,192,757; 4,248,720; 4,201,683; 4,289,635; and 4,479,883) that oil-soluble molybdenum compounds are useful as lubricant additives. In particular, the addition of molybdenum compounds to oil, particularly molybdenum dithiocarbamate compounds, provides the oil with improved boundary friction characteristics and bench tests demonstrate that the coefficient of friction of oil containing such molybdenum compounds is generally lower than that of oil containing organic friction modifiers. This reduction in coefficient of friction results in improved antiwear properties and may contribute to enhanced fuel economy in gasoline or diesel fired engines, including both short- and long-term fuel economy properties (i.e., fuel economy retention properties). To provide antiwear effects, molybdenum compounds are generally added in amounts introducing from about 350 ppm up to 2,000 ppm of molybdenum into

fuel economy benefits, such molybdenum compounds are expensive relative to more conventional, metal-free (ashless) organic friction modifiers

[0004] Therefore, it is desirable to find a lubricating oil composition that provides improved fuel economy benefit; demonstrates excellent wear protection characteristics, is relatively low in cost.

SUMMARY

[0005] Provided herein are lubricating oil compositions that provide an improved friction reduction. The lubricating oil compositions comprising

- i) a major amount of a base oil,
- ii) at least one oil-soluble molybdenum compound and
- iii) a zinc dialkyldithiophosphate compound,

wherein the molybdenum content derived from the molybdenum compound is at least about 10 ppm based on the total weight of the lubricating oil composition and the phosphorus content derived from the zinc dialkyldithiophosphate compound is about 200 to 500 ppm based on the total weight of the lubricating oil composition.

[0006] In certain aspects, the base oil is present in an amount greater than about 40%, 50%, 60% or about 70% by weight of the lubricating oil compositions.

[0007] In certain embodiments, the lubricating oil composition disclosed herein further comprises at least one additive selected from the group consisting of antioxidants, antiwear agents, detergents, rust inhibitors, demulsifiers, friction modifiers, multi-functional additives, viscosity index improvers, pour point depressants, foam inhibitors, metal deactivators, dispersants, corrosion inhibitors, lubricity improvers, thermal stability improvers, anti-haze additives, dyes, markers, and combinations thereof.

[0008] Also provided herein are methods of making lubricating oil compositions. In one aspect, the methods comprise the step of mixing

- i) a major amount of a base oil,
- ii) at least one oil-soluble molybdenum compound and
- iii) a zinc dialkyldithiophosphate compound,

wherein the molybdenum content derived from the molybdenum compound is at least about 10 ppm based on the total weight of the lubricating oil composition and the

phosphorus content derived from the zinc dialkyldithiophosphate compound is about 200 to 500 ppm based on the total weight of the lubricating oil composition. In certain embodiments, the molybdenum compound and the zinc dialkyldithiophosphate compound used as described herein show synergy and resulting low friction coefficient in prototype GF-5 lubricating compositions.

[0009] Also provided herein are methods of lubricating a motor engine with a lubricating oil compositions provided herein. In one aspect, the methods comprise the step of operating the engine with the lubricating oil composition of provided herein.

[0010] Other embodiments will be in part apparent and in part pointed out hereinafter.

DESCRIPTION OF THE DRAWINGS

[0011] Figure 1 depicts a plot of friction by High Frequency Reciprocating Rig test (HFRR) versus phosphorus content of the lubricant oil compositions described herein.

Definitions

[0012] To facilitate the understanding of the subject matter disclosed herein, a number of terms, abbreviations or other shorthand as used herein are defined below. Any term, abbreviation or shorthand not defined is understood to have the ordinary meaning used by a skilled artisan contemporaneous with the submission of this application.

[0013] “A major amount” of a base oil refers to the amount of the base oil is at least 40 wt.% of the lubricating oil composition. In some embodiments, “a major amount” of a base oil refers to an amount of the base oil more than 50 wt.%, more than 60 wt.%, more than 70 wt.%, more than 80 wt.%, or more than 90 wt.% of the lubricating oil composition.

[0014] “Sulfated ash content” refers to the amount of metal-containing additives (*e.g.*, calcium, magnesium, molybdenum, zinc, *etc.*) in a lubricating oil and is typically measured according to ASTM D874, which is incorporated herein by reference.

[0015] A composition that is “substantially free” of a compound refers to a composition which contains less than 20 wt.%, less than 10 wt.%, less than 5 wt.%, less

than 4 wt.%, less than 3 wt.%, less than 2 wt.%, less than 1 wt.%, less than 0.5 wt.%, less than 0.1 wt.%, or less than 0.01 wt.% of the compound, based on the total weight of the composition.

[0016] A composition that is “free” of a compound refers to a composition which contains from 0.001 wt.% to 0 wt.% of the compound, based on the total weight of the composition.

[0017] In the following description, all numbers disclosed herein are approximate values, regardless whether the word “about” or “approximate” is used in connection therewith. They may vary by 1 percent, 2 percent, 5 percent, or, sometimes, 10 to 20 percent. Whenever a numerical range with a lower limit, R^L , and an upper limit, R^U , is disclosed, any number falling within the range is specifically disclosed. In particular, the following numbers within the range are specifically disclosed: $R = R^L + k * (R^U - R^L)$, wherein k is a variable ranging from 1 percent to 100 percent with a 1 percent increment, *i.e.*, k is 1 percent, 2 percent, 3 percent, 4 percent, 5 percent,..., 50 percent, 51 percent, 52 percent,..., 95 percent, 96 percent, 97 percent, 98 percent, 99 percent, or 100 percent. Moreover, any numerical range defined by two R numbers as defined in the above is also specifically disclosed.

DESCRIPTION OF EMBODIMENTS

[0018] Provided herein are lubricating oil compositions comprising:

- i) a major amount of a base oil,
- ii) at least one oil-soluble molybdenum compound and
- iii) a zinc dialkyldithiophosphate compound,

wherein the molybdenum content derived from the molybdenum compound is at least about 10 ppm based on the total weight of the lubricating oil composition and the phosphorus content derived from the zinc dialkyldithiophosphate compound is 200 to 500 ppm based on the total weight of the lubricating oil composition.

[0019] In certain embodiments, the phosphorus content of the composition is about 200 to 500 ppm. In other embodiments, the phosphorus content of the composition is about 250 to 400 ppm, about 300 to 400 ppm. In certain embodiments, the SAE viscosity of the composition is 5W-20.

i). The Base Oil of Lubricating Viscosity

[0020] The lubricating oil compositions disclosed herein generally comprise at least one oil of lubricating viscosity. Any base oil known to a skilled artisan can be used as the oil of lubricating viscosity disclosed herein. Some base oils suitable for preparing the lubricating oil compositions have been described in Mortier *et al.*, “*Chemistry and Technology of Lubricants*,” 2nd Edition, London, Springer, Chapters 1 and 2 (1996); and A. Sequeria, Jr., “*Lubricant Base Oil and Wax Processing*,” New York, Marcel Decker, Chapter 6, (1994); and D. V. Brock, *Lubrication Engineering*, Vol. 43, pages 184-5, (1987), all of which are incorporated herein by reference. Generally, the amount of the base oil in the lubricating oil composition may be from about 50 to about 99.5 wt.%, based on the total weight of the lubricating oil composition. In some embodiments, the amount of the base oil in the lubricating oil composition is from about 75 to about 99 wt.%, from about 80 to about 98.5 wt.%, or from about 80 to about 98 wt.%, based on the total weight of the lubricating oil composition. In certain embodiments, the amount of base oil in the lubricant oil compositions provided herein is about 45%, 50%, 52%, 54%, 56%, 58%, 60%, 62%, 64%, 66%, 68%, 70%, 75%, 80%, 85% or about 90% by total weight of the composition.

[0021] In certain embodiments, the base oil is or comprises any natural or synthetic lubricating base oil fraction. Some non-limiting examples of synthetic oils include oils, such as polyalphaolefins or PAOs, prepared from the polymerization of at least one alpha-olefin, such as ethylene, or from hydrocarbon synthesis procedures using carbon monoxide and hydrogen gases, such as the Fisher-Tropsch process. In certain embodiments, the base oil comprises less than about 10 wt.% of one or more heavy fractions, based on the total weight of the base oil. A heavy fraction refers to a lube oil fraction having a viscosity of at least about 20 cSt at 100 °C. In certain embodiments, the heavy fraction has a viscosity of at least about 25 cSt or at least about 30 cSt at 100 °C. In further embodiments, the amount of the one or more heavy fractions in the base oil is less than about 10 wt.%, less than about 5 wt.%, less than about 2.5 wt.%, less than about 1 wt.%, or less than about 0.1 wt.%, based on the total weight of the base oil. In still further embodiments, the base oil comprises no heavy fraction.

[0022] In certain embodiments, the lubricating oil compositions comprise a major amount of a base oil of lubricating viscosity. In some embodiments, the base oil has a

kinematic viscosity at 100 °C from about 2 centistokes (cSt) to about 20 cSt, from about 4 centistokes (cSt) to about 16 cSt, or from about 5 cSt to about 13 cSt. The kinematic viscosity of the base oils or the lubricating oil compositions disclosed herein can be measured according to ASTM D 445, which is incorporated herein by reference.

[0023] In other embodiments, the base oil is or comprises a base stock or blend of base stocks. In further embodiments, the base stocks are manufactured using a variety of different processes including, but not limited to, distillation, solvent refining, hydrogen processing, oligomerization, esterification, and rerefining. In some embodiments, the base stocks comprise a rerefined stock. In further embodiments, the rerefined stock shall be substantially free from materials introduced through manufacturing, contamination, or previous use.

[0024] In some embodiments, the base oil comprises one or more of the base stocks in one or more of Groups I-V as specified in the American Petroleum Institute (API) Publication 1509, Fourteen Edition, December 1996 (*i.e.*, API Base Oil Interchangeability Guidelines for Passenger Car Motor Oils and Diesel Engine Oils), which is incorporated herein by reference. The API guideline defines a base stock as a lubricant component that may be manufactured using a variety of different processes. Groups I, II and III base stocks are mineral oils, each with specific ranges of the amount of saturates, sulfur content and viscosity index. Group IV base stocks are polyalphaolefins (PAO). Group V base stocks include all other base stocks not included in Group I, II, III, or IV.

[0025] The saturates levels, sulfur levels and viscosity indices for Group I, II, III, IV and V base stocks are listed in Table 1 below.

Table 1.

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.	Greater than or equal to 0.03% sulfur.	Greater than or equal to 80 and less than 120.
II	Greater than or equal to 90% saturates.	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.	Less than or equal to 0.03% sulfur.	Greater than or equal to 120.
IV	Defined as polyalphaolefins (PAO)		
V	All other base stocks not included in Groups I, II, III or IV		

[0026]

[0027] In some embodiments, the base oil comprises one or more of the base stocks in Group I, II, III, IV, V or a combination thereof. In other embodiments, the base oil comprises one or more of the base stocks in Group II, III, IV or a combination thereof. In further embodiments, the base oil comprises one or more of the base stocks in Group II, III, IV or a combination thereof wherein the base oil has a kinematic viscosity from about 2.5 centistokes (cSt) to about 20 cSt, from about 4 cSt to about 20 cSt, or from about 5 cSt to about 16 cSt at 100 °C.

[0028] The base oil may be selected from the group consisting of natural oils of lubricating viscosity, synthetic oils of lubricating viscosity and mixtures thereof. In some embodiments, the 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. In other embodiments, the base oil of lubricating viscosity includes natural oils, such as animal oils, vegetable oils, mineral oils (*e.g.*, liquid petroleum oils and solvent treated or acid-treated mineral oils of the paraffinic, naphthenic or mixed paraffinic-naphthenic types), oils derived from coal or shale, and combinations thereof. Some non-limiting examples

of animal oils include bone oil, lanolin, fish oil, lard oil, dolphin oil, seal oil, shark oil, tallow oil, and whale oil. Some non-limiting examples of vegetable oils include castor oil, olive oil, peanut oil, rapeseed oil, corn oil, sesame oil, cottonseed oil, soybean oil, sunflower oil, safflower oil, hemp oil, linseed oil, tung oil, oiticica oil, jojoba oil, and meadow foam oil. Such oils may be partially or fully hydrogenated.

[0029] In some embodiments, the synthetic oils of lubricating viscosity 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. In other embodiments, the synthetic oils include alkylene oxide polymers, interpolymers, copolymers and derivatives thereof wherein the terminal hydroxyl groups can be modified by esterification, etherification, and the like. In further embodiments, the synthetic oils include the esters of dicarboxylic acids with a variety of alcohols. In certain embodiments, the synthetic oils include esters made from C₅ to C₁₂ monocarboxylic acids and polyols and polyol ethers. In further embodiments, the synthetic oils include tri-alkyl phosphate ester oils, such as tri-n-butyl phosphate and tri-iso-butyl phosphate.

[0030] In some embodiments, the synthetic oils of lubricating viscosity include silicon-based oils (such as the polyakyl-, polyaryl-, polyalkoxy-, polyaryloxy-siloxane oils and silicate oils). In other embodiments, the synthetic oils include liquid esters of phosphorus-containing acids, polymeric tetrahydrofurans, polyalphaolefins, and the like.

[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] In further embodiments, the base oil comprises a poly-alpha-olefin (PAO). In general, the poly-alpha-olefins may be derived from an alpha-olefin having from about 2 to about 30, from about 4 to about 20, or from about 6 to about 16 carbon atoms. Non-limiting examples of suitable poly-alpha-olefins include those derived from octene, decene, mixtures thereof, and the like. These poly-alpha-olefins may have a viscosity from about 2 to about 15, from about 3 to about 12, or from about 4 to about 8 centistokes

at 100 °C. In some instances, the poly-alpha-olefins may be used together with other base oils such as mineral oils.

[0033] In further embodiments, the base oil comprises a polyalkylene glycol or a polyalkylene glycol derivative, where the terminal hydroxyl groups of the polyalkylene glycol may be modified by esterification, etherification, acetylation and the like. Non-limiting examples of suitable polyalkylene glycols include polyethylene glycol, polypropylene glycol, polyisopropylene glycol, and combinations thereof. Non-limiting examples of suitable polyalkylene glycol derivatives include ethers of polyalkylene glycols (*e.g.*, methyl ether of polyisopropylene glycol, diphenyl ether of polyethylene glycol, diethyl ether of polypropylene glycol, *etc.*), mono- and polycarboxylic esters of polyalkylene glycols, and combinations thereof. In some instances, the polyalkylene glycol or polyalkylene glycol derivative may be used together with other base oils such as poly-alpha-olefins and mineral oils.

[0034] In further embodiments, the base oil comprises any of 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 acid, alkyl malonic acids, alkenyl malonic acids, and the like) with a variety of alcohols (*e.g.*, butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol, and the like). Non-limiting 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, and the like.

[0035] In further embodiments, the base oil comprises a hydrocarbon prepared by the Fischer-Tropsch process. The Fischer-Tropsch process prepares hydrocarbons from gases containing hydrogen and carbon monoxide using a Fischer-Tropsch catalyst. These hydrocarbons may require further processing in order to be useful as base oils. For example, the hydrocarbons may be dewaxed, hydroisomerized, and/or hydrocracked using processes known to a person of ordinary skill in the art.

[0036] In further embodiments, the base oil comprises an unrefined oil, a refined oil, a rerefined oil, or a mixture thereof. Unrefined oils are those obtained directly from a

natural or synthetic source without further purification treatment. Non-limiting examples of unrefined oils include shale oils obtained directly from retorting operations, petroleum oils obtained directly from primary distillation, and ester oils obtained directly from an esterification process and used without further treatment. Refined oils are similar to the unrefined oils except the former have been further treated by one or more purification processes to improve one or more properties. Many such purification processes are known to those skilled in the art such as solvent extraction, secondary distillation, acid or base extraction, filtration, percolation, and the like. Rerefined oils are obtained by applying to refined oils processes similar to those used to obtain refined oils. Such rerefined oils are also known as reclaimed or reprocessed oils and often are additionally treated by processes directed to removal of spent additives and oil breakdown products.

ii). Oil Soluble Molybdenum Compounds

[0037] For the lubricating oil compositions provided herein, any suitable oil-soluble molybdenum compound can be employed. Exemplary of such oil-soluble molybdenum compounds include, but are not limited to dithiocarbamates, dithiophosphates, dithiophosphinates, xanthates, thioxanthates, sulfides, and the like, and mixtures thereof. In certain embodiments, the molybdenum compounds are molybdenum dithiocarbamates, dialkyldithiophosphates, alkyl xanthates and alkylthioxanthates.

[0038] The molybdenum compound may be mono-, di-, tri- or tetra-nuclear. In certain embodiments, the compound is a dinuclear or trinuclear molybdenum compound. In one embodiment, the molybdenum compound is an organo-molybdenum compound. In another embodiment, the molybdenum compound is selected from the group consisting of molybdenum dithiocarbamates (MoDTC), molybdenum dithiophosphates, molybdenum dithiophosphinates, molybdenum xanthates, molybdenum thioxanthates, molybdenum sulfides and mixtures thereof. In another embodiment, the molybdenum compound is present as a molybdenum dithiocarbamate or a trinuclear organo-molybdenum compound. In one embodiment, the oil-soluble molybdenum compound is selected from molybdenum dithiocarbamate, molybdenum-succinimide complex and a mixture thereof.

[0039] In certain aspects, the molybdenum compound may be an acidic molybdenum compound. These compounds will react with a basic nitrogen compound as

measured by ASTM test D-664 or D-2896 titration procedure and are typically hexavalent. Examples of such compounds include molybdic acid, ammonium molybdate, sodium molybdate, potassium molybdate, and other alkaline metal molybdates and other molybdenum salts, *e.g.*, hydrogen sodium molybdate, MoOCl_4 , $\text{MoO}_2 \text{ Br}_2$, $\text{Mo}_2 \text{ O}_3 \text{ Cl}_6$, molybdenum trioxide or similar acidic molybdenum compounds. Alternatively, the compositions herein comprise molybdenum/sulfur complexes of basic nitrogen compounds as described, for example, in U.S. Pat. Nos. 4,263,152; 4,285,822; 4,283,295; 4,272,387; 4,265,773; 4,261,843; 4,259,195; 4,259,194 and 6,562,765; and WO 94/06897.

[0040] The basic nitrogen compound used to prepare the oxymolybdenum compounds for use herein have at least one basic nitrogen and are, in certain embodiments, 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.

[0041] 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 exemplary succinimides and the related materials are described in U.S. Pat. Nos. 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. In certain embodiments, succinimides for use herein are commercial available succinimides, such as those 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 characterized by ethylene diamine, diethylene triamine, triethylene tetramine, and tetraethylene pentamine. In one embodiment, the succinimides include succinimides prepared from polyisobutenyl

succinic anhydride of 70 to 128 carbon atoms and tetraethylene pentamine or triethylene tetramine or mixtures thereof.

[0042] Also included in the succinimides 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. In certain embodiments, the cooligomers have an average molecular weight between 1,500 and 50,000. In one embodiment, the molybdenum compound for use in the compositions herein is prepared by reacting polyisobutenyl succinic anhydride and ethylene dipiperazine.

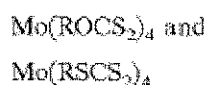
[0043] In certain embodiment, carboxylic acid amide compositions are also suitable starting materials for preparing the oxymolybdenum compounds used herein. Typical of such compounds are those disclosed in U.S. Pat. No. 3,405,064, the disclosure of which is hereby incorporated by reference. These compositions can be prepared by reacting a carboxylic acid or anhydride or ester thereof, having at least 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. In one embodiment, the amides are prepared from (1) a carboxylic acid of the formula $R'COOH$, where R' is C_{12-20} alkyl or a mixture of this acid with a polyisobutenyl carboxylic acid in which the polyisobutenyl group contains from 72 to 128 carbon atoms and (2) an ethylene amine, especially triethylene tetramine or tetraethylene pentamine or mixtures thereof.

[0044] Another class of compounds which can be used to prepare molybdenum compounds are hydrocarbyl monoamines and hydrocarbyl polyamines, such as those disclosed in U.S. Pat. No. 3,574,576, the disclosure of which is hereby incorporated by reference. The hydrocarbyl group, for example alkyl, or olefinic having one or two sites of unsaturation, usually contains from 9 to 350, preferably from 20 to 200 carbon atoms. Exemplary of such 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.

[0045] Another class of compounds useful for supplying basic nitrogen are the Mannich base compositions. These compositions are prepared from a phenol or C₉₋₂₀₀ 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 C₈₀₋₁₀₀ alkylphenol. Typical Mannich bases which can be used 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.

[0046] Another class of composition useful for preparing the oxymolybdenum complexes employed in the lubricating oil compositions provided herein are the phosphoramides and phosphonamides such as those disclosed in U.S. Pat. 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 2 to 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, alkyldiamine, alkylpolyamine, or an alkyleneamine, such as ethylene diamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, and the like.

[0047] Further molybdenum compounds useful in the compositions provided herein are organo-molybdenum compounds of the formulae



[0048] wherein R is an organic group selected from the group consisting of alkyl, aryl, aralkyl and alkoxyalkyl, generally of from 1 to 30 carbon atoms, and in one

embodiment, from 2 to 12 carbon atoms and in another embodiment, alkyl of 2 to 12 carbon atoms.

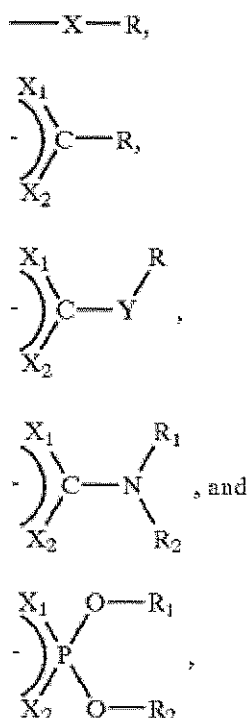
[0049] In one embodiment, the molybdenum compounds are dithiocarbamates of molybdenum represented by the formula:



[0050] wherein, R₁, R₂, R₃ and R₄ are each independently a straight-chain or branched-chain alkyl group or a straight-chain or branched-chain alkenyl group having four to eighteen carbons; and X₁, X₂, X₃ and X₄ are each independently an oxygen atom or a sulfur atom, the ratio between the number of the oxygen atom or atoms and that of the sulfur atom or atoms with respect to X₁ through X₄ being 1/3 to 3/1. In one embodiment, R₁, R₂, R₃ and R₄, are each alkyl. In one embodiment, the alkyl is butyl, 2-ethylhexyl, isotridecyl or stearyl. The R₁, R₂, R₃ and R₄ groups in one molybdenum dithiocarbamate may be identical with or different from each other. Further, two or more molybdenum dithiocarbamates having different R₁, R₂, R₃ and R₄ groups may be used in a mixed state.

[0051] In one embodiment, organo-molybdenum compounds useful in the lubricating compositions herein are trinuclear molybdenum compounds, including those of the formula Mo₃ S_k L_n Q_z and mixtures thereof, wherein L are independently selected ligands having organic groups with a sufficient number of carbon atoms to render the compound soluble or dispersible in the oil, n is from 1 to 4, k varies from 4 through 7, Q is selected from the group of neutral electron donating compounds such as water, amines, alcohols, phosphines, and ethers, and z ranges from 0 to 5 and includes non-stoichiometric values. In certain embodiments, at least 21 total carbon atoms are present among all the ligands' organic groups, such as at least 25, at least 30, or at least 35 carbon atoms.

[0052] The ligands are independently selected from the group of:



[0053] and mixtures thereof, wherein X, X₁, X₂, and Y are independently selected from the group of oxygen and sulfur, and wherein R₁, R₂, and R are each independently selected from hydrogen and organic groups that may be the same or different. In one embodiment, the organic groups are hydrocarbyl groups such as alkyl (e.g., in which the carbon atom attached to the remainder of the ligand is primary or secondary), aryl, substituted aryl and ether groups. In one embodiment, each ligand has the same hydrocarbyl group.

[0054] The term "hydrocarbyl" denotes a substituent having carbon atoms directly attached to the remainder of the ligand and is predominantly hydrocarbyl in character, exemplary substituents include the following:

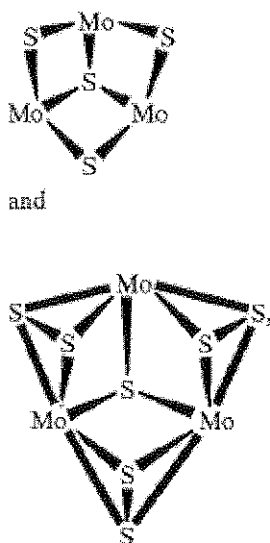
[0055] 1. Hydrocarbon substituents, that is, aliphatic (for example alkyl or alkenyl), alicyclic (for example cycloalkyl or cycloalkenyl) substituents, aromatic-, aliphatic- and alicyclic-substituted aromatic nuclei and the like, as well as cyclic substituents wherein the ring is completed through another portion of the ligand (that is, any two indicated substituents may together form an alicyclic group).

[0056] 2. Substituted hydrocarbon substituents, that is, those containing non-hydrocarbon groups which do not alter the predominantly hydrocarbyl character of the substituent. Those skilled in the art are aware of suitable groups (*e.g.*, halo, especially chloro and fluoro, amino, alkoxyl, mercapto, alkylmercapto, nitro, nitroso, sulfoxy, and the like).

[0057] 3. Hetero substituents, that is, substituents which, while predominantly hydrocarbon in character, contain atoms other than carbon present in a chain or ring otherwise composed of carbon atoms.

[0058] In certain embodiments, the organic groups of the ligands have a sufficient number of carbon atoms to render the compound soluble or dispersible in the oil. For example, the number of carbon atoms in each group will generally range between about 1 to about 100, from about 1 to about 30 or between about 4 to about 20. In certain embodiments, the ligands include dialkyldithiophosphate, alkylxanthate, and dialkyldithiocarbamate. In one embodiment, the ligand is dialkyldithiocarbamate. Organic ligands containing two or more of the above functionalities can also serve as ligands by binding to one or more of the cores. Those skilled in the art will realize that formation of the compounds provided herein requires selection of ligands having the appropriate charge to balance the core's charge.

[0059] Compounds having the formula $\text{Mo}_3 \text{S}_k \text{L}_n \text{Q}_z$ to have cationic cores surrounded by anionic ligands and are represented by structures such as



[0060]

[0061] and have net charges of +4. Consequently, in order to solubilize these cores the total charge among all the ligands must be -4. In one embodiment, four monoanionic ligands are present. Without wishing to be bound by any theory, it is believed that two or more trinuclear cores may be bound or interconnected by means of one or more ligands and the ligands may be multidentate. This includes the case of a multidentate ligand having multiple connections to a single core. It is believed that oxygen and/or selenium may be substituted for sulfur in the core(s).

[0062] Oil-soluble or dispersible trinuclear molybdenum compounds can be prepared by reacting in the appropriate liquid(s)/solvent(s) a molybdenum source such as $(\text{NH}_4)_2 \text{Mo}_3 \text{S}_{13} \cdot n(\text{H}_2 \text{O})$, where n varies between 0 and 2 and includes non-stoichiometric values, with a suitable ligand source such as a tetraalkylthiuram disulfide. Other oil-soluble or dispersible trinuclear molybdenum compounds can be formed during a reaction in the appropriate solvent(s) of a molybdenum source such as of $(\text{NH}_4)_2 \text{Mo}_3 \text{S}_{13} \cdot n(\text{H}_2 \text{O})$, a ligand source such as tetraalkylthiuram disulfide, dialkyldithiocarbamate, or dialkyldithiophosphate, and a sulfur abstracting agent such as cyanide ions, sulfite ions, or substituted phosphines. Alternatively, a trinuclear molybdenum-sulfur halide salt such as $[\text{M}']_2 [\text{Mo}_3 \text{S}_7 \text{A}_6]$, where M' is a counter ion, and A is a halogen such as Cl , Br , or I , may be reacted with a ligand source such as a dialkyldithiocarbamate or dialkyldithiophosphate in the appropriate liquid(s)/solvent(s) to form an oil-soluble or dispersible trinuclear molybdenum compound. The appropriate liquid/solvent may be, for example, aqueous or organic.

[0063] A compound's oil solubility or dispersibility may be influenced by the number of carbon atoms in the ligand's organic groups. In the compounds herein, at least 21 total carbon atoms should be present among all the ligands' organic groups. In certain embodiments, the ligand source chosen has a sufficient number of carbon atoms in its organic groups to render the compound soluble or dispersible in the lubricating composition.

[0064] The terms "oil-soluble" or "dispersible" used herein do not necessarily indicate that the compounds or additives are soluble, dissolvable, miscible, or capable of being suspended in the oil in all proportions. These do mean, however, that they are, for instance, soluble or stably dispersible in oil to an extent sufficient to exert their intended

effect in the environment in which the oil is employed. Moreover, the additional incorporation of other additives may also permit incorporation of higher levels of a particular additive, if desired.

[0065] The lubricating compositions provided herein contain the molybdenum compound at a concentration of at least about 10 ppm in terms of molybdenum content. In certain embodiments, the molybdenum compound is at a concentration from about 10 ppm to about 10,000 ppm in terms of molybdenum content. In certain embodiments, the molybdenum compound at a concentration from about 50 to 1500 ppm, or about 250 to 1200 ppm in terms of molybdenum content. In one embodiment, the molybdenum compound is at a concentration of about 10 ppm, 50 ppm, 100 ppm, 250 ppm, 500 ppm, 750 ppm, or 1000 ppm in terms of molybdenum content.

[0066] The amount of molybdenum may be determined by Inductively Coupled Plasma (ICP) emission spectroscopy using the method described in ASTM D5185.

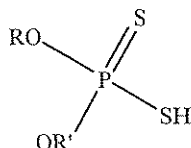
iii). Zinc dialkyldithiophosphate compounds

[0067] The lubricating oil compositions provided herein additionally contain a zinc dialkyldithiophosphate compound. The alkyl group in the zinc dialkyldithiophosphate compound is, for example, branched or non-branched alkyl containing 3 to 30 carbon atoms. In another embodiment, the alkyl group has 3 to 8 carbon atoms. Examples of alkyl groups include a straight or branched ethyl, propyl, butyl, pentyl, methylpentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, and octadecyl groups.

[0068] These zinc dialkyldithiophosphate salts can be prepared in accordance with known techniques by first forming a dihydrocarbyl dithiophosphoric acid (DDPA), usually by reaction of one or more alcohol or a phenol with P_2S_5 and then neutralizing the formed DDPA with a zinc compound. For example, a dithiophosphoric acid may be made by reacting mixtures of primary and secondary alcohols. Alternatively, multiple dithiophosphoric acids can be prepared where the hydrocarbyl groups on one are entirely secondary in character and the hydrocarbyl groups on the others are entirely primary in character. To make the zinc salt, any basic or neutral zinc compound could be used but the oxides, hydroxides and carbonates are most often employed. Commercial additives

frequently contain an excess of zinc due to the use of an excess of the basic zinc compound in the neutralization reaction.

[0069] In one embodiment, the oil soluble zinc dialkyldithiophosphates may be produced from dialkyldithiophosphoric acids (DDPA) of the formula:



[0070] The hydroxyl alkyl compounds from which the dialkyldithiophosphoric acids are derived can be represented generically by the formula ROH or R'OH, wherein R or R' is alkyl or substituted alkyl, in one embodiment, branched or non-branched alkyl containing 3 to 30 carbon atoms. In another embodiment, R or R' is a branched or non-branched alkyl containing 3 to 8 carbon atoms. Examples of alkyl groups include a straight or branched ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, and octadecyl groups.

[0071] In certain embodiments, the dialkyldithiophosphoric acids are prepared from mono-, di-, tri-, tetra-, and other polyhydroxy alkyl compounds, or mixtures of two or more of the foregoing. In one embodiment, the zinc dialkyldithiophosphate is derived from a single primary alcohol. In one embodiment, the single primary alcohol is 2-ethylhexanol. In one embodiment, the zinc dialkyldithiophosphate is derived from one or more secondary alkyl alcohols. In one embodiment, the mixture of secondary alcohols is a mixture of 2-butanol and 4-methyl-2-pentanol.

[0072] The zinc salts can be prepared from the dihydrocarbyl dithiophosphoric acids by reacting with a zinc compound. In some embodiments, a basic or a neutral zinc compound is used. In other embodiments, an oxide, hydroxide or carbonate of zinc is used.

[0073] The phosphorus pentasulfide reactant used in the dialkyldithiophosphoric acid formation step may contain certain amounts of one or more of P₂S₃, P₄S₃, P₄S₇, or P₄S₉. Compositions as such may also contain minor amounts of free sulfur. In certain embodiments, the phosphorus pentasulfide reactant is substantially free of any of P₂S₃,

P_4S_3 , P_4S_7 , and P_4S_9 . In certain embodiments, the phosphorus pentasulfide reactant is substantially free of free sulfur.

[0074] The phosphorus content derived from the zinc dialkyldithiophosphate compound is about 200 to 500 ppm based on the total weight of the lubricating oil composition. In certain embodiments, the phosphorus content derived from the zinc dialkyldithiophosphate compound is about 200 to 400 ppm. In one embodiment, the phosphorus content derived from the zinc dialkyldithiophosphate compound is about 200, 250, 300, 350, 400, 450, 500 ppm. In one embodiment, phosphorus content derived from the zinc dialkyldithiophosphate compound is about 250 ppm.

[0075] 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

[0076] In some embodiments, the lubricating oil composition provided herein comprises at least a neutral or overbased metal detergent as an additive, or additive components. In certain embodiments, the metal detergents in lubricating oil compositions acts as a neutralizer of acidic products within the oil. In certain embodiments, the metal detergent prevents the formation of deposits on the surface of an engine. Depending on the nature of the acid used, the detergent may have additional functions, for example, antioxidant properties. In certain aspects, lubricating oil compositions contain metal detergents comprising either overbased detergents or mixtures of neutral and overbased detergents. The term "overbased" is intended to define additives which contain a metal content in excess of that required by the stoichiometry of the particular metal and the particular organic acid used. The excess metal exists in the form of particles of inorganic base, e.g. a hydroxide or carbonate, surrounded by a sheath of metal salt. The sheath serves to maintain the particles in dispersion in a liquid oleaginous vehicle. The amount of excess metal is commonly expressed as the ratio of total equivalence of excess metal to equivalence of organic acid and is typically 0.1 to 30.

[0077] Some non-limiting examples of suitable metal detergents include sulfurized or unsulfurized alkyl or alkenyl phenates, alkyl or alkenyl aromatic sulfonates, borated 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 alkanoic acids, metal salts of an alkyl or alkenyl multiacid, and chemical and physical mixtures thereof. Other non-limiting examples of suitable metal detergents include metal sulfonates, phenates, salicylates, phosphonates, thiophosphonates and combinations thereof. The metal can be any metal suitable for making sulfonate, phenate, salicylate or phosphonate detergents. Non-limiting examples of suitable metals include alkali metals, alkaline metals and transition metals. In some embodiments, the metal is Ca, Mg, Ba, K, Na, Li or the like. An exemplary metal detergent which may be employed in the lubricating oil compositions includes overbased calcium phenate.

[0078] Generally, the amount of the metal detergent additive can be less than 10000 ppm, less than 1000 ppm, less than 100 ppm, or less than 10 ppm, based on the total weight of the lubricating oil composition. In some embodiments, the amount of the metal detergent is from about 0.001 wt.% to about 5 wt.%, from about 0.05 wt.% to about 3 wt.%, or from about 0.1 wt.% to about 1 wt.%, based on the total weight of the lubricating oil composition. Some suitable detergents have been described in Mortier *et al.*, “*Chemistry and Technology of Lubricants*,” 2nd Edition, London, Springer, Chapter 3, pages 75-85 (1996); and Leslie R. Rudnick, “*Lubricant Additives: Chemistry and Applications*,” New York, Marcel Dekker, Chapter 4, pages 113-136 (2003), both of which are incorporated herein by reference.

2) Anti Wear and/or Extreme Pressure Agents

[0079] In certain embodiments, the lubricating oil compositions disclosed herein can additionally comprise anti wear or extreme pressure agents. Wear occurs in all equipment that has moving parts in contact. Specifically, three conditions commonly lead to wear in engines: (1) surface-to-surface contact; (2) surface contact with foreign matter; and (3) erosion due to corrosive materials. Wear resulting from surface-to-surface contact is friction or adhesive wear, from contact with foreign matter is abrasive wear, and from contact with corrosive materials is corrosive wear. Fatigue wear is an additional

type of wear that is common in equipment where surfaces are not only in contact but also experience repeated stresses for prolonged periods. Abrasive wear can be prevented by installing an efficient filtration mechanism to remove the offending debris. Corrosive wear can be addressed by using additives which neutralize the reactive species that would otherwise attack the metal surfaces. The control of adhesive wear requires the use of additives called antiwear and extreme-pressure (EP) agents.

[0080] Under optimal conditions of speed and load, the metal surfaces of the equipment should be effectively separated by a lubricant film. Increasing load, decreasing speed, or otherwise deviating from such optimal conditions promote metal-to-metal contact. This contact typically causes a temperature increase in the contact zone due to frictional heat, which in turn leads to the loss of lubricant viscosity and hence its film-forming ability. In certain embodiments, antiwear additive and EP agents offer protection by a similar mechanism. In certain embodiments, EP additives require higher activation temperatures and load than antiwear additives.

[0081] Without being bound to any particular theory, it is believed that antiwear and/or EP additives function by thermal decomposition and by forming products that react with the metal surface to form a solid protective layer. This solid metal film fills the surface asperities and facilitates effective film formation, thereby reducing friction and preventing welding and surface wear.

[0082] Most antiwear and extreme pressure agents contain sulfur, chlorine, phosphorus, boron, or combinations thereof. The classes of compounds that inhibit adhesive wear include, for example, alkyl and aryl disulfides and polysulfides; dithiocarbamates; chlorinated hydrocarbons; and phosphorus compounds such as alkyl phosphites, phosphates, dithiophosphates, and alkenylphosphonates.

[0083] Exemplary antiwear agents that can be included in the lubricant oil compositions provided herein include metal (*e.g.*, Pb, Sb, and the like) salts of dithiophosphate, metal (*e.g.*, Pb, Sb, and the like) salts of dithiocarbamate, metal (*e.g.*, Pb, Sb and the like) salts of fatty acids, boron compounds, phosphate esters, phosphite esters, amine salts of phosphoric acid esters or thiophosphoric acid esters, reaction products of dicyclopentadiene and thiophosphoric acids and combinations thereof. The amount of the anti-wear agent may vary from about 0.01 wt.% to about 5 wt.%, from about 0.05 wt.% to

about 3 wt.%, or from about 0.1 wt.% to about 1 wt.%, based on the total weight of the lubricating oil composition. Some suitable anti-wear agents have been described in Leslie R. Rudnick, "*Lubricant Additives: Chemistry and Applications*," New York, Marcel Dekker, Chapter 8, pages 223-258 (2003), which is incorporated herein by reference.

[0084] In one embodiment, the sulfated ash content of the total lubricating oil composition is less than 5 wt.%, less than 4 wt.%, less than 3 wt.%, less than 2 wt.%, or less than 1 wt.%, as measured according to ASTM D874.

[0085] In one embodiment, the EP agents for use in the lubricant oil compositions include alkyl and aryl disulfides and polysulfides, dithiocarbamates, chlorinated hydrocarbons, dialkyl hydrogen phosphites, and salts of alkyl phosphoric acids. Methods of making these EP agents are known in the art. For example, polysulfides are synthesized from olefins either by reacting with sulfur or sulfur halides, followed by dehydrohalogenation. Dialkyldithiocarbamates are prepared either by neutralizing dithiocarbamic acid (which can be prepared by reacting a dialkylamine and carbon disulfide at low temperature) with bases, such as antimony oxidized, or by its addition to activated olefins, such as alkyl acrylates.

[0086] In certain embodiments, the lubricating oil compositions comprise one or more EP agents. In one embodiment, use of more than one EP agent leads to synergism. For example, synergism may be observed between sulfur and chlorine-containing EP agents. An exemplary lubricating oil composition provided herein includes one or more EP agents selected from: zinc dialkyldithiophosphate (primary alkyl type & secondary alkyl type), sulfurized oils, diphenyl sulfide, methyl trichlorostearate, chlorinated naphthalene, fluoroalkylpolysiloxane, and lead naphthenate.

3. Rust Inhibitors (Anti Rust Agents)

[0087] Protection against rust is an important consideration in formulating lubricants. Without protection, rust ultimately causes a loss of metal, thereby lowering the integrity of the equipment, and resulting in engine mal-function. In addition, corrosion exposes fresh metal that can wear at an accelerated rate, perpetuated by the metal ions that might be released into the fluid and act as oxidation promoters.

[0088] The lubricating oil composition disclosed herein can optionally comprise a rust inhibitor that can inhibit the corrosion of metal surfaces. Any rust inhibitor known by a person of ordinary skill in the art may be used in the lubricating oil composition. The rust inhibitors attach themselves to metal surfaces to form an impenetrable protective film, which can be physically or chemically adsorbed to the surface. Specifically, film formation occurs when the additives interact with the metal surface via their polar ends and associate with the lubricant via their nonpolar ends. Suitable rust inhibitors may include, for example, various nonionic polyoxyethylene surface active agents such as 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 mono-oleate, and polyethylene glycol monooleate. Suitable rust inhibitors may further include other compounds such as, for example, monocarboxylic acids (*e.g.*, 2-ethylhexanoic acid, lauric acid, myristic acid, palmitic acid, oleic acid, linoleic acid, linolenic acid, behenic acid, cerotic acid and the like), oil-soluble polycarboxylic acids (*e.g.*, those produced from tall oil fatty acids, oleic acid, linoleic acid and the like), alkenylsuccinic acids in which the alkenyl group contains 10 or more carbon atoms (*e.g.*, tetrapropenylsuccinic acid, tetradecenylsuccinic acid, hexadecenylsuccinic acid, and the like); long-chain alpha,omega-dicarboxylic acids having a molecular weight in the range of 600 to 3000 daltons and combinations thereof. Further examples of rust agents include metal soaps, fatty acid amine salts, metal salts of heavy sulfonic acid, partial carboxylic acid ester of polyhydric alcohol, and phosphoric ester.

4. Demulsifiers

[0089] The lubricating oil composition disclosed herein can optionally comprise a demulsifier that can promote oil-water separation in lubricating oil compositions that are exposed to water or steam. Any demulsifier known by a person of ordinary skill in the art may be used in the lubricating oil composition. Non-limiting examples of suitable demulsifiers include anionic surfactants (*e.g.*, alkyl-naphthalene sulfonates, alkyl benzene sulfonates and the like), nonionic alkoxylated alkylphenol resins, polymers of alkylene oxides (*e.g.*, polyethylene oxide, polypropylene oxide, block copolymers of ethylene oxide, propylene oxide and the like), esters of oil soluble acids, polyoxyethylene sorbitan

ester and combinations thereof. In certain embodiments, the demulsifiers for use herein include block copolymers of propylene oxide or ethylene oxide and initiators, such as, for example, glycerol, phenol, formaldehyde resins, soloxanes, polyamines, and polyols. In certain embodiments, the polymers contain about 20 to about 50% ethylene oxide. These materials concentrate at the water-oil interface and create low viscosity zones, thereby promoting droplet coalescence and gravity-driven phase separation. Low molecular weight materials, such as, for example, alkali metal or alkaline earth metal salts of dialkyl naphthalene sulfonic acids, are also useful in certain applications. The amount of the demulsifier may vary from about 0.01 wt.% to about 10 wt.%, from about 0.05 wt.% to about 5 wt.%, or from about 0.1 wt.% to about 3 wt.%, based on the total weight of the lubricating oil composition. Some suitable demulsifiers have been described in Mortier *et al.*, "Chemistry and Technology of Lubricants," 2nd Edition, London, Springer, Chapter 6, pages 190-193 (1996), which is incorporated herein by reference.

5. Friction Modifiers

[0090] The lubricating oil composition disclosed herein can optionally comprise a friction modifier that can lower the friction between moving parts. Any friction modifier known by a person of ordinary skill in the art may be used in the lubricating oil composition. They are typically long-chain molecules with a polar end group and a nonpolar linear hydrocarbon chain. The polar end groups either physically adsorb onto the metal surface or chemically react with it, while the hydrocarbon chain extends into the lubricant. The chains associate with one another and the lubricant to form a strong lubricant film.

[0091] Non-limiting examples of suitable friction modifiers include fatty carboxylic acids; derivatives (*e.g.*, alcohol, esters, borated esters, amides, metal salts and the like) of fatty carboxylic acid; mono-, di- or tri-alkyl substituted phosphoric acids or phosphonic acids; derivatives (*e.g.*, esters, amides, metal salts and the like) of mono-, di- or tri-alkyl substituted phosphoric acids or phosphonic acids; mono-, di- or tri-alkyl substituted amines; mono- or di-alkyl substituted amides and combinations thereof.

[0092] In one embodiment, the friction modifier is a saturated fatty acid containing a 13 to 18 carbon chains. The amount of the friction modifier may vary from about 0.01 wt.% to about 10 wt.%, from about 0.05 wt.% to about 5 wt.%, or from about

0.1 wt.% to about 3 wt.%, based on the total weight of the lubricating oil composition. Some suitable friction modifiers have been described in Mortier *et al.*, “*Chemistry and Technology of Lubricants*,” 2nd Edition, London, Springer, Chapter 6, pages 183-187 (1996); and Leslie R. Rudnick, “*Lubricant Additives: Chemistry and Applications*,” New York, Marcel Dekker, Chapters 6 and 7, pages 171-222 (2003), both of which are incorporated herein by reference.

6. Pour Point Depressants

[0093] The lubricating oil composition disclosed herein can optionally comprise a pour point depressant that can lower the pour point of the lubricating oil composition. Any pour point depressant known by a person of ordinary skill in the art may be used in the lubricating oil composition. In certain embodiments, pour point depressants possess one or more structural features selected from: (1) polymeric structure; (2) waxy and non-waxy components; (3) comb structure comprising a short backbone with long pendant groups; and (4) broad molecular weight distribution. Non-limiting examples of suitable pour point depressants include polymethacrylates, alkyl acrylate polymers, alkyl methacrylate polymers, alkyl fumarate polymers, di(tetra-paraffin phenol)phthalate, condensates of tetra-paraffin phenol, condensates of a chlorinated paraffin with naphthalene, alkylated naphthalenes, styrene esters, oligomerized alkyl phenols, phthalic acid esters, ethylene-vinyl acetate copolymers and combinations thereof. In one embodiment, the pour point depressant is selected from tetra (long-chain) alkyl silicates, phenyltristearoyloxysilane, and pentaerythritol tetrastearate. In some embodiments, the pour point depressant comprises an ethylene-vinyl acetate copolymer, a condensate of chlorinated paraffin and phenol, polyalkyl styrene or the like. The amount of the pour point depressant may vary from about 0.01 wt.% to about 10 wt.%, from about 0.05 wt.% to about 5 wt.%, or from about 0.1 wt.% to about 3 wt.%, based on the total weight of the lubricating oil composition. Some suitable pour point depressants have been described in Mortier *et al.*, “*Chemistry and Technology of Lubricants*,” 2nd Edition, London, Springer, Chapter 6, pages 187-189 (1996); and Leslie R. Rudnick, “*Lubricant Additives: Chemistry and Applications*,” New York, Marcel Dekker, Chapter 11, pages 329-354 (2003), both of which are incorporated herein by reference.

7. Foam Inhibitors

[0094] The lubricating oil composition disclosed herein can optionally comprise a foam inhibitor or an anti-foam that can break up foams in oils. Any foam inhibitor or anti-foam known by a person of ordinary skill in the art may be used in the lubricating oil composition. Non-limiting examples of suitable anti-foams include silicone oils or polydimethylsiloxanes, fluorosilicones, alkoxyated aliphatic acids, polyethers (e.g., polyethylene glycols), branched polyvinyl ethers, alkyl acrylate polymers, alkyl methacrylate polymers, polyalkoxyamines and combinations thereof. In some embodiments, the anti-foam comprises glycerol monostearate, polyglycol palmitate, a trialkyl monothiophosphate, an ester of sulfonated ricinoleic acid, benzoylacetone, methyl salicylate, glycerol monooleate, or glycerol dioleate. The amount of the anti-foam may vary from about 0.01 wt.% to about 5 wt.%, from about 0.05 wt.% to about 3 wt.%, or from about 0.1 wt.% to about 1 wt.%, based on the total weight of the lubricating oil composition. Some suitable anti-foams have been described in Mortier *et al.*, "*Chemistry and Technology of Lubricants*," 2nd Edition, London, Springer, Chapter 6, pages 190-193 (1996), which is incorporated herein by reference.

8. Metal Deactivators

[0095] In some embodiments, the lubricating oil composition comprises at least a metal deactivator. Some non-limiting examples of suitable metal deactivators include disalicylidene propylenediamine, triazole derivatives, thiadiazole derivatives, and mercaptobenzimidazoles.

9. Dispersants

[0096] The lubricating oil composition disclosed herein can optionally comprise a dispersant that can prevent sludge, varnish, and other deposits by keeping particles suspended in a colloidal state. In certain embodiments, dispersants perform these functions via one or more means selected from: (1) solubilizing polar contaminants in their micelles; (2) stabilizing colloidal dispersions in order to prevent aggregation of their particles and their separation out of oil; (3) suspending such products, if they form, in the bulk lubricant; (4) modifying soot to minimize its aggregation and oil thickening; and (5) lowering surface/interfacial energy of undesirable materials to decrease their tendency to adhere to surfaces. The undesirable materials are typically formed as a result of oxidative degradation of the lubricant, the reaction of chemically reactive species such as

carboxylic acids with the metal surfaces in the engine, or the decomposition of thermally unstable lubricant additives such as, for example, extreme pressure agents.

[0097] In certain aspects, a dispersant molecule comprises three distinct structural features: (1) a hydrocarbyl group; (2) a polar group; and (3) a connecting group or a link. In certain embodiments, the hydrocarbyl group is polymeric in nature, and has a molecular weight of at or above about 2000 Daltons, in one embodiment, at or above about 3000 Daltons, in another embodiment, at or above about 5000 Daltons, and in yet another embodiment, at or above about 8000 Daltons. A variety of olefins, such as polyisobutylene, polypropylene, polyalphaolefins, and mixtures thereof, can be used to make suitable polymeric dispersants. In certain embodiments, the polymeric dispersant is a polyisobutylene-derived dispersant. Typically the number average molecular weight of polyisobutylene in those dispersants ranges between about 500 and about 3000 Daltons, or, in some embodiments, between about 800 to about 2000 Daltons, or in further embodiments, between about 1000 to about 2000 Daltons. In certain embodiments, the polar group in the dispersant is nitrogen- or oxygen-derived. Nitrogen-based dispersants are typically derived from amines. The amines from which the nitrogen-based dispersants are derived are often polyalkylenepolyamines, such as, for example, diethylenetriamine and trethylenetetramine. Amine-derived dispersants are also called nitrogen- or amine-dispersants, while those derived from alcohol are also called oxygen or ester dispersants. Oxygen-based dispersants are typically neutral while the amine-based dispersants are typically basic.

[0098] Non-limiting examples of suitable dispersants include alkenyl succinimides, alkenyl succinimides modified with other organic compounds, alkenyl succinimides modified by post-treatment with ethylene carbonate or boric acid, succinamides, succinate esters, succinate ester-amides, pentaerythritols, phenate-salicylates and their post-treated analogs, alkali metal or mixed alkali metal, alkaline earth metal borates, dispersions of hydrated alkali metal borates, dispersions of alkaline-earth metal borates, polyamide ashless dispersants, benzylamines, Mannich type dispersants, phosphorus-containing dispersants, and combinations thereof. The amount of the dispersant may vary from about 0.01 wt.% to about 10 wt.%, from about 0.05 wt.% to about 7 wt.%, or from about 0.1 wt.% to about 4 wt.%, based on the total weight of the lubricating oil composition. Some suitable dispersants have been described in Mortier *et*

al., "Chemistry and Technology of Lubricants," 2nd Edition, London, Springer, Chapter 3, pages 86-90 (1996); and Leslie R. Rudnick, "Lubricant Additives: Chemistry and Applications," New York, Marcel Dekker, Chapter 5, pages 137-170 (2003), both of which are incorporated herein by reference.

10. Anti-Oxidants

[0099] Optionally, the lubricating oil composition disclosed herein can further comprise an additional antioxidant that can reduce or prevent the oxidation of the base oil. Any antioxidant known by a person of ordinary skill in the art may be used in the lubricating oil composition. Examples of anti oxidants useful in the compositions 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' 5 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 butyl-phenol, 2,6 di tert l dimethylamino p cresol, 2,6 di tert 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-10 butylbenzyl) sulfide, and bis(3,5 di tert butyl 4 hydroxybenzyl). Diphenylamine type oxidation inhibitors include, but are not limited to, alkylated diphenylamine, phenyl alpha naphthylamine, and alkylated alpha naphthylamine, sulfur-based antioxidants (e.g., dilauryl-3,3'-thiodipropionate, sulfurized phenolic antioxidants and the like), phosphorous-based antioxidants (e.g., phosphites and the like), zinc dithiophosphate, oil-soluble copper compounds and combinations thereof.. Other types of oxidation inhibitors include metal dithiocarbamate (e.g., zinc dithiocarbamate), and 15 methylenebis(dibutylldithiocarbamate). The amount of the antioxidant may vary from about 0.01 wt.% to about 10 wt.%, from about 0.05 wt.% to about 5 wt.%, or from about 0.1 wt.% to about 3 wt.%, based on the total weight of the lubricating oil composition. Some suitable antioxidants have been described in Leslie R. Rudnick, "Lubricant Additives: Chemistry and Applications," New York, Marcel Dekker, Chapter 1, pages 1-28 (2003), which is incorporated herein by reference.

11. Multifunctional Additives

[00100] Various additives mentioned or not mentioned herein can provide a multiplicity of effects to the lubricant oil composition provided herein. Thus, for example, a single additive may act as a dispersant as well as an oxidative inhibitor. Multi-functional additives are well known in the art. Other suitable multi-functional additives may include, for example, sulfurized oxymolybdenum dithiocarbamate, sulfurized oxymolybdenum organo phosphoro dithioate, oxymolybdenum monoglyceride, amine-molybdenum complex compound, and sulfur-containing molybdenum complex compounds.

12. Viscosity Index Improvers

[00101] In certain embodiments, the lubricating oil composition comprises at least a viscosity index improver. Some non-limiting examples of suitable viscosity index improvers include polymethacrylate type polymers, ethylene-propylene copolymers, styrene-isoprene copolymers, hydrated styrene-isoprene copolymers, polyisobutylene, and dispersant type viscosity index improvers.

Processes of Preparing Lubricating Oil Compositions

[00102] The lubricating oil compositions disclosed herein can be prepared by any method known to a person of ordinary skill in the art for making lubricating oils. In some embodiments, the base oil is blended or mixed with an oil-soluble molybdenum compound; a zinc dialkyldithiophosphate and optionally an additive. In certain embodiments, the oil-soluble molybdenum compound; a zinc dialkyldithiophosphate are premixed followed by addition of the base oil. In other embodiments, the oil-soluble molybdenum compound and zinc dialkyldithiophosphate can be added to the base oil individually or simultaneously. In some embodiments, the oil-soluble molybdenum compound, zinc dialkyldithiophosphate and the optional additives are added to the base oil individually in one or more additions and the additions may be in any order. In other embodiments, the ester base stocks and the additives are added to the base oil simultaneously. In some embodiments, the oil-soluble molybdenum compound, zinc

dialkyldithiophosphate and the optional additives are premixed and the premix is added to the base oil along with a viscosity index improver.

[00103] Any mixing or dispersing equipment known to a person of ordinary skill in the art may be used for blending, mixing or solubilizing the ingredients. The blending, mixing or solubilizing may be carried out with a blender, an agitator, a disperser, a mixer (*e.g.*, planetary mixers and double planetary mixers), a homogenizer (*e.g.*, Gaulin homogenizers and Rannie homogenizers), a mill (*e.g.*, colloid mill, ball mill and sand mill) or any other mixing or dispersing equipment known in the art.

Applications of the Lubricating Oil Compositions

[00104] In certain embodiments, the lubricating oil compositions provided herein is suitable for use as motor oils (that is, engine oils or crankcase oils), in a gasoline or diesel engine.

[00105] In one embodiment, the lubricating oil composition provided herein is used to cool hot engine parts, keep the engine free of rust and deposits, and seal the rings and valves against leakage of combustion gases. The motor oil composition comprises a base oil, oil-soluble molybdenum compound and a zinc dialkyldithiophosphate. Optionally, the motor oil composition may further comprises one or more other additives. In some embodiments, the motor oil composition further comprises a pour point depressant, a detergent, a dispersant, an anti-wear, an antioxidant, a friction modifier, a rust inhibitor, or a combination thereof.

[00106] The following examples are presented to exemplify embodiments of the lubricant oil compositions provided herein but are not intended to limit the subject matter to the specific embodiments set forth. Unless indicated to the contrary, all parts and percentages are by weight. All numerical values are approximate. When numerical ranges are given, it should be understood that embodiments outside the stated ranges may still fall within the scope of the claimed subject matter. Specific details described in each example should not be construed as necessary features of the claimed subject matter.

EXAMPLES

Example 1

[00107] A lubricating oil composition was prepared and used for assessing boundary lubrication properties in the High Frequency Reciprocating Rig (HFRR) test (ASTM D 6079). The composition contained a major amount of a base oil of lubricating viscosity and the following additives, to provide an SAE 5W-20 finished oil;

- (1) 700 ppm in terms of molybdenum content, of a molybdenum dithiocarbamate
- (2) 1 wt % of a borated bis-succinimide dispersant
- (3) 4 wt % of an ethylene carbonate post-treated bis-succinimide
- (4) 164 ppm in terms of calcium content, of a 17 TBN calcium sulfonate detergent
- (5) 2220 ppm in terms of calcium content, of a 148 TBN calcium salicylate
- (6) 1 wt % of an alkylated diphenylamine
- (7) 0.2 wt % of hindered phenol
- (8) 0.2 wt % of a pour point depressant
- (9) 4.8 wt % of a non-dispersant ethylene-propylene copolymer concentrate
- (10) 5 ppm in terms of Silicon content, of a foam inhibitor
- (11) The remainder was diluent oil. Diluent oil can be a Gp 1 or Gp 2 base oil.

However, any diluent oil known to one of skill in the art could be used.

Example 2

[00108] A lubricating oil was prepared in accordance with the formulation of Example 1 except that 250 ppm in terms of phosphorus content of a zinc dialkyldithiophosphate was added. The composition contained 250 ppm phosphorus based on the total weight of the lubricating oil composition.

[00109] The zinc dialkyldithiophosphate is synthesized using a mixture of C4 and C6 secondary alcohols. The resulting zinc dialkyldithiophosphate is a zinc bis(O,O'-di-(2-butyl/4-methyl-2-pentyl) dithiophosphate.

Example 3

[00110] A lubricating oil was prepared in accordance with the formulation of Example 1 except that 500 ppm in terms of phosphorus content of the zinc

dialkyldithiophosphate was added. The composition contained 500 ppm phosphorus based on the total weight of the lubricating oil composition.

Example 4

[00111] A lubricating oil was prepared in accordance with the formulation of Example 1 except that 750 ppm in terms of phosphorus content of the zinc dialkyldithiophosphate was added. The composition contained 750 ppm phosphorus based on the total weight of the lubricating oil composition.

Example 5

[00112] A lubricating oil was prepared in accordance with the formulation of Example 1 except that 1000 ppm in terms of phosphorus content of the zinc dialkyldithiophosphate was added. The composition contained 1000 ppm phosphorus based on the total weight of the lubricating oil composition.

Example 6

[00113] A lubricating oil was prepared in accordance with the formulation of Example 1 except that 700 ppm in terms of molybdenum content of an oxymolybdenum-succinimide complex was used in place of the molybdenum dithiocarbamate.

Example 7

[00114] A lubricating oil was prepared in accordance with the formulation of Example 6 except that 250 ppm in terms of phosphorus content of the zinc dialkyldithiophosphate was added. The composition contained 250 ppm phosphorus based on the total weight of the lubricating oil composition.

Example 8

[00115] A lubricating oil was prepared in accordance with the formulation of Example 6 except that 500 ppm in terms of phosphorus content of the zinc dialkyldithiophosphate was added. The composition contained 500 ppm phosphorus based on the total weight of the lubricating oil composition.

Example 9

[00116] A lubricating oil was prepared in accordance with the formulation of Example 6 except that 750 ppm in terms of phosphorus content of the zinc

dialkyldithiophosphate was added. The composition contained 750 ppm phosphorus based on the total weight of the lubricating oil composition.

Example 10

[00117] A lubricating oil was prepared in accordance with the formulation of Example 6 except that 1000 ppm in terms of phosphorus content of the zinc dialkyldithiophosphate was added. The composition contained 1000 ppm phosphorus based on the total weight of the lubricating oil composition.

Example 11

[00118] A lubricating oil was prepared in accordance with the formulation of Example 1 except that the amount of molybdenum dithiocarbamate was reduced to 150 ppm in terms of molybdenum content, and 550 ppm in terms of molybdenum content of the oxymolybdenum-succinimide complex was added.

Example 12

[00119] A lubricating oil was prepared in accordance with the formulation of Example 11 except that 250 ppm in terms of phosphorus content of the zinc dialkyldithiophosphate was added. The composition contained 250 ppm phosphorus based on the total weight of the lubricating oil composition.

Example 13

[00120] A lubricating oil was prepared in accordance with the formulation of Example 11 except that 500 ppm in terms of phosphorus content of the zinc dialkyldithiophosphate was added. The composition contained 500 ppm phosphorus based on the total weight of the lubricating oil composition.

Example 14

[00121] A lubricating oil was prepared in accordance with the formulation of Example 11 except that 750 ppm in terms of phosphorus content of the zinc dialkyldithiophosphate was added. The composition contained 750 ppm phosphorus based on the total weight of the lubricating oil composition.

Example 15

[00122] A lubricating oil was prepared in accordance with the formulation of Example 10 except that 1000 ppm in terms of phosphorus content of the zinc

dialkyldithiophosphate was added. The composition contained 1000 ppm phosphorus based on the total weight of the lubricating oil composition.

Test Procedure

The High Frequency Reciprocating Rig (HFRR) test (ASTM D 6079) is designed to evaluate boundary lubrication properties. In this method, a 2 mL sample is placed in the test reservoir of an HFRR and adjusted to a standard temperature. When the sample temperature has stabilized, a vibrator arm holding a non-rotating steel ball is lowered until it contacts a test disk completely submerged in the sample. The ball is caused to rub against the disk.

[00123] The compositions of Examples 1-15 were tested using a 120°C oil reservoir temperature and were subjected to a 1000 g load. The ball was caused to rub against the disk with a 1 mm stroke at a frequency of 20 Hz for 60 min.

[00124] This test was run using samples from Examples 1 – 15 and the results are shown in Table 2. A graphic description of these results is found in Figure 1.

TABLE 2

Example	Mo Source	P ⁴ content (ppm)	Overall Average Friction Coefficient	Last 10 Min Average Friction Coefficient
1	MoDTC ¹	0	0.10	0.068
2	MoDTC ¹	250	0.079	0.053
3	MoDTC ¹	500	0.083	0.069
4	MoDTC ¹	750	0.077	0.071
5	MoDTC ¹	1000	0.078	0.076
6	Mo-succ ²	0	0.16	0.16
7	Mo-succ ²	250	0.065	0.050
8	Mo-succ ²	500	0.080	0.058
9	Mo-succ ²	750	0.080	0.064
10	Mo-succ ²	1000	0.086	0.073
11	Mixed ³	0	0.17	0.16

12	Mixed ³	250	0.052	0.052
13	Mixed ³	500	0.083	0.065
14	Mixed ³	750	0.074	0.060
15	Mixed ³	1000	0.076	0.066

¹Lubricating oil compositions with molybdenum dithiocarbamate had a total molybdenum content of 700 ppm.

²Lubricating oil compositions with molybdenum-succinimide complex had a total molybdenum content of 700 ppm.

³Lubricating oil composition contained a mixture of 150 ppm Mo of MoDTC and of 550 ppm Mo of molybdenum-succinimide complex. The lubricating oil composition had a total molybdenum content of 700 ppm (150 ppm Mo from MoDTC and 550 ppm Mo from Mo-succinimide complex).

⁴Phosphorous content in ppm of the zinc dialkyldithiophosphate employed in Examples 1 – 15.

[00125] In addition to measurement of the overall average friction coefficient, the last 10 minute average friction coefficient was determined. This coefficient is useful because it takes approximately 15 minutes from the start of the test until there is a low friction film on the metal surface. Both sets of data show friction coefficient minima at phosphorus levels of 250 ppm.

[00126] While the lubricant oil compositions provided herein have been described with respect to a limited number of embodiments, the specific features of one embodiment should not be attributed to other embodiments of the subject matter claimed herein. No single embodiment is representative of all aspects of the claimed subject matter. In some embodiments, the methods may include numerous steps not mentioned herein. In other embodiments, the methods do not include, or are substantially free of, steps not enumerated herein. Variations and modifications from the described embodiments exist. It is noted that the methods for producing the compositions disclosed herein are described with reference to a number of steps. These steps can be practiced in any sequence. One or more steps may be omitted or combined but still achieve substantially the same results. The appended claims intend to cover all such variations and modifications as falling within the scope of the claims.

[00127] All publications and patent applications mentioned in this specification are herein incorporated by reference to the same extent as if each individual publication or

patent application was specifically and individually indicated to be incorporated by reference. Although the foregoing has been described in some detail by way of illustration and example for purposes of clarity of understanding, it will be readily apparent to those of ordinary skill in the art in light of the teachings herein that certain changes and modifications may be made thereto without departing from the spirit or scope of the appended claims.

CLAIMS

What is claimed is:

1. A lubricating oil composition comprising:
 - i) a major amount of a base oil,
 - ii) at least one oil-soluble molybdenum compound and
 - iii) a zinc dialkyldithiophosphate compound, wherein the molybdenum content derived from the molybdenum compound is at least 10 ppm Molybdenum based on the total weight of the lubricating oil composition and the phosphorus content derived from the zinc dialkyldithiophosphate compound is about 200 ppm to 500 ppm based on the total weight of the lubricating oil composition.
2. The lubricating oil composition of claim 1, wherein the oil-soluble molybdenum compound is selected from molybdenum dithiocarbamate, molybdenum dithiophosphate, molybdenum dithiophosphinate, molybdenum xanthate, molybdenum thioxanthate, molybdenum sulfide and a mixture thereof.
3. The lubricating oil composition of any one of the preceding claims, wherein the oil-soluble molybdenum compound is selected from molybdenum dithiocarbamate, molybdenum-succinimide complex and a mixture thereof.
4. The lubricating oil composition of any one of the preceding claims, wherein the molybdenum content derived from the molybdenum compound is from about 10 to 10,000 ppm molybdenum based on the total weight of the lubricating oil composition.
5. The lubricating oil composition of any one of the preceding claims, wherein the molybdenum content derived from the molybdenum compound is from about 50 to 1500 ppm molybdenum based on the total weight of the lubricating oil composition.
6. The lubricating oil composition of any one of the preceding claims, wherein the molybdenum content derived from the molybdenum compound is from about 250 to 1200 ppm molybdenum based on the total weight of the lubricating oil composition.

7. The lubricating oil composition of any one of the preceding claims, wherein the zinc dialkyldithiophosphate comprises a straight or branched alkyl group having 3 to 30 carbon atoms.

8. The lubricating oil composition of any one of the preceding claims, wherein the zinc dialkyldithiophosphate comprises an alkyl selected from ethyl, propyl, butyl, pentyl, methylpentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, and octadecyl.

9. The lubricating oil composition of any one of the preceding claims, wherein the phosphorus content derived from the zinc dialkyldithiophosphate compound is about 200, 250, 300, 350, 400, 450 or 500 ppm based on the total weight of the lubricating oil composition.

10. The lubricating oil composition of any one of the preceding claims, wherein the phosphorus content derived from the zinc dialkyldithiophosphate compound is about 250 ppm based on the total weight of the lubricating oil composition.

11. The lubricating oil composition of any one of the preceding claims further comprising at least one additive selected from the group consisting of antioxidants, antiwear agents, detergents, rust inhibitors, demulsifiers, friction modifiers, multi-functional additives, viscosity index improvers, pour point depressants, foam inhibitors, metal deactivators, dispersants, corrosion inhibitors, lubricity improvers and combinations thereof.

12. A method of making a lubricating oil composition comprising the step of mixing:

- i) a major amount of a base oil,
- ii) at least one oil-soluble molybdenum compound and
- iii) a zinc dialkyldithiophosphate compound, wherein the molybdenum content derived from the molybdenum compound is at least 10 ppm based on the total weight of the lubricating oil composition and the phosphorus content derived from the zinc dialkyldithiophosphate compound is about 200 to 500 ppm based on the total weight of the lubricating oil composition.

13. A method of lubricating a motor engine comprising the step of operating the engine with the lubricating oil composition of any one of claims 1 to 11.

14. The method of claim 12, wherein the molybdenum content derived from the molybdenum compound is from 10 to 10,000 ppm based on the total weight of the lubricating oil composition.

15. The method of any one of claims 12 and 14, wherein the phosphorus content derived from the zinc dialkyldithiophosphate compound is about 200, 250, 300, 350, 400, 450 or 500 ppm based on the total weight of the lubricating oil composition.

16. The method of claim 15, wherein the phosphorus content derived from the zinc dialkyldithiophosphate compound is about 250 ppm based on the total weight of the lubricating oil composition.