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GUEVREMONT et al.(10) **Pub. No.: US 2010/0292113 A1**(43) **Pub. Date: Nov. 18, 2010**(54) **LUBRICANT FORMULATIONS AND METHODS**(75) Inventors: **Jeffrey M. GUEVREMONT**,
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C10M 137/10 (2006.01)(52) **U.S. Cl.** **508/369**(57) **ABSTRACT**

The embodiments described herein relate to particular formulations and methods that may provide improved fuel economy characteristics for an engine lubricant. The compositions and methods include a (a) a base oil; (b) a zinc dialkyldithiophosphate compound; and (c) a hydrocarbon soluble metal compound. The hydrocarbon soluble metal compound is devoid of phosphorus and sulfur atoms and the metal is selected from the group consisting essentially of selected from the group consisting essentially of cobalt, nickel, zinc, zirconium, manganese, vanadium, scandium, yttrium, tungsten, gold, platinum, and iron. A weight ratio of total metal in the lubricant composition from the zinc dialkyl-dithiophosphate compound and the hydrocarbon soluble metal compound to phosphorus in the lubricant composition ranges from greater than about 1.5 to 1 to about 15 to 1.

LUBRICANT FORMULATIONS AND METHODS

TECHNICAL FIELD

[0001] The embodiments described herein relate to particular formulations and methods that provide improved lubricant performance for internal combustion engines.

BACKGROUND AND SUMMARY

[0002] For over fifty (50) years automotive engine oils have been formulated with zinc dialkyldithiophosphate (ZDDP) resulting in low levels of wear, oxidation, and corrosion. The additive is truly ubiquitous and found in nearly every modern engine oil. ZDDP may impart multifunctional performance in the areas of anti-wear, anti-oxidation, and anti-corrosion and is considered one of the most cost-effective additives in general use by engine oil manufacturers and marketers. In general, ZDDP may form a thick glassy polyphosphate film that is effective to prevent wear between metal parts of an engine.

[0003] However, while ZDDP may reduce wear, the polyphosphate films may cause friction to increase between the metal parts thereby reducing a fuel economy performance of the lubricant in the engine. In addition, increased levels of phosphorus may poison engine emission catalyst. Accordingly, there is a need for additives which, in combination with ZDDP, provide improved friction properties without increasing the amount of phosphorus compound in the lubricant that is required for suitable engine wear performance.

[0004] In view of the above, an embodiments of the disclosure relate to particular formulations and methods that may provide improved fuel economy characteristics for an engine lubricant. The compositions and methods include a (a) a base oil; (b) a zinc dialkyldithiophosphate compound; and (c) a hydrocarbon soluble metal compound. The hydrocarbon soluble metal compound is devoid of phosphorus and sulfur atoms and the metal is selected from the group consisting essentially of cobalt, nickel, zinc, zirconium, manganese, vanadium, scandium, yttrium, tungsten, gold, platinum, and iron. A weight ratio of total metal in the lubricant composition from the zinc dialkyldithiophosphate compound and the hydrocarbon soluble metal compound to phosphorus in the lubricant composition ranges from greater than about 1.5 to 1 to about 15 to 1.

[0005] An embodiment of the disclosure may provide additive concentrate for an engine crankcase lubricant. The additive concentrate includes a zinc dialkyldithiophosphate compound, and a hydrocarbon soluble metal compound other than a dispersant or a detergent. The hydrocarbon soluble metal compound is devoid of phosphorus and sulfur atoms and the metal is selected from the group consisting essentially of cobalt, nickel, zinc, zirconium, manganese, vanadium, scandium, yttrium, tungsten, gold, platinum, and iron. A weight ratio of total metal in the concentrate from the zinc dialkyldithiophosphate compound and the hydrocarbon soluble metal compound to phosphorus in the concentrate ranges from greater than about 1.5 to 1 to about 15 to 1.

[0006] Another embodiment of the disclosure provides a method for improving a fuel economy of an internal combustion engine. According to the disclosure, the engine is lubricated with a lubricant composition that includes, (a) a base oil; (b) a zinc dialkyldithiophosphate compound; and (b) a hydrocarbon soluble metal compound other than a dispersant or a detergent. The hydrocarbon soluble metal compound is

devoid of phosphorus and sulfur atoms and the metal is selected from the group consisting essentially of zinc cobalt, nickel, zinc, zirconium, manganese, vanadium, scandium, yttrium, tungsten, gold, platinum, and iron. A weight ratio of total metal in the concentrate from the zinc dialkyldithiophosphate compound and the hydrocarbon soluble metal compound to phosphorus in the lubricant composition ranges from greater than about 1.5 to 1 to about 15 to 1.

[0007] Another embodiment of the disclosure provides a method for improving a friction characteristic of a lubricant for an internal combustion engine. According to the disclosure, the engine is lubricated with a lubricant composition that includes, (a) a base oil; (b) a zinc dialkyldithiophosphate compound; and (b) a hydrocarbon soluble metal compound other than a dispersant or a detergent. The hydrocarbon soluble metal compound is devoid of phosphorus and sulfur atoms and the metal is selected from the group consisting essentially of cobalt, nickel, zinc, zirconium, manganese, vanadium, scandium, yttrium, tungsten, gold, platinum, and iron. A weight ratio of total metal in the concentrate from the zinc dialkyldithiophosphate compound and the hydrocarbon soluble metal compound to phosphorus in the lubricant composition ranges from greater than about 1.5 to 1 to about 15 to 1.

[0008] The compositions and methods described may be particularly suitable for improving boundary friction characteristics of lubricant compositions containing from about 100 to about 1000 ppm phosphorus from a zinc dialkyldithiophosphate compound without adversely affecting thin film friction characteristics of the lubricant composition. Other features and advantages of the compositions and methods described herein may be evident by reference to the following detailed description which is intended to exemplify aspects of the embodiments without intending to limit the embodiments described herein.

[0009] It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are intended to provide further explanation of the embodiments disclosed and claimed.

DETAILED DESCRIPTION

[0010] Lubricant compositions according to embodiments described herein may comprise a base oil; a zinc dialkyldithiophosphate (ZDDP) compound and a hydrocarbon soluble metal compound, wherein the metal of the metal compound is a transition metal selected from cobalt, nickel, zinc, zirconium, manganese, vanadium, scandium, yttrium, tungsten, gold, platinum, and iron. It is particularly desirable that the transition metal compound be substantially devoid of phosphorus and sulfur atoms. The lubricant composition may also include other hydrocarbon soluble metal compounds, such as organomolybdenum compounds that are devoid of phosphorus and sulfur atoms. However, for purposes of this disclosure, the metal to phosphorus weight ratio is determined on the basis of the ZDDP and the hydrocarbon soluble transition metal compounds described above. Lubricant compositions of the disclosure are also substantially devoid of non-metal containing phosphorus compounds.

[0011] The lubricant compositions may be suitable for use in a variety of applications, including but not limited to engine oil applications and/or heavy duty engine oil applications. Examples may include the crankcase of spark-ignited and

compression-ignited internal combustion engines, automobile and truck engines, marine and railroad diesel engines, and the like.

[0012] The lubricant compositions may comprise a base oil and one or more suitable additive components. The additive components may be combined to form an additive package which is combined with the base oil. Or, alternatively, the additive components may be combined directly with the base oil.

Base Oil

[0013] Base oils suitable for use with present embodiments may comprise one or more oils of lubricating viscosity such as mineral (or natural) oils, synthetic lubricating oils, vegetable oils, and mixtures thereof. Such base oils include those conventionally employed as crankcase lubricating oils for spark-ignited and compression-ignited internal combustion engines, such as automobile and truck engines, marine and railroad diesel engines, and the like. Suitable base oils may have a NOACK volatility of from about 5 to about 15. As another example, suitable base oils may have a NOACK volatility of from about 10 to about 15. As even further example, suitable base oils may have a NOACK volatility of from about 9 to about 13. Base oils are typically classified as Group I, Group II, Group III, Group IV and Group V, as described in Table 1 below.

TABLE 1

Group I-V Base Oils				
Base Oil	% Sulfur		% Saturates	Viscosity Index
Group I	>0.03	and/or	<90	80-120
Group II	≤0.03	and/or	≥90	80-120
Group III	≤0.03	and/or	≥90	≥120
Group IV	*			
Group V	**			

* Group IV base oils are defined as all polyalphaolefins

** Group V base oils are defined as all other base oils not included in Groups I, II, III and IV and may include gas to liquid base oils.

[0014] Lubricating base oils may also include oils made from a waxy feed. The waxy feed may comprise at least 40 weight percent n-paraffins, for example greater than 50 weight percent n-paraffins, and more desirably greater than 75 weight percent n-paraffins. The waxy feed may be a conventional petroleum derived feed, such as, for example, slack wax, or it may be derived from a synthetic feed, such as, for example, a feed prepared from a Fischer-Tropsch synthesis.

[0015] Non-limiting examples of synthetic base oils include alkyl esters of dicarboxylic acids, polyglycols and alcohols, poly-alpha-olefins, including polybutenes, alkyl benzenes, organic esters of phosphoric acids, polysilicone oils, and alkylene oxide polymers, interpolymers, copolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, and the like.

[0016] Mineral base oils include, but are not limited to, animal oils and vegetable oils (e.g., castor oil, lard oil), liquid petroleum oils and hydrorefined, solvent-treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic and mixed paraffinic-naphthenic types. Oils of lubricating viscosity derived from coal or shale are also useful base oils.

ZDDP Compound

[0017] A primary component of the lubricant composition is a phosphorus-containing metal compound such as ZDDP.

Suitable ZDDPs may be prepared from specific amounts of primary or secondary alcohols, or mixtures thereof. For example, the alcohols may be combined in a ratio of from about 100:0 to about 0:100 primary-to-secondary alcohols. As an even further example, the alcohols may be combined in a ratio of about 60:40 primary-to-secondary alcohols. An example of a suitable ZDDP may comprise the reaction product obtained by combining: (i) about 50 to about 100 mol % of about C₁ to about C₁₈ primary alcohol; (ii) up to about 50 mol % of about C₃ to C₁₈ secondary alcohol; (iii) a phosphorus-containing component; and (iv) a zinc-containing component. As a further example, the primary alcohol may be a mixture of from about C₁ to about C₁₈ alcohols. As an even further example, the primary alcohol may be a mixture of a C₄ and a C₈ alcohol. The secondary alcohol may also be a mixture of alcohols. As an example, the secondary alcohol may comprise a C₃-C₆ alcohol. The alcohols may contain any of branched, cyclic, or straight chains. The ZDDP may comprise the combination of about 60 mol % primary alcohol and about 40 mol % secondary alcohol. In the alternative, the ZDDP may comprise 100 mol % secondary alcohols, or 100 mol % primary alcohols.

[0018] The phosphorus-containing component used to make the ZDDP compound may comprise any suitable phosphorus-containing component such as, but not limited to a phosphorus sulfide. Suitable phosphorus sulfides may include phosphorus pentasulfide or tetraphosphorus trisulfide.

[0019] The zinc-containing component used to make the ZDDP compound may comprise any suitable zinc-containing component such as, but not limited to zinc oxide, zinc hydroxide, zinc carbonate, zinc propylate, zinc chloride, zinc propionate, or zinc acetate.

[0020] The reaction product may comprise a resulting mixture, component, or mixture of components. The reaction product may or may not include unreacted reactants, chemically bonded components, products, or polar bonded components.

[0021] The ZDDP compound may be present in an amount sufficient to contribute from about 0.03 wt % to about 0.15 wt % phosphorus in the lubricant composition.

Hydrocarbon Soluble Metal Compound

[0022] The hydrocarbon soluble metal compounds that are used in combination with the ZDDP compound to provide lubricants having improved friction characteristics may include a wide variety of transition metal compounds that are soluble in hydrocarbons such as natural and synthetic lubricating oils. As described above, suitable transition metals for the hydrocarbon soluble metal compounds include, but are not limited to cobalt, nickel, zinc, zirconium, manganese, vanadium, scandium, yttrium, tungsten, gold, platinum, and iron.

[0023] The metal compounds may be selected from metal alkoxides, carboxylates, acetylacetonates, aminocarboxylates, aminoacetylacetonates, naphthenates, and polymeric derivatives thereof containing M-O-M linkages, wherein M is the metal of the metal compound. Desirably, the transition metal compound is substantially devoid of sulfur and phosphorus atoms. The metal carboxylates may be derived from carboxylic acids. The carboxylic acids may be mono- or polycarboxylic acids such as di- or tricarboxylic acids.

[0024] Monocarboxylic acids include C₁₋₇ lower acids (acetic, propionic, etc.) and higher C₈₊ acids (e.g., octanoic,

decanoic, etc.) as well as the fatty acids of about 12-30 carbon atoms. The neo acids such as neooctanoic and neodecanoic and the like are also useful.

[0025] Fatty acids are often mixtures of straight and branched chain acids containing, for example, from 5% to about 30% straight chain acids and about 70% to about 95% (mole) branched chain acids. Other commercially available fatty acid mixtures containing much higher proportions of straight chain acids are also useful. Mixtures produced from dimerization of unsaturated fatty acids can also be used.

[0026] Examples of aminocarboxylic acids that may be used to provide the metal compound include, but not limited to, ethylenediaminetetraacetic acid (EDTA), trans-1,2-diaminocyclohexane-N,N',N'-tetraacetic acid (CDTA), ethylenediaminedisuccinic acid (EDDS), diethylenetriaminepentaacetic acid (DTPA), triethylenetetraaminhexaacetic acid (TTHA) and ethylenebis [2(hydroxyphenyl) glycine] (ED-DHA).

[0027] Acetylacetonates, tert-butyl acetylacetonates may be used as the metal compounds. A particularly suitable hydrocarbon soluble metal compound is a metal chelate with 2,2,6,6-tetramethyl-3,5-heptanedionate ligands.

[0028] The amount of metal compound used in the lubricant composition in combination with the ZDDP compound is that amount of compound which is sufficient to provide a total metal content, based on ZDDP and the metal compound of from about 300 to about 1500 ppm by weight based on the total weight of the lubricant composition. Accordingly, the weight ratio of total metal to phosphorus in the lubricant composition, based on the ZDDP and hydrocarbon soluble transition metal compound may range from above 1.5 to 1 to about 15 to 1 or higher. In another embodiment, the weight ratio of total metal to phosphorus may range from about 3 to 1 to about 10 to 1.

[0029] The ZDDP compound and transition metal compound mixture disclosed herein is used in combination with other additives. The additives are typically blended into the base oil in an amount that enables that additive to provide its desired function. Representative effective amounts of the phosphorus-containing and transition metal compound mixtures and additives, when used in crankcase lubricants, are listed in Table 2 below. All the values listed are stated as weight percent active ingredient.

TABLE 2

Component	Wt. % (Broad)	Wt. % (Typical)
Dispersant	0.5-10.0	1.0-5.0
Oxidation Inhibitors	0-10.0	0.1-6.0
Metal Detergents	0.1-15.0	0.2-8.0
Corrosion Inhibitor	0-5.0	0-2.0
Antifoaming agent	0-5.0	0.001-0.15
Pour point depressant	0.01-5.0	0.01-1.5
Viscosity modifier	0.01-20.00	0.25-10.0
ZDDP compound	0.1-10.0	0.25-5.0
Transition metal compound	0.05-5.0	0.075-3.0
Base oil	Balance	Balance
Total	100	100

Dispersant Components

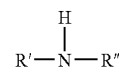
[0030] Dispersants that may be used in an additive package with the ZDDP and metal compounds include, but are not limited to, ashless dispersants that have an oil soluble poly-

meric hydrocarbon backbone having functional groups that are capable of associating with particles to be dispersed. Typically, the dispersants comprise amine, alcohol, amide, or ester polar moieties attached to the polymer backbone often via a bridging group. Dispersants may be selected from Mannich dispersants as described in U.S. Pat. Nos. 3,697,574 and 3,736,357; ashless succinimide dispersants as described in U.S. Pat. Nos. 4,234,435 and 4,636,322; amine dispersants as described in U.S. Pat. Nos. 3,219,666, 3,565,804, and 5,633,326; Koch dispersants as described in U.S. Pat. Nos. 5,936,041, 5,643,859, and 5,627,259, and polyalkylene succinimide dispersants as described in U.S. Pat. Nos. 5,851,965; 5,853,434; and 5,792,729.

Oxidation Inhibitor Components

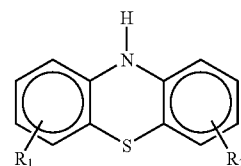
[0031] Oxidation inhibitor may also be used in combination with the ZDDP and metal compounds in a lubricant additive package. Oxidation inhibitors or antioxidants reduce the tendency of base stocks to deteriorate in service which deterioration can be evidenced by the products of oxidation such as sludge and varnish-like deposits that deposit on metal surfaces and by viscosity growth of the finished lubricant. Such oxidation inhibitors include hindered phenols, sulfurized hindered phenols, alkaline earth metal salts of alkylphenolthioesters having C₅ to C₁₂ alkyl side chains, sulfurized alkylphenols, metal salts of either sulfurized or nonsulfurized alkylphenols, for example calcium nonylphenol sulfide, ashless oil soluble phenates and sulfurized phenates, phosphorusulfurized or sulfurized hydrocarbons, phosphorus esters, metal thiocarbamates, and oil soluble copper compounds as described in U.S. Pat. No. 4,867,890. Other antioxidants that may be used include diarylamines, alkylated phenothiazines, sulfurized compounds, and ashless dialkyldithiocarbamates. Sterically hindered phenols and mixtures thereof as described in U.S. Publication No. 2004/0266630.

[0032] Diarylamine antioxidants include, but are not limited to diarylamines having the formula:



wherein R' and R'' each independently represents a substituted or unsubstituted aryl group having from 6 to 30 carbon atoms. Illustrative of substituents for the aryl group include aliphatic hydrocarbon groups such as alkyl having from 1 to 30 carbon atoms, hydroxy groups, halogen radicals, carboxylic acid or ester groups, or nitro groups.

[0033] Another class of aminic antioxidants includes phenothiazine or alkylated phenothiazine having the chemical formula:



wherein R_1 is a linear or branched C_1 to C_{24} alkyl, aryl, heteroalkyl or alkylaryl group and R_2 is hydrogen or a linear or branched C_1 - C_{24} alkyl, heteroalkyl, or alkylaryl group.

[0034] The sulfur containing antioxidants include, but are not limited to, sulfurized olefins that are characterized by the type of olefin used in their production and the final sulfur content of the antioxidant. High molecular weight olefins, i.e. those olefins having an average molecular weight of 168 to 351 g/mole, are preferred. Examples of olefins that may be used include alpha-olefins, isomerized alpha-olefins, branched olefins, cyclic olefins, and combinations of these.

[0035] Sulfur sources that may be used in the sulfurization reaction of olefins include: elemental sulfur, sulfur monochloride, sulfur dichloride, sodium sulfide, sodium polysulfide, and mixtures of these added together or at different stages of the sulfurization process.

[0036] Unsaturated oils, because of their unsaturation, may also be sulfurized and used as an antioxidant. Examples of oils or fats that may be used include corn oil, canola oil, cottonseed oil, grapeseed oil, olive oil, palm oil, peanut oil, coconut oil, rapeseed oil, safflower seed oil, sesame seed oil, soyabean oil, sunflower seed oil, tallow, and combinations of these. The foregoing aminic, phenothiazine, and sulfur containing antioxidants are described for example in U.S. Pat. No. 6,599,865.

[0037] The ashless dialkyldithiocarbamates which may be used as antioxidant additives include compounds that are soluble or dispersable in the additive package. It is also preferred that the ashless dialkyldithiocarbamate be of low volatility, preferably having a molecular weight greater than 250 daltons, most preferably having a molecular weight greater than 400 daltons. Examples of dialkyldithiocarbamates that may be used are disclosed in the following patents: U.S. Pat. Nos. 5,693,598; 4,876,375; 4,927,552; 4,957,643; 4,885,365; 5,789,357; 5,686,397; 5,902,776; 2,786,866; 2,710,872; 2,384,577; 2,897,152; 3,407,222; 3,867,359; and 4,758,362.

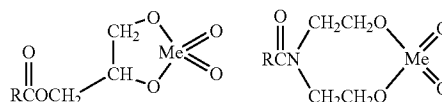
[0038] Organomolybdenum containing compounds used as friction modifiers may also exhibit antioxidant functionality. U.S. Pat. No. 6,797,677 describes a combination of organomolybdenum compound, alkylphenothiazine and alkyl-diphenylamines for use in finished lubricant formulations. Examples of suitable molybdenum containing friction modifiers are described below under friction modifiers.

[0039] Friction Modifier Components

[0040] A sulfur- and phosphorus-free organomolybdenum compound that may be used as a friction modifier may be prepared by reacting a sulfur- and phosphorus-free molybdenum source with an organic compound containing amino and/or alcohol groups. Examples of sulfur- and phosphorus-free molybdenum sources include molybdenum trioxide, ammonium molybdate, sodium molybdate and potassium molybdate. The amino groups may be monoamines, diamines, or polyamines. The alcohol groups may be mono-substituted alcohols, diols or bis-alcohols, or polyalcohols. As an example, the reaction of diamines with fatty oils produces a product containing both amino and alcohol groups that can react with the sulfur- and phosphorus-free molybdenum source.

[0041] Examples of sulfur- and phosphorus-free organomolybdenum compounds include compounds described in the following patents: U.S. Pat. Nos. 4,259,195; 4,261,843; 4,164,473; 4,266,945; 4,889,647; 5,137,647; 4,692,256; 5,412,130; 6,509,303; and 6,528,463.

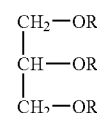
[0042] Molybdenum compounds prepared by reacting a fatty oil, diethanolamine, and a molybdenum source as described in U.S. Pat. No. 4,889,647 are sometimes illustrated with the following structure, where R is a fatty alkyl chain, although the exact chemical composition of these materials is not fully known and may in fact be multi-component mixtures of several organomolybdenum compounds.



[0043] Sulfur-containing organomolybdenum compounds may be used and may be prepared by a variety of methods. One method involves reacting a sulfur and phosphorus-free molybdenum source with an amino group and one or more sulfur sources. Sulfur sources can include for example, but are not limited to, carbon disulfide, hydrogen sulfide, sodium sulfide and elemental sulfur. Alternatively, the sulfur-containing molybdenum compound may be prepared by reacting a sulfur-containing molybdenum source with an amino group or thiuram group and optionally a second sulfur source.

[0044] Examples of sulfur-containing organomolybdenum compounds include compounds described in the following patents: U.S. Pat. Nos. 3,509,051; 3,356,702; 4,098,705; 4,178,258; 4,263,152; 4,265,773; 4,272,387; 4,285,822; 4,369,119; 4,395,343; 4,283,295; 4,362,633; 4,402,840; 4,466,901; 4,765,918; 4,966,719; 4,978,464; 4,990,271; 4,995,996; 6,232,276; 6,103,674; and 6,117,826.

[0045] Glycerides may also be used alone or in combination with other friction modifiers. Suitable glycerides include glycerides of the formula:



wherein each R is independently selected from the group consisting of H and $C(O)R'$ where R' may be a saturated or an unsaturated alkyl group having from 3 to 23 carbon atoms. Examples of glycerides that may be used include glycerol monolaurate, glycerol monomyristate, glycerol monopalmitate, glycerol monostearate, and mono-glycerides derived from coconut acid, tallow acid, oleic acid, linoleic acid, and linolenic acids. Typical commercial monoglycerides contain substantial amounts of the corresponding diglycerides and triglycerides. These materials are not detrimental to the production of the molybdenum compounds, and may in fact be more active. Any ratio of mono- to di-glyceride may be used, however, it is preferred that from 30 to 70% of the available sites contain free hydroxyl groups (i.e., 30 to 70% of the total R groups of the glycerides represented by the above formula are hydrogen). A preferred glyceride is glycerol monooleate, which is generally a mixture of mono, di, and tri-glycerides derived from oleic acid, and glycerol.

Other Additives

[0046] Rust inhibitors selected from the group consisting of nonionic polyoxyalkylene polyols and esters thereof, polyoxyalkylene phenols, and anionic alkyl sulfonic acids may be used.

[0047] A small amount of a demulsifying component may be used. A preferred demulsifying component is described in EP 330,522. Such demulsifying component may be obtained by reacting an alkylene oxide with an adduct obtained by reacting a bis-epoxide with a polyhydric alcohol. The demulsifier should be used at a level not exceeding 0.1 mass % active ingredient. A treat rate of 0.001 to 0.05 mass % active ingredient is convenient.

[0048] Pour point depressants, otherwise known as lube oil flow improvers, lower the minimum temperature at which the fluid will flow or can be poured. Such additives are well known. Typical of those additives which improve the low temperature fluidity of the fluid are C₈ to C₁₈ dialkyl fumarate/vinyl acetate copolymers, polyalkylmethacrylates and the like.

[0049] Foam control can be provided by many compounds including an antifoamant of the polysiloxane type, for example, silicone oil or polydimethyl siloxane.

[0050] Seal swell agents, as described, for example, in U.S. Patent Nos. 3,794,081 and 4,029,587, may also be used.

[0051] Viscosity modifiers (VM) function to impart high and low temperature operability to a lubricating oil. The VM used may have that sole function, or may be multifunctional.

[0052] Multifunctional viscosity modifiers that also function as dispersants are also known. Suitable viscosity modifiers are polyisobutylene, copolymers of ethylene and propylene and higher alpha-olefins, polymethacrylates, polyalkylmethacrylates, methacrylate copolymers, copolymers of an unsaturated dicarboxylic acid and a vinyl compound, inter polymers of styrene and acrylic esters, and partially hydrogenated copolymers of styrene/isoprene, styrene/butadiene, and isoprene/butadiene, as well as the partially hydrogenated homopolymers of butadiene and isoprene and isoprene/divinylbenzene.

when used, ranges up to about 20% by weight based on the weight of the lubricating oil composition, and in one embodiment from about 0.001% to about 20% by weight, and in one embodiment about 0.01% to about 10% by weight based on the weight of the lubricating oil composition.

[0055] The ZDDP and hydrocarbon soluble metal compounds may be added directly to the lubricating oil composition. In one embodiment, however, they are diluted with a substantially inert, normally liquid organic diluent such as mineral oil, synthetic oil, naphtha, alkylated (e.g. C₁₀ to C₁₃ alkyl) benzene, toluene or xylene to form an additive concentrate. These concentrates usually contain from about 1% to about 100% by weight and in one embodiment about 10% to about 90% by weight of the additive mixture.

[0056] In order to illustrate an advantage of the disclosed embodiments with respect to improving friction characteristics of lubricating oils, the following non-limiting example is given.

EXAMPLE

[0057] The following example is not intended to limit the embodiments in any way. Inventive and comparative lubricant compositions containing the ZDDP compound and metal compound were tested to provide boundary friction characteristics and thin film friction characteristics. The friction characteristics of the compositions were determined using a Mini Traction Machine with a Spacer Layer Imaging System (MTM-SLIM). The metal compounds were added to the mixture in the form of a chelate of 2,2,6,6-tetramethyl-3,5-heptanedionate ligands. The results of each mixture are given in the following table.

TABLE 3

ZDDP Compound (ppm by wt. P)	Metal Compound (ppm by wt.)	Total Metal (ppm by wt.)	Total Metal to Phosphorus Ratio	Boundary Friction at 130° C.
ZDDP, 400 ppm P	—	400	1 to 1	0.150
ZDDP, 600 ppm P	—	600	1 to 1	0.178
ZDDP, 400 ppm P	40 ppm Zn	440	1.1 to 1	0.152
ZDDP, 400 ppm P	200 ppm Zn	600	1.5 to 1	0.141
ZDDP, 400 ppm P	400 ppm Zn	800	2 to 1	0.134
ZDDP, 400 ppm P	4000 ppm Zn	4400	11 to 1	0.142
ZDDP, 400 ppm P	200 ppm Ti	600	1.5 to 1	0.133
ZDDP, 400 ppm P	200 ppm Fe	600	1.5 to 1	0.159
ZDDP, 400 ppm P	200 ppm Ca	600	1.5 to 1	0.152
ZDDP, 400 ppm P	200 ppm Zr	600	1.5 to 1	0.152

[0053] Functionalized olefin copolymers that may be used include interpolymers of ethylene and propylene which are grafted with an active monomer such as maleic anhydride and then derivatized with an alcohol or amine. Other such copolymers are copolymers of ethylene and propylene which are grafted with nitrogen compounds.

[0054] Each of the foregoing additives, when used, is used at a functionally effective amount to impart the desired properties to the lubricant. Thus, for example, if an additive is a corrosion inhibitor, a functionally effective amount of this corrosion inhibitor would be an amount sufficient to impart the desired corrosion inhibition characteristics to the lubricant. Generally, the concentration of each of these additives,

[0058] The foregoing table 3 illustrates that increasing an amount of ZDDP compound to provide from 400 ppm total metal to 600 ppm total metal significantly increase boundary friction from 0.150 at 400 ppm total metal to 0.178 at 600 ppm total metal. However, when non-phosphorus-containing metal compounds are combined with ZDDP to provide a total metal content of 600 ppm, the boundary friction is about the same or lower than with 400 ppm total metal and only ZDDP in the lubricant composition. Based on the foregoing analysis, increasing the metal to phosphorus ratio to above about 1.5 to 1 in a lubricant composition using a non-phosphorus metal compound may be useful for increasing engine fuel economy.

[0059] In order to further illustrate the advantages of using certain transition metal compounds in combination with the

ZDDP compound, the thin film friction characteristics of the forging blends were determined and are listed in the following table.

TABLE 4

ZDDP Compound (ppm by wt. P)	Metal Compound (ppm by wt.)	Total Metal (ppm by wt.)	Total Metal to Phosphorus Ratio	Thin Film Friction at 100° C.
ZDDP, 400 ppm P	—	400	1 to 1	0.042
ZDDP, 600 ppm P	—	600	1 to 1	0.045
ZDDP, 400 ppm P	40 ppm Zn	440	1.1 to 1	0.040
ZDDP, 400 ppm P	200 ppm Zn	600	1.5 to 1	0.043
ZDDP, 400 ppm P	400 ppm Zn	800	2 to 1	0.041
ZDDP, 400 ppm P	4000 ppm Zn	4400	11 to 1	0.024
ZDDP, 400 ppm P	200 ppm Ti	600	1.5 to 1	0.045
ZDDP, 400 ppm P	200 ppm Fe	600	1.5 to 1	0.040
ZDDP, 400 ppm P	200 ppm Ca	600	1.5 to 1	0.056
ZDDP, 400 ppm P	200 ppm Zr	600	1.5 to 1	0.038

[0060] The foregoing table 4 illustrates that not all metals in the lubricant composition have a beneficial effect on friction characteristics. In particular, non-transition metals, such as calcium, may significantly increase the thin film friction of a lubricant composition compared to the same or greater total metal content provided by ZDDP and a transition metal compound such as Zn, Ti, Fe, or Zr.

[0061] At numerous places throughout this specification, reference has been made to a number of U.S. Patents and publications. All such cited documents are expressly incorporated in full into this disclosure as if fully set forth herein.

[0062] The foregoing embodiments are susceptible to considerable variation in its practice. Accordingly, the embodiments are not intended to be limited to the specific exemplifications set forth hereinabove. Rather, the foregoing embodiments are within the spirit and scope of the appended claims, including the equivalents thereof available as a matter of law.

[0063] The patentees do not intend to dedicate any disclosed embodiments to the public, and to the extent any disclosed modifications or alterations may not literally fall within the scope of the claims, they are considered to be part hereof under the doctrine of equivalents.

What is claimed is:

1. A lubricant composition for providing improved friction characteristics:

- (a) a base oil;
- (b) a zinc dialkyldithiophosphate compound; and
- (c) a hydrocarbon soluble metal compound, wherein the hydrocarbon soluble metal compound is devoid of phosphorus and sulfur atoms and the metal is selected from the group consisting essentially of cobalt, nickel, zinc, zirconium, manganese, vanadium, scandium, yttrium, tungsten, gold, platinum, and iron,

wherein a weight ratio of total metal in the lubricant composition from the zinc dialkyl-dithiophosphate compound and the hydrocarbon soluble metal compound to phosphorus in the lubricant composition ranges from greater than about 1.5 to 1 to about 15 to 1.

2. The lubricant composition of claim 1, wherein the lubricant composition is an engine oil.

3. The lubricant composition of claim 1, wherein the lubricant composition is a heavy duty engine oil.

4. The lubricant composition of claim 1, wherein the base oil comprises a mineral oil, a synthetic oil, or a mixture thereof.

5. The lubricant composition of claim 1, wherein the base oil comprises one or more of a member selected from the group consisting of: a group I base oil, a group II base oil, a group III base oil, a group IV base oil, and a group V base oil.

6. The lubricant composition of claim 1, wherein a total amount of metal in the lubricant composition from the zinc dialkyldithiophosphate compound and the hydrocarbon soluble metal compound ranges from about 300 to about 1500 ppm by weight based on the total weight of the lubricant composition.

7. The lubricant composition of claim 1, wherein a total amount of phosphorus in the lubricant composition from the zinc dialkyldithiophosphate compound ranges from about 200 to about 1000 ppm by weight based on the total weight of the lubricant composition.

8. The lubricant composition of claim 1, wherein a boundary friction characteristic at 130° C. is less than a boundary friction characteristic at 130° C. of a lubricant composition comprising zinc dialkyldithiophosphate and having a total metal to phosphorus weight ratio of less than about 1.5 to 1, wherein the lubricant composition is devoid of the hydrocarbon soluble metal compound.

9. The lubricant composition of claim 1, wherein a boundary friction characteristic at 130° C. is less than a boundary friction characteristic at 130° C. of a lubricant composition comprising zinc dialkyldithiophosphate, wherein the lubricant composition is devoid of the hydrocarbon soluble metal compound.

10. The lubricant composition of claim 1, wherein the weight ratio of total metal in the lubricant composition from the zinc dialkyl-dithiophosphate compound and the hydrocarbon soluble metal compound to phosphorus in the lubricant composition ranges from greater than about 3.0 to 1 to about 10 to 1.

11. An additive concentrate for an engine crankcase lubricant comprising:

- (a) a zinc dialkyldithiophosphate compound; and
- (b) a hydrocarbon soluble metal compound other than a dispersant or a detergent,

wherein the hydrocarbon soluble metal compound is devoid of phosphorus and sulfur atoms and the metal is selected from the group consisting essentially of cobalt, nickel, zinc, zirconium, manganese, vanadium, scandium, yttrium, tungsten, gold, platinum, and iron, wherein a weight ratio of total metal

in the concentrate from the zinc dialkyl-dithiophosphate compound and the hydrocarbon soluble metal compound to phosphorus in the concentrate ranges from greater than about 1.5 to 1 to about 15 to 1.

12. The additive concentrate of claim **11**, wherein the additive concentrate provides a total amount of metal from the zinc dialkyldithiophosphate compound and the hydrocarbon soluble metal compound to a lubricant composition containing the concentrate ranging from about 300 to about 1500 ppm by weight based on the total weight of the lubricant composition.

13. The additive concentrate of claim **11**, wherein the additive concentrate provides a total amount of phosphorus from the zinc dialkyldithiophosphate compound to a lubricant composition containing the concentrate ranging from about 200 to about 1000 ppm by weight based on the total weight of the lubricant composition.

14. A method for improving a fuel economy of an internal combustion engine, comprising lubricating the engine with a lubricant composition comprising:

- (a) a base oil;
- (b) a zinc dialkyldithiophosphate compound; and
- (b) a hydrocarbon soluble metal compound other than a dispersant or a detergent,

wherein the hydrocarbon soluble metal compound is devoid of phosphorus and sulfur atoms and the metal is selected from the group consisting essentially of cobalt, nickel, zinc, zirconium, manganese, vanadium, scandium, yttrium, tungsten, gold, platinum, and iron, wherein a weight ratio of total metal in the concentrate from the zinc dialkyl-dithiophosphate compound and the hydrocarbon soluble metal compound to phosphorus in the lubricant composition ranges from greater than about 1.5 to 1 to about 15 to 1.

15. The method of claim **14**, wherein a total amount of metal in the lubricant composition from the zinc dialkyldithiophosphate compound and the hydrocarbon soluble metal compound ranges from about 300 to about 1500 ppm by weight based on the total weight of the lubricant composition.

16. The method of claim **14**, wherein a total amount of phosphorus in the lubricant composition from the zinc dialkyldithiophosphate compound ranges from about 200 to about 1000 ppm by weight based on the total weight of the lubricant composition.

17. The method of claim **14**, wherein a boundary friction characteristic at 130° C. is less than a boundary friction characteristic at 130° C. of a lubricant composition comprising zinc dialkyldithiophosphate and having a total metal to phosphorus weight ratio of less than about 1.5 to 1, wherein the lubricant composition is devoid of the hydrocarbon soluble metal compound.

18. A method for improving a friction characteristic of a lubricant for an internal combustion engine, comprising formulating a lubricant composition with:

- (a) a base oil;
- (b) a zinc dialkyldithiophosphate compound; and
- (b) a hydrocarbon soluble metal compound other than a dispersant or a detergent,

wherein the hydrocarbon soluble metal compound is devoid of phosphorus and sulfur atoms and the metal is selected from the group consisting essentially of cobalt, nickel, zinc, zirconium, manganese, vanadium, scandium, yttrium, tungsten, gold, platinum, and iron, wherein a weight ratio of total metal in the concentrate from the zinc dialkyl-dithiophosphate compound and the hydrocarbon soluble metal compound to phosphorus in the lubricant composition ranges from greater than about 1.5 to 1 to about 15 to 1.

19. The method of claim **18**, wherein a total amount of metal in the lubricant composition from the zinc dialkyldithiophosphate compound and the hydrocarbon soluble metal compound ranges from about 300 to about 1500 ppm by weight based on the total weight of the lubricant composition.

20. The method of claim **18**, wherein a total amount of phosphorus in the lubricant composition from the zinc dialkyldithiophosphate compound ranges from about 200 to about 1000 ppm by weight based on the total weight of the lubricant composition.

21. The method of claim **18**, wherein a boundary friction characteristic at 130° C. is less than a boundary friction characteristic at 130° C. of a lubricant composition comprising zinc dialkyldithiophosphate and having a total metal to phosphorus weight ratio of less than about 1.5 to 1, wherein the lubricant composition is devoid of the hydrocarbon soluble metal compound.

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