**Lubricant formulations and methods**

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 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 dialkyldithiophosphate compound and the hydrocarbon soluble metal compound to phosphorus in the lubricant composition ranges from greater than 1.5 to 1 to 15 to 1.
DESCRIPTION

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 anticorrosion 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, 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 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 1.5 to 1 to 15 to 1.

[0005] An embodiment of the disclosure provides 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 1.5 to 1 to 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 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 1.5 to 1 to 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 1.5 to 1 to 15 to 1.

[0008] The compositions and methods described may be particularly suitable for improving boundary friction characteristics of lubricant compositions containing from 100 to 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

Lubricant compositions according to embodiments described herein may comprise a base oil; a zinc dialkylidithiophosphate (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.

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.

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

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 5 to 15. As another example, suitable base oils may have a NOACK volatility of from 10 to 15. As even further example, suitable base oils may have a NOACK volatility of from 9 to 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>
<thead>
<tr>
<th>Base Oil</th>
<th>% Sulfur</th>
<th>% Saturates</th>
<th>Viscosity Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group I</td>
<td>&gt; 0.03</td>
<td>&lt;90</td>
<td>80-120</td>
</tr>
<tr>
<td>Group II</td>
<td>≤ 0.03</td>
<td>≥90</td>
<td>80-120</td>
</tr>
<tr>
<td>Group III</td>
<td>≤ 0.03</td>
<td>≥90</td>
<td>≥120</td>
</tr>
</tbody>
</table>

* 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.

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.

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, interpolymeromers, copolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, and the like.

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.
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 100:0 to 0:100 primary-to-secondary alcohols. As an even further example, the alcohols may be combined in a ratio of 60:40 primary-to-secondary alcohols. An example of a suitable ZDDP may comprise the reaction product obtained by combining: (i) 50 to 100 mol % of C1 to C18 primary alcohol; (ii) up to 50 mol % of 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 C1 to C18 alcohols. As an even further example, the primary alcohol may be a mixture of a C2 and a C8 alcohol. The secondary alcohol may also be a mixture of alcohols. As an example, the secondary alcohol may comprise a C2-C8 alcohol. The alcohols may contain any of branched, cyclic, or straight chains. The ZDDP may comprise the combination of 60 mol % primary alcohol and 40 mol % secondary alcohol. In the alternative, the ZDDP may comprise 100 mol % secondary alcohol, or 100 mol % primary alcohols.

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.

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.

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.

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

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.

The metal compounds may be selected from metal alkoxides, carboxylates, acetylacetonates, aminocarboxylates, aminoacetylacetonates, napthenates, 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.

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 12-30 carbon atoms. The neo acids such as neooctanoic and neodecanoic and the like are also useful.

Fatty acids are often mixtures of straight and branched chain acids containing, for example, from 5% to 30% straight chain acids and 70% to 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.

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',N'-tetraacetic acid (CDTA), ethylenediaminedisuccinic acid (EDDS), diethylenetriaminepentaacetic acid (DTPA), triethylenetetraminehexaacetic acid (TTHA) and ethylened [2(hydroxyphenyl) glycine] (EDDA).

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.

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 300 to 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 15 to 1 or higher. In another embodiment, the weight ratio of total metal to phosphorus may range from 3 to 1 to 10 to 1.

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

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

**Dispersant Components**

[D0030] 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 polymeric 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 succcinimide 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**

[D0031] 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 C6 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, phosphosulfurized 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.

[D0032] Diarylamine antioxidants include, but are not limited to diarylamines having the formula:

\[
\begin{align*}
\text{H} \\
\text{R'} & \text{N} & \text{R''}
\end{align*}
\]

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:
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.

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.

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

\[ \text{CH}_2\text{OR} \]
\[ \text{CH} \]
\[ \text{CH}_2\text{OR} \]

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., from 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

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

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.

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.

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

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

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.  

**[0051]** 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/1,3-propene, styrene/butadiene, and isoprene/butadiene, as well as the partially hydrogenated homopolymers of butadiene and isoprene and isoprene/divinylbenzene.

**[0052]** 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.

**[0053]** 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, when used, ranges up to 20% by weight based on the weight of the lubricating oil composition, and in one embodiment from 0.001 % to 20% by weight, and in one embodiment 0.01 % to 10% by weight based on the weight of the lubricating oil composition.

**[0054]** 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 1% to 100% by weight and in one embodiment 10% to 90% by weight of the additive mixture.

**[0055]** 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**

**[0056]** 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.

<p>| Table 3 |
|-------------------|-------------------|----------------|------------------|------------------|</p>
<table>
<thead>
<tr>
<th>ZDDP Compound (ppm by wt. P)</th>
<th>Metal Compound (ppm by wt.)</th>
<th>Total Metal (ppm by wt.)</th>
<th>Total Metal to Phosphorus Ratio</th>
<th>Boundary Friction at 130° C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZDDP, 400 ppm P</td>
<td>----</td>
<td>400</td>
<td>1 to 1</td>
<td>0.150</td>
</tr>
<tr>
<td>ZDDP, 600 ppm P</td>
<td>----</td>
<td>600</td>
<td>1 to 1</td>
<td>0.178</td>
</tr>
<tr>
<td>ZDDP, 400 ppm P</td>
<td>40 ppm Zn</td>
<td>440</td>
<td>1.1 to 1</td>
<td>0.152</td>
</tr>
<tr>
<td>ZDDP, 400 ppm P</td>
<td>200 ppm Zn</td>
<td>600</td>
<td>1.5 to 1</td>
<td>0.141</td>
</tr>
<tr>
<td>ZDDP, 400 ppm P</td>
<td>400 ppm Zn</td>
<td>800</td>
<td>2 to 1</td>
<td>0.134</td>
</tr>
<tr>
<td>ZDDP, 400 ppm P</td>
<td>4000 ppm Zn</td>
<td>4400</td>
<td>11 to 1</td>
<td>0.142</td>
</tr>
<tr>
<td>ZDDP, 400 ppm P</td>
<td>200 ppm Ti</td>
<td>600</td>
<td>1.5 to 1</td>
<td>0.133</td>
</tr>
<tr>
<td>ZDDP, 400 ppm P</td>
<td>200 ppm Fe</td>
<td>600</td>
<td>1.5 to 1</td>
<td>0.159</td>
</tr>
<tr>
<td>ZDDP, 400 ppm P</td>
<td>200 ppm Ca</td>
<td>600</td>
<td>1.5 to 1</td>
<td>0.152</td>
</tr>
<tr>
<td>ZDDP, 400 ppm P</td>
<td>200 ppm Zr</td>
<td>600</td>
<td>1.5 to 1</td>
<td>0.152</td>
</tr>
</tbody>
</table>

**[0057]** 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.

[0058] 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 forgoing blends were determined and are listed in the following table.

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

[0059] 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.

[0060] 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.

[0061] 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 scope of the appended claims, including the equivalents thereof available as a matter of law.

[0062] 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.

Claims

1. A lubricant composition for providing improved friction characteristics including:
   (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 cobalt, nickel, zinc, zirconium, manganese, vanadium, scandium, yttrium, tungsten, gold, platinum, and iron, and wherein 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 1.5 to 1 to 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 any one of claims 1-3, wherein the base oil comprises a mineral oil, a synthetic oil, or
5. The lubricant composition of any one of claims 1-4, wherein the base oil comprises on 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 any one of claims 1-5, wherein a total amount of metal in the lubricant composition from the zinc dialkyldithiophosphate compound and the hydrocarbon soluble metal compound ranges from 300 to 1500 ppm by weight based on the total weight of the lubricant composition.

7. The lubricant composition of any one of claims 1-6, wherein a total amount of phosphorus in the lubricant composition from the zinc dialkyldithiophosphate compound ranges from 200 to 1000 ppm by weight based on the total weight of the lubricant composition.

8. The lubricant composition of any one of claims 1-7, wherein a boundary friction characteristic of the lubricant composition at 130°C is less than a boundary friction characteristic at 130°C of a lubricant composition comprising zinc dialkyldithiophosphate, having a total metal to phosphorus weight ratio of less than 1.5 to 1, and which is devoid of the hydrocarbon soluble metal compound.

9. The lubricant composition of any one of claims 1-7, wherein a boundary friction characteristic of the lubricant composition at 130°C is less than a boundary friction characteristic at 130°C of a lubricant composition comprising zinc dialkyldithiophosphate and which is devoid of the hydrocarbon soluble metal compound.

10. The lubricant composition of any one of claims 1-9, wherein the 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 3.0 to 1 to 10 to 1.

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

(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 cobalt, nickel, zinc, zirconium, manganese, vanadium, scandium, yttrium, tungsten, gold, platinum, and iron, and wherein 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 1.5 to 1 to 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 300 to 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 200 to 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 the step of lubricating the engine with a lubricant composition as claimed in any one of claims 1-10.

15. A method for improving a friction characteristic of a lubricant for an internal combustion engine, comprising the step of formulating a lubricant composition as claimed in any one of claims 1-10.
REFERENCES CITED IN THE DESCRIPTION

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