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(54) **LOW PHOSPHORUS LUBRICATING OIL COMPOSITION HAVING LEAD CORROSION CONTROL**

(75) Inventor: **Alexander B. Boffa**, San Francisco, CA (US)

Correspondence Address:
CHEVRON CORPORATION
P.O. BOX 6006
SAN RAMON, CA 94583-0806

(73) Assignee: **Chevron Oronite Company LLC**

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(57) **ABSTRACT**

The present invention provides a low phosphorus lubricating oil composition containing a mixture of zinc dithiophosphates in a certain ratio surprisingly yields improved lead corrosion. The synergistic combination of mixed zinc dithiophosphates containing a zinc primary dialkyl dithiophosphate, zinc secondary dialkyl dithiophosphate and zinc diaryl dithiophosphate in a respective ratio, based on the phosphorus content, of the zinc primary dialkyl dithiphosphate to zinc secondary dialkyl dithiophosphate from about 2:1 to about 1:2 and the ratio of the mixture of zinc primary dialkyl dithiophosphate and zinc secondary dialkyl dithiophosphate to zinc diaryl dithiophosphate from about 6:1 to about 1:1. When used in a lubricating oil composition having a total phosphorus content less than about 0.06 wt %, based on the total weight of the lubricating oil composition to lubricate internal combustion engines. The mixture of zinc dithiophosphates greatly reduces lead corrosion.

LOW PHOSPHORUS LUBRICATING OIL COMPOSITION HAVING LEAD CORROSION CONTROL

[0001] The present invention is related, in part, to a lubricating oil composition. More particularly, the present invention relates to a low phosphorus lubricating oil composition employing a mixture of zinc dithiophosphates and wherein the lubricating oil composition has less than about 0.06 wt % total phosphorus content based on the total weight of the lubricating oil composition. The low phosphorus lubricating oil composition of the present invention is effective in lead corrosion control when used as a lubricating oil composition in internal combustion engines.

BACKGROUND OF THE INVENTION

[0002] Emissions arising from automotive exhaust has been a problem for several decades and approaches for addressing this problem have included the use of unleaded fuel (to deal, in part, with lead pollution arising from leaded fuels), oxygenated fuel (to reduce hydrocarbon emissions), the use of catalytic converters (also to reduce hydrocarbon emissions), etc.

[0003] Catalytic converters are now universally employed with gasoline powered vehicles and the efficiency of these converters is directly related to the ability of the catalyst to effect conversion of unburnt or partially burnt hydrocarbons generated during combustion to carbon dioxide and water. One problem arising with the use of such converters is poisoning of the catalyst resulting in reduced catalyst efficiency. Since catalytic converters are intended for extended use, catalyst poisoning results in higher levels of atmospheric discharges of pollutants from internal combustion engines over prolonged periods of time.

[0004] In order to minimize such poisoning, the industry has set standards for both fuel and lubricant contents. For example, standards for fuels have included the use of unleaded gasoline in order to avoid lead poisoning of the catalyst as well as lead discharge into the environment. See, for example, Buckley, III, "Long Chain Aliphatic Hydrocarbyl Amine Additive Having an Oxyalkylene Hydroxy Connecting Group", U.S. Pat. No. 4,975,096, issued Dec. 4, 1990.

[0005] As to the lubricants, one additive family currently being addressed by industry standards is the phosphorus-containing additives such as zinc dithiophosphate wear inhibitors used in lubricant compositions employed to lubricate internal combustion engines. Specifically, phosphorus-containing additives reach the catalytic converter as a result of, for example, exhaust gas recirculation and/or oil blow-by processes as well as other methods known in the are. See, for example, Beck, et al. "*Impact of Oil-Derived Catalyst Poisons on FTP Performance of LEV Catalyst Systems*", SAE Technical Paper 972842 (1997) and Darr et al. "*Effects of Oil-Derived Contaminants on Emissions from TWC-Equipped Vehicles*", SAE 2000-01-1881 (2000). In any event, the phosphorus is known to accumulate in the catalytic converter, at active metal sites; thus reducing catalyst efficiency and effectively over time, poisoning the catalyst. As a result of the above, a new focus is to lower phosphorus in the lubricating oils. For example, the draft GF-4 specifications for lubricant compositions have proposed significantly lower phosphorus contents than heretofore employed.

[0006] A problem arises when the level of phosphorus is reduced in a lubricant composition containing an oil-soluble, phosphorus-containing, anti-wear compound in that there is a significant reduction in anti-wear performance arising from the diminution in phosphorus content. One well known class of antiwear additives are metal alkylphosphates, especially zinc dialkyl dithiophosphates, are generally employed in lubricating oils at phosphorous levels above 0.1 weight percent when used for wear control. At lower levels, it is not found to be an effective antiwear additive. For instance, as exemplified in U.S. Pat. No. 6,696,393, issued Feb. 24, 2004, lowering the level of phosphorus glue to the presence of a metal dithiophosphate additive in a lubricant composition by one-half from 0.095 weight percent to 0.048 weight percent phosphorus results in about a seven-fold increase in engine wear.

[0007] Zinc dithiophosphates have either dialkyl or diaryl groups. Zinc dialkyl dithiophosphates are further subdivided into primary alkyl and secondary alkyl zinc dithiophosphates. Pentan-1-ol and 3-methylbutan-2-ol are illustrative of the primary and secondary alcohols used to prepare primary and secondary zinc dithiophosphates. Different zinc dithiophosphate chemical types perform differently (See below).

	Primary Alkyl	Secondary Alkyl	Aryl
Thermal Stability	Medium	Low	High
Antiwear Protection	Medium	High	Low
Hydrolytic Stability	Medium	High	Low

[0008] Each type has important applications in modern additive packages. It is therefore important to have the right mix of zinc dithiophosphates in any given lubricating oil composition to provide adequate anti-wear performance and at the same time keeping the phosphorus levels, due to the presence of a metal dithiophosphate additive below 0.1 wt % because phosphorus has a tendency to accumulate in the catalytic converter thus reducing catalyst efficiency, poisoning the catalyst.

SUMMARY OF THE INVENTION

[0009] As previously mentioned, the present invention is related, in part, to a lubricating oil composition. More particularly, the present invention relates to a low phosphorus lubricating oil composition employing a mixture of zinc dithiophosphates in a certain ratio and wherein the lubricating oil composition has less than about 0.06 wt % total phosphorus content, based on the total weight of the lubricating oil composition. The low phosphorus lubricating oil composition of the present invention is effective in lead corrosion control when used as a lubricating oil composition in internal combustion engines.

[0010] Accordingly, in its broadest aspect, the present invention is related to a lubricating oil composition comprising a major amount of bases oil of lubricating viscosity and a minor amount of a mixture of a zinc primary dialkyl dithiophosphate, a zinc secondary dialkyl dithiophosphate and a zinc diaryl dithiophosphate wherein the respective ratio, based on the phosphorous content, of the zinc primary dialkyl dithiophosphate to zinc secondary dialkyl dithiophosphate is from about 2:1 to about 1:2 and the ratio of the mixture of zinc primary dialkyl dithiophosphate and zinc secondary dialkyl dithiophosphate to zinc diaryl dithiophosphate is from about 6:1 to about 1:1 and wherein the total phosphorus content of the lubricating oil composition is less than about 0.06 wt %, based on the total weight of the lubricating oil composition.

[0011] The minor amount of the mixture of a zinc primary dialkyl dithiophosphate, a zinc secondary dialkyl dithiophosphate and a zinc diaryl dithiophosphate employed in the lubricating oil composition of the present invention is from about 0.1 wt % to about 1.5 wt % to about 1.0 wt %, based on the total weight of the lubricating oil composition.

[0012] The lubricating oil composition of the present invention will contain from about 0.05 wt % to about 1.2 wt % of a zinc primary dialkyl dithiophosphate, from about 0.05 wt % to about 1.2 wt % of a zinc secondary dialkyl dithiophosphate and from about 0.02 wt % to about 0.7 wt % of a zinc diaryl dithiophosphate, based on the total weight of the lubricating oil composition. Preferably, the lubricating oil composition of the present invention will contain from about 0.1 wt % to about 0.7 wt % of a zinc primary dialkyl dithiophosphate, from about 0.1 wt % to about 0.7 wt % of a zinc secondary dialkyl dithiophosphate and from about 0.05 wt % to about 0.5 wt % of a zinc diaryl dithiophosphate, based on the total weight of the lubricating oil composition. More preferably, the lubricating oil composition of the present invention will contain from about 0.2 wt % to about 0.5 wt % of a zinc primary dialkyl dithiophosphate, from about 0.2 wt % to about 0.5 wt % of a zinc secondary dialkyl dithiophosphate and from about 0.1 wt % to about 0.3 wt % of a zinc diaryl dithiophosphate, based on the total weight of the lubricating oil composition.

[0013] The primary alkyl group of the zinc primary dialkyl dithiophosphate has from about C_1 to about C_{13} carbon atoms, preferably from about C_3 to about C_{10} carbon atoms and more preferably, from about C_6 to about C_8 carbon atoms.

[0014] The secondary alkyl group of the zinc secondary dialkyl dithiophosphate has from about C_3 to about C_{13} carbon atoms, preferably from about C_3 to about C_8 carbon atoms and more preferably, from about C_3 to about C_6 carbon atoms.

[0015] The aryl group of the zinc diaryl dithiophosphate has from about C_6 to about C_{30} carbon atoms, preferably from about C_6 to about C_{24} carbon atoms and more preferably, from about C_6 to about C_{20} carbon atoms.

[0016] In a preferred embodiment, the respective ratio, based on the phosphorus content, of zinc primary dialkyl dithiophosphate to zinc secondary dialkyl dithiophosphate is from about 3:2 to about 2:3. More preferably, the ratio is about 1:1.

[0017] In a preferred embodiment, the respective ratio, based on the phosphorus content, of the mixture of zinc primary dialkyl dithiophosphate and zinc secondary dialkyl dithiophosphate to zinc diaryl dithiophosphate is from about 4:1 to about 1:1. More preferably, the ratio is about 2:1.

[0018] In an especially preferred embodiment, the respective ratio, based on the phosphorus content, of the mixture of zinc primary dialkyl dithiophosphate to zinc secondary dialkyl dithiophosphate to zinc diaryl dithiophosphate is 1:1:1.

[0019] In another embodiment, the total phosphorus content in the lubricating oil composition of the present invention is preferably less than about 0.05 wt %, more preferably, based on the total weight of the lubricating oil composition.

[0020] In still another embodiment, the sulfur content in the lubricating oil composition of the present invention is less than about 0.5 wt % and, preferably, less than about 0.2 wt %, based on the total weight of the lubricating oil composition and the total sulfated ash content in the lubricating oil composition of the present invention is less than about 1.2 wt %, preferably, less than about 1.0 wt %, and more preferably less than about 0.8 wt %, based on the total weight of the lubricating oil composition.

[0021] In one of its method aspects, the present invention further relates to a method for improving lead corrosion. The method involves operating an internal combustion engine with a lubricating oil composition comprising a major amount of base oil of lubricating viscosity and a minor amount of mixture of a zinc primary dialkyl dithiophosphate, a zinc secondary dialkyl dithiophosphate and a zinc diaryl dithiophosphate wherein the respective ratio, based on the phosphorus content, of the zinc primary dialkyl dithiophosphate to zinc secondary dialkyl dithiophosphate is from about 2:1 to about 1:2 and the ratio of the mixture of zinc primary dialkyl dithiophosphate and zinc secondary dialkyl dithiophosphate to zinc diaryl dithiophosphate is from about 6:1 to about 1:1 and wherein the total phosphorus content of the lubricating oil composition is less than about 0.06 wt %, based on the total weight of the lubricating oil composition.

[0022] Among other factors, the present invention provides a low phosphorus lubricating oil composition containing a mixture of zinc dithiophosphates in a certain ratio surprisingly yields improved lead corrosion. The mixture of zinc dithiophosphates contains a zinc primary dialkyl dithiophosphate, a zinc secondary dialkyl dithiophosphate and a zinc diaryl dithiophosphate. The synergistic combination of mixed zinc dithiophosphates wherein the respective ratio, based on the phosphorus content, of the zinc primary dialkyl dithiophosphate to zinc secondary dialkyl dithiophosphate is from about 2:1 to about 1:2 and the ratio of the mixture of zinc primary dialkyl dithiophosphate and zinc secondary dialkyl dithiophosphate to zinc diaryl dithiophosphate is from about 6:1 to about 1:1 when used in a lubricating oil composition having a total phosphorus content less than about 0.06 wt %, based on the total weight of the lubricating oil composition, greatly reduces lead corrosion when used to lubricate internal combustion engines.

DETAILED DESCRIPTION OF THE INVENTION

[0023] The present invention is related, in part, to a lubricating oil composition. More particularly, the present invention relates to a low phosphorus lubricating oil composition employing a mixture of zinc dithiophosphates containing a zinc primary dialkyl dithiophosphate, a zinc secondary dialkyl dithiophosphate and a zinc diaryl dithiophosphate wherein the respective ratio, based on the phosphorus content, of the zinc primary dialkyl dithiophosphate to zinc secondary dialkyl dithiophosphate is from about 2:1 to about 1:2 and the ratio of the mixture of zinc primary dialkyl dithiophosphate and zinc secondary dialkyl dithiophosphate to zinc diaryl dithiophosphate is from about 6:1 to 1:1 and wherein the lubricating oil composition has less than about 0.06 wt % total phosphorus content, based on the total weight of the lubricating oil composition. The low phosphorus lubricating oil composition of the present invention is effective in lead corrosion control when used as a lubricating oil in internal combustion engines.

[0024] Each of these components in the claimed composition will be described in detail herein. However, prior to such a description, the following terms will first be defined.

[0025] The term "alkyl" refers to both straight- and branched-chain alkyl groups.

[0026] The term "aryl" refers to a substituted or unsubstituted aromatic group, such as the phenyl, tolyl, xylyl, ethylphenyl and cumenyl groups.

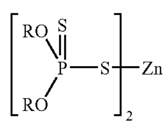
[0027] The term "low phosphorus" refers to the phosphorus content of the lubricating oil composition of the present invention. The phosphorus content is in the range of about 0.005 weight percent to about 0.06 weight percent based on the total weight of the lubricating oil composition.

[0028] The term "total phosphorus" refers to the total amount of phosphorus in the lubricant composition regardless of whether such phosphorus is present as part of an oil-soluble, phosphorus-containing, anti-wear compound or in the form of a contaminant in the lubricant composition such as residual phosphorus remaining due to the presence of P_2S_5 used to prepare metal dihydrocarbyl dithiophosphates. In either event, the amount of phosphorus permitted in the lubricant composition is independent of source. Preferably, however, the phosphorus is part of a lubricant additive.

[0029] Unless otherwise specified, all percentages are in weight percent.

The Zinc Dithiophosphate Compound

[0030] The lubricating oil composition of the present invention will employ, in part, a mixture of zinc dithiophosphates. The zinc dithiophosphates are independently characterized by formula I:



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wherein each R is independently a group containing from about 1 to about 30 carbon atoms.

[0031] The R groups in the dithiophosphate can independently be about C_1 to about C_{13} primary alkyl, about C_3 to about C_{13} secondary alkyl, and about C_6 to about C_{30} aryl group. Preferably, the R groups in the dithiophosphate can independently be about C_3 to about C_{10} primary alkyl, about C_3 to about C_8 secondary alkyl, and about C_6 to about C_{24} aryl group. More preferably, the R groups in the dithiophosphate can independently be about C_6 to about C_8 primary alkyl, about C_3 to about C_6 secondary alkyl, and about C_6 to about C_{20} aryl group. The R groups may be a substantially hydrocarbon group. By "substantially hydrocarbon" is meant hydrocarbons that contain substituent groups such as ether, ester, nitro, or halogen which do not materially affect the hydrocarbon character of the group.

[0032] The R group of the zinc dithiophosphate may be derived, for example, from a primary alcohol such as methanol, ethanol, propanol, butanol, pentanol, hexanol, heptanol, octanol, nonanol, decanol, dodecanol, octadecanol, propenol, butenol, 2-ethylhexanol: a secondary alcohol such as isopropyl alcohol, secondary butyl alcohol, isobutanol, 3-methylbutan-2-ol, 2-pentanol, 4-methyl-2-pentanol, 2-hexanol, 3-hexanol, amyl alcohol, an aryl alcohol such as phenol, substituted phenol (particularly alkylphenol such as butylphenol, octylphenol, nonylphenol, dodecylphenol), disubstituted phenol.

[0033] Preferably the R group will be independently a primary alkyl, a secondary alkyl or an aryl group.

[0034] For the present invention it is contemplated that the mixture of a zinc primary dialkyl dithiophosphate, a zinc secondary dialkyl dithiophosphate and a zinc diaryl dithiophosphate will be in a respective ratio, based on the phosphorus content, in the lubricating oil composition of the present invention. The ratio of zinc primary dialkyl dithiophosphate to zinc secondary dialkyl dithiophosphate will be from about 2:1 to about 1:2 and the ratio of the mixture of zinc primary dialkyl dithiophosphate and zinc secondary dialkyl dithiophosphate to zinc diaryl dithiophosphate is from about 6:1 to about 1:1. Preferably, the respective ratio, based on the phosphorus content, of zinc primary dialkyl dithiophosphate to zinc secondary dialkyl dithiophosphate is a range from about 3:2 to about 2:3, more preferably about 1:1. Preferably, the respective ratio, based on the phosphorus content, of the mixture of zinc primary dialkyl dithiophosphate and zinc secondary dialkyl dithiophosphate to zinc diaryl dithiophosphate is a range from about 4:1 to about 1:1, more preferably about 2:1. Most preferably, the respective ratio, based on the phosphorus content, of the mixture of zinc primary dialkyl dithiophosphate to zinc secondary dialkyl dithiophosphate to zinc diaryl dithiophosphate is 1:1:1.

[0035] Many of the zinc dithiophosphates useful in the present invention are available commercially. However, zinc dithiophosphates are widely known in the art and a skilled artisan can readily synthesize such compounds for the purposes of the present invention. Typically, zinc dithiophosphates can be made by initial reaction of phosphorous pentasulfide and an alcohol or phenol or mixtures of alcohols and/or phenols such as those illustrated above for the R group. The reaction involves four moles of the alcohol or phenol per mole of phosphorous pentasulfide, and may be carried out within the temperature range from about 50° C. to about 200° C. Thus, the preparation of O,O-di-n-hexyl phosphorodithioic acid, for example, involves the reaction of phosphorous pentasulfide with four moles of n-hexyl alcohol at about 100° C. for about two hours. Hydrogen sulfide is liberated and the residue is phosphorodithioic acid. The preparation of the metal salt of this acid may be affected by reaction with either zinc oxide or zinc hydroxide to yield the zinc dithiophosphate. Simply mixing and heating these two reactants is sufficient to cause the reaction to take place and the resulting product is sufficiently pure for the purposes of the present invention.

[0036] Patents describing the synthesis of such zinc dithiophosphates include U.S. Pat. Nos. 2,680,123; 3,000,822; 3,151,075; 3,385,791; 4,377,527; 4,495,075 and 4,778,906. Each of these patents is incorporated herein by reference in their entirety.

The Lubricating Oil Composition

[0037] The mixture of zinc dithiophosphates of the present invention is typically added to a base oil in sufficient amounts to provide lead corrosion control in internal combustion engines. Generally, the lubricating oil composition of the present invention will contain a major amount of base oil of lubricating viscosity and a minor amount of the mixture of zinc dithiophosphates of the present invention.

Base Oil of Lubricating Viscosity

[0038] Base oil as used herein is defined as a base stock or blend of base stocks which is a lubricant component that is produced by each manufacturer to the same specifications (independent of feed source or manufacturer's location); that meets the same manufacturer's specification; and that is identified by a unique formula, product identification number, or both. Base stocks may be manufactured using a variety of different processes including but not limited to distillation, solvent refining, hydrogen processing, oligomerization, esterification, and rerefining.

[0039] Refined stock shall be substantially free from materials introduced through manufacturing, contamination, or previous use. The base oil of this invention may be any natural or synthetic lubricating base oil fraction particularly those having a kinematic viscosity at 100° Centigrade (° C.) and about 4 centistokes (cSt) to about 20 cSt. Hydrocarbon synthetic oils may include, for example, oils prepared from the polymerization of ethylene, polyalphaolefin or PAO, or from hydrocarbon synthesis procedures using carbon monoxide and hydrogen gases such as in a Fisher-Tropsch process. A preferred base oil is one that comprised little, if any, heavy fraction; e.g., little, if any, tube oil fraction of viscosity about 20 cSt or higher at about 100° C. Oils used as the base oil will be selected or blended depending on the desired end use and the additives in the finished oil to give the desired of engine oil, e.g. a lubricating oil composition having an SAE Viscosity Grade of 0W, 0W-20, 0W-30, 0W-40, 0W-50, 0W-60, 5W, 5W-20, 5W-30, 5W-40, 5W-50, 5W-60, 10W, 10W-20, 10W-20, 10W-30, 10W-40, 10W-50, 15W, 15W-20, 15W-30, 15W-40.

[0040] The base oil may be derived from natural lubricating oils, synthetic lubricating oils or mixtures thereof. Suitable base oil includes base stocks obtained by isomerization of synthetic wax and slack wax, as well as hydrocrackate base stocks produced by hydrocracking (rather than solvent extracting) the aromatic and polar components of the crude. Suitable base oils include those in all API categories, I, II, III, IV and V as defined in API Publication 1509, 14th Edition, Addendum I, December 1998. Saturates levels and viscosity indices for Group I, II and III base oils are listed in Table I. Group IV base oils are polyalphaolefins (PAO). Group V base oils include all other base oils not included in Group I, II, III, or IV. Group III base oils are preferred.

TABLE I

SATURATES, SULFUR AND VISCOSITY INDEX OF GROUP I, II, III, IV AND V BASE STOCKS

Group	Saturates (As determined by ASTM D2007) Sulfur (As determined by ASTM D2270)	Viscosity Index (As determined by ASTM D4294, ASTM D4297 or ASTM D3120)
I	Less than 90% saturates and/or Greater than to 0.03% sulfur	Greater than or equal to 80 and less than 120
II	Greater than or equal to 90% saturates and less than or equal to 0.03% sulfur	Greater than or equal to 80 and less than 120
III	Greater than or equal to 90% saturates and less than or equal to 0.03% sulfur	Greater than or equal to 120
IV	All Polyalphaolefins (PAOs)	
V	All others not included in Groups I, II, III, or IV	

[0041] Natural lubricating oils may include animal oils, vegetable oils (e.g., rapeseed oils, castor oils and lard oil), petroleum oils, mineral oils, and oils derived from coal or shale.

[0042] Synthetic oils may include hydrocarbon oils and halo-substituted hydrocarbon oils such as polymerized and inter-polymerized olefins, alkylbenzenes, polyphenyls, alkylated diphenyl ethers, alkylated diphenyl sulfides, as well as their derivatives, analogues and homologues thereof, interpolymers, copolymers and derivatives thereof wherein the terminal hydroxyl groups have been modified by esterification, etherification, etc. Another suitable class of synthetic lubricating oils comprises the esters of dicarboxylic acids with a variety of alcohols. Esters useful as synthetic oils also include those made from about C_5 to about C_{12} monocarboxylic acids and polyols and polyol ethers. Tri-alkyl phosphate ester oils such as those exemplified by tri-n-butyl phosphate and tri-iso-butyl phosphate are also suitable for use as base oils.

[0043] Silicon-based oils (such as the polyalkyl-, polyaryl-, polyalkoxy-, or polyaryloxy-siloxane oils and silicate oils) comprise another useful class of synthetic lubricating oils. Other synthetic lubricating oils include esters of phosphorus-containing acids, polymeric tetrahydrofurans, polyalphaolefins, and the like.

[0044] The base oil may be derived from unrefined, refined, rerefined oils, or mixtures thereof. Unrefined oils are obtained directly from a natural source or synthetic source (e.g., coal, shale, or tar sand bitumen) without further purification or treatment. Examples of unrefined oils include a shale oil obtained directly from a retorting operation, a petroleum oil obtained directly from distillation, or an ester oil obtained directly from an esterification process, each of which may then be used without further treatment. Refined oils are similar to the unrefined oils except that refined oils have been treated in one or more purification steps to improve one or more properties. Suitable purification techniques include distillation, hydrocracking, hydrotreating, dewaxing, solvent extraction, acid or base extraction, filtration, and percolation, all of which are known to those skilled in the art. Rerefined oils are obtained by treating used oils in processes similar to those used to obtain the refined oils. These rerefined oils are also known as reclaimed or reprocessed oils and often are additionally processed by techniques for removal of spent additives and oil breakdown products.

[0045] 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.

[0046] Such wax isomerate oil is produced by the hydroisomerization of natural or synthetic waxes or mixtures thereof over a hydroisomerization catalyst.

[0047] It is preferred to use a major amount of base oil in the lubricating oil composition of the present invention. A major amount of base oil as defined herein comprises about 40 wt % or more. Preferred amounts of base oil comprise about 40 wt % to about 97 wt %, preferably greater than about 50 wt % to about 97 wt %, more preferably about 60 wt % to about 97 wt % and most preferably about 80 wt % to about 95 wt % of the lubricating oil composition. (When weight percent is used herein, it is referring to weight percent of the lubricating oil unless otherwise specified.

[0048] The amount of the mixture of zinc dithiophosphates employed in the lubricating oil composition of the present invention will be in a minor amount compared to the base oil of lubricating viscosity. Generally, it will be in an amount from about 0.1 wt % to about 1.5 wt %, preferably from about 0.3 wt % to about 1.2 wt % and more preferably from about 0.5 wt % to about 1.0 wt %, based on the total weight of the lubricating oil composition.

[0049] The lubricating oil composition of the present invention will contain from about 0.05 wt % to about 1.2 wt %, preferably from about 0.1 wt % to about 0.7 wt %, and more preferably from about 0.2 wt % to about 0.5 wt % of a zinc primary dialkyl dithiophosphate, based on the total weight of the lubricating oil composition.

[0050] The lubricating oil composition of the present invention will contain from about 0.05 wt % to about 1.2 wt %, preferably from about 0.1 wt % to about 0.7 wt %, and more preferably from about 0.2 wt % to about 0.5 wt % of a zinc secondary dialkyl dithiophosphate, based on the total weight of the lubricating oil composition.

[0051] The lubricating oil composition of the present invention will contain from about 0.02 wt % to about 0.7 wt %, preferably from about 0.05 wt % to about 0.5 wt %, and more preferably from about 0.1 wt % to about 0.3 wt % of a zinc primary diaryl dithiophosphate, based on the total weight of the lubricating oil composition.

[0052] In a preferred embodiment, the lubricating oil composition of the present invention will have a phosphorus content preferably less than about 0.05 wt %, based on the total weight of the lubricating oil composition.

[0053] In another embodiment, the lubricating oil composition of the present invention will further have a sulfur content less than about 0.5 wt % and, preferably less than about 0.2 wt %, based on the total weight of the lubricating oil composition and the total sulfated ash content in the lubricating oil composition of the present invention is less than about 1.2 wt %, preferably, less than about 1.0 wt %, and more preferably less than about 0.8 wt %, based on the total weight of the lubricating oil composition.

Other Additive Components

[0054] The following additive components are examples of components that can be favorably employed in combination with the lubricating additive of the present invention. These examples of additives are provided to illustrate the present invention, but they are not intended to limit it.

[0055] (A) Detergents are additives designed to hold the acid-neutralizing compounds in solution in the oil. They are usually alkaline and react with the strong acids (sulfuric and nitric) which form during the combustion of the fuel and which would cause corrosion to the engine parts if left unchecked. Examples are carboxylates, sulfurized or unsulfurized alkyl or alkenyl phenates, alkyl or alkenyl aromatic sulfonates, sulfurized or unsulfurized metal salts of multi-hydroxy alkyl or alkenyl aromatic compounds, alkyl or alkenyl hydroxy aromatic sulfonates, sulfurized or unsulfurized alkyl or alkenyl naphthenates, metal salts of alkanoic acids, metal salts of an alkyl or alkenyl multiacids and chemical and physical mixtures thereof.

[0056] (B) Dispersants are additives that keep soot and combustion products in suspension in the body of the oil and therefore prevent deposition as sludge or lacquer. Typically, the ashless dispersants are nitrogen-containing dispersants formed by reacting alkenyl succinic acid anhydride with an amine. Examples are alkenyl succinimides, alkenyl succinimides modified with other organic compounds, e.g., ethylene carbonating post-treatment and alkenyl succinimides modified with boric acid, polysuccinimides, alkenyl succinic ester.

[0057] (C) Oxidation Inhibitors:

[0058] 1) Phenol type (phenolic) oxidation inhibitors: 4,4'-methylenebis (2,6-di-tert-butylphenol), 4,4'-bis(2,6-di-tert-butylphenol), 4,4'-bis(2-methyl-6-tert-butylphenol), 2,2'-methylenebis(4-methyl-6tert-butyl-phenol, 4,4'-butyldienebis(3-methyl-6-tert-butylphenol), 4,4'-isopropylidenebis(2,6-di-tert-butylphenol), 2,2'-methylenebis(4-methyl-6-nonylphenol), 2,2'isobutyldiene-bis(4,6-dimethylphenol), 2,2'-methylenebis(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-α-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-4hydroxy-5-tert-butylbenzyl)-sulfide and bis (3,5-di-tert-butyl-4-hydroxybenzyl).

[0059] 2) Diphenylamine type oxidation inhibitor: alkylated diphenylamine, phenyl-α-naphthylamine and alkylated α-naphthylamine.

[0060] 3) Other types: metal dithiocarbamate (e.g., zinc dithiocarbamate) and methylenebis(dibutyldithiocarbamate).

[0061] (D) Rust inhibitors (Anti-rust agents)

[0062] 1) Nonionic polyoxyethylene surface active agents: 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.

[0063] 2) Other compounds: stearic acid and other fatty acids, dicarboxylic acids, metal soaps, fatty acid amine salts, metal salts of heavy sulfonic acid, partial carboxylic acid ester of polyhydric alcohol and phosphoric ester.

[0064] (E) Demulsifiers: addition product of alkylphenol and ethyleneoxide, polyoxyethylene alkyl ether and polyoxyethylene sorbitane ester.

[0065] (F) extreme pressure agents (EP agents): sulfurized oils, diphenyl sulfide, methyl trichlorostearate, chlorinated naphthalene, benzyl iodide, fluoroalkylpolysiloxane and lead naphthenate.

[0066] (G) Friction modifiers: fatty alcohol, fatty acid, amine, borated ester and other esters.

[0067] (H) Multifunctional additives: sulfurized oxymolybdenum dithiocarbamate, sulfurized oxymolybdenum organo phosphorodithioate, oxymolybdenum monoglyceride, oxymolybdenum diethylate amide, amine-molybdenum complex compound and sulfur-containing molybdenum complex compound.

[0068] (I) Viscosity Index Improvers (VII): polymethacrylate type polymers, ethylene-propylene copolymers, styrene-isoprene copolymers, hydrogenated styrene-isoprene copolymers, hydrogenated star-branched polyisoprene, polyisobutylene, hydrogenated star-branched styrene-isoprene copolymer and dispersant type viscosity index improvers.

[0069] (J) Pour point depressants: polymethyl methacrylates, alkylmethacrylates and dialkyl fumarate-vinyl acetate copolymers.

[0070] (K) Foam Inhibitors: alkyl methacrylate polymers and dimethyl silicone polymers.

EXAMPLES

[0071] The present invention will be further illustrated by the following examples, which set forth particularly advantageous method embodiments. While the Examples are provided to illustrate the present invention, they are not intended to limit it.

Example 1

[0072] The low phosphorus lubricating oil composition of the present invention was prepared by blending a 0.78 wt % mixture of zinc bis(O,O'-di-(2-ethyl-1-hexyl) dithiophosphate (0.24 wt %, primary), zinc bis(O,O'-di-(2-butyl/4-methyl-2-pentyl) dithiophosphate (0.15 wt %, secondary) and zinc bis(O,O'-di-(dodecylphenyl) dithiophosphate (0.39 wt %, aryl) with a Group II base oil of lubricating viscosity. The ratio of zinc bis(O,O'-di-(2-ethyl-1-hexyl) dithiophosphate to zinc bis(O,O'-di-(2-butyl/4-methyl-2-pentyl) dithiophosphate was about 1:1, based on the phosphorus content. The ratio of the mixture of zinc bis(O,O'-di-(2-ethyl-1-hexyl) dithiophosphate and zinc bis(O,O'-di-(2-butyl/4-methyl-2-pentyl)dithiophosphate to zinc bis(O,O'-di-(dodecylphenyl) dithiophosphate was about 2:1, based on the phosphorus content. The resulting ratio of the three-way mixture of zinc bis(O,O'-di-(2-ethyl-1-hexyl) dithiophosphate to zinc bis(O,O'-di-(2-butyl/4-methyl-2phenyl) dithiophosphate to zinc bis(O,O'-di-(dodecylphenyl) dithiophosphate was 1:1:1, based on the phosphorus content. The wt % of phosphorus in the prepared lubricating oil composition was less than about 0.06 wt % based on the total weight of the lubricating oil composition. Further, the sulfur content and sulfated ash content 0.2 wt % and 0.8 wt % balance of the lubricating oil composition containing a 1200 molecular weight (MW) isobutylene bis-succinimide dispersant, a 2300 MW isobutylene bis-succinimide dispersant, a neutral sulfonate detergent, an overbased calcium phenate, a molybdenum oxidation inhibitor, diphenylamine oxidation inhibitor, a phenolic oxidation inhibitor, anti-foam agent, pour point depressant and a viscosity index improver to complete the 100 wt % lubricating oil composition.

Comparative Example A

[0073] Comparative Example A was prepared according to Example 1 except only about 1.16 wt % aryl zinc bis(O,O'-di-(dodecylphenyl) dithiophosphate was added, instead of the mixture of zinc bis(O,O'-di-(2-ethyl-1-hexyl) dithiophosphate, zinc bis(O,O'-di-(2-butyl/4-methyl-2pentyl) dithiophosphate and zinc bis(O,O'-di-(dodecylphenyl) dithiophosphate.

Comparative Example B

[0074] Comparative Example B was prepared according to Example 1 except only about 0.46 wt % zinc bis(O,O'-di-(2-butyl/4-methyl-2-pentyl) dithiophosphate was added, instead of the mixture of zinc bis(O,O'-di-(2-ethyl-1-hexyl) dithiophosphate, zinc bis(O,O'-di-(2-butyl/4-methyl-2-pentyl) dithiophosphate and zinc bis(O,O'-di-(dodecylphenyl) dithiophosphate.

Comparative Example C

[0075] Comparative Example C was prepared according to Example 1 except only about 0.71 wt % zinc bis(O,O'-di-(2-ethyl-1-hexyl) dithiophosphate, zinc bis(O,O'-di-(2-butyl/4-methyl-2-pentyl) dithiophosphate and zinc bis(O,O'-di-(dodecylphenyl) dithiophosphate.

Comparative Example D

[0076] Comparative Example D was prepared according Example 1 except about 0.81 wt % of a mixture of zinc bis (O,O'-di-(2-butyl/4-methyl-2-pentyl) dithiophosphate and zinc bis (O,O'-di-(dodecylphenyl) dithiophosphate in about a 1:1 ratio were added, instead of the mixture of zinc bis(O,O'-di-(2-ethyl1-hexyl) dithiophosphate, zinc bis(O,O'-di-(2-butyl/4-methyl-2pentyl) dithiophosphate and zinc bis (O,O'-di-(dodecylphenyl) dithiophosphate.

Comparative Example E

[0077] Comparative Example E was prepared according to Example 1 except about 0.94 wt % of a mixture of zinc bis(O,O'-di-(2-ethyl-1-hexyl) dithiophosphate and zinc bis (O,O'-di-(dodecylphenyl) dithiophosphate in about a 1:1 ratio were added, instead of the mixture of zinc bis(O,O'-di-(2-ethyl-1-hexyl) dithiophosphate, zinc bis(O,O'-di-(2-butyl/4-methyl-2-pentyl) dithiophosphate and zinc bis(O,O'-di-(dodecylphenyl) dithiophosphate.

Comparative Example F

[0078] Comparative Example F was prepared according to Example 1 except about 0.59 wt % of a mixture of zinc bis(O,O'-di-(2-ethyl-1-hexyl) dithiophosphate and zinc bis (O,O'-di-(2-butyl/4-methyl-2-pentyl) dithiophosphate in about a 1:1 ratio were added, instead of the mixture of zinc bis(O,O'-di-(2-ethyl-1-hexyl) dithiophosphate, zinc bis(O, O'-di-(2-butyl/4-methyl-2pentyl) dithiophosphate and zinc bis(O,O'-di-(dodecylphenyl) dithiophosphate.

[0079] Each formulation according to Example 1 and Comparative Example A-F were tested for lead corrosion using the High Temperature Corrosion Bench Test (HTCBT) (ASTM D6594) which is an industry standard bench test to measure corrosion performance of a motor oil. Briefly, four metal specimens of copper, lead, tin, and phosphor bronze are immersed in a measured amount of engine oil. The oil, at an elevated temperature, is blown with air for a period of time. When the test is completed, the lead specimen and the stressed oil are examined to detect corrosion and corrosion products, respectively. A reference oil is tested with each group of tests to verify test acceptability.

[0080] The test results are summarized in Table II.

TABLE II

HTCBT Results

		Comparative Examples					
	Example 1	A	B	C	D	E	F
Lead, ppm	48.4	113.4	93.4	305	64.6	87.3	99.4

[0081] These results demonstrate that the low phosphorus lubricating oil composition of the present invention (Example 1) containing a mixture of zinc primary dialkyl dithiophosphate, zinc secondary dialkyl dithiophosphate and zinc diaryl dithiophosphate in a 1:1:1 ratio, and wherein the phosphorus content of the lubricating oil composition is less than 0.06 wt %, provides excellent lead corrosion performance when compared to the comparative examples not having a mixture of all three dithiophosphates. The amount of lead corrosion is significantly reduced by the lubricating oil composition of the present invention.

What is claimed is:

1. A lubricating oil composition comprising a major amount of base oil of lubricating viscosity and a minor amount of a mixture of a zinc primary dialkyl dithiophosphate, a zinc secondary dialkyl dithiophosphate and a zinc diaryl dithiophosphate wherein the respective ratio, based on the phosphorus content, of the zinc primary dialkyl dithiophosphate to zinc secondary dialkyl dithiophosphate is from about 2:1 to about 1:2 and the ratio of the mixture of zinc primary dialkyl dithiophosphate and zinc secondary dialkyl dithiophosphate to zinc diaryl dithiophosphate is from about 6:1 to about 1:1 and wherein the lubricating oil composition has less than about 0.06 wt % total phosphorus content, based on the total weight of the lubricating oil composition.

2. The lubricating oil composition according to claim **1**, wherein the minor amount of the mixture of zinc primary dialkyl dithiophosphate, zinc secondary dialkyl dithiophosphate and zinc diaryl dithiophosphate is from about 0.1 wt % to about 1.5 wt %, based on the total weight of the lubricating oil compression.

3. The lubricating oil composition according to claim **1**, wherein the minor amount of them mixture of zinc primary dialkyl dithiophosphate, zinc secondary dialkyl dithiophosphate and zinc diaryl dithiophosphate is from about 0.3 wt % to about 1.2 wt %, based on the total weight of the lubricating oil composition.

4. The lubricating oil composition according to claim **1**, wherein the minor amount of the mixture of zinc primary dialkyl dithiophosphate, zinc secondary dialkyl dithiophosphate and zinc diaryl dithiophosphate is from about 0.5 wt % to about 1.0 wt %, based on the total weight of the lubricating oil composition.

5. The lubricating oil composition according to claim **1**, wherein the mixture contains from about 0.05 wt % to about 1.2 wt % zinc primary dialkyl dithiophosphate, from about 0.05 wt % to about 1.2 wt % zinc secondary dialkyl dithiophosphate and from about 0.02 wt % to about 0.7 wt % zinc diaryl dithiophosphate, based on the total weight of the lubricating oil composition.

6. The lubricating oil composition according to claim **5**, wherein the mixture contains from about 0.1 wt % to about 0.7 wt % zinc primary dialkyl dithiophosphate, from about 0.1 wt % to about 0.7 wt % zinc secondary dialkyl dithiophosphate and from about 0.05 wt % to about 0.5 wt % zinc diaryl dithiophosphate, based on the total weight of the lubricating oil composition.

7. The lubricating oil composition according to claim **6**, wherein the mixture contains from about 0.2 wt % to about 0.5 wt % zinc primary dialkyl dithiophosphate, from 0.2 wt % to about 0.5 wt % zinc secondary dialkyl dithiophosphate and from about 0.1 wt % to about 0.3 wt % zinc diaryl dithiophosphate, based on the total weight of the lubricating oil composition.

8. The lubricating oil composition according to claim **1**, wherein the primary alkyl group of the zinc primary dialkyl dithiophosphate has from about C_1 to about C_{13} carbon atoms.

9. The lubricating oil composition according to claim **8**, wherein the primary alkyl group of the zinc primary dialkyl dithiophosphate has from about C_3 to about C_{10} carbon atoms.

10. The lubricating oil composition according to claim **9**, wherein the primary alkyl group of the zinc primary dialkyl dithiophosphate has from about C_6 to about C_8 carbon atoms.

11. The lubricating oil composition according to claim **1**, wherein the secondary alkyl group of the zinc secondary dialkyl dithiophosphate has from about C_3 to about C_{13} carbon atoms.

12. The lubricating oil composition according to claim **11**, wherein the secondary alkyl group of the zinc secondary dialkyl dithiophosphate has from about C_3 to about C_8 carbon atoms.

13. The lubricating oil composition according to claim **12**, wherein the secondary alkyl group of the zinc secondary dialkyl dithiophosphate has from about C_3 to about C_6 carbon atoms.

14. The lubricating oil composition according to claim **1**, wherein the aryl group of the zinc diaryl dithiophosphate has from about C_6 to about C_{30} carbon atoms.

15. The lubricating oil composition according to claim **14**, wherein the aryl group of the zinc diaryl dithiophosphate has from about C_8 to about C_{24} carbon atoms.

16. The lubricating oil composition according to claim **15**, wherein the aryl group of the zinc diaryl dithiophosphate has from about C_6 to about C_{20} carbon atoms.

17. The lubricating oil composition according to claim **1**, wherein the respective ratio of zinc primary dithiophosphate to zinc secondary dialkyl dithiophosphate is a range from about 3:2 to about 2:3, based on the phosphorus content.

18. The lubricating oil composition according to claim **17**, wherein the secondary dialkyl dithiophosphate is about 1:1, based on the phosphorus content.

19. The lubricating oil composition according to claim **1**, wherein the respective ratio of the mixture of zinc primary dialkyl dithiophosphate and zinc secondary dialkyl dithiophosphate to zinc diaryl dithiophosphate is a range from about 4:1 to about 1:1, based on the phosphorus content.

20. The lubricating oil composition according to claim **19**, wherein the respective ratio of the mixture of zinc primary dialkyl dithiophosphate and zinc secondary dialkyl dithiophosphate to zinc diaryl dithiophosphate is a about 2:1 based on the phosphorus content.

21. The lubricating oil composition according to claim **1**, wherein the respective ratio of the mixture of zinc primary dialkyl dithiophosphate zinc secondary dialkyl dithiophosphate to zinc diaryl dithiophosphate is 1:1:1, based on the phosphorus content.

22. The lubricating oil composition according to claim **1**, wherein the total phosphorus content of the lubricating oil composition in less than 0.05 wt %, based on the total weight of the lubricating oil composition.

23. The lubricating oil composition according to claim **1**, wherein the total sulfur content of the lubricating oil composition in less than 0.5 wt %, based on the total weight of the lubricating oil composition.

24. The lubricating oil composition according to claim **23**, wherein the total sulfur content of the lubricating oil composition in less than 0.2 wt %, based on the total weight of the lubricating oil composition.

25. The lubricating oil composition according to claim **1**, wherein the total sulfated ash content of the lubricating oil composition in less than 1:2 wt %, based on the total weight of the lubricating oil composition.

26. The lubricating oil composition according to claim **25**, wherein the total sulfated ash content of the lubricating oil composition in less than 1.0 wt %, based on the total weight of the lubricating oil composition.

27. The lubricating oil composition according to claim **26**, wherein the total sulfated ash content of the lubricating oil composition in less than 0.8 wt %, based on the total weight of the lubricating oil composition.

28. A method for improving lead corrosion, said method comprising operating an internal combustion engine with a lubricating oil composition comprising a major amount of base oil of lubricating viscosity and a minor amount of a mixture of zinc primary dialkyl dithiophosphate, zinc secondary dialkyl dithiophosphate and zinc diaryl dithiophosphate wherein the respective ratio, based on the phosphorus content, of the zinc primary dialkyl dithiophosphate to zinc secondary dialkyl dithiophosphate is from about 2:1 to about 1:2 and the ratio of the mixture of zinc primary dialkyl dithiophosphate and zinc secondary dialkyl dithiophosphate to zinc diaryl dithiophosphate is from about 6:1 to about 1:1 and wherein the lubricating oil composition has less than about 0.06 wt % total phosphorus content, based on the total weight of the lubricating oil composition.

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