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(54) **LOW SAP ENGINE LUBRICANT CONTAINING SILANE AND ZINC DITHIOPHOSPHATE LUBRICANT ADDITIVE AND COMPOSITION**

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(57) **ABSTRACT**

The present invention is directed to a lubricating oil composition comprising a lubricating oil basestock, an organic silane containing additive of at least 0.1 and less than 2.0 weight percent of the composition, a dispersant-detergent-inhibitor system of less than 15 weight percent of the composition, an organic boron additive of at least 0.1 and less than 8.0 weight percent of the composition, a zinc dithiophosphate additive of at least 0.1 weight percent of the composition and less than 1.6 weight percent of the composition and the composition having at least 80 PPM and less than 1600 RPM silicon, at least 100 PPM and less than 630 PPM phosphorus, at least 105 PPM and less than 710 PPM zinc, at least 1,000 PPM and less than 4,000 PPM sulfur, at least 800 PPM, less than 10,000 PPM ash and less than 450 PPM boron. In a second embodiment, an additive composition for lubricating oils is disclosed. In a third embodiment, a method of obtain a favorable lubricating properties is disclosed.

LOW SAP ENGINE LUBRICANT CONTAINING SILANE AND ZINC DITHIOPHOSPHATE LUBRICANT ADDITIVE AND COMPOSITION

CROSS-REFERENCE TO RELATED APPLICATION:

[0001] This application claims benefit of Provisional Application 60/791,805 filed Apr. 13, 2006.

[0002] This application claims benefit of Provisional Application 60/791,805 filed Apr. 13, 2006.

BACKGROUND OF THE INVENTION

[0003] 1. Field of the Invention

[0004] This invention relates to lubricating oil compositions suitable for use in internal combustion engines. More particularly, this invention relates to a low sulfur, ash and phosphorous lubricating oil composition containing is additives.

[0005] 2. Background

[0006] Many means have been employed to reduce overall wear and friction as well as to control oxidation/cleanliness in modern engines, particularly automobile engines. The primary methods include prolonging engine life by reducing engine wear and increasing the resistance to oxidation by reducing the engine's sludge/deposit build-up through degradation. Some of the solutions to reducing wear have been primarily mechanical including building engines with wear resistant alloy or ceramic parts, modifying the contact geometry and adding special coating materials. Other solutions to improve cleanliness also involve modifications to the oil, including the use of metal containing detergents. Recently, considerable work has also been done with lubricating oils to enhance their anti-wear/anti-oxidation properties by modifying them with ashless antioxidants and anti-wear components.

[0007] Contemporary lubricants such as engine oils use mixtures of additive components to achieve numerous performance benefits. Examples of additives components include, anti-wear and extreme pressure components, fuel economy improving components, friction reducers, dispersants, detergents, corrosion inhibitors and viscosity index improving additive.

[0008] These additives provide energy conservation, engine cleanliness and durability and high performance levels to the lubricating oil under a wide range of engine operating conditions including temperature, pressure and lubricant service life.

[0009] Throughout the world, legislation aimed at reducing automotive emissions is forcing down the level of sulfur in fuels. Recently, lubricants are coming under scrutiny as a source of air pollution and emission catalyst deactivation. Phosphorus is known to be poisonous to automotive three-way HC conversion catalysts.

[0010] Conventional engine oil technology relies heavily on zinc (dialkyl) dithiophosphate ("ZnDTP" or "ZDDP"). ZnDTP is a versatile, anti-wear/anti-oxidant component that provides extremely low cam and lifter wear and favorable oxidation protection under severe conditions. ZnDTPs are disadvantageous, especially at high treat rates because they contain the three disfavorable elements of Zn, S, P and no reduction in phosphorus and zinc levels can be realized until new additive technology permits replacing or eliminating zinc dithiophosphates. Sulfur is known to be poisonous to deNox catalysts and zinc phosphates cause plugging of the exhaust particulate filters. The sulfur, ash and phosphorous components in oil are commonly referred to as "SAP" or "SAPS" in the art.

[0011] The major problem with ZnDTP is the poisoning effects to after-treatment devices that may aggravate emission problems. In addition, ZnDTP has strong interactions with dispersants, detergents, other anti-wear components and moly dithiocarbamates causing antagonistic effects on friction, sludge and deposit, if inappropriate concentrations are utilized. Replacing ZnDTP additives is not a simple endeavor because the wear protection demand for today's engine is extremely high and extremely rigorous chemical limits on any reductions in ZnDTP treat levels.

[0012] Engine lubricating oils are often used in high temperature applications, where extreme temperatures can significantly reduce the useful life of the lubricant. Under high temperatures, the lubricant can become oxidized prematurely unless a strong antioxidant system can also be employed in the oil to prevent this degradation process. Good piston, ring, cam and lifter wear protection are also an important characteristic of today's engine oil. Additionally, many engine oils are often required to perform well in the presence of water, therefore, protecting against rust formation. Traditionally, ZnDTPs are used to provide adequate protection as described above. Engine designers are now requiring even greater anti-wear protection and more demanding test protocols are being put in place to insure that lubricants can meet these more stringent specifications. However, stringent regulations in emission control have forced lubricant formulators to move away from ZnDTPs for the reasons discussed above.

[0013] Accordingly, there is a need for an additive or additive system for engine oils that has the ability to improve both rust and wear protection, and at the same time significantly enhance oxidative stability, while meeting stringent emission requirements. This invention satisfies that need.

SUMMARY OF THE INVENTION

[0014] In a first embodiment, a lubricating oil composition is disclosed. This composition, comprises a lubricating oil basestock, an organic silane containing additive present in the amount of at least 0.1 and less than 2.0 weight percent of the composition, a dispersant-detergent-inhibitor system of less than 15 weight percent of the composition, an organic boron additive present in the amount of at least 0.1 and less than 8.0 weight percent of the composition, a zinc dithiophosphate additive present in the amount of at least 0.1 weight percent of the composition and less than 1.6 weight percent of the composition. The final formulation of the composition has at least 80 PPM and less than 1600 PPM silicon, at least 100 PPM and less than 630 PPM phosphorus, at least 10 5 PPM and less than 710 PPM zinc, at least 1,000 PPM and less than 4,000 PPM sulfur, at least 800 PPM, less than 10,000 PPM ash and at least 80 PPM and less than 450 PPM Boron.

[0015] In a second embodiment, an additive composition for lubricating oils is disclosed. This composition comprises an organic silane containing additive present in the amount of at least 0.4 and less than 8.0 weight percent of the additive a dispersant-detergent-inhibitor system of less than 60 weight percent of the additive, an organic boron additive present in the amount of at least 0.4 and less than 32.0

weight percent of the additive, a zinc dithiophosphate additive present in the amount of at least 0.4 weight percent of the additive and less than 6.4 weight percent of the additive. The final formulation of the composition has at least 80 PPM and less than 1600 PPM silicon, at least 100 PPM and less than 630 PPM phosphorus, at least 105 PPM and less than 710 PPM zinc, at least 1,000 PPM and less than 4,000 PPM sulfur, at least 800 PPM, less than 10,000 PPM ash and less than 450 PPM Boron.

[0016] In a third embodiment, a method of obtain a favorable lubricating properties is disclosed. This method, comprises obtaining a composition comprising a lubricating oil basestock, an organic silane containing additive present in the amount of at least 0.1 and less than 2.0 weight percent of the composition, a dispersant-detergent-inhibitor system of less than 15 weight percent of the composition, an organic boron additive present in the amount of at least 0.1 and less than 8.0 weight percent of the composition, a zinc dithiophosphate additive present in the amount of at least 0.1 weight percent of the composition and less than 1.6 weight percent of the composition. The final formulation of the composition has at least 80 PPM and less than 1600 PPM silicon, at least 100 PPM and less than 630 PPM phosphorus, at least 105 PPM and less than 710 PPM zinc, at least 10,000 PPM and less than 4,000 PPM sulfur, at least 800 PPM, less than 1,000 PPM ash and less than 450 PPM Boron and lubricating an engine with the composition.

DETAILED DESCRIPTION OF THE INVENTION

[0017] This invention relates to engine lubricants formulated with unique functional fluids and/or additives to achieve performance improvements. One embodiment is a low SAP engine lubricant composition comprising combinations of borates, high levels of ashless antioxidants, and low levels of ZnDTP to achieve high level of performance equal to or better than using high level of ZnDTP alone. In one embodiment, the component synergy is built upon a variety of functionalities to achieve well balanced performance features. In a preferred embodiment, these performance features favorably exceed engine oils formulated with high levels of zinc dithiophosphates and metallic detergents.

[0018] In a second embodiment, the lubricating oils maintain low frictional properties of film under various operating conditions. This embodiment favorably maintains sufficiently high film thickness at high operating temperatures to provide a minimum lubricant film to protect against wear at a variety of temperatures.

[0019] In a third embodiment, the lubricating oil maintains cleanliness over the entire range of operating conditions while reducing wear to an absolute minimum. In a fourth embodiment, the lubricating oil provides favorable oxidation, deposit and corrosion control, under the most severe operating conditions.

[0020] It has been discovered that organic silanes when blended with high levels of organic borates, and low levels of zinc dithiophosphates provide substantial property benefits. U.S. Pat. No. 6,887,835 discloses suitable silanes including organic silane additives for lubricants. U.S. Pat. No. 6,887,835 is incorporated by reference herein.

[0021] In a preferred embodiment, high levels of ashlees antioxidants are added to the compounds to achieve even more favorable property benefits. An even more preferred embodiment combines the synergistic benefits of low levels of non-corrosive sulfur, organic silanes, high levels of organic borates with ashless antioxidants and low levels of ZnDTP. These benefits include but are not limited to reductions in wear, corrosion, and increases in oil induction temperature or time (OIT) during oxidative conditions that result in potentially significant improvements in engine service life and durability with excellent overall performance benefits. In an additional embodiment, these benefits can be achieved without deleterious effects such as instability, undesirable high viscosity, deposits and the like, when added to lubricating oils.

[0022] This new engine oil technology is based on an advanced anti-wear, anti-friction and antioxidant system, suitable for combination with typical, contemporary dispersants, ashless antioxidants, detergents, defoamants and others including contemporary DI additive packages. These additives enhance anti-wear, anti-oxidation and anti-corrosion performance.

[0023] Persons skilled in the art with the benefit of the disclosure herein will recognize the ability to include additives that favorably enhances lubricant performance including anti-friction, anti-oxidation and anti-wear performance while successfully meeting the stringent wear, oxidation and cleanliness performance requirements in modern engines. Examples of suitable additives include but are not limited to contemporary ZDDP in low levels, borated or non-borated dispersants, phenolic and aminic ashless anti-oxidants, high and low levels of metal detergents, molybdenum or organic friction modifiers, defoamants, seal swell additives, pour point depressants including contemporary DDI additive packages, and any combination thereof.

[0024] Suitable dispersants include borated and non-borated succinimides, succinic acid-esters and amides, alkylphenol-polyamine coupled Mannich adducts, other related components and any combination thereof. In some embodiments, it can often be advantageous to use mixtures of such above described dispersants and other related dispersants. Examples include additives that are borated, those that are primarily of higher molecular weight, those that consist of primarily mono-succinimide, bis-succinimide, or mixtures of above, those made with different amines, those that are end-capped, dispersants wherein the back-bone is derived from polymerization of branched olefins such as polyisobutylene or from polymers such as other polyolefins other than polyisobutylene, such as ethylene, propylene, butene, similar dispersants and any combination thereof. The averaged molecular weight of the hydrocarbon backbone of most dispersants, including polyisobutylene, is in the range from 1000 to 6000, preferably from 1500 to 3000 and most preferably around 2200.

[0025] The preferred organic borates are borated hydroxyl esters, such as borated glycerol mono-oleate (GMO), borated glycerol di-oleate (GDO), borated glycerol tri-oleate (GTO), borated glycerol mono-cocoate (GMC), borated mono-talloate (GMT), borated glycerol mono-sorbitate (GMS), borated polyol esters with pendant hydroxyl groups, such as borated pentaerythritol di-C8 ester, and any combination thereof. Short chain tri-hydroxyl orthoborates may be used but are not desirable due to their relatively poor thermal/oxidative stability properties when compared to borated hydroxyl esters. Borated dispersants and borated detergents can be used as a source of boron. However, in order to achieve best overall performance, specific organic borates, such as borated hydroxyl esters are more preferable.

[0026] Suitable detergents include but are not limited to calcium phenates, calcium sulfonates, calcium salicylates, magnesium phenates, magnesium sulfonates, magnesium salicylates, metal carbonates, related components including borated detergents, and any combination thereof. The detergents can be neutral, mildly overbased, or highly overbased. The amount of detergents usually contributes a total base number (TBN) in a range from 1 to 9 for the formulated lubricant composition. Metal detergents have been chosen from alkali or alkaline earth calcium or magnesium phenates, sulfonates, salicylates, carbonates and similar components.

[0027] Antioxidants have been chosen from hindered phenols, arylamines, dihydroquinolines, phosphates, thiol/thioester/disulfide/trisulfide, low sulfur peroxide decomposers and other related components. These additives are rich in sulfur, phosphorus and/or ash content as they form strong chemical films to the metal surfaces and thus need to be used in limited amount to reduce sulfur, ash and phosphorous.

[0028] Inhibitors and antirust additives may be used as needed. Seal swell control components and defoamants may be used with the mixtures of this invention. Various friction modifiers may also be utilized. Examples include but are not limited to amines, alcohols, esters, diols, triols, polyols, fatty amides, various molybdenum phosphorodithioates (MoDTP), molybdenum dithiocarbamates (MoDTC), sulfur/phosphorus free organic molybdenum components, molybdenum trinuclear components, and any combination thereof.

[0029] The preferred non-corrosive sulfur compounds are chosen from the group consisting of ashless derivatives of thiadiazoles, ashless derivatives of benzothiazoles, ashless alkyl or aryl sulfides/di-sulfides/tri-sulfide including thianthrene, and its alkylates, diphenyl sulfide and disulfide, and their alkylates, dinonyl sulfide or disulfide, dipyridyl sulfide or disulfide, and their alkylates, ashless dithiocarbamates, and thioesters/sulfurized esters including thioglycolates, dialkyl thiodipropionates, dialkyl dithiopropionates. Examples of ashless thiadiazoles are Vanlube 87™, Cuvan 826™ and Cuvan 484™. Examples of ashless dithiocarbamates are Vanlube 7723™ and Vanlube 981. A prerequisite to the selection of sulfur additives is that they all need to meet copper corrosion requirements according to ASTM (D130) and low temperature storage compatibility tests.

[0030] The anti-corrosion performance can be judged by the copper corrosion test ASTDM D130 under normal conditions. For ASTDM test D130-6 normal conditions are 250 degrees Fahrenheit at 3 hours. For ASTDM test D130-8, normal conditions are 210 degrees Fahrenheit for 6 hours with 1 percent water, as well as a more severe condition at 250 degrees Fahrenheit for 24 hours. For purposes of this invention, non-corrosive sulfur shall be defined as any sulfur that provides a performance classification of 2B or better under the ASTM D-130 Copper Corrosion Test.

[0031] For example, dibenzyl disulfide was found to have deficiency in a severe copper corrosion test at degrees Fahrenheit for 24 hours and 2,2'-dipyridyl disulfide has poor low temperature compatibility in engine oils. Therefore, both these additives are deemed less favorable, despite their strong EP performance.

[0032] Sulfur additives containing a small portion of polysulfides (tri-sulfide/tetra-sulfide and higher order of polysulfides) are still acceptable providing that they could meet the copper corrosion requirements. The preferred ashless antioxidants are hindered phenols and arylamines. Typical examples are butylated/octylated/styrenated/nonylated/dodecylated diphenylamines, 4,4'-methylene bis-(2,6-di-tert-butylphenol), 2,6-di-tert-butyl-p-cresol, octylated phenyl-alpha-naphthylamine, alkyl ester of 3,5-di-tert-butyl-4-hydroxy-phenyl propionic acid, and many others. Sulfur-containing antioxidants, such as sulfur linked hindered phenols and thiol esters can also be used.

[0033] In a preferred embodiment, this new synergistic combination of lubricant base stocks and additives provide favorable performance parameters while maintaining excellent compatibility to exhaust after-treatment devices. This embodiment comprises a novel anti-wear, friction reduction and antioxidant system consisting of multi-functional, organic silane additives, organic borates, high level of ashless antioxidants and low level of zinc dithiophosphates. More specifically, this formulated engine oil embodiment comprises about 80 to 1600 PPM silicon, about 100 to 630 PPM phosphorus, and about 0.1 to 0.3 weight percent sulfur, less than 1 weight percent ash and from about 80 to 450 PPM boron, and about 0.5 to 3.0 wt % ashless antioxidants such as total amounts of hindered phenols and arylamines.

[0034] In one example embodiment, the general formulation of the low SAP engine oil containing the organic silanes is summarized in Table 1. In this table and throughout the application weight percent is intended to be active weight percent of the entire composition unless otherwise stated.

TABLE 1

Component Type	Wt %	Elements in Formulated Oils (ppm) + Other Restrictions
Organic boron additive	0.1–8.0%	80 to 450 PPM boron
Zinc dithiophosphate additive	0.1–1.0%	100 to 630 PPM phosphorous and 105 to 710 PPM zinc
Dispersant-detergent-inhibitor system	<15.0%	
Organic Silane additive	0.1–2.0%	80 to 1600 PPM silicon
Ashless antioxidants	0.5–3.0%	

[0035] These components can be used with a variety of base stocks, including group I, II, III, IV, and V, and gas-to-liquids ("GTL") as well as a variety of mixtures thereof. However, due to other performance requirements including volatility, stability, viscometrics, and cleanliness feature, premium engine oils preferably utilize group II and higher ("Group II+") base oils to ensure that they can achieve desirable overall performance levels as well as maximizing the full potential of the unique synergies among additives. Additional significant synergies were identified among alkylated aromatics and Group II+ high performance base stocks including Group II, III, IV, V, VI or GTL base stocks.

[0036] Groups I, II, III, IV and V are broad categories of base oil stocks developed and defined by the American Petroleum Institute (API Publication 1509; www.API.org) to create guidelines for lubricant base oils. Group I base stocks generally have a viscosity index of a range about 80 to 120 and contain greater than about 0.03% sulfur and/or less than about 90% saturates. Group II base stocks generally have a viscosity index of between about 80 to 120, and contain less than or equal to about 0.03% sulfur and greater than or equal to about 90% saturates. Group III stock generally has a viscosity index greater than about 120 and contains less than or equal to about 0.03 % sulfur and greater than about 90% saturates. Group IV includes polyalphaolefins (PAO). Group V base stocks include base stocks not included in Groups I-IV. Table 2 summarizes properties of each of these five groups.

TABLE 2

Base Stock Properties

	Saturates	Sulfur	Viscosity Index
Group I	<90% and/or	>0.03% and	≧80 and <120
Group II	≧90% and	≦0.03% and	≧80 and <120
Group III	≧90% and	≦0.03% and	≧120
Group IV	Polyalphaolefins (PAO)		
Group V	All other base oil stocks not included in Groups I, II, III, or IV		

[0037] Base stocks having a high paraffinic/naphthenic and saturation nature less than 90 weight percent can often be used advantageously in certain embodiments. Such base stocks include Group II and/or Group III hydroprocessed or hydrocracked base stocks, or their synthetic counterparts such as polyalphaolefin oils, GTL or similar base oils or mixtures of similar base oils.

[0038] In a preferred embodiment, at least about 20% of the total composition should consist of such Group II or Group III base stocks or GTL, with at least about 30% being preferable, and more than about 80% on being most preferable. Gas to liquid base stocks can also be preferentially used with the components of this invention as a portion or all of the base stocks used to formulate the finished lubricant. We have discovered, favorable improvement when the components of this invention are added to lubricating systems comprising primarily Group II, Group III and/or GTL base stocks compared to lesser quantities of alternate fluids.

[0039] GTL materials are materials that are derived via one or more synthesis, combination, transformation, rearrangement, and/or degradation/deconstructive processes from gaseous carbon-containing compounds, hydrogen-containing compounds, and/or elements as feedstocks such as hydrogen, carbon dioxide, carbon monoxide, water, methane, ethane, ethylene, acetylene, propane, propylene, propyne, butane, butylenes, and butynes. GTL base stocks and base oils are GTL materials of lubricating viscosity that are generally derived from hydrocarbons, for example waxy synthesized hydrocarbons, that are themselves derived from simpler gaseous carbon-containing compounds, hydrogen-containing compounds and/or elements as feedstocks. GTL base stock(s) include oils boiling in the lube oil boiling range separated/fractionated from GTL materials such as by, for example, distillation or thermal diffusion, and subsequently subjected to well-known catalytic or solvent dewaxing processes to produce lube oils of reduced/low pour point; wax isomerates, comprising, for example, hydroisomerized or isodewaxed synthesized hydrocarbons; hydroisomerized or isodewaxed Fischer-Tropsch ("F-T") material (i.e., hydrocarbons, waxy hydrocarbons, waxes and possible analogous oxygenates); preferably hydroisomerized or isodewaxed F-T hydrocarbons or hydroisomerized or isodewaxed F-T waxes, hydro-isomerized or isodewaxed synthesized waxes, or mixtures thereof.

[0040] GTL base stock(s) derived from GTL materials, especially, hydroisomerized/isodewaxed F-T material derived base stock(s). These base stocks are hydroisomerized/isodewaxed wax derived base stock(s) are characterized typically as having kinematic viscosities at 100° C. of from about 2 mm^2/s to about 50 mm^2/s, preferably from about 3 mm^2/s to about 50 mm^2/s, more preferably from about 3.5 mm^2/s to about 30 mm^2/s. For example, a GTL base stock derived by the isodewaxing of F-T wax, has a is kinematic viscosity of about 4 mm^2/s at 100° C. and a viscosity index of about 130 or greater. The term GTL base oil/base stock and/or wax isomerate base oil/base stock as used herein and in the claims is to be understood as embracing individual fractions of GTL base stock/base oil or wax isomerate base stock/base oil as recovered in the production process. Other examples, include mixtures of two or more GTL base stocks/base oil fractions and/or wax isomerate base stocks/base oil fractions, as well as mixtures of one or two or more low viscosity GTL base stock(s)/base oil fraction(s) and/or wax isomerate base stock(s)/base oil fraction(s) with one, two or more high viscosity GTL base stock(s)/base oil fraction(s) and/or wax isomerate base stock (s)/base oil fraction(s) to produce a dumbbell blend wherein the blend exhibits a viscosity within the aforesaid recited range. Reference herein to Kinematic viscosity refers to a measurement made by ASTM method D445.

[0041] GTL base stocks and base oils derived from GTL materials, especially hydroisomerized/isodewaxed F-T material derived base stock(s), and other hydroisomerized/isodewaxed wax-derived base stock(s), such as wax hydroisomerates/isodewaxates, which can be used as base stock components of this invention are further characterized typically as having pour points of about −5° C. or lower, preferably about −10° C. or lower, more preferably about −15° C. or lower, still more preferably about −20° C. or lower, and under some conditions may have advantageous pour points of about −25° C. or lower, with useful pour points of about −30° C. to about −40° C. or lower. If necessary, a separate dewaxing step may be practiced to achieve the desired pour point. References herein to pour point refer to measurement made by ASTM D97 and similar automated versions.

[0042] The GTL base stock(s) derived from GTL materials, especially hydroisomerized/isodewaxed F-T material derived base stock(s), and other hydroisomerized/isodewaxed wax-derived base stock(s) which are base stock components which can be used in this invention are also characterized typically as having viscosity indices of 80 or greater, preferably 100 or greater, and more preferably 120 or greater. Additionally, in certain particular instances, viscosity index of these base stocks may be preferably 130 or greater, more preferably 135 or greater, and even more preferably 140 or greater. For example, GTL base stock(s) that derive from GTL materials preferably F-T materials especially F-T wax generally have a viscosity index of 130 or greater. References herein to viscosity index refer to ASTM method D2270.

[0043] In addition, the GTL base stock(s) are typically highly paraffinic (>90% saturates), and may contain mixtures of monocycloparaffins and multicycloparaffins in combination with non-cyclic isoparaffins. The ratio of the naphthenic (i.e., cycloparaffin) content in such combinations varies with the catalyst and temperature used. Further, GTL base stocks and base oils typically have very low sulfur and nitrogen content, generally containing less than about 10 ppm, and more typically less than about 5 ppm of each of these elements. The sulfur and nitrogen content of GTL base stock and base oil obtained by the hydroisomerization/isodewaxing of F-T material, especially F-T wax is essentially nil.

[0044] In a preferred embodiment, the GTL base stock(s) comprises paraffinic materials that consist predominantly of non-cyclic isoparaffins and only minor amounts of cycloparaffins. These GTL base stock(s) typically comprise paraffinic materials that consist of greater than 60 weight percent non-cyclic isoparaffins, preferably greater than 80 weight percent non-cyclic isoparaffins, more preferably greater than 85 weight percent non-cyclic isoparaffins, and most preferably greater than 90 weight percent non-cyclic isoparaffins.

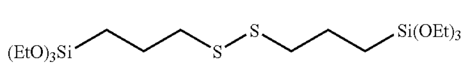
[0045] Useful compositions of GTL base stock(s), hydroisomerized or isodewaxed F-T material derived base stock(s), and wax-derived hydroisomerized/isodewaxed base stock(s), such as wax isomerates/isodewaxates, are recited in U.S. Pat. Nos. 6,080,301; 6,090,989, and 6,165,949 for example.

[0046] Typically, engine oils have multi-component oxidation inhibition systems including ZDTP and other ashless antioxidants such as hindered phenols, arylamines and/or low sulfur peroxide decomposers to prevent oil from oxidation through different mechanisms. As the levels of ZnDTP are reduced, the anti-wear, anti-oxidation and anti-corrosion protection must rely on the new multi-functional additive system.

[0047] The absence of ZDDP antioxidancy may be compensated by other antioxidants. The principle advantage of a preferred embodiment of this invention is the unique synergistic combination of organic borates, organic silane additives in the presence of low level zinc dithiophosphates and high level of ashless antioxidants that provides favorable oxidation, corrosion stability, deposit control, and more importantly, anti-wear performance. These favorable performance levels can be achieved while reducing the levels of sulfur, ash, phosphorus, and zinc in the engine oil formulations compared to the typical engine oil used today.

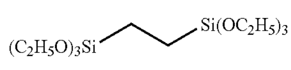
EXAMPLES

[0048] As illustrated in the attached Table 3, very good oxidation and corrosion resistance can be achieved with Silane additives. In table 2, a commercial silane additive sold by Chemtura Chemical Company as Silquest A-1589 is used with both PAO/ester synthetic blends and group I mineral oils. The chemical structure for Silquest A-1589 is shown below:



[1]

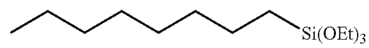
[0049] Another suitable Silane is Silquest Y-9805 and is sold by Chemtura Chemical Company. The chemical structure for Silquest Y-9805 is shown below:



[2]

[0050] The general chemical composition of Silquest Y-9805 is $(R_1—O)(R_2—O)(R_3—O)Si—(CRR')_n—Si(OR_3)(OR_2)(OR_1)$ where R_1, R_2, R_3 are H or C1 to C9 hydrocarbyl groups, R and R' are H or C1 to C4 hydrocarbyl groups, and n=2-6.

[0051] Another suitable silane is Silquest A-137 sold by Chemutra Chemical Company. The chemical structure for A-137 is



[3]

[0052] The general structure for Silane A-137 is (R1-O)(R2-O)(R3-O)Si—R where R could be a C1 to C30 hydrocarbyl group.

[0053] As shown by the Pressure Differential Scanning Calorimetry ("PDSC") Table in 3(a) and 3(b), the onset temperature of oil 2 and oil 4 is 8 to 10 degrees higher than that of oil 1 and oil 3 in the ramping method because oxidation rates generally double with about 10 degrees Celsius increase in temperature, theses results can be translated into about 60 percent to 100 percent better control of viscosity or acid number increases or any other comparable measurements for control of oxidation.

TABLE 3(a)

	Oil 1	Oil 2
Test Oil = PAO/Ester Base Blend 1 (80:20)		1% A-1589 99% Base Blend 1

TABLE 3(b)

Solubility			Clear & bright
PDSC (Ramp 10° C./min)	Onset T (° C.)	206.4	216.4
		Oil 3	Oil 4
Test Oil = 100 SPN	Stock 142		1% A-1589
Group I Base Blend 2			99% Base Blend 2
Solubility			Clear & bright
PDSC (Ramp 10° C./min)	Onset T (° C.)		
		201.8	210.1
Test Oil = 100 SPN			
Cu Corrosion (D130-6)	3 hrs/250° F.	1A	1B

[0054] Table 4 illustrates very good oxidation control with Silquest A-1589 silane additive in a low P engine oil with less than 0.025% P as in oil 5. The antioxidation performance of oil 5 is even better than reference oil A and B when more ZnDTP, instead of silane, was added to Base oil 3 as evidenced by the PDSC data of approximately 5 degree higher onset temperature in the ramping method). Also, excellent corrosion resistance can be maintained with oils formulated with silane additives as shown in oils 5 and 6. The 4-Ball wear results are all consistent and promising.

TABLE 4

Entry		Reference oil A	Reference oil B	Base	Oil 5	Oil 6
Engine Oil (0.025% P)	Base Blend 3	Reference (0.10% P)	Reference (0.05% P)	Base Blend 3 0.025% P	1% A-1589 Base blend 3 0.025% P	1% Y-9805 Base Blend 3 0.025% P
Solubility Appearance		C & B	C & B	C & B	C & B	C & B
Condition Set 1 4 Ball Wear (D4172)	WSD (mm)	0.39	0.4	1.66	0.33	0.59
40 Kg/1800 rpm/30 min./200 F.	K Factor				0.2	6
Condition Set 2 4 Ball Wear	WSD (mm)	0.4	0.38	0.47	0.36	0.33
40 Kg/1200 rpm/60 min./200 F.	K Factor	0.6	1.9	1.4	0.3	0.1
Condition Set 3 4 Ball Wear	WSD (mm)	0.35	0.43	0.47	0.36	0.47
40 Kg/600 rpm/30 min./200 F.	K Factor	0.9	3.9	5.8	1.1	5.9
4 Ball EP (D2783)	LNS (Kg)	80	50	63	80	63
30 C./10 sec./1760 rpm	Weld Ld (Kg)	250	250	250	250	250
	LWI	37	32	26	36	30
Cu Corrosion (D130-6)	3 hrs/250 F.	1A	1A	1A	1B	1B
Cu Corrosion (D130-8)	3 hrs/210 F./1 wt % H_2O	1A	1A	1A	1A	1A
Cu Corrosion (D130-9)	24 hrs/250 F.	1B	1B	2A	1B	1B
PDSC (Ramp 10 C./min)	Onset T (C.)	235.8	235.7	233.6	240.6	234
HFRR	Ave. Friction	0.13	0.12	0.12	0.12	0.12
0.7 Kg/60 Hz/0.5 mm/60 min./75 C.	% Ave. film	0	14.4	82.1	79.1	89.2
High Temperature	week 1	C & B	C & B	C & B	C & B	C & B
Storage Stability Test	week 2	C & B	C & B	C & B	C & B	C & B
Temperature = 80 C.	week 3	C & B	C & B	C & B	C & B	C & B
Duration: 1 to 4 weeks	week 4	C & B	C & B	C & B	C & B	C & B
Low Temperature	week 1	C & B	C & B	C & B	C & B	C & B
Storage Stability	week 2	C & B	C & B	C & B	C & B	C & B
Temperature = 10° C.	week 3	C & B	C & B	C & B	C & B	C & B
	week 4	C & B	C & B	C & B	C & B	C & B

[0055] Adding a silane additive to the 0.025% P base formulation (Base), results in a 64 to 80 percent reduction in wear scar diameter for condition set 1. Furthermore, a 23 to 30 percent reduction is found for condition set 2 and a 0 to 23 percent reduction can be seen in condition set 3. The High Frequency Reciprocating Rig (HFRR) data demonstrates silanes can help maintain strong film formation and excellent frictional properties, while adding more ZnDTP may destroy the film formation mechanism.

[0056] All silanes dissolve easily in engine oils and remained clear and bright on the shelf at both low and elevated temperatures over a period of four weeks at both 10 degrees Celsius and 80 degrees Celsius. Apparently, the stability of silane containing oils is satisfactory and silanes cause no adverse effects to compatibility in the presence of other commonly used additives in engine oil compositions. The 4-Ball EP test, demonstrate significant improvements in last non-seizure (LNS) load and load wear index (LWI) with oils formulated with a silane additive. This improvement is most prevalent, in is oil containing disulfide-silanes such as, Silquest A-1589 as shown in oil 5. An increase of 4 to 10 units in LWI over base oil is significant as this performance is almost identical or better than what ZnDTP provides when comparing oil 5 versus reference oils A and B.

[0057] As illustrated in Table 5, very good oxidation control can be achieved when silanes and ZnDTP were used together in a low phosphorous, low ash engine oil of less than 0.05% phosphorous. The anti-oxidation performances of oils at columns 7 and 8 are much better than that of reference oil D as evidenced by PDSC data of 2 to 8 degrees higher onset temperature by the ramping method. In fact, oil 7 is even better than reference oil C as adding more Silquest A-1589 gives better performance than adding ZnDTP. Also, excellent corrosion resistance can be maintained with oils formulated with silane additives as shown by oils 7 and 8.

TABLE 5

Entry	Reference oil C	Reference Oil D	Base	Oil 7	Oil 8
Base Blend 4 is a P-free	1.0% ZnDDP 99% Base Blend 4	0.5% ZnDDP 99.5% Base Blend 4	Base Blend 4 0% P	1% Silquest A-1589 0.5% ZnDDP 98.5% Base Blend 4	1% Silquest A-137 0.5% ZnDDP 98.5% Base Blend 4

TABLE 5-continued

Entry		Reference oil C	Reference Oil D	Base	Oil 7	Oil 8
Partially formulated engine oil		(0.10% P)	(0.05% P)	(0% P)	(0.05% P)	(0.05% P)
Solubility/Compatibility		Good	Good	Good	Good	Good
Appearance		Clear & bright	Clear & bright	Clear & bright	Clear & bright	Clear & bright
4 Ball Wear	WSD (mm)	0.37	0.4	0.45	0.4	0.43
40 Kg/600 rpm/30 min./200 F.	K Factor	1.4	2.5	4.9	2.5	3.9
4 Ball EP (D2783)	LNS (Kg)	80	80	50	80	80
30 C./10 sec./1760 rpm	Weld Ld (Kg)	200	200	160	250	200
	LWI	35	34	22	42	34
Cu Corrosion (D130-6)	3 hrs/250 F.	1A	1A	1B	1A	1A
Cu Corrosion (D130-8)	3 hrs/210 F./H_2O	1A	1B	3A	1A	1A
Cu Corrosion (D130-9)	24 hrs/250 F.	1A	1A	2A	1A	1A
PDSC (Ramp 10 C./min)	Onset T (C.)	232	229.7	233.5	238.4	232
Hot Tube Test (288 C./16 hr)						
Tube Rating (1 = Clean, 9 = dirty)		3.8	3.5	1	3	3.5
HFRR	Ave. Friction	0.14	0.15	0.14	0.13	0.13
0.7 Kg/60 Hz/0.5 mm/	Scar X/Y (mm)	0.32/0.7	0.3/0.77	0.37/0.73	0.3/0.73	0.3/0.73
60 min./75 C.	Calc. Sc. Area	0.17	0.18	0.21	0.17	0.17
D2896	TBN	4.27	4.23	4.12		
D874 (wt %)	Sulfated Ash	0.53	0.38	0.32		
D6443 (wt %)	Phosphorus	0.1003	0.0507	<0.002	0.0474	
D6443 (wt %)	Zinc	0.1118	0.0577	<0.002	0.0545	
D6443 (wt %)	Calcium	0.0329	0.0332	0.0334	0.0326	
D6443 (wt %)	Magnesium	0.0595	0.0496	0.494	0.0525	
D6443 (wt %)	Copper	<0.002	<0.002	<0.002	<0.002	
D6443 (wt %)	Chlorine	0.0047	0.0049	0.0047	0.0061	
D6443 (wt %)	Sulfur	0.2799	0.1783	0.072	0.3165	
High Temperature	week 1	C & B	C & B	C & B	C & B	
Storage Stability Test	week 2	C & B	C & B	C & B	C & B	
Temperature = 80 C.	week 3	C & B	C & B	C & B	C & B	
Duration: 1 to 4 weeks	week 4	C & B	C & B	C & B	C & B	
Low Temperature	week 1	C & B	C & B	C & B	C & B	
Storage Stability Test	week 2	C & B	C & B	C & B	C & B	
Temperature = 10° C.	week 3	C & B	C & B	C & B	C & B	
Duration: 1 to 4 weeks	week 4	C & B	C & B	C & B	C & B	

[0058] The 4-Ball wear results are good as equivalent wear scar diameters are reported. The HFRR data showed that silanes can help reduce the calculated wear scar area while maintaining excellent frictional properties. The Hot Tube test which is a typical test to assess cleanliness features of engine oils under high temperature oxidation conditions. As indicated, oils 7 and 8 both have equivalent or slightly better Hot Tube results than reference oil D with the lower the rating, the better the cleanliness. These results demonstrate that silane additives contribute no adverse effects to cleanliness. All silanes dissolved easily in engine oils and remained clear and bright on the shelf at both low and elevated temperatures over a period of four weeks at 10 degrees Celsius and 80 degrees Celsius. Apparently the storage stability of silane containing oils is satisfactory and silanes cause no adverse compatibility effects in the presence of other commonly used additives in engine oil compositions. Perhaps, the most significant improvement of all is the exceptionally good load-carrying property. Evaluating silane containing oils in a 4-Ball EP test, illustrate significant improvements in last non-seizure (LNS) load and load wear index (LWI) can be observed as shown by oil 7 with 1 percent Silquest A-1589. An increase of 8 units in LWI over reference oil D is significant and an increase of 7 units in LWI over reference oil C is even more significant as this performance level exceeds what ZnDTP can provide.

[0059] In a preferred embodiment, very low levels of metals are present in the final composition of the formulation. As shown in Table 4 only trace amounts of copper iron, barium, aluminum, potassium, chromium, manganese, nickel, lead, silver, sodium, tin, and vanadium are present.

[0060] A synergistic combination of organic silanes and low level of zinc dithiophosphates in the low SAP engine oil formulations can reduce wear and increase oxidative stability. Table 6 illustrates this example embodiment.

[0061] As shown in the attached Table 6, three engine oils were formulated and compared to each other. Reference oil E is an oil of relatively high ash as evidenced by high sulfated ash level (0.94 weight percent) and high TBN number (7.73). Reference oil F is a low ash oil with essentially almost identical formulation to oil A except at much reduced detergent level (888 ppm versus 2169 ppm calcium). Inventive oil 9 has similar detergent level as oil F except that 1 weight percent of a sulfur containing silane was added. As a result, the sulfur level is higher in oil 9 (0.3266%, still below the industry standard limit of 0.5%), but the ash level is still much lower than the level is in reference oil E. Clearly, the silane additives have shown strong synergistic effect with low level of zinc dithiophosphates in low ash oils. Therefore, the silane additives are more suitable for low ash engine oil application. Comparing reference oils E and F the Four-ball wear performance of oil F is not as good as oil E when the total amount of detergents is reduced. The K-factor indicates a factor of 3 times weaker in anti-wear control in oil F compared to oil E (6.22/2.06).

However, when silane was added to oil F to form oil 9, the anti-wear performance improves significantly (by a factor of 4.5, 6.22/1.37), which is even better than the performance of oil A at higher ash level. Also, as shown in Pressure Differential Scanning Calorimetry (PDSC), the onset temperature of oil 9 is 8.3 to 25 degrees higher than results of oil A and oil B (ramping method). Since oxidation rates generally double with about every 10° C. increase in temperature, these results are impressive with respect to the ability to reduce and control oxidation by these oils. If translated directly into the control of viscosity or acid number increases, or other measurements of control of oxidation, oil 9 is estimated to be 83% to 565.7% better than reference oils E and F.

[0062] In this embodiment, we have identified a new engine oil system based on very unique combination of additives that demonstrate outstanding and unexpected performance improvements. This unique component synergism concept is believed to be applicable to similar formulations containing (a) low TBN detergent system of less than 6 for the finished oils, (b) a low ash level of less than 0.8 weight percent ash, (c) a low level of ZnDTP of less than <0.08 weight percent phosphorus in the finished oil), and (d) a silane additives which are preferably sulfur containing silanes.

TABLE 6

Entry		Reference oil E	Reference oil F	Oil 9
Metal Detergent		3.0% Ca Detergent	1.2% Ca Detergent	1.2% Ca Detergent
Zinc Dithiophosphate		.75% ZDTP	.75% ZDTP	.75% ZDTP
Partial engine oil formulation (0% P)		96.25%	98.05%	97.05%
Silane				1.0 wt % A-1589
		(0.075% P)	(0.075% P)	(0.075% P)
Solubility Appearance		C & B	C & B	C & B
4 Ball Wear	WSD (mm)	0.389	0.6	0.367
40 Kg/600 rpm/30 min./200 F.	K Factor	2.06	6.22	1.37
4 Ball EP (D2783)	LNS (Kg)	100	100	100
30 C/10 sec./1760 rpm	Weld Ld (Kg)	250	250	250
	LWI	42.5	42.9	43.1
Cu Corrosion (D130-6)	3 hrs/250 F.	1A	1A	1A
Cu Corrosion (D130-8)	3 hrs/ 210 F/H_2O	1A	1A	1A
Cu Corrosion (D130-9)	24 hrs/250 F.	1A	1A	1A
PDSC	700 Kpa O_2			
Ramp method (Onset temp)	10 C./min	259.4 C.	276.1 C.	284.4 C.
D2896	TBN	7.73	4.53	5.3
D874 (wt %)	Sulfated Ash	0.93	0.54	0.78
D6443 (wt %)	Phosphorus	0.0776	0.0774	0.0771
D6443 (wt %)	Zinc	0.083	0.0841	0.0855
D6443 (wt %)	Calcium	0.2169	0.0888	0.0866
D6443 (wt %)	Magnesium	0.0028	<0.002	<0.002
D6443 (wt %)	Copper	<0.002	<0.002	<0.002
D6443 (wt %)	Chlorine	<0.002	<0.002	0.0037
D6443 (wt %)	Sulfur	0.2041	0.1987	0.3266
Comment		High detergent	Low detergent	Low detergent

[0063] In summary, a new engine oil system is presented based on very unique combinations of silane additives and low levels of ZnDTP that demonstrate outstanding and unexpected performance to modern engines. This offers an effective way to reduce the amount of ZnDTP for contemporary engine oils while maintain excellent wear, oxidation and corrosion protection.

What is claimed is:

1. A composition, comprising:

a. a lubricating oil basestock;

b. an organic silane containing additive present in an amount of at least 0.1 and less than 2.0 weight percent of the composition;

c. a dispersant-detergent-inhibitor system of less than 15 weight percent of the composition;

d. an organic boron additive present in an amount of at least 0.1 and less than 8.0 weight percent of the composition;

e. a zinc dithiophosphate additive present in an amount of at least 0.1 weight percent of the composition and less than 1.6 weight percent of the composition; and

f. the composition having at least 80 PPM and less than 1600 PPM silicon, at least 100 PPM and less than 630 PPM phosphorus, at least 105 PPM and less than 710 PPM zinc, at least 1,000 PPM and less than 4,000 PPM sulfur, at least 800 PPM, less than 10,000 PPM ash and less than 450 PPM Boron.

2. The composition of claim **1** further comprising at least one performance wherein the additives are chosen form the group comprising borated or non-borated dispersants, phenolic and aminic ashless anti-oxidants, metal detergents, molybdenum or organic friction modifiers, defoamants, seal swell additives, pour point depressants, organic borates, contemporary dispersant-detergent-inhibitor (DDI) additive packages, and any combination thereof.

3. The composition of claim **1** wherein the base stock is chosen from the group consisting of group II base stocks, group III base stocks, group IV base stocks, and group V base stocks, gas-to-liquids base stocks, and any combination thereof.

4. The composition of claim **1** wherein the dispersant systems comprises additives chosen from the group consisting of borated and non-borated succinimides, succinic acid-esters and amides, alkylphenol-polyamine coupled Mannich adducts, and any combination thereof.

5. The composition of claim **1** further comprising an ashless antioxidant additive.

6. The composition of claim **1** further comprising a metallic detergent or detergent system.

7. The composition of claim **6** wherein the detergent system provides a total base number (TBN) less than 9, preferably less than 7 and most preferably less than 5, to the formulated lubricant composition.

8. The composition of claim **1** further comprising a viscosity modifier additive.

9. The composition of claim **1** wherein the organic borate is a borated hydroxyl esters chosen from the group consisting of borated glycerol mono-oleate, borated glycerol di-oleate, borated glycerol tri-oleate, borated glycerol mono-cocoate, borated mono-talloate, borated glycerol mono-sorbitate, borated polyol esters and any combination thereof.

10. The composition of claim **1** further comprising a non-corrosive organic sulfur additive.

11. The composition of claim **10** wherein the non-corrosive sulfur additive is chosen from the group consisting of ashless derivatives of thiadiazoles, ashless derivatives of benzothiazoles, ashless alkyl, aryl sulfides/di-sulfides/tri-sulfide including thianthrene, diphenyl disulfide, dinonyl disulfide, dipyridyl disulfide, and their alkylates, ashless dithiocarbamates, thioetsers/sulfurized esters, thioglycolates, dialkyl thiodipropionates, dialkyl dithiopropionates, and any combination thereof.

12. A lubricant additive system for a lubricant composition, comprising:

a. an organic silane containing additive of at least 0.4 and less than 8.0 weight percent of the additive;

b. a dispersant-detergent-inhibitor system of less than 60 weight percent of the additive;

c. an organic boron additive of at least 0.4 and less than 32.0 weight percent of the additive; and

d. a zinc dithiophosphate additive of at least 0.4 weight percent of the composition and less than 6.4 weight percent of the additive.

13. The lubricant additive of claim **12** wherein the total lubricant additive treat is in the range of at least 0.01 weight percent and less than 25 weight percent of the lubricant composition.

14. The lubricant additive of claim **12** further comprising a non-corrosive sulfur additive.

15. The lubricant additive of claim **12** further comprising an ashless antioxidant.

16. A method comprising:

a. obtaining a composition comprising a lubricating oil basestock, an organic silane containing additive of at least 0.1 and less than 2.0 weight percent of the composition, a dispersant-detergent-inhibitor system of less than 15 weight percent of the composition, an organic boron additive of at least 0.1 and less than 8.0 weight percent of the composition, a zinc dithiophosphate additive of at least 0.1 weight percent of the composition and less than 1.6 weight percent of the composition and the composition having at least 80 PPM and less than 1600 PPM silicon, at least 100 PPM and less than 630 PPM phosphorus, at least 105 PPM and less than 710 PPM zinc, at least 1,000 PPM and less than 4,000 PPM sulfur, at least 800 PPM, less than 10,000 PPM ash and less than 450 PPM Boron; and

b. lubricating an engine with the composition to achieve favorable oxidation.

17. A method for reducing sulfur, phosphorus and ash in a lubricating oil for an internal combustion engine, comprising:

a. obtaining a composition comprising a lubricating oil basestock, an organic silane containing additive present in the amount of of at least 0.1 and less than 2.0 weight percent of the composition, a dispersant-detergent-inhibitor system of less than 15 weight percent of the composition, an organic boron additive present in the amount of at least 0.1 and less than 8.0 weight percent of the composition, a zinc dithiophosphate additive present in the amount of at least 0.1 weight percent of the composition to 1.6 weight percent of the composition and the composition having at least 100 PPM and less than 630 PPM phosphorus, at least 105 PPM and less than 710 PPM zinc, at least 1,000 PPM and less than 4,000 PPM sulfur, at least 800 PPM, less than 10,000, and;

b. lubricating the internal combustion engine with the composition.

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