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(54) LOW SAP ENGINE LUBRICANT ADDITIVE AND COMPOSITION CONTAINING NON-CORROSIVE SULFUR COMPOUND AND ORGANIC BORATES

LOW-SAP-MOTORSCHMIERMITTELZUSATZ UND ZUSAMMENSETZUNG MIT NICHT-KORROSIVER SCHWEFELVERBINDUNG UND ORGANISCHEN BORATEN

ADDITIF ET COMPOSITION LUBRIFIANTES POUR MOTEUR À FAIBLE TAUX DE SOUFRE, DE CENDRE ET DE PHOSPHORE CONTENANT UN COMPOSÉ SOUFRÉ NON CORROSIF ET DES BORATES ORGANIQUES

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DescriptionBACKGROUND OF THE INVENTION5 FIELD OF THE INVENTION

[0001] This invention relates to lubricating oil compositions suitable for use in internal combustion engines. More particularly, this invention relates to a low ash, sulfur, and phosphorous lubricating oil composition.

10 BACKGROUND

[0002] 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 oil degradation. Some of the solutions to reducing wear have been strictly mechanical including building engines with wear resistant alloy or ceramic parts, modifying the contact geometry and adding special coating materials. Solutions to improve cleanliness also involve modification of 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.

[0003] Contemporary lubricants such as engine oils use mixtures of additive components to include 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. These additives provide energy conservation, engine cleanliness and durability and high performance levels to the lubricating oil under a wide range of engine operability conditions including temperature, pressure and lubricant service life.

[0004] 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.

[0005] 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 carry the three unfavorable 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.

[0006] 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 MoDTC 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 place extremely rigorous chemical limits on any reductions in ZnDTP treat levels.

[0007] 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. WO 03/070863 relates to low phosphorus lubricating oil composition comprising ashless sulfurized olefin and composition containing a molybdenum and sulfur.

[0008] 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.

55 SUMMARY OF THE INVENTION

[0009] In a first embodiment, a lubricating oil composition is disclosed. This composition comprises a lubricating oil basestock, a boron-containing additive present in the amount in the range of from 0.01 weight percent of the composition

to less than 8.0 weight percent, a non-corrosive ashless sulfur additive chosen from ashless dithiocarbamates present in the amount in the range of from at least 0.1 weight percent of the composition and to less than 4.0 weight percent, a dispersant-detergent-inhibitor system of less than 15 percent weight percent of the composition, a zinc dithiophosphate additive present in the amount in the range of from at least 0.2 weight percent of the composition and to less than 2.0 weight percent of the composition wherein weight percent is active ingredient weight of the composition. The formulated oil composition having at least 100 and less than 630 ppm phosphorus, at least 1,000 ppm and less than 3,000 ppm sulfur, and at least 105 ppm and less than 710 ppm zinc, at least 80 ppm and less than 450 ppm boron.

[0010] In a second embodiment, an additive composition for lubricating oils is disclosed. This composition comprises an organic boron containing additive present in the amount in the range of from at least 0.4 weight percent to less than 32 weight percent of the additive, a detergent-dispersant system of less than 60 percent weight percent of the additive, a zinc dithiophosphate additive present in the amount in the range of at least 0.8 weight percent to less than 8.0 weight percent of the additive, a non-corrosive ashless sulfur additive present in the amount in the range of from at 0.4 to less than 16.0 weight percent of the additive.

[0011] A method of obtain a favorable lubricating properties is disclosed. This method, comprises obtaining a composition comprising a lubricating oil basestock, an organic boron containing additive of at least 0.01 and less than 8 weight percent of the composition, a dispersant-detergent-inhibitor system of less than 15 percent weight percent of the composition, zinc dithiophosphate additive of at least 0.2 weight percent of the composition and less than 2.0 weight percent of the composition, a non corrosive ashless sulfur additive of at 0.1 and less than 4.0 weight percent of the composition. The formulated oil composition having at least 100 and less than 630 PPM phosphorus, at least 1,000 PPM and less than 3,000 PPM sulfur, and at least 105 PPM and less than 710 PPM zinc, at least 80 PPM and less than 45.0 PPM boron.

DETAILED DESCRIPTION OF THE INVENTION

[0012] 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 organic borates, non-corrosive sulfur compounds, optional 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, 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.

[0013] 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.

[0014] In a third embodiment, the lubricating oil maintains cleanliness over the entire range of operating conditions while reducing wear to a minimum. In a fourth embodiment, the lubricating oil provides favorable oxidation and corrosion control, under the most severe operating conditions.

[0015] It has been discovered that non-corrosive, organic sulfur compounds when blended with high levels of organic borates, and low level of zinc dithiophosphates provide substantial property benefits. In a preferred embodiment, high levels of ashless antioxidants are added to the compounds to achieve even more favorable property benefits. 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 oil 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 the additives are added to lubricating oils. This new engine oil technology is based on an advanced anti-wear, anti-friction and antioxidant system, in combination of some typical, contemporary dispersants, ashless antioxidants, detergents, defoamants and other additives including contemporary DI additive packages. These additives enhance anti-wear, anti-oxidation and anti-corrosion performance.

[0016] 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 zinc dithiophosphates 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.

[0017] 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.

[0018] The non-corrosive sulfur compounds are chosen from the group consisting of ashless dithiocarbamates. 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.

[0019] The anti-corrosion performance can be judged by the copper corrosion test ASTM D130 under normal conditions. For ASTM test D130-6 normal conditions are at 121 °C (250 degrees Fahrenheit) at 3 hours. For ASTM test D130-8, normal conditions are set at 99°C (210 degrees Fahrenheit) for 6 hours with percent water, as well as a more severe condition at 121°C (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.

[0020] Dibenzyl disulfide was deficient 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 additives are deemed less favorable, despite of their strong EP performance. 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.

[0021] 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.

[0022] Suitable dispersants include borated and non-borated succinimides, succinic acid-esters and amides, alkyl-phenol-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.

[0023] 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.

[0024] Antioxidants have been chosen from hindered phenols, arylamines, dihydroquinolines, phosphates, thiol/thiolester/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 in reduced sulfur, ash and phosphorous lubricating oils.

[0025] 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 tri-nuclear components, and any combination thereof.

[0026] In a preferred embodiment, this new synergistic combination has significantly improved these critical 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 organic borates, non-corrosive sulfur additives, high level of ashless antioxidants and low levels of zinc dithiophosphates. More specifically, this formulated engine oil embodiment comprises about 100 to 630 ppm phosphorus, and about 0.1 to 0.3 wt% sulfur 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.

[0027] 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 prefer to use 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.

[0028] 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 between 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 1 summarizes properties of each of these five groups.

Table 1: 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		

[0029] Base stocks having a high paraffinic/naphthenic and saturation nature of greater 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.

[0030] In a preferred embodiment, at least about 20 percent of the total composition should consist of such Group II or Group III base stocks or GTL, with at least about 30 percent being preferable, and more than about 80 percent 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.

[0031] 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, hydroisomerized or isodewaxed synthesized waxes, or mixtures thereof.

[0032] 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) are characterized typically as having kinematic viscosities at 100°C of from about 2 mm²/s to about 50 mm²/s, preferably from about 3 mm²/s to about 50 mm²/s, more preferably from about 3.5 mm²/s to about 30 mm²/s, as exemplified by a GTL base stock derived by the isodewaxing of F-T wax, which has a kinematic viscosity of about 4 mm²/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, 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.

[0033] 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.

[0034] 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.

[0035] In addition, the GTL base stock(s) are typically highly paraffinic of greater than 90 percent 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.

[0036] 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 wt% non-cyclic isoparaffins, preferably greater than 80 wt% non-cyclic isoparaffins, more preferably greater than 85 wt% non-cyclic isoparaffins, and most preferably greater than 90 wt% non-cyclic isoparaffins.

[0037] 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.

[0038] The principle advantage of one embodiment of this invention is the unique synergistic combination of organic borates, non-corrosive sulfur additives in the presence of low level zinc dithiophosphates and high level of ashless antioxidants that provides favorable oxidation, corrosion stability, and more importantly, anti-wear performance. These favorable performance levels can be achieved while reducing the levels of sulfur, phosphorus and zinc in the engine oil formulations compared to the typical engine oil used today.

[0039] In one embodiment, the general formulation of the low SAP engine oil is summarized in Table 2. In this table and throughout the application weight percent is intended to be active ingredient weight percent of the entire composition unless otherwise stated.

Table 2

Component Type	Wt%	Elements in Formulated Oils (ppm) + Other Restrictions
Organic-containing boron additive	0.1 - 8.0%	80 to 450 PPM boron
Zinc dithiophosphate additive	0.2 - 2.0%	100 to 530 PPM phosphorous and 105 to 710 PPM zinc
Dispersant-detergent-inhibitor system	<15.0%	
Non-corrosive ashless sulfur additive	0.1 - 4.0%	1,000 to 3,000 PPM sulfur
Ashless antioxidants	0.5 - 3.0%	

EXAMPLES

[0040] Table 3 illustrates low temperature stabilities for different ashless antiwear additives for low phosphorous lubricant oils with a phosphorous level of 0.05 weight percent of the composition. Table 3 illustrates various embodiments for two reference base oils formulations. Both base Reference oils A and B are formulated with the premium Group III base oils.

Table 3

Entry		1	2	3	4	5	6	7
		Reference oil A	Comparative oil 1	Comparative oil 2	Comparative oil 3	Comparative oil 4	Reference oil B	Comparative oil 5
								RN 4717
Ashless AW additive			0.2%Ald-4 S ₂ -pyridine	0.3%Ald-4 S ₂ -pyridine	0.2%Ald-2 S ₂ -pyridine	0.3%Ald-2 S ₂ -pyridine	25%Dibenzyl	.25%Dibenzyl
		0.05% P	0.05% P	0.05% P	0.05% P	0.05% P	(0.05% P)	Disulfide
								(0.05% P)
Solubility		C&B	Dropout	Dropout	C&B	C&B	C&B	C&B
Appearance			at 5C	At 5C				
Cu Corrosion (D130-6)	3 hrs/121°C (250°F)						1A	1A
Cu Corrosion (D130-8)	3 hrs/99°C (210°F)/ H ₂ O	2C	1B	1B	2B	2C	1B	1B
Cu Corrosion (D130-9)	24 hrs/121°C (250°F)	1A	2A	2A	3A	4A	1A	4A
PDSC (Ramp 10°C/min)	Onset T (°C)	246.7	239.6	245	242.7	238.8	229.7	228.5
288° C, 16hrs								
Tube Rating (1 = Clean)		3	6	6.9	4.5	5.5	3.8	3.3
4 Ball Wear (D4172)	WSD (mm)						0.6	0.6
40Kg/1800r pm/30min./ 93° C 200° F	K Factor						7	6.2

(continued)

Entry	1	2	3	4	5	6	7
		Aldrithiol-4	4,4'-dipyridyl	Disulfide	[2645-22-9]		
4 Ball EP (D2783)		Aldrithiol-2	2,2'-dipyridyl	Disulfide	[2127-03-9]	80	80
30°C/10sec./1760rpm						200	200
						34.5	35.2
HFR						0.147	0.107
0.7Kg/60Hz /0.5mm/						12.3	10.7
60min./75° °C						0.3/0.77	0.30/0.73
						0.181	0.173

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[0041] Now referring to Table 3, comparative oils 1, 2, 3 and 4 are variations of reference oil A. The formulation for reference oil A is disclosed in Table 4.

Table 4

	Descriptions	Low ash engine oil
Blend Code		4866XNP005-D
Batch Number		1
Additive Sytem 1	Antioxidants	2
Additive System 2	Detergents/dispersants	9.25
Additive System 3	Viscosity modifiers	14
Additive System 4	Other performance additives	0.3
Base oil System	Group III	Balance
		BASELINE
D 130 8	Corrosion of Cu by Petroleum	2C
D 130 9 250F / 24hrs	Corrosion of Cu by Petroleum	1A
D 445 5 KV at 100C, CST	Kinematic Viscosity @100 C	9.868
D5293 6 AppVis CCS -30, CP	App. Viscosity @ Low Temp	4400
D6443 MAGNESIUM, WT%	Add Metals in Lubes	0.0469
D6443 SULFUR, WT%	Add Metals in Lubes	0.1825
D6443 PHOSPHORUS, WT%	Add Metals in Lubes	0.0476
D6443 CALCIUM, WT%	Add Metals in Lubes	0.0329
D6443 CHLORINE, WT%	Add Metals in Lubes	0.0095
D6443 COPPER, WT%	Add Metals in Lubes	<0.0020000001
D6443 ZINC, WT%	Add Metals in Lubes	0.0554

[0042] Again referring to table 3, comparative oil 5 is a variations of reference oil B. The formulation for reference oil B is disclosed in Table 5.

Table5

Blend Code		OSCARLOWSPA-C
Batch Number	ZnDTP free base blend	1
Base oil System	Group III Base Oi)	Balance
Additive System 1	Antioxidants	1.5
Additive System 2	Dispersants/Detergents	9.5
Additive System 3	Viscosity Modifiers	7
Additive System 4	All other performance additives	0..05
REFERENCE		
		Group III Base Oil with a minimum VI of 120, a typical pour point of -15C and a typical sulfur <10 ppm
D 445 5 KV at 100C, CST	Kinematic Viscosity at 100 C	12.1
D 874 Sulfated Ash, WT%	Sulfated Ash from Lubes, Addtv	0.32
D2896	TBN of Petroleum Products	4.12
D4683 , CP	HTHS Tapered Bearing Visc Test	3.53
D4684 6 Yield Stress, PA	Yield Stress, App. Viscosity	>350
D4684 6 Appar Viscos 1, CP	Yield Stress, App. Viscosity	>500000
D4684 6 Appar Viscos 2, CP	Yield Stress, App. Viscosity	>500000
D4684 6 Appar Viscos 3, CP	Yield Stress, App. Viscosity	>500000
D5293 6 AppVis CCS -30, CP	App. Viscosity @ Low Temp	5080
D6443 MAGNESIUM, WT%	Add Metals in Lubes	0.0494
D6443 SULFUR, WT%	Add Metals in Lubes	0.072
D6443 PHOSPHORUS, WT%	Add Metals in Lubes	<0.0020000001
D6443 CALCIUM, WT%	Add Metals in Lubes	0.0334
D6443 CHLORINE, WT%	Add Metals in Lubes	0.0047
D6443 COPPER, WT%	Add Metals in Lubes	<0.0020000001
D6443 ZINC, WT%	Add Metals in Lubes	<0.0020000001
D5185 Boron, PPM		170
D5185 Molybdenum, PPM		<0.5

[0043] Table 3 also illustrates copper corrosion test from the ASTM D-130 method. Table 6 illustrates the various classifications from the ASTM Copper Corrosion test. As shown in table 6, Classifications 1A, 1B, 2A, and 2B are the non-corrosive preferred classifications with classifications 2C, 2D, 2E, 3A, 3B, 4A, 4B, and 4C being the non preferred classifications.

Table 6: ASTM D-130 Copper Corrosion Tests

Classification	Designation	Description	Corrosion Comment
Freshly polished strip	-	-	Non-corrosive, preferred
1A	Slightly tarnish	Light orange, almost the same as freshly pol. Strip	Non-corrosive, preferred
1B	Slightly tarnish	Dark orange	Non-corrosive, preferred
2A	Moderate tarnish	Claret red	Non-corrosive, preferred
2B	Moderate tarnish	Lavender	Non-corrosive, preferred

(continued)

Classification	Designation	Description	Corrosion Comment
2C	Moderate tarnish	Multicolored with lavender blue or silver	Not preferred
2D	Moderate tarnish	Silvery	Not preferred
2E	Moderate tarnish	Brassy or gold	Not preferred
3A	Dark tarnish	Magenta overcast on brassy strip	Not preferred
3B	Dark tarnish	Multicolored with red and green, but no gray	Not preferred
4A	Corrosion	Transparent black, dark gray or brown with green	Not preferred
4B	Corrosion	Green barely showing	Not preferred
4C	Corrosion	Graphite or lusterless black glassy or jet black	Not preferred

[0044] As shown in columns 2 and 3 of table 3, very poor low temperature stability, labeled as solubility appearance is observed when 0.2 to 0.3% of Aldrithiol-4 was respectively added to the low phosphorous reference A base oil formulation in column 1. This poor oil compatibility issue correlates well with the poor hot tube deposit test results. As shown in columns 4 and 5 adding 0.2 and 0.3% of Aldrithiol-2 improves the oil compatibility but the copper corrosion becomes unacceptable in columns 4 and 5.

[0045] A similar evaluation was conducted when 0.25% dibenzyl disulfide described in comparative oil 5 is added to reference oil B base formulation as described in table 3. In this example, the 4-Ball wear and EP performance improves slightly, and the average friction and calculated wear scar area in High Frequency Reciprocating Rig (HFRR) reduces significantly comparing reference oil B with comparative oil 5. However, the copper corrosion at 250 °F for the 24 hour test conditions remains poor as shown by a 4A rating for comparative oil 5.

[0046] Now referring to table 6, any ratings in classification categories 2C-2E, 3 and 4 are not preferred as they can cause darkening and discoloration of the copper coupons that strongly indicate corrosive or near corrosive behavior. To achieve the additive synergy embodiment described in this invention, a very stringent preferred range is established for defining non-corrosive sulfur additives. Accordingly, dibenzyl disulfide and Aldrithiol-2 are not preferred due to their corrosive sulfur species and thus not recommended for low SAP engine oils.

[0047] Reference oil B is a ZnDTP free blend developed so different amounts of ZnDTP as well as other non-corrosive organic sulfur additives can be added to show comparative performance results. The base formulation is formulated with Group III base oils with a minimum of 120 viscosity index, a typical pour point of -15°C, a typical Noack of 15 and a typical sulfur of 10 ppm with a maximum sulfur content less than 30 ppm. Similarly, the base engine oil formulated is also formulated with GTL oils with a minimum of 135 viscosity index, a typical pour point of -17°C and a typical sulfur of less than 1 ppm.

[0048] Table 7, illustrates that very good oxidation/corrosion control can be achieved with combinations of non-corrosive sulfur additives, borated dispersants, high level of ashless antioxidants and low level of zinc dithiophosphates in a low Phosphorus engine oil. Columns one and two represent reference oils C and D and Columns 3, 4 and 5 represent respectively comparative oils 6, 7, and 8 which are variation of reference oil D. Reference oil C is a low SAP group III base oil with 0.1 weight percent phosphorous. Whereas, reference oil D and example comparative oils 6, 7, and 8 are Group III low SAP base oils with 0.05 weight percent phosphorous. Slight variations in the formulations are also documented in Table 7.

Table 7

Entry	1	2	3	4	5
	Reference oil C	Reference oil D	Comparative oil 6 Ashless DTC	Comparative oil 7 Sulfur ester	Comparative oil 8 DTC/Sulfur
ZnDTP Ashless AW additive Ashless AW additive	1%	0.50%	0.50% .25%VL981	0.50% .5%RC-2411	0.50% .25%VL981 .25%RC-2515
Borated Dispersant and Ashless Antioxidant	9.5%	9.5%	9.5%	9.5%	9.5%
Low ash/S/P Gp III	(0.10% P)	(0.05% P)	(0.05% P)	(0.05% P)	(0.05% P)
Solubility	Clear and bright	Clear and bright	Clear and bright	Clear and bright	Clear and bright
Appearance					
4 Ball Wear (D4172) 40Kg/1800rpm/.5 hr/93°C(200F)	0.59 5.7	0.62 7.0	0.57 5.0	0.57 4.8	0.53 3.7
4 Ball EP (D2783) 30°C/10sec./1760rpm	80 200 35.1	80 200 34.5	80 200 41.5	100 200 41.5	100 200 41.8
Cu Corrosion (D130-6) Cu Corrosion (D130-8)	1A 1A	1A 1B	1A 1B	1A 1B	1A 1A
Cu Corrosion (D130-9)	1A	1A	1B	1B	1B
PDSC (Ramp 10°C/min)	232	229.7	233.6	237.6	237.7
Hot Tube Test (288C/16hr)					
	3.5	3.8	3	2.8	3.3
HFRR 0.7Kg/60Hz/0.5mm/ 60min./75°C	0.139 0.174	0.147 0.181	0.118 0.173	0.105 0.173	0.121 0.154

(continued)

Entry	1	2	3	4	5
TBN	4.27	4.23	4.14	4.04	4.23
Sulfated Ash (wt%)	0.53	0.38	0.38	0.32	0.38
Boron (wt%)	0.017	0.017	0.017	0.017	0.017
Phosphorus (wt%)	0.1003	0.0507	0.0488	0.0482	0.0494
Zinc (wt%)	0.1118	0.0577	0.0573	0.0564	0.0569
Calcium (wt%)	0.0329	0.0332	0.0331	0.0328	0.0327
Magnesium (wt%)	0.0595	0.0496	0.0507	0.0505	0.0479
Copper (wt%)	<0.002	<0.002	<0.002	<0.002	<0.002
Chlorine (wt%)	0.0047	0.0049	0.0052	0.0053	0.0049
Sulfur (wt%)	0.2799	0.1783	0.2109	0.2198	0.2526
Pin-on-V Block		Pass	Pass	Pass	
500Lb, 210 minutes	Ave Scar (mm)	0.432	0.418	0.387	

[0049] The non-corrosive sulfur additives in comparative example embodiment oil 6 is an ashless dithiocarbamates ("DTC") called Vanlube™981. Vanlube™981 is an experimental additive available from R.T. Vanderbilt Chemical Company. Comparative oils 7 and 8 are specific sulfurized ester/olefins with low sulfur content with or without DTC as in comparative oils 7 and 8 and are respectively labeled RC-2411 and RC-2515. RC-2411 and RC-2515 are commercially available from Rhein Chemie Chemical Company] The good corrosion control is evidenced by 1A to 2B copper corrosion ratings under various conditions. The anti-oxidation performance of oils 6, 7, and 8 are slightly better than reference oil D. These properties are evidenced by Pressurized Differential Scanning Calorimetry ("PDSC") by about 4 to 8 degrees higher onset temperature. In the ramping method of PDSC of 10 degrees Celsius per minute, the higher the onset temperature, the better the resistance to oxidation. Generally, oxidation rates generally double with about 10 degrees Celsius increase in temperature. Therefore, these results can be translated into about 40 percent to 80 percent better in terms of control of viscosity or acid number increases or any other comparable measurements for control of oxidation.

[0050] When non-corrosive sulfur additives were added as in comparative embodiment oils 6, 7 and 8, the 4-Ball wear and 4-Ball EP results are all consistently better than the Reference oil D. A slight reduction in wear scar diameter of between 8 to 14 percent can be observed for the ASTM D4172 4-Ball wear conditions which translate into a 29 to 47 percent calculated reduction in wear volume shown as the K-factor. The last non-seizure load ("LNS") and load-wear index ("LWI") are 21 to 25 percent better for oils 6, 7, and 8 when compared to the performance of reference 4 in the 4-Ball EP tests.

[0051] The HFRR data showed that those non-corrosive sulfur additives can help maintain excellent frictional properties as well as wear reduction as evidenced by the lower average coefficients of friction of between 18 to 29 and approximately 4 to 15 percent smaller calculated scar area. Overall, example comparison oils 6, 7, and 8 formulated with 0.05% phosphorus plus non-corrosive sulfur additives provide favorable performance when compared to a typical engine oil, with full load of ZDDP as in the 1 weight percent reference oil C. This demonstrates the strong synergistic effect exists of the various embodiments of example oils 6, 7, and 8. All the additive components of examples 6, 7, and 8 are fully compatible with engine oils as evidenced by their clear and bright appearance in storage over a period of several months. Table 7 demonstrates satisfactory stability for oils containing non-corrosive sulfur additives. Lastly, the pin-on-V block shown as Falex wear test results correlate well with 4-Ball wear/EP results indicating better wear control with comparative oils 6 and 7 versus Reference oil D.

[0052] In Table 8, another low SAP oil was also evaluated. Comparative oil 9 is a low SAP Group III base with a final composition of 0.025 weight percent phosphorous.

Table 8

Entry		1	2	3	4
		Base	Reference E	Reference F	Comparative oil 9 DTC/S ester
ZnDTP Ashless AW additive	Secondary ZDDP	0%	0.25%	0.50%	0.25% .25%VL981 .25%RC-2411
Borated Dispersant and Ashless Antioxidant		9.5%	9.5%	9.5%	9.5%
Low ash/S/P Gp III		(0% P)	(0.025% P)	(0.05% P)	(0.025% P)
Solubility Appearance		C&B	C&B	C&B	C&B
4 Ball EP (D2783) 30C/10sec./1760rpm	LNS (Kg) Weld Ld (Kg) LWI	50 160 22.0	63 200 28.21	80 200 34.5	80 200 34.4
Cu Corrosion (D130-6) Cu Corrosion (D130-8)	3 hrs/250°F 3 hrs/99°C (210°F)/H ₂ O	1B 3A	1B 1A	1A 1B	1B 1B
HFRR 0.7Kg/60Hz/0.5mm/ 60min./75°C	Ave. Friction Calc. Sc. Area	0.144 0.211	0.127 0.173	0.147 0.181	0.126 0.173

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(continued)

Entry		1	2	3	4
TBN	D2896	4.12	5.45	4.23	4.52
Sulfated Ash (wt%)	D874	0.32	0.33	0.38	0.33
Boron (wt%)	D5185	0.017	0.017	0.017	0.017
Phosphorus (wt%)	D6443	<0.002	0.0244	0.0507	0.0258
Zinc (wt%)	D6443	<0.002	0.0287	0.0577	0.03
Calcium (wt%)	D6443	0.4859	0.0331	0.0332	0.0323
Magnesium (wt%)	D6443	0.0034	0.0501	0.0496	0.0508
Copper (wt%)	D6443	<0.002	<0.002	<0.002	<0.002
Chlorine (wt%)	D6443	0.0055	0.0048	0.0049	0.0049
Sulfur (wt%)	D6443	0.072	0.124	0.1783	0.1849

[0053] Equivalent average friction coefficients and calculated wear scar area were observed in HFRR tests, but much improved last non-seizure (LNS) load and load-wear index (LWI) were found in 4-Ball EP test when comparative oil 9 is compared to Reference oil E. Actually, the 4-Ball EP performance of comparative oil D is almost equivalent to that of Reference F where twice the amount of ZDDP is used as shown by a final phosphorus weight percent of 0.05. Although Reference oil E has strong 4-Ball EP performance, the HFRR data are not as good as comparative oil 9 and Reference oil E. This data clearly indicates that too much ZDDP can be antagonistic to the frictional property. The base formulation, shown as base in column of 1 of table 8 was also used to blend oils in Tables 6 and 7 and is fully described in Table 5 for reference.

[0054] Table 9 illustrates the evaluation of non-corrosive sulfur additives in low SAP commercial vehicle lubricants ("CVL"). Table 9 is formulated with a low SAP base oil with no phosphorous.

Table 9

Entry		1	2	3	4
Commercial Engine Oil		Reference Oil G	Comparative oil 10 Ashless DTC	Comparative oil 11 Borated GMO	Comparative oil 12 DTC + B-GMO
ZnDTP	Secondary ZDDP	0.30%	0.30%	0.30%	0.30%
Ashless Antiwear			0.3% VL 981		0.3% VL 981
Ashless Friction Modifier				0.5% B-GMO	0.5% B-GMO
Borated Dispersants and		9.71%	9.71%	9.71%	9.71%
Antioxidants					
Low ash/S/P		(0.03% P)	(0.03% P)	(0.03% P)	(0.03% P)
Solubility Appearance		C&B	C&B	C&B	C&B
4 Ball Wear 40Kg/1200rpm/60min./93 °C (200°F)	WSD (mm) K Factor	0.61 4.86	0.52 2.36	0.48 1.71	0.47 1.44
4 Ball Wear 40Kg/600rpm/30min./93°C (200°F)	WSD (mm) K Factor	0.41 2.67	0.40 2.46	0.33 0.57	0.40 2.46
4 Ball EP (D2783)	LNS (Kg)	80	100	80	80

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(continued)

Entry		1	2	3	4
30C/10sec./1760rpm	Weld Ld (Kg)	200	200	200	200
	LWI	33.6	41.2	34.0	34.2
Cu Corrosion (D130-6)	3hrs/121°C (250°F)	1A	1A	1A	1B
Cu Corrosion (D130-8)	3 hrs/99°C (210°F)/H ₂ O	1A	1A	1A	1A
Cu Corrosion (D130-9)	24 hrs/121°C (250°F)	1B	1B	1B	1B
TBN	D2896	7.88	8.04	8	7.98
Sulfated Ash (wt%)	D874	0.76	0.79	0.77	0.77
Phosphorus (wt%)	D6443	0.0286	0.0287	0.0291	0.0285
Zinc (wt%)		0.0324	0.0326	0.0332	0.0325
Calcium (wt%)		0.1983	0.1986	0.1983	0.1967
Magnesium (wt%)		0.0038	0.0025	0.0024	0.0024
Copper (wt%)		<0.002	<0.002	<0.002	<0.002
Chlorine (wt%)		0.008	0.008	0.0076	0.0077
Sulfur (wt%)		0.2237	0.2663	0.2233	0.2645

[0055] The composition of the base formulation of Table 9 is listed in Table 10 As shown in Table 10 and column 3 of Table 9, this base oil has no phosphorous. The base oil system consists of about 50% Group III and roughly about 20% Group I base oils. All oils containing ZDDP and other sulfur/boron additives in Table 9 and 11 are formulated from the base formulation. Similarly, another base formulation is formulated with GTL base oils. The base oil system consists of more than 50% GTL and less than 20% Group I base oils.

Table 10

	Descriptions	Commercial engine oil
Blend Code		LSAP01-A
Batch Number	ZnDTP free base blend	1
Base oil system	Mixed Group I & III base oils	Balanced
Additive system 1	Antioxidants	0.5
Additive system 2	Detergent/dispersants	17.8
Additive system 3	Viscosity modifiers	9
Additive system 4	Other performance additives	1.2

[0056] Now referring to table 9, in example oil 10, a 0.3 weight percent of a non-corrosive sulfur additive, in this example an ashless dithiocarbamate, is included in the engine oil formulated with 0.03 weight percent phosphorus as shown by reference oil G. The 4-Ball wear performance resulted in 2 to 15 percent improvement in wear reduction or wear scar diameter ("WSD") and 8 to 51 percent improvement in calculated wear volume or K-factor. Comparative oils 11 and 12 illustrate the synergists effect of combining borated GMO with borated dispersants.

[0057] Similarly, Table 11 illustrates the 4-Ball EP and Hot Tube performance of the combination of 0.3 percent ZDDP and 0.3 percent of a non-corrosive sulfur additive for comparative oil 13 versus the 0.6 percent ZDDP reference oil H. The total AW/EP additive treat rate is the same 0.6 percent and the EP performance is about the same, but the Hot Tube of Entry 4 is much better indicating a cleaner environment. The 4-Ball EP performance of comparative oil 13 is stronger than reference oil I with reduced ZDDP at 0.3% and the base oil in column 3 with 0% ZDDP.

Table 11

Entry		1	2	3	4
Commercial Engine Oil		Reference oil H	Reference oil I	Base	Comparative oil 13 Ashless DTC
ZnDTP Ashless Antiwear		0.60%	0.30%	0%	0.30% 0.3% VL 981
Ashless Friction Modifier					
Borated Dispersants		9.71%	9.71%	9.71%	9.71%
Antioxidants					
Low ash/S/P		(0.06% P)	(0.03% P)	0%P	(0.03% P)
Solubility Appearance		C&B	C&B	C&B	C&B
4 Ball EP (D2783)	LNS (Kg)	100	80	63	100
30C/10sec./1760rpm	Weld Ld (Kg)	200	200	160	200
	LWI	41.5	33.6	26.5	41.2
Cu Corrosion (D130-6)	3 hrs/12.1°C (250F)	1A	1A	1B	1A
Cu Corrosion (D130-8)	3 hrs/99°C (210F)/H ₂ O	1A	1A	1B	1A
Cu Corrosion (D130-9)	24 hrs/121 °C (250F)	1A	1B	2A	1B
Hot Tube Test (305C/16 hr)		4.0			1.5

[0058] In summary, a new low SAP engine oil system has been discovered based on very unique combinations of non-corrosive sulfur additives, low level of ZDDP, borated components, with preferably high level of ashless anti-oxidants. This formulation exhibits outstanding and unexpected performance to modern engines. One embodiment of this discovery provides an effective way to reduce the amount of ZDDP for contemporary engine oils while maintaining excellent wear, oxidation and corrosion protection. This unique component synergism concept is believed to be applicable to similar formulations containing low sulfur base oils of less than 300 ppm, borated additives with borated hydroxyesters such as borated GMO, and alternate organic borates such as borated dispersants, non-corrosive sulfur additives, and preferably with ashless antioxidants.

Claims

1. A 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 3,000 ppm sulfur, at least 80 ppm and less than 450 ppm boron, comprising:
 - a. a lubricating oil basestock;
 - b. from 0.01 to less than 8.0 weight percent of the composition of a organic boron containing additive;
 - c. from 0.1 to less than 4.0 weight percent of the composition of a non-corrosive ashless sulfur additive chosen from ashless dithiocarbamates;
 - d. from 0.2 weight percent to less than 2.0 weight percent of the composition of a zinc dithiophosphahte additive; and
 - e. less than 15 weight percent of the composition of a dispersant-detergent-inhibitor system.
2. 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.
3. 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.

4. The composition of claim 1, further comprising a metal detergent system providing a total base number (TBN) less than 9.
5. The composition of claim 4, having a TBN of less than 7.
6. The composition of claim 4, having a TBN of less than 5.
7. The composition of claim 1, further comprising a viscosity modifier additive.
8. The composition of claim 1, wherein the organic borate is a borated hydroxyl ester chosen from the group consisting of borated glycerol mono-oleate, borated glycerol di-oleate, borated glycerol tri-oleate, borated glycerol mono-cocotate, borated mono-talloate, borated glycerol mono-sorbitate, borated polyol esters and any combination thereof.
9. A lubricant additive system for a lubricant composition, comprising:
 - a. from 0.4 weight percent to less than 32 weight percent of the additive of an organic boron containing additive;
 - b. from 0.8 weight percent to less than 8.0 weight percent of the additive of a zinc dithiophosphate additive;
 - c. from at least 0.4 to less than 16.0 weight percent of the additive of a non-corrosive ashless sulfur additive chosen from the group consisting of ashless dithiocarbamates; and
 - d. less than 60 weight percent of the additive of a detergent-dispersant system
10. The lubricant additive of claim 9, further comprising an organic molybdenum additive.
11. The lubricant additive of claim 9, wherein the zinc dithiophosphate additive comprises a primary alkyl alcohol derived, or a secondary alkyl alcohol derived zinc dithiophosphate or a combination thereof.
12. Use of the composition according to claim 1 in an engine to achieve favorable anti-wear measured according to the 4-Ball wear tests and oxidation measured by Pressurized Differential Scanning Calorimetry.
13. Use of the composition according to claim 1 in an internal combustion engine.

Patentansprüche

1. Zusammensetzung mit mindestens 100 ppm und weniger als 630 ppm Phosphor, mindestens 105 ppm und weniger als 710 ppm Zink, mindestens 1000 ppm und weniger als 3000 ppm Schwefel, mindestens 80 ppm und weniger als 450 ppm Bor, umfassend:
 - a. einen Schmieröl-Grundstock;
 - b. von 0,01 bis weniger als 8,0 Gew.-% der Zusammensetzung eines Additivs, das organisches Bor enthält;
 - c. von 0,1 bis weniger als 4,0 Gew.-% der Zusammensetzung eines nicht-korrosiven, aschefreien Schwefeladditivs, das aus aschefreien Dithiocarbamaten ausgewählt ist.
 - d. von 0,2 Gew.-% bis weniger als 2,0 Gew.-% der Zusammensetzung eines Zinkdithiophosphatadditivs und
 - e. weniger als 15 Gew.-% der Zusammensetzung eines Dispergiermittel-Tensid-Inhibitorsystems.
2. Zusammensetzung nach Anspruch 1, wobei der Grundstock aus der Gruppe bestehend aus Gruppe II Grundstöcken, Gruppe III Grundstöcken, Gruppe IV Grundstöcken, Gruppe V Grundstöcken, Grundstöcke aus verflüssigten Gasen und irgendeiner Kombination davon ausgewählt ist.
3. Zusammensetzung nach Anspruch 1, wobei das Dispergiermittelsystem Additive umfasst, die aus der Gruppe bestehend aus borierten und nicht-borierten Succinimiden, Bernsteinsäureestern und -amiden, Alkylphenol-Polyamin-gekoppelten Mannich-Addukten und irgendeiner Kombination davon ausgewählt sind.
4. Zusammensetzung nach Anspruch 1, die ferner ein Metalltensidsystem umfasst, das eine Gesamtbasenzahl (TBN) von weniger als 9 zur Verfügung stellt.

5. Zusammensetzung nach Anspruch 4 mit einer TBN von weniger als 7.
6. Zusammensetzung nach Anspruch 4 mit einer TBN von weniger als 5.
- 5 7. Zusammensetzung nach Anspruch 1, die ferner ein viskositätsmodifizierendes Additiv umfasst.
8. Zusammensetzung nach Anspruch 1, wobei das organische Borat ein borierter Hydroxylester ist, der aus der Gruppe bestehend aus boriertem Glycerinmonooleat, boriertem Glycerindioleat, boriertem Glycerintrioleat, boriertem Glycerinmonococoat, boriertem Monotallowat, boriertem Glycerinmonosorbitat, borierten Polyolestern und irgendeiner
10 Kombination davon ausgewählt ist.
9. Schmiermitteladditiv system für eine Schmiermittelzusammensetzung, umfassend:
 - a. von 0,4 Gew.-% bis weniger als 32 Gew.-% des Additivs eines Additivs, das organisches Bor enthält;
 - 15 b. von 0,8 Gew.-% bis weniger als 8,0 Gew.-% des Additivs eines Zinkdithiophosphatadditivs;
 - c. von mindestens 0,4 bis weniger als 16,0 Gew.-% des Additivs eines nicht-korrosiven, aschefreien Schwefeladditivs, das aus der Gruppe bestehend aus aschefreien Dithiocarbamaten ausgewählt ist;
 - d. weniger als 60 Gew.-% des Additivs eines Dispergiermittel-Tensidsystems.
- 20 10. Schmiermitteladditiv nach Anspruch 9, das ferner ein organisches Molybdänadditiv umfasst.
11. Schmiermitteladditiv nach Anspruch 9, wobei das Zinkdithiophosphatadditiv Zinkdithiophosphat, das von einem primären Alkylalkohol oder einem sekundären Alkylalkohol abgeleitet ist, oder eine Kombination davon umfasst.
- 25 12. Verwendung der Zusammensetzung gemäß Anspruch 1 in einem Motor, um eine günstige Antiverschleißwirkung, bestimmt mittels des 4-Ball Verschleißtests, und eine günstige Oxidation, bestimmt durch eine unter Druck ausgeführte Differential-Scanning-Kalorimetrie, zu gewährleisten.
13. Verwendung der Zusammensetzung gemäß Anspruch 1 in einem Verbrennungsmotor.
- 30

Revendications

- 35 1. Composition ayant au moins 100 ppm et moins de 630 ppm de phosphore, au moins 105 ppm et moins de 710 ppm de zinc, au moins 1000 ppm et moins de 3000 ppm de soufre, au moins 80 ppm et moins de 450 ppm de bore, comprenant :
 - a. une huile lubrifiante de base ;
 - 40 b. de 0,01 à moins de 8,0 pour cent en poids de la composition d'un additif organique contenant du bore ;
 - c. de 0,1 à moins de 4,0 pour cent en poids de la composition d'un additif soufré sans cendres non corrosif choisi parmi les dithiocarbamates sans cendres ;
 - d. de 0,2 pour cent en poids à moins de 2,0 pour cent en poids de la composition d'un additif au dithiophosphate de zinc ; et
 - 45 e. moins de 15 pour cent en poids de la composition d'un système dispersant-détergent-inhibiteur.
2. Composition selon la revendication 1, dans laquelle l'huile de base est choisie dans le groupe constitué par les huiles de base du groupe II, les huiles de base du groupe III, les huiles de base du groupe IV et les huiles de base du groupe V, les huiles de base de transformation de gaz en liquides, et toutes les combinaisons de celles-ci.
- 50 3. Composition selon la revendication 1, dans laquelle le système dispersant comprend des additifs choisis dans le groupe constitué par les succinimides borés et non borés, les esters et amides d'acide succinique, les adduits de Mannich couplés à une alkylphénolpolyamine, et toutes les combinaisons de ceux-ci.
4. Composition selon la revendication 1, comprenant en outre un système détergent métallique fournissant un indice de basicité total (TBN) inférieur à 9.
- 55 5. Composition selon la revendication 4, ayant un TBN inférieur à 7.

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6. Composition selon la revendication 4, ayant un TBN inférieur à 5.

7. Composition selon la revendication 1, comprenant en outre un additif modificateur de viscosité.

5 8. Composition selon la revendication 1, dans laquelle le borate organique est un ester hydroxylé boré choisi dans le groupe constitué par le monooléate de glycérol boré, le dioléate de glycérol boré, le trioléate de glycérol boré, le monococoate de glycérol boré, le monotalloate boré, le monosorbitate de glycérol boré, les esters de polyols borés et toutes les combinaisons de ceux-ci.

10 9. Système additif lubrifiant pour une composition lubrifiante, comprenant :

- a. de 0,4 pour cent en poids à moins de 32 pour cent en poids de l'additif d'un additif organique contenant du bore ;
- b. de 0,8 pour cent en poids à moins de 8,0 pour cent en poids de l'additif d'un additif au dithiophosphate de zinc ;
- c. d'au moins 0,4 à moins de 16,0 pour cent en poids de l'additif d'un additif soufré sans cendres non corrosif
- 15 choisi dans le groupe constitué par les dithiocarbamates sans cendres ; et
- d. moins de 60 pour cent en poids de l'additif d'un système dispersant-détergent.

10. Additif lubrifiant selon la revendication 9, comprenant en outre un additif organique au molybdène.

20 11. Additif lubrifiant selon la revendication 9, dans lequel l'additif au dithiophosphate de zinc comprend un dithiophosphate de zinc dérivé d'un alcool alkylique primaire, ou dérivé d'un alcool alkylique secondaire, ou une combinaison de ceux-ci.

25 12. Utilisation de la composition selon la revendication 1 dans un moteur pour obtenir une anti-usure mesurée selon les tests d'usure à 4 billes et une oxydation mesurée par calorimétrie différentielle à balayage sous pression favorables.

13. Utilisation de la composition selon la revendication 1 dans un moteur à combustion interne.

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REFERENCES CITED IN THE DESCRIPTION

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