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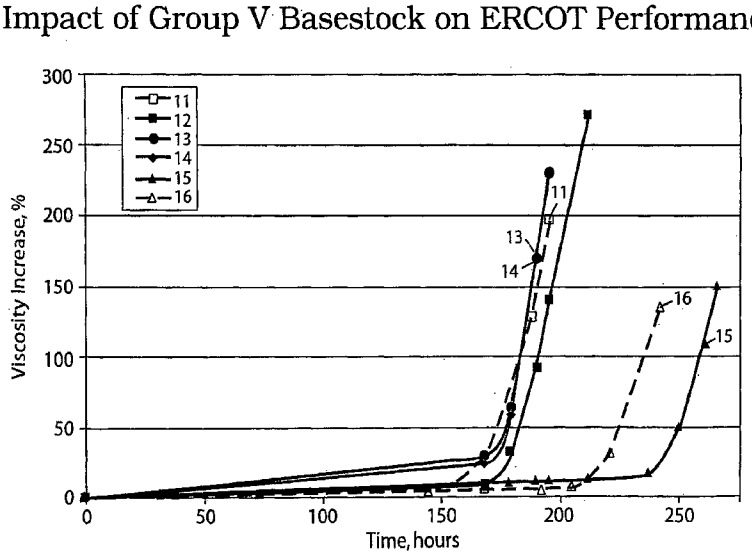
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(54) **Title:** LOW SULFUR, LOW ASH AND LOW PHOSPHOROUS LUBRICANT ADDITIVE AND COMPOSITION



(57) **Abstract:** A lubricating oil composition is disclosed. This composition, comprises a lubricating oil basestock, an alkylated aromatic additive of at least 0.01 and less than 20 weight percent of the composition, a dispersant-detergent-inhibitor system of less than 15 percent weight percent of the composition, a zinc dithiophosphate additive of at least 0.1 weight percent of the composition and no more than 1.0 weight percent of the composition, the composition having less than 630 PPM phosphorus, less than 710 PPM zinc, less than 5,000 PPM sulfur, less than 8 TBN5 less than 1.0 weight percent ash. 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.

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LOW SULFUR, LOW ASH AND LOW PHOSPHOROUS LUBRICANT ADDITIVE AND COMPOSITION

BACKGROUND OF THE INVENTION

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.

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 reasons include prolonging engine life by reducing engine wear and increasing the resistance to oxidation by reducing the engine's sludge/deposit through degradation. Many of the solutions to reducing wear have been strictly mechanical including building engines with wear resistant parts, modifying the contact geometry and adding special coating materials. Other solutions to improve cleanliness involve 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. Examples of additives components include, anti-wear and extreme pressure components, fuel economy improving components, friction reducers, dispersants, detergents, inhibitors and viscosity index improving additive. These

additives provide energy conservation, engine cleanliness and durability and high performance levels under a wide range of performance conditions including temperature, pressure and lubricant service life.

[0004] Throughout the world, legislation aimed at reducing automotive emissions is pushing 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. Sulfur is known to be poisonous to deNox catalysts and zinc/moly phosphates are key contributors to cause plugging of the exhaust particulate filters. The sulfur, ash and phosphorous components are commonly referred to as "SAP" or "SAPS" in the art. Accordingly, there is a need for a low sulfur, ash, and phosphorous component additive for lubricating oils that provides favorable performance properties.

[0005] Conventional engine oil technology relies heavily on zinc 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. ZnDTP is disadvantageous, especially at high treat rates. 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 since the wear protection demand for today's engine is extremely high and extremely rigorous chemical limits on ZnDTP.

[0006] Based on the above, there is a need for the development of a low phosphorus, low sulfur and low ash lubricating oil and additive with low levels of ZDNTP. Accordingly, this invention satisfies that need.

SUMMARY OF THE INVENTION

[0007] In a first embodiment, a lubricating oil composition is disclosed. This composition, comprises a lubricating oil basestock, an alkylated aromatic additive of at least 0.01 and less than 20 weight percent of the composition, a dispersant–detergent-inhibitor system of less than 15 percent weight percent of the composition, a zinc dithiophosphate additive of at least 0.1 weight percent of the composition and no more than 1.0 weight percent of the composition. The composition having less than 630 PPM phosphorus, less than 710 PPM zinc, less than 5,000 PPM sulfur, less than 8 TBN, less than 1.0 weight percent ash.

[0008] In a second embodiment, an additive composition for lubricating oils is disclosed. This composition comprises an alkylated aromatic additive of less than 20 weight percent of the composition, a dispersant–detergent-inhibitor system of less than 15 percent weight percent of the composition, a zinc dithiophosphate additive of at least 0.1 weight percent of the composition and no more than 1.0 weight percent of the composition.

[0009] 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 alkylated aromatic additive of at least 0.01 and less than 20 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 0.1 weight percent of the composition and no more than 1.0 weight percent of the composition, wherein the composition has

less than 630 PPM phosphorus, less than 710 PPM zinc, less than 5,000 PPM sulfur, less than 8 TBN, less than 1.0 weight percent ash and a lubricating an engine with the composition to achieve favorable anti-wear properties, oxidation resistance and cleanliness.

BRIEF DESCRIPTION OF THE DRAWING

[0010] Figure 1 illustrates the viscosity increase profiles for a Group V base stock with different additive embodiments.

DETAILED DESCRIPTION OF THE INVENTION

[0011] This invention relates to engine lubricants formulated with functional fluids and/or additives and compositions. One embodiment is a low ash, sulfur, phosphorus engine lubricant compositions comprising oils of lubricant viscosity containing a minor amount of multi-functional anti-wear/anti-oxidation additive. The anti-wear/anti-oxidation additive may be a functional fluid of certain sulfur-containing alkylated aromatics or mixtures of sulfur and non-sulfur alkylated aromatics.

[0012] 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.

[0013] 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 and corrosion control, under the most severe operating conditions.

[0014] Traditionally, antiwear and extreme pressure additives have been chosen from zinc dithiophosphates, phosphites, sulfurized olefins/esters, sulfur-nitrogen additives and similar components. Friction reducers have been chosen from molybdenum additives including Moly dithiocarbamates ("MoDTC"), Molydithiophosphates ("MoDTP"), and other organic moly-containing compounds), amines, amides and similar components. Metal detergents have been chosen from calcium or magnesium phenates, sulfonates, salicylates, carbonates and similar components. Antioxidants have been chosen from hindered phenols, arylamines, dihydroquinolines, phosphites and thiol/thiolester/disulfide/trisulfide compounds. These additives are rich in sulfur, phosphorus and/or ash content as they form strong chemical films to the metal surfaces.

[0015] Diphenyl sulfide, diphenyl oxide, biphenyl, diphenylmethane, and many other related analogs are utilized as heat transfer fluids since they are stable materials that can resist thermal stress under severe conditions. However, the direct use of the non-alkylated aromatics in lubricants are relatively limited to low concentrations due to the limited compatibility with other hydrocarbon base stocks.

[0016] Alkylated aromatics, especially sulfur containing alkylated aromatics have been developed by applying alkylation technique to functional or non-functional aromatics providing good thermal-oxidative stability while maintaining good compatibility. These alkylated aromatics have excellent compatibility with other base oils and superb solvency and stability making them unique synthetic oils including Group V or functional fluids. U.S. Patent Nos.

5,105,042, and 5,177,284 disclose the process conditions of making alkylated naphthalenes. US. Patent Nos. 5,372,734, 5,552,071, 5,371,248, and 5,286,396 disclose the preparation of alkylated benzothiophene-derived lubricants, alkylated diphenyl ether lubricants, alkylated benzofuran-derived lubricants and alkylated phenoxathins for lubricants.

[0017] The prior art literature referenced above fails to disclose the use of alkylated aromatics in a low SAP environment with high quality base stocks. In addition, the prior art fails to disclose the favorable anti-wear/anti-oxidation properties and unexpected, superb cleanliness features which make the alkylated aromatics functional fluids suitable for low ash and low phosphorus engine oils. In different embodiments the preferred degree of alkylation varies ranging from mono- to di- to multiple alkylates. However, mono-alkylates are more desirable than others. The desired carbon to sulfur and oxygen ratio is in a range from 10:1 to 400:1 on atomic basis with a more preferred range of 20:1 to 200:1 and an even more preferred range of 25:1 to 100:1.

[0018] In one embodiment, lubricating oils, especially synthetic oils, when blended with low level of zinc dithiophosphates and/or optionally molybdenum friction modifiers can provide substantial reductions in wear and oxidation. These combinations provide improvements in engine service life and durability with excellent overall performance benefits. In addition, these combinations typically minimize deleterious effects such as instability, undesirable high viscosity, high friction, deposits and the like, when added to lubricating oils. Combinations of alkylated aromatics with low level of sulfur-free detergents such as, salicylates, ashless phenols and arylamines, and boron containing additives, and any combination thereof further provide synergies.

[0019] In another embodiment, novel highly stable, sulfur containing, alkylated aromatics have been synthesized and evaluated as functional fluids and/or additives for lubricants including low ash, sulfur, phosphorus engine lubricants. The novel compositions possess multi-functional anti-wear/anti-oxidation/cleanliness/friction reducing-fuel economy properties. In addition, these combinations can improve the wear protection of most lubricants used in both automotive and commercial diesel engine applications, while maintaining desirable viscometrics. In this embodiment, the composition is favorable suited for low ash passenger car engine oils. When used as Group V base stocks including functional fluids or co-base stocks, the typical alkylated aromatic concentration is in the range of 0.1 to 20 wt%, preferably 0.5 to 8 wt%. When used as lubricant additives, the typical treat, sometimes referred to as treat rate, is in the range of 0.01 to 4 wt% with a more preferred range of 0.02 to 2 wt% and an even more preferred range of 0.1 to 1 wt%. The treat for an additive is based on the weight percent of the active ingredient in the desired lubricant.

[0020] In a preferred embodiment, this invention is referred to as a low ash, sulfur and phosphorus engine oil formulated with extremely stable, sulfur functional fluids. However, this invention is not limited to sulfur functional fluids. Other suitable functional fluids include alkylated diphenyl sulfides, alkylated diphenyl disulfides/polysulfides, alkylated naphthalenes, alkylated benzenes, alkylated diphenyl ether, alkylated diphenylmethanes, alkylated phenothiazines, alkylated phenoxazines, alkylated benzothiazines, alkylated benzothiophenes, alkylated thiophenol, alkylated thianthrene, similar and related components, and any combinations thereof.

[0021] Preferably, the highly stable engine oil fluids has a very low viscosity of less than 20 cSt at 400°C, with fully saturated structures with an Iodine value less than 1, low volatility of less than 15 wt% loss in Noack and even more

preferably high resistance to oxidation/thermal breakdown. The most preferred embodiment provides favorable viscometrics for engine oils since fuel economy is heavily influenced by viscometrics. A variety of alkylated aromatics are suitable for different embodiments of this invention. For example, ADPS-1 is an experimental synthetic fluid made by the alkylation of diphenyl sulfide with long chain alkenes over the USY catalyst.

[0022] In a preferred embodiment, the lubricant compositions, besides being built around the unique sulfur containing alkylated aromatics, also contain low levels of zinc, phosphorus and sulfur components. Persons skilled in the art 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, 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.

[0023] In some embodiments, we have discovered that these new synergistic combination has favorably improved lubricant performance parameters while maintaining excellent compatibility to exhaust after-treatment devices. The core of the preferred embodiment comprises stable sulfur containing functional fluid and a significantly reduced amount of ZnDTP and metal detergents, and enhanced amount of ashless anti-oxidants and friction modifiers. The resulting formulation provides an engine oil lubricant with less than 630 PPM phosphorus, less than 710 PPM zinc, less than 5,000 PPM sulfur, less than 8 TBN, less than 1.0 wt% ash and high nitrogen/zinc or nitrogen/phosphorus ratios. In one

embodiment, the general formulation of the low SAP engine oil containing the alkylated aromatics is summarized in Table 1.

Table 1

Component Type	Wt%	Elements in Formulated Oils (ppm) + Other Restrictions
Sulfur aromatic functional fluid/additive	0.01 - 20.0%	< 4500 ppm sulfur, volatility <10 wt%
Zinc dithiophosphate additive	0.1 - 1.0%	100 - 630 ppm phosphorus, 105-710 ppm zinc
Dispersant-detergent-inhibitor system	<15.0%	<1800 ppm nitrogen, <1.0 wt ash, TBN <8, N/P >1 (wt/wt) N/Zn >1 (wt/wt)
Molybdenum additive	0 -2.0%	<210 ppm molybdenum
Boron additive	0 -8.0%	<400 ppm boron

[0024] These components can be used with a variety of base stocks, including group I, II, III, IV, and V, and 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.

[0025] Base stocks having a high paraffinic/naphthenic and saturation nature (>90 wt%) 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.

[0026] 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.

[0027] 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 embodiment, 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.

[0028] 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.

[0029] The antioxidants include hindered phenols, arylamines, low sulfur peroxide decomposers and other related components. 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.

[0030] ZnDTP is widely utilized for providing anti-wear protection to modern engine oils with few other components sharing similar functions. As the levels of ZnDTP are reduced, the wear protection must rely on a new anti-wear system. Preferably, that new anti-wear system will be low in ash, sulfur and substantially free of phosphorus components to provide favorable performance with the new exhaust systems. Typically, the sulfur-containing alkylated aromatics possess moderate level of highly stable, less volatile sulfur, that is different from the volatile sulfur liberated from zinc dithiophosphates. Therefore, these sulfur-containing alkylated aromatics are harmless to exhaust after-treatment devices but effective in protecting engine parts against wear mechanism.

[0031] In one embodiment, the principle advantage of this new invention is the synergistic combination of multi-functional, alkylated sulfur aromatics and small

amount of zinc dithiophosphate additives that favorably provides oxidation, corrosion, seal stability and frictional properties. Even more important is the ability to provide anti-wear protection with lower levels of sulfur, phosphorus and zinc in the engine oil formulations are significantly less than that typically used in today's engine oils. Another principle advantage of this invention is the unique combination of alkylated sulfur aromatics with boron-containing additives for superb cleanliness features, such as the effective control of undercrown deposit formation. Another principle advantage in one embodiment is the synergistic combination of alkylated sulfur aromatics and low level of sulfur-free metal detergents including calcium and magnesium salicylates and carbonates. An additional synergistic combination is an alkylated sulfur aromatics with ashless anti-oxidants to improve oxidation protection and extended drain intervals. Another potential advantage is the unique combination embodiment of alkylated sulfur aromatics with friction reducers to improve fuel economy.

Examples

[0032] Table 2 below discloses bench and tribology testing data for alkylated diphenyl sulfide (experimental sample "ADPS-1") in Passenger Vehicle Engine Oils.

Table 2

Lubricant Example		1	2	3
ADPS-1 =93-59386 01-60665 = 0% P EO		 1.0% ZnDTP 99% 01-60665	 0.5% ZnDTP 99.5% 01-60665	4% ADPS-1 0.5% ZnDTP 95.5% 01-60665
Phosphorus, %		0.10	0.05	0.05
Sample Number		02-713	02-714	02-33611
Solubility Appearance		C & B	C & B	C & B
4 Ball Wear 40Kg/1200rpm/60min./200 F	WSD (mm) K Factor	0.44 1.11	0.48 1.62	0.42 0.78
4 Ball EP (D2783) 30C/10sec./1760rpm	LNS (Kg) Weld Ld (Kg) LWI	80 200 35.1	80 200 34.5	100 200 41.7
Cu Corrosion (D130-9)	24 hrs/250F	1A	1A	1A
PDSC (Ramp 10C/min)	Onset T (C)	232	229.7	235.1
288° C, 16hrs Tube Rating (1 = Clean)		3.8	3.5	3.3

HFRR 0.7Kg/60Hz/0.5mm/ 60min./75C	Scar X/Y (mm) Calc. Sc. Area	0.317/0.7 0.174	0.3/0.767 0.181	0.26/0.70 0.147

D2896	TBN	4.27	4.23	-
D874 (wt%)	Sulfated Ash	0.53	0.38	0.35
D6443 (wt%)	Phosphorus	0.1003	0.0507	0.0497
D6443 (wt%)	Zinc	0.1118	0.0577	0.0572
D6443 (wt%)	Calcium	0.0329	0.0332	0.0317
D6443 (wt%)	Magnesium	0.0595	0.0496	0.0482
D6443 (wt%)	Copper	<0.002	<0.002	<0.002
D6443 (wt%)	Chlorine	0.0047	0.0049	0.0048
D6443 (wt%)	Sulfur	0.2799	0.1783	0.4761

[0033] The base formulation (01-60665) is a phosphorus-free, partially formulated engine oil with Group III base stocks, ashless antioxidants, ashless

dispersants, metal detergents, defoamants, viscosity modifiers and other performing components.

[0034] As illustrated in the above Table 2, very good anti-wear, anti-oxidation and corrosion control can be achieved with sulfur-derived alkylated aromatics in the low P passenger vehicle lubricants ("PVL"). As shown in the High Frequency Reciprocating Rig ("HFRR") and Four-Ball EP wear test, the functional fluids formulated low SAPS engine oils can help to improve anti-wear properties evidenced by the low wear scar areas and wear coefficients ("K Factor") measured.

[0035] In addition, there are synergistic benefits of low SAP additives with Group II and higher base stocks. The synergistic benefits include favorable cleanliness, wear properties, catalyst compatibility and oxidation.

[0036] Comparing lubricant example 1 by adding 1000 ppm phosphorus and lubricant example 2 by adding 500 ppm phosphorus, noticeable anti-wear performance differences can be seen, which are believed to be directly affected by ZnDTP concentrations. Typically, the more ZnDTP, the better anti-wear protection. However, when 4% alkylated diphenyl sulfide was added to make lubricant example 3, which has the same level of 500 ppm phosphorus as lubricant example 2, a significant 19% reduction of wear scar areas and an observed 52% reduction in wear coefficients was measured.

[0037] The Table 2 results for lubricant example 3 are even better when compared to lubricant example 1. In the presence of more ZnDTP, for example 1000 ppm P in lubricant example 1 versus 500 ppm P in lubricant example 2, a reduction of calculated scar area from 0.18 mm^2 to 0.174 mm^2 is expected.

However, a significant reduction to 0.147 mm^2 range for lubricant example 3 is an unexpected result.

[0038] In the Four-Ball EP test, lubricant example 3 also demonstrated superb load carrying property as evidenced by the higher last non-seizure load of 100 kg and a greater Load Wear Index of 41.7 when compared to lubricant examples 1 and 2. The improvement in Load Wear Index from lubricant examples 2 to lubricant examples 3 is almost 21%. The high temperature stability of lubricant example 3 is also shown by the Pressured differential Scanning Calorimetry ("PDSC") data on ramping method. Comparing lubricant examples 2 to 3, the onset temperature is raised from 229.7°C to 235.1°C respectively providing 54% better oxidation control, assuming the oxidation rates doubled with every 10 °C increase in temperature. Therefore, lubricant example 3 could provide 54 % better oxidation resistance than lubricant 2 if we quantify the control by viscosity or acid value increases or any other measurements.

[0039] The hot tube test is also used to assess cleanliness features of engine oils under high temperature oxidation conditions. As exhibited in Table 2, lubricant example 3 has slightly better cleanliness result than both lubricant examples 1 and 2 as the lower the rating, the better the cleanliness. This data illustrates that more ZnDTP reduces lubricant cleanliness as lubricant example 1 has the worst result as ZnDTP is known to decompose to various species at elevated temperatures. The copper corrosion results indicated that adding ADPS to the engine oil formulations causes no adverse impact to their copper corrosivity. Adding ADPS will certainly increase the sulfur content of the engine oil. However, the final sulfur level of 0.476 wt% for lubricant example 3 is still under the current ILSAC GF-4 standard of 0.5 wt%. In conclusion, exceptionally good oxidative stability and low wear in low phosphorous engine oils can be achieved by using alkylated sulfur aromatics such as, ADPS thus providing favorable performance properties suitable for modern engine oils.

[0040] The outstanding anti-oxidation/anti-wear performance is further verified by another set of Four-ball EP and hot tube tests. Table 3 is a Table similar to Table 2 comparing lubricant examples 1 and 2 from Table 2 with additional lubricant example tests. As shown in the Table 3 data, when the low phosphorus engine oil was formulated with extremely low level of ZnDTP such as, 0.025 wt% phosphorous, the last non-seizure load dropped to 63 kg and the load wear index also dropped to 28.2 comparing table 4 lubricant example 4 versus lubricant examples 2 and 1. This is clearly not desirable as poor EP performance indicates weak load carrying property. Adding a conventional sulfur EP additive, Rhein-Chemie's RC-2411™, could not improve the load carrying property significantly as shown in lubricant example 5. However, as shown in example 6, adding 2 wt% of ADPS to the base engine oil formulation provides significant improvement.

Table 3

Lubricant Example		1	2	4	5	6
Funct'lized fluids or cobase oil						2% ADPS-1
01-60665 = 0% P EO		1% ZnDTP 99% 01-60665	0.5% ZnDTP 99.5% 01-60665	0.25% ZnDTP 99.75%01-60665	0.25% ZnDTP 99.5%01-60665	0.25% ZnDTP 97.5%01-60665
					.25%RC2411	.25%RC2411
		(0.10% P)	(0.05% P)	0.025% P	0.025% P	0.025% P
Sample Number		02-713	02-714	02-31205	02-35335	02-35333
Solubility/ Appearance		C & B	C & B	C & B	C & B	C & B
4 Ball EP (D2783) 30C/10sec./1760rpm	LNS (Kg)	80	80	63	63	80
	Weld Ld (Kg)	200	200	200	200	250
	LWI	35.1	34.47	28.21	28.41	36.16
Cu Corrosion (D130-8)	3hrs/ 210F/H2O	1A	1B	1A	1B	1B
Cu Corrosion (D130-9)	24 hrs/250F	1A	1A	2A	2B	2A
288° C, 16hrs Tube Rating (1 = Clean)		3.8	3.5		2.8	2.8

D2896	TBN	4.27	4.23	5.45	4.11	5.59
D874 (wt%)	Sulfated Ash	0.53	0.38	0.33	0.33	0.32
D6443 (wt%)	Phosphorus	0.1003	0.0507	0.0244	0.0245	0.0246
D6443 (wt%)	Zinc	0.1118	0.0577	0.0287	0.0278	0.028
D6443 (wt%)	Calcium	0.0329	0.0332	0.0331	0.0331	0.0325
D6443 (wt%)	Magnesium	0.0595	0.0496	0.0505	0.0501	0.0514
D6443 (wt%)	Copper	<0.002	<0.002	<0.002	<0.002	<0.002
D6443 (wt%)	Chlorine	0.0047	0.0049	0.0048	0.005	0.0049
D6443 (wt%)	Sulfur	0.2799	0.1783	0.124	0.1463	0.2988

[0041] RC-2411™ is an aliphatic sulfur additive, which has even higher sulfur content than the ADPS used in lubricant example 6 of table 3. Some sulfur-containing additives, including aliphatic sulfur species, could provide equivalent favorable antiwear/extreme pressure performance as alkylated sulfur aromatics providing that they are thermally stable and non-corrosive. However, many sulfur-containing aliphatic sulfur additives, used by themselves alone, are not sufficient to provide anti-wear protection while maintaining satisfactory anti-corrosion properties as demonstrated in example 4 and 5 of table 3. Lubricant example 6 (with levels of 0.025 wt% phosphorus) of table 3 illustrates the last non-seizure load and the load-wear index improved to be equivalent to or better than the lubricant example 1 with levels of 0.1 wt% phosphorus engine oil. In addition, the weld load increased to 250 kg when comparing lubricant example 6 to lubricant example 1. Lubricant example 6 shows a synergistic benefits of using an ADPS aliphatic sulfur compound with group II and higher base stock.

[0042] These results are exceptional favorable in the presence of additive treat level of ADPS. As stated before, the hot-tube test is used to measure the relative cleanliness of engine oils with the higher the rating on the scale form 1 to 9, the dirtier the lubricant. Lubricant example 6, ADPS formulated oil, demonstrated better cleanliness than oils with higher levels of ZnDTP including lubricant examples 1 and 2. As shown in table 3 for lubricant example 5, the total sulfur of the ADPS containing formulation is below the ILSAC GF-4 requirements.

[0043] Figure 1 illustrates the viscosity increase profiles for a Group V base stock with different additive embodiments. Reference numerals 11 and 12 represent viscosity increase profiles for two runs for 7 wt% alkylated naphthanates additives. Reference numeral 13 represents viscosity increase profiles for 7 wt% of TMP ester and 14 represents a viscosity increase profile for 7% dibasic acid ester (adipate ester). Finally, the reference numerals 15 and 16

represent viscosity increase profiles for 7 wt% and 1 wt% ADPS additive respectively.

[0044] Figure 1 demonstrates that alkylated sulfur aromatics 15 and 16 can provide favorable performance advantages in oxidation control versus other group V synthetic fluids in the presence of equal amount of ashless anti-oxidants. This performance benefit was shown using the ExxonMobil Research Catalytic Oxidation Test ("ERCOT"). In the ERCOT test, 50 ppm of soluble iron is added to 100g of test fluid. The fluid is heated at 165°C while air is bubbled through the sample at a rate of 1L/hour. The kinematic viscosity at 40°C of the catalyzed oil is monitored as a function of time. When the antioxidants in the fluid are consumed, a significant increase in viscosity is observed. The base engine oil formulation has about 450 ppm phosphorus from reduced ZnDTP, and a total of 1.0 wt% hindered phenol and alkylated arylamine ashless anti-oxidants. In the presence of 7 wt% experimental ADPS-1, the oil induction time has been increased by 70-80 hours in the ERCOT test. Even present in just 1 wt% ADPS, the oil induction time can still be 40-50 hours longer than synthetic esters or alkylated naphthalenes. Therefore, Figure 1 illustrates the strong synergy of ADPS with an ashless anti-oxidant.

[0045] Another important performance feature of the current invention is after-treatment compatibility. To measure after-treatment compatibility, a series of engine oil samples were prepared where each sample contained a single sulfur containing species as shown in Table 4. Thus, the fully formulated engine oils studied contained only the single source of sulfur listed in Table 4. Secondary ZDDP, Primary ZDDP, Thiadiazole, Sulfur-phenol, sulfurized olefin, and ADPS were studied. These fully formulated engine oils contain typical non-sulfur containing performance additives such as hindered phenols, alkylated arylamines, ashless dispersants, metal and ashless detergents, friction modifiers, defoamants,

corrosion inhibitors, copper passivators, pour point depressants and seal swell agents. The single sulfur containing species in Table 4 were the last components added. Samples were volatilized at 250°C for 15 minutes using D 5800 and a comparison of the percent sulfur lost between the new oil and the oil remaining at the end of the volatilization test was made. In a direct comparison of Table 4, primary and secondary zinc dithiophosphates volatized at 12.0% and 37.0% respectively. Commercial sulfur-containing antioxidants volatized at 6.1%, thiadiazole at 21.8%, molybdenum dithiocarbamate at 12.7%, and sulfurized olefin additive at 10.5%. ADPS exhibited extraordinarily low volatility at 2.0%. This data provides strong evidence for the favorable low emission performance benefit of using ADPS in engine oils. In this embodiment, the invention provides favorable benefit in sustaining the useful life of the after-treatment system by identifying a method to reduce volatile sulfur species to the exhaust system.

Table 4

15 Minute D5800 Sulfur Volatilization Study	
	Sulfur Volatilized, %
2° ZDDP	37.0
Thiadiazole	21.8
Moly Dithiocarbamate	12.7
1° ZDDP	12.0
Sulfurized Olefin	10.5
Sulfur Phenol*	6.1
ADPS	2.0

[0046] All alkylated aromatics dissolved easily in engine oils and remained clear and bright on the shelf at ambient temperatures over period of six months or longer. Apparently, the stability of alkylated sulfur aromatics-containing oils is satisfactory and they cause no adverse effects to compatibility in the presence of other commonly used additives in engine oil compositions.

[0047] Besides unique, synergistic additive effects, it is evidenced that other highly refined, low sulfur Group II/III based oils including both hydro-processed oils and HDP as well as other Group IV/V synthetic base oils can be used to achieve favorable lubricant performance.

[0048] In summary, in one embodiment, we have discovered a new class of low sulfur, low ash and low phosphorous ("SAP") engine oils with favorable oxidation and wear protection based on alkylated sulfur-containing aromatics. This offers an effective way to reduce the amount of ZnDTP for contemporary engine oils while maintaining excellent wear, friction and oxidation performance as well as meeting stringent emission requirements. This embodiment further provides favorable synergisms to similar formulations comprising alkylated sulfur aromatics, base oils of less than 300 ppm sulfur, low levels of ZnDTP wherein the ZnDTP contributes less than 630 ppm phosphorus and/or less than 710 ppm zinc, sulfur containing additives and molybdenum containing additives.

CLAIMS:

1. A composition, comprising,

a. a lubricating oil basestock;

b. an alkylated aromatic additive of at least 0.01 and less than 20 weight percent of the composition;

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

d. a zinc dithiophospahte additive of at least 0.1 weight percent of the composition and no more than 1.0 weight percent of the composition

e. the composition having less than 630 PPM phosphorus, less than 710 PPM zinc, less than 5,000 PPM sulfur, less than 8 TBN and less than 1.0 weight percent ash.

2. The composition of claim 1 further comprising a molybdenum additive wherein the molybdenum additive is less than 2 weight percent of the composition.

3. The composition of claim 1 further comprising a boron additive wherein the boron additive is less than 8 weight percent of the composition.

4. The composition of claim 1 further comprising a sulfur additive.

5. The composition of claim 1 wherein the composition has a viscosity less than 20 cSt at 400 °C, fully saturated structures with an iodine value less than 1 and a volatility less than 15 weight percent loss in Noack.

6. The composition of claim 1 wherein the alkylated aromatic concentration is at least 0.5 weight percent and no more than 8 weight percent of the composition.

7. The composition of claim 1 further comprising additives to provide favorable lubricant performance wherein the additives are chosen form the group comprising zinc dithiophosphates, 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 and others including contemporary dispersant-detergent-inhibitor (DDI) additive packages, and any combination thereof.

8. 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.

9. 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.

10. The composition of claim 1 wherein the alkylated aromatic additive is a mano-alkylate comprising a carbon and oxygen atomic ratio of at least 10:1 and less than 400:1.

11. The composition of claim 1 wherein the alkylated aromatic additive is an alkylated diphenyl sulfide.

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

13. The composition of claim 1 further comprising a sulfur free metal detergent.

14. The composition of claim 11 further comprising an aliphatic sulfur additive.

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

a. an alkylated aromatic additive of less than 20 weight percent of the lubricant composition;

b. a sulfur-free detergent-dispersant system of less than 15 percent weight percent of the lubricant composition;

c. a zinc dithiophospahte additive of at least 0.1 weight percent of the composition and no more than 1.0 weight percent of the lubricant composition;

d. an alkylated diphenyl sulfide additive

16. The lubricant additive of claim 15 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.

17. The lubricant additive of claim 15 further a molybdenum additive.

18. The lubricant additive of claim 15 wherein the molybdenum additive is an organic molybdenum additive.

19. The lubricant additive of claim 17 further comprising a non volatile sulfur additive.

20. A method comprising

a. obtaining a composition comprising a lubricating oil basestock, an alkylated aromatic additive of at least 0.01 and less than 20 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 0.1 weight percent of the composition and no more than 1.0 weight percent of the composition, wherein the composition has less than 630 PPM phosphorus, less than 710 PPM zinc, less than 5,000 PPM sulfur, less than 8 TBN, less than 1.0 weight percent ash;

b. lubricating an engine with the composition to achieve favorable anti-wear properties, oxidation resistance and cleanliness.

21. A method for reducing sulfur in exhaust gasses in an internal combustion engine, comprising:

a. obtaining a composition comprising a lubricating oil base stock, an alkylated aromatic additive of at least 0.01 and less than 20 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 0.1 weight percent of the composition and no more than 1.0 weight percent of the composition, wherein the composition has less than 630 PPM phosphorus, less than 710 PPM zinc, less than 5,000 PPM sulfur, less than 8 TBN, less than 1.0 weight percent ash;

b. lubricating the internal combustion engine with the composition.

Figure 1
Impact of Group V Basestock on ERCOT Performance

