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(54) USE OF A LUBRICANT FOR PREVENTING OR REDUCING LOW SPEED PRE-IGNITION

VERWENDUNG EINES SCHMIERSTOFFS ZUR VERHINDERUNG ODER REDUZIERUNG DER FRÜHZÜNDUNG BEI NIEDRIGEN DREHZAHLEN

UTILISATION D'UN LUBRIFIANT À RÉDUIRE OU PRÉVENIR LE PRÉALLUMAGE À VITESSE BASSE

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(56) References cited:
US-A1- 2009 082 233

- **KAZUO TAKEUCHI ET AL: "Investigation of Engine Oil Effect on Abnormal Combustion in Turbocharged Direct Injection - Spark Ignition Engines", SAE INTERNATIONAL JOURNAL OF FUELS AND LUBRICANTS, vol. 5, no. 3, 30 January 2012 (2012-01-30), pages 1017-1024, XP055203823, ISSN: 1946-3960, DOI: 10.4271/2012-01-1615**
- **AKRAM ZAHDEH ET AL: "Fundamental Approach to Investigate Pre-Ignition in Boosted SI Engines", SAE INTERNATIONAL JOURNAL OF ENGINES, vol. 4, no. 1, 12 April 2011 (2011-04-12), pages 246-273, XP055203891, ISSN: 1946-3944, DOI: 10.4271/2011-01-0340**

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Description

FIELD

[0001] This disclosure relates to the use of a formulated oil as lubricating oil for preventing or reducing low speed pre-ignition (LSPI) in an engine lubricated with a lubricating oil by using as the lubricating oil a formulated oil that has at least one zinc-containing compound or at least one antiwear agent, preferably at least one zinc dialkyl dithiophosphate compound derived at least in part from a secondary alcohol, present in a particular amount in the formulated oil. The lubricating oils of this disclosure are useful as passenger vehicle engine oil (PVEO) products.

BACKGROUND

[0002] Pre-ignition in a flame propagation (or "spark-ignition") engine describes an event wherein the air/fuel mixture in the cylinder ignites before the spark plug fires. Pre-ignition is initiated by an ignition source other than the spark, such as hot spots in the combustion chamber, a spark plug that runs too hot for the application, or carbonaceous deposits in the combustion chamber heated to incandescence by previous engine combustion events.

[0003] Many passenger car manufacturers have observed intermittent pre-ignition in their production turbocharged gasoline engines, particularly at low speeds and medium-to-high loads. At these elevated loads, pre-ignition usually results in severe engine knock that can damage the engine. The cause of the pre-ignition is not fully understood, and may in fact be attributed to multiple phenomena such as hot deposits within the combustion chamber, elevated levels of lubricant vapor entering from the PCV system, oil seepage past the turbocharger compressor seals or oil and/or fuel droplet auto-ignition during the compression stroke.

[0004] Pre-ignition can sharply increase combustion chamber temperatures and lead to rough engine operation or loss of performance. Traditional methods of eliminating pre-ignition include, for example, proper spark plug selection, proper fuel/air mixture adjustment, and periodic cleaning of the combustion chambers. Hardware solutions such as cooled exhaust gas recirculation (EGR) are known, but these can be costly to implement and present packaging problems.

[0005] Low speed pre-ignition (LSPI) is a type of abnormal combustion affecting engines operating at high brake mean effective pressure (BMEP) and low engine speed (RPM). Downsized, downspeeded, turbocharged engines are most susceptible to operating under these engine conditions and are thus more susceptible to LSPI. SAE International Journal of Fuels and Lubricants Vol.5, no.3, pages 1017-1024 and SAE International Journal of Engines, vol.4, no.1, pages 246-273 provides studies on that problems. As the automobile industry continues to move towards further downsizing, downspeeding, and increased turbocharging to increase vehicle fuel economy and reduce carbon dioxide emissions, the concern over LSPI continues to grow.

[0006] The further development of downspeeded, turbocharged gasoline engines is being impeded by LSPI. A solution to this problem or even a mitigation of its occurrence would remove barriers for original equipment manufacturer (OEM) technology and efficiency improvement. A lubricant formulation solution would enable product differentiation with regard to LSPI. US 2009/0082233 discloses lubricant formulation for power transmission devices and engines.

[0007] Although pre-ignition problems can be and are being resolved by optimization of internal engine components and by the use of new component technology such as electronic controls, modification of the lubricating oil compositions used to lubricate such engines is desirable. For example, it would be desirable develop new lubricating oil formulations which are particularly useful in internal combustion engines and, when used in internal combustion engines, will prevent or minimize the pre-ignition problems. It is desired that the lubricating oil composition be useful in lubricating gasoline-fueled, spark-ignited engines.

[0008] Despite the advances in lubricant oil formulation technology, there exists a need for an engine oil lubricant that effectively prevents or reduces low speed pre-ignition especially for downsized, downspeeded, turbocharged engines.

SUMMARY

[0009] This disclosure also relates to the use of a formulated oil as lubricating oil for preventing or reducing low speed pre-ignition in an internal combustion engine as set out in claim 1 said. The formulated oil has a composition comprising a lubricating oil base stock as a major component; and at least one zinc-containing compound or at least one antiwear agent, as a minor component. The at least one antiwear agent comprises at least one zinc dialkyl dithiophosphate compound derived from a secondary alcohol. The engine exhibits greater than about 20% reduced low speed pre-ignition, based on normalized low speed pre-ignition (LSPI) counts per 25,000 engine cycles, engine operation at 2000 revolutions per minute (RPM) and brake mean effective pressure (BMEP) at 18 bar, as compared to low speed pre-ignition performance achieved in an engine using a lubricating oil that does not comprise at least one zinc-containing compound or antiwear agent.

[0010] According to this invention, the minor component further comprises at least one boron-containing compound

and at least one detergent. The boron-containing compound comprises at least one borated dispersant, or a mixture of a boron-containing compound and a non-borated dispersant. The detergent comprises at at least one magnesium salt of an organic acid.

[0011] It has been surprisingly found that, in accordance with this disclosure, prevention or reduction of LSPI can be attained in an engine lubricated with a lubricating oil by using as the lubricating oil the formulated oil as set out in claim 1 that includes at least one zinc-containing compound or at least one antiwear agent, preferably at least one zinc dialkyl dithiophosphate compound derived at from a secondary alcohol, present in an amount of from 0.1 weight percent to 5.0 weight percent, based on the total weight of the lubricating oil, in the lubricating oil, at least one boron-containing compound and at least one magnesium based detergent. In particular, for lubricating oil formulations containing the at least one zinc-containing compound or at least one antiwear agent, it has been surprisingly found that the engine exhibits greater than about 20% reduced low speed pre-ignition, based on normalized low speed pre-ignition (LSPI) counts per 25,000 engine cycles, engine operation at 2000 revolutions per minute (RPM) and brake mean effective pressure (BMEP) at 18 bar, as compared to low speed pre-ignition performance achieved in an engine using a lubricating oil containing a minor component other than the at least one zinc-containing compound or antiwear agent, and in an amount other than the amount of the at least one zinc-containing compound or antiwear agent, in the lubricating oil. In addition, it has been surprisingly found that, in accordance with this disclosure, reduction of LSPI can be attained in an engine lubricated with a lubricating oil by using as the lubricating oil a formulated oil that has a particular base stock (e.g., a Gas-To-Liquids base stock or an ester base stock).

[0012] Deleted

[0013] Other objects and advantages of the present disclosure will become apparent from the detailed description that follows.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] All concentrations outlined in the figures are quoted on a "as delivered" basis.

Fig. 1 shows formulation details in weight percent based on the total weight percent of the formulation, of various lubricating oil formulations, and the results of testing the various lubricating oil formulations, as detailed in Example A.

Fig. 2 shows formulation details in weight percent based on the total weight percent of the formulation, of various lubricating oil formulations, as detailed in Example B.

Fig. 3 shows the results of testing the various lubricating oil formulations set forth in Fig. 2, as detailed in Example B.

Fig. 4 shows formulation details in weight percent based on the total weight percent of the formulation, of various lubricating oil formulations, as detailed in Example C.

Fig. 5 shows the results of testing the various lubricating oil formulations set forth in Fig. 4, as detailed in Example C.

Fig. 6 shows formulation details in weight percent based on the total weight percent of the formulation, of the formulation embodiments of this disclosure, as detailed in Example D.

Fig. 7 shows the expected results of testing the various lubricating oil formulations of Fig. 6, as detailed in Example D.

Fig. 8 shows formulation details in weight percent based on the total weight percent of the formulation, of the formulation embodiments of this disclosure, as detailed in Example E.

Fig. 9 shows the expected results of testing the various lubricating oil formulations of Fig. 8, as detailed in Example E.

Fig. 10 shows formulation details in weight percent based on the total weight percent of the formulation, of the formulation embodiments of this disclosure, as detailed in Example F.

Fig. 11 shows the expected results of testing the various lubricating oil formulations of Fig. 10, as detailed in Example F.

Fig. 12 shows the results of engine performance mapping as detailed in Example A.

DETAILED DESCRIPTION

[0015] All numerical values within the detailed description and the claims take into account experimental error and variations that would be expected by a person having ordinary skill in the art.

[0016] It has now been found that prevention or reduction of LSPI can be attained in an engine lubricated with a lubricating oil by using as the lubricating oil a formulated oil as set out in claim 1. The lubricating oils of this disclosure are particularly advantageous as PVEO products.

[0017] The lubricating oil compositions of this disclosure are particularly used in lubricating gasoline-fueled, spark-ignited engines

[0018] As described herein, the lubricant formulation chemistry of this disclosure can be used to prevent or control the detrimental effect of LSPI in engines which have already been designed or sold in the marketplace as well as future engine technology. The lubricant formulation chemistry of this disclosure removes barriers for OEM technology and efficiency improvement, and enables further development of downspeeded, turbocharged gasoline engines that is currently being impeded by LSPI. The lubricant formulation solution afforded by this disclosure for preventing or reducing LSPI enables product differentiation with regard to LSPI.

Lubricating Oil Base Stocks

[0019] A wide range of lubricating base oils is known in the art. Lubricating base oils that are useful in the present disclosure are both natural oils, and synthetic oils, and unconventional oils (or mixtures thereof) can be used unrefined, refined, or rerefined (the latter is also known as reclaimed or reprocessed oil). Unrefined oils are those obtained directly from a natural or synthetic source and used without added purification. These include shale oil obtained directly from retorting operations, petroleum oil obtained directly from primary distillation, and ester oil obtained directly from an esterification process. Refined oils are similar to the oils discussed for unrefined oils except refined oils are subjected to one or more purification steps to improve at least one lubricating oil property. One skilled in the art is familiar with many purification processes. These processes include solvent extraction, secondary distillation, acid extraction, base extraction, filtration, and percolation. Rerefined oils are obtained by processes analogous to refined oils but using an oil that has been previously used as a feed stock.

[0020] Groups I, II, III, IV and V are broad base oil stock categories 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 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 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 stocks have a viscosity index greater than about 120 and contain less than or equal to about 0.03 % sulfur and greater than about 90% saturates. Group IV includes polyalphaolefins (PAO). Group V base stock includes base stocks not included in Groups I-IV. The table below summarizes properties of each of these five groups.

	Base Oil 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	Includes polyalphaolefins (PAO)		
Group V	All other base oil stocks not included in Groups I, II, III or IV		

[0021] Natural oils include animal oils, vegetable oils (castor oil and lard oil, for example), and mineral oils. Animal and vegetable oils possessing favorable thermal oxidative stability can be used. Of the natural oils, mineral oils are preferred. Mineral oils vary widely as to their crude source, for example, as to whether they are paraffinic, naphthenic, or mixed paraffinic-naphthenic. Oils derived from coal or shale are also useful. Natural oils vary also as to the method used for their production and purification, for example, their distillation range and whether they are straight run or cracked, hydrorefined, or solvent extracted.

[0022] Group II and/or Group III hydroprocessed or hydrocracked base stocks, including synthetic oils such as polyalphaolefins, alkyl aromatics and synthetic esters are also well known base stock oils.

[0023] Synthetic oils include hydrocarbon oil. Hydrocarbon oils include oils such as polymerized and interpolymerized

olefins (polybutylenes, polypropylenes, propylene isobutylene copolymers, ethylene-olefin copolymers, and ethylene-alphaolefin copolymers, for example). Polyalphaolefin (PAO) oil base stocks are commonly used synthetic hydrocarbon oil. By way of example, PAOs derived from C_6, C_8, C_{10}, C_{12}, C_{14} olefins or mixtures thereof may be utilized. See U.S. Patent Nos. 4,956,122; 4,827,064; and 4,827,073.

[0024] The number average molecular weights of the PAOs, which are known materials and generally available on a major commercial scale from suppliers such as ExxonMobil Chemical Company, Chevron Phillips Chemical Company, BP, and others, typically vary from about 250 to about 3,000, although PAO's may be made in viscosities up to about 150 cSt (100°C). The PAOs are typically comprised of relatively low molecular weight hydrogenated polymers or oligomers of alphaolefins which include, but are not limited to, C_2 to about C_{32} alphaolefins with the C_6 to about C_{16} alphaolefins, such as 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, and the like, being preferred. The preferred poly-alphaolefins are poly-1-hexene, poly-1-octene, poly-1-decene and poly-1-dodecene, 1 tetradecene, and mixtures thereof and mixed olefin-derived polyolefins. However, the dimers of higher olefins in the range of C_{14} to C_{18} may be used to provide low viscosity base stocks of acceptably low volatility. Depending on the viscosity grade and the starting oligomer, the PAOs may be predominantly trimers and tetramers of the starting olefins, with minor amounts of the higher oligomers, having a viscosity range of 1.5 to 12 cSt. PAO fluids of particular use may include 3.0 cSt, 3.4 cSt, and/or 3.6 cSt and combinations thereof. Bi-modal mixtures of PAO fluids having a viscosity range of 1.5 to 150 cSt may be used if desired.

[0025] The PAO fluids may be conveniently made by the polymerization of an alphaolefin in the presence of a polymerization catalyst such as the Friedel-Crafts catalysts including, for example, aluminum trichloride, boron trifluoride or complexes of boron trifluoride with water, alcohols such as ethanol, propanol or butanol, carboxylic acids or esters such as ethyl acetate or ethyl propionate. For example the methods disclosed by U.S. Patent Nos. 4,149,178 or 3,382,291 may be conveniently used herein. Other descriptions of PAO synthesis are found in the following U.S. Patent Nos. 3,742,082; 3,769,363; 3,876,720; 4,239,930; 4,367,352; 4,413,156; 4,434,408; 4,910,355; 4,956,122; and 5,068,487. The dimers of the C_{14} to C_{18} olefins are described in U.S. Patent No. 4,218,330.

[0026] Other useful lubricant oil base stocks include wax isomerate base stocks and base oils, comprising hydroisomerized waxy stocks (e.g. waxy stocks such as gas oils, slack waxes, fuels hydrocracker bottoms, etc.), hydroisomerized Fischer-Tropsch waxes, Gas-to-Liquids (GTL) base stocks and base oils, and other wax isomerate hydroisomerized base stocks and base oils, or mixtures thereof Fischer-Tropsch waxes, the high boiling point residues of Fischer-Tropsch synthesis, are highly paraffinic hydrocarbons with very low sulfur content. The hydroprocessing used for the production of such base stocks may use an amorphous hydrocracking/hydroisomerization catalyst, such as one of the specialized lube hydrocracking (LHDC) catalysts or a crystalline hydrocracking/hydroisomerization catalyst, preferably a zeolitic catalyst. For example, one useful catalyst is ZSM-48 as described in U.S. Patent No. 5,075,269. Processes for making hydrocracked/hydroisomerized distillates and hydrocracked/hydroisomerized waxes are described, for example, in U.S. Patent Nos. 2,817,693; 4,975,177; 4,921,594 and 4,897,178 as well as in British Patent Nos. 1,429,494; 1,350,257; 1,440,230 and 1,390,359. Particularly favorable processes are described in European Patent Application Nos. 464546 and 464547. Processes using Fischer-Tropsch wax feeds are described in U.S. Patent Nos. 4,594,172 and 4,943,672.

[0027] Gas-to-Liquids (GTL) base oils, Fischer-Tropsch wax derived base oils, and other wax-derived hydroisomerized (wax isomerate) base oils be advantageously used in the instant disclosure, and may have useful kinematic viscosities at 100°C of about 3 cSt to about 50 cSt, preferably about 3 cSt to about 30 cSt, more preferably about 3.5 cSt to about 25 cSt, as exemplified by GTL 4 with kinematic viscosity of about 4.0 cSt at 100°C and a viscosity index of about 141. These Gas-to-Liquids (GTL) base oils, Fischer-Tropsch wax derived base oils, and other wax-derived hydroisomerized base oils may have useful pour points of 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. Useful compositions of Gas-to-Liquids (GTL) base oils, Fischer-Tropsch wax derived base oils, and wax-derived hydroisomerized base oils are recited in U.S. Patent Nos. 6,080,301; 6,090,989, and 6,165,949 for example.

[0028] The hydrocarbyl aromatics can be used as base oil or base oil component and can be any hydrocarbyl molecule that contains at least about 5% of its weight derived from an aromatic moiety such as a benzenoid moiety or naphthenoid moiety, or their derivatives. These hydrocarbyl aromatics include alkyl benzenes, alkyl naphthalenes, alkyl diphenyl oxides, alkyl naphthols, alkyl diphenyl sulfides, alkylated bis-phenol A, alkylated thiodiphenol, and the like. The aromatic can be mono-alkylated, dialkylated, polyalkylated, and the like. The aromatic can be mono- or poly-functionalized. The hydrocarbyl groups can also be comprised of mixtures of alkyl groups, alkenyl groups, alkynyl, cycloalkyl groups, cycloalkenyl groups and other related hydrocarbyl groups. The hydrocarbyl groups can range from about C_6 up to about C_{60} with a range of about C_8 to about C_{20} often being preferred. A mixture of hydrocarbyl groups is often preferred, and up to about three such substituents may be present. The hydrocarbyl group can optionally contain sulfur, oxygen, and/or nitrogen containing substituents. The aromatic group can also be derived from natural (petroleum) sources, provided at least about 5% of the molecule is comprised of an above-type aromatic moiety. Viscosities at 100°C of approximately 3 cSt to about 50 cSt are preferred, with viscosities of approximately 3.4 cSt to about 20 cSt often being more preferred for the hydrocarbyl aromatic component. In one embodiment, an alkyl naphthalene where the alkyl group is primarily comprised of 1-hexadecene is used. Other alkylates of aromatics can be advantageously used. Naphthalene or methyl

naphthalene, for example, can be alkylated with olefins such as octene, decene, dodecene, tetradecene or higher, mixtures of similar olefins, and the like. Useful concentrations of hydrocarbyl aromatic in a lubricant oil composition can be about 2% to about 25%, preferably about 4% to about 20%, and more preferably about 4% to about 15%, depending on the application.

[0029] Alkylated aromatics such as the hydrocarbyl aromatics of the present disclosure may be produced by well-known Friedel-Crafts alkylation of aromatic compounds. See Friedel-Crafts and Related Reactions, Olah, G. A. (ed.), Interscience Publishers, New York, 1963. For example, an aromatic compound, such as benzene or naphthalene, is alkylated by an olefin, alkyl halide or alcohol in the presence of a Friedel-Crafts catalyst. See Friedel-Crafts and Related Reactions, Vol. 2, part 1, chapters 14, 17, and 18, See Olah, G. A. (ed.), Interscience Publishers, New York, 1964. Many homogeneous or heterogeneous, solid catalysts are known to one skilled in the art. The choice of catalyst depends on the reactivity of the starting materials and product quality requirements. For example, strong acids such as $AlCl_3$, BF_3, or HF may be used. In some cases, milder catalysts such as $FeCl_3$ or $SnCl_4$ are preferred. Newer alkylation technology uses zeolites or solid super acids.

[0030] Esters comprise a useful base stock. Additive solvency and seal compatibility characteristics may be secured by the use of esters such as the esters of dibasic acids with monoalkanols and the polyol esters of monocarboxylic acids. Esters of the former type include, for example, the esters of dicarboxylic acids such as phthalic acid, succinic acid, alkyl succinic acid, alkenyl succinic acid, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkyl malonic acid, alkenyl malonic acid, etc., with a variety of alcohols such as butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, etc. Specific examples of these types of esters include dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, etc.

[0031] Particularly useful synthetic esters are those which are obtained by reacting one or more polyhydric alcohols, preferably the hindered polyols (such as the neopentyl polyols, e.g., neopentyl glycol, trimethylol ethane, 2-methyl-2-propyl-1,3-propanediol, trimethylol propane, pentaerythritol and dipentaerythritol) with alkanoic acids containing at least about 4 carbon atoms, preferably C_5 to C_{30} acids such as saturated straight chain fatty acids including caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, arachic acid, and behenic acid, or the corresponding branched chain fatty acids or unsaturated fatty acids such as oleic acid, or mixtures of any of these materials.

[0032] Suitable synthetic ester components include the esters of trimethylol propane, trimethylol butane, trimethylol ethane, pentaerythritol and/or dipentaerythritol with one or more monocarboxylic acids containing from about 5 to about 10 or more carbon atoms. These esters are widely available commercially, for example, the Mobil P-41 and P-51 esters of ExxonMobil Chemical Company.

[0033] Preferred synthetic esters useful in this disclosure have a kinematic viscosity at 100°C of about 3 cSt to about 50 cSt, preferably about 3 cSt to about 30 cSt, more preferably about 3.5 cSt to about 25 cSt, and even more preferably about 2 cSt to about 8 cSt. Group V base oils useful in this disclosure preferably comprise an ester at a concentration of about 2% to about 20%, preferably from about 5% to about 15%.

[0034] Also useful are esters derived from renewable material such as coconut, palm, rapeseed, soy, sunflower and the like. These esters may be monoesters, di-esters, polyol esters, complex esters, or mixtures thereof. These esters are widely available commercially, for example, the Mobil P-51 ester of ExxonMobil Chemical Company.

[0035] Engine oil formulations containing renewable esters are included in this disclosure. For such formulations, the renewable content of the ester is typically greater than about 70 weight percent, preferably more than about 80 weight percent and most preferably more than about 90 weight percent.

[0036] Other useful fluids of lubricating viscosity include non-conventional or unconventional base stocks that have been processed, preferably catalytically, or synthesized to provide high performance lubrication characteristics.

[0037] Non-conventional or unconventional base stocks/base oils include one or more of a mixture of base stock(s) derived from one or more Gas-to-Liquids (GTL) materials, as well as isomerate/isodewaxate base stock(s) derived from natural wax or waxy feeds, mineral and or non-mineral oil waxy feed stocks such as slack waxes, natural waxes, and waxy stocks such as gas oils, waxy fuels hydrocracker bottoms, waxy raffinate, hydrocrackate, thermal crackates, or other mineral, mineral oil, or even non-petroleum oil derived waxy materials such as waxy materials received from coal liquefaction or shale oil, and mixtures of such base stocks.

[0038] 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 feed stocks such as hydrogen, carbon dioxide, carbon monoxide, water, methane, ethane, ethylene, acetylene, propane, propylene, propyne, butane, butylenes, and butynes. GTL base stocks and/or 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 feed stocks. GTL base stock(s) and/or base oil(s) include oils boiling in the lube oil boiling range (1) separated/fractionated from synthesized GTL materials such as, for example, by distillation and subsequently subjected to a final wax processing step which involves either or both of a catalytic dewaxing process,

or a solvent dewaxing process, to produce lube oils of reduced/low pour point; (2) synthesized wax isomerates, comprising, for example, hydrodewaxed or hydroisomerized cat and/or solvent dewaxed synthesized wax or waxy hydrocarbons; (3) hydrodewaxed or hydroisomerized cat and/or solvent dewaxed Fischer-Tropsch (F-T) material (i.e., hydrocarbons, waxy hydrocarbons, waxes and possible analogous oxygenates); preferably hydrodewaxed or hydroisomerized/followed by cat and/or solvent dewaxing dewaxed F-T waxy hydrocarbons, or hydrodewaxed or hydroisomerized/followed by cat (or solvent) dewaxing dewaxed, F-T waxes, or mixtures thereof.

[0039] GTL base stock(s) and/or base oil(s) derived from GTL materials, especially, hydrodewaxed or hydroisomerized/followed by cat and/or solvent dewaxed wax or waxy feed, preferably F-T material derived base stock(s) and/or base oil(s), are characterized typically as having kinematic viscosities at 100°C of from about 2 mm^2/s to about 50 mm^2/s (ASTM D445). They are further characterized typically as having pour points of -5°C to about -40°C or lower (ASTM D97). They are also characterized typically as having viscosity indices of about 80 to about 140 or greater (ASTM D2270).

[0040] The term GTL base stock and/or base oil and/or wax isomerate base stock and/or base oil is to be understood as embracing individual fractions of such materials of wide viscosity range as recovered in the production process, mixtures of two or more of such fractions, as well as mixtures of one or two or more low viscosity fractions with one, two or more higher viscosity fractions to produce a blend wherein the blend exhibits a target kinematic viscosity.

[0041] The GTL material, from which the GTL base stock(s) and/or base oil(s) is/are derived is preferably an F-T material (i.e., hydrocarbons, waxy hydrocarbons, wax).

[0042] In addition, the GTL base stock(s) and/or base oil(s) are typically highly paraffinic (>90% saturates), and may contain mixtures of monocycloparaffins and multicycloparaffins in combination with non-cyclic isoparaffins. The ratio of the naphthenic (i.e., cycloparaffin) content in such combinations varies with the catalyst and temperature used. Further, GTL base stock(s) and/or base oil(s) and hydrodewaxed, or hydroisomerized/cat (and/or solvent) dewaxed base stock(s) and/or base oil(s) 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(s) and/or base oil(s) obtained from F-T material, especially F-T wax, is essentially nil. In addition, the absence of phosphorous and aromatics make this material especially suitable for the formulation of low sulfur, sulfated ash, and phosphorus (low SAP) products.

[0043] Base oils for use in the formulated lubricating oils useful in the present disclosure are any of the variety of oils corresponding to API Group I, Group II, Group III, Group IV, and Group V oils and mixtures thereof, preferably API Group II, Group III, Group IV, and Group V oils and mixtures thereof, more preferably the Group III to Group V base oils, and mixtures thereof, due to their exceptional volatility, stability, viscometric and cleanliness features. The above base stocks when used in combination with the additive components disclosed in this disclosure can be used to formulate SAE 0W-8, SAE 0W-12, SAE 0W-16, SAE 0W-20, SAE 0W-30, SAE 0W-40, SAE 5W-12, SAE 5W-16, SAE 5W-20, SAE 5W-30, and SAE 10W-40 products with exceptional LSPI performance. These base stocks when used in combination with the additive components disclosed in this disclosure are particularly effective in formulating SAE 0W-8, SAE 0W-12, SAE 0W-16, SAE 0W-20, SAE 0W-30, SAE 0W-40, and SAE 5W-30 oils with exceptional LSPI performance.

[0044] The base oil constitutes the major component of the engine oil lubricant composition of the present disclosure and typically is present in an amount ranging from about 50 to about 99 weight percent, preferably from about 70 to about 95 weight percent, and more preferably from about 85 to about 95 weight percent, based on the total weight of the composition. The base oil may be selected from any of the synthetic or natural oils typically used as crankcase lubricating oils for spark-ignited and compression-ignited engines. The base oil conveniently has a kinematic viscosity, according to ASTM standards, of about 2.5 cSt to about 12 cSt (or mm^2/s) at 100°C and preferably of about 2.5 cSt to about 9 cSt (or mm^2/s) at 100°C, and more preferably of about 3.5 cSt to about 7 cSt (or mm^2/s) at 100°C and even more preferred in some application of 3.5 cSt to about 5 cSt (or mm^2/s) at 100°C. Mixtures of synthetic and natural base oils may be used if desired. Mixtures of Group III, IV, and V may be preferably used if desired.

Antiwear Agent

[0045] A zinc dialkyl dithio phosphate (ZDDP) derived from a secondary alcohol is a component of the lubricating oils of this disclosure. The preferred ZDDP compounds generally are represented by the formula

$$Zn[SP(S)(OR^1)(OR^2)]_2$$

wherein R^1 and R^2 are independently primary and/or secondary provided at least one of R^1 and R^2 is a secondary C_1 to C_8 alkyl group. Mixtures of primary alcohol derived ZDDP and secondary alcohol derived ZDDP where R^1 and R^2 are C_1 to C_8 alkyl groups can be used. These alkyl groups may be straight chain or branched. Alkyl aryl groups may also be used.

[0046] Preferable zinc dithiophosphates which are commercially available include secondary zinc dithiophosphates such as those available from for example, The Lubrizol Corporation under the trade designations "LZ 677A", "LZ 1095",

"LZ 1389" and "LZ 1371", from for example Chevron Oronite under the trade designation "OLOA 262" from for example Afton Chemical under the trade designation "HITEC 7169 and from for example Infineum under the trade designation Infineum C9417, and Infineum C9414.

[0047] Preferably, the primary or secondary C_1 to C_8 alkyl groups of the zinc dialkyl dithiophosphate compound are derived in part from an alcohol selected from the group consisting of: 2-propanol (C3), 1-butanol (n-C4), 1-isobutanol (1-i-C4), 2-butanol (2-C4), 1-pentanol (primary C-5), 3-methyl-1-butanol (primary C-5), 2-pentanol (C5), 3-pentanol (C5), 3-methyl-2-butanol (C5), 1-hexanol (primary C6), 4-methyl-1-pentanol (primary C6), 4-methyl-2-pentanol (C6), and 2-ethyl-1-hexanol (primary C8), and mixtures thereof. In some cases ZDDP derived from alcohols having an average carbon number of 5 and less are desirable. In some cases ZDDP derived from alcohols having an average carbon number of greater than 5 are desirable. Table 1 below shows alcohol mixtures used to make ZDDP which can be advantageously used in this disclosure.

Table 1. Alcohol Mixtures Useful in Preparing ZDDPs (wt%)

i-C3,	2-C4, -	1-i-C4,	n-C4, -	i-C5	n-C5	i-C6	C6	C8
Secondary	Secondary	Primary	Primary	Secondary	Primary	Secondary	Primary	Primary
20.2%	4.0%					75.7%		
8.4%	3.2%	11.7%						76.6%
45.2%	6.2%	19.4%	1.4%	8.8%	19.1%			
42.3%	2.4%					55.3%		
23.2%	13.3%							63.6%
5.7%	2.3%					92.1%		
4.6%	63.1%					32.3%		
4.1%	2.4%	52.6%						40.9%
7.7%	1.8%							90.6%
9.1%		0.4%				89.3%	0.4%	0.8%
42.0%		0.5%				56.5%	0.2%	0.9%
33.9%						66.1%		
0.3%		0.2%				99.6%		
	85.6%							14.4%

[0048] The R^1 and R^2 primary or secondary alkyl groups of the zinc dialkyl dithiophosphate compound, and the amount of the zinc dialkyl dithiophosphate compound having the R^1 and R^2 primary or secondary alkyl groups in the lubricating oil, are sufficient for an engine to exhibit reduced low speed pre-ignition, as compared to low speed pre-ignition performance achieved in an engine using a lubricating oil containing a minor component other than the particular zinc dialkyl dithiophosphate compound, and in an amount other than the amount of the particular zinc dialkyl dithiophosphate compound, in the lubricating oil.

[0049] In general, the ZDDP is used in amounts of from 0.4 weight percent to 1.2 weight percent, preferably from 0.5 weight percent to 1.0 weight percent, and more preferably from 0.6 weight percent to 0.8 weight percent, based on the total weight of the lubricating oil, although more or less can often be used advantageously. Preferably, the ZDDP is a primary, secondary or mixture ZDDP and present in an amount of from 0.6 to 1.0 weight percent of the total weight of the lubricating oil.

[0050] Preferably, the zinc dialkyl dithiophosphate compounds having the R^1 and R^2 primary or secondary alkyl groups, in which the R^1 and R^2 primary or secondary alkyl groups are derived from 2-ethyl-1-hexanol (Primary C8), are present in an amount of from 0.1 weight percent to 5.0 weight percent, preferably from 0.1 to 1.2 weight percent, and more preferably from 0.2 to 0.8 weight percent, based on the total weight of the lubricating oil.

[0051] Preferably, the zinc dialkyl dithiophosphate compounds having the R^1 and R^2 primary or secondary alkyl groups, in which the R^1 and R^2 primary or secondary alkyl groups are derived from 4-methyl-2-pentanol (i-C6), are present in an amount of from 0.1 weight percent to 5.0 weight percent, preferably from 0.1 to 1.2 weight percent, and more preferably from 0.2 to 0.8 weight percent, based on the total weight of the lubricating oil.

[0052] Preferably, the zinc dialkyl dithiophosphate compound is derived from a C_3 to C_8 secondary alcohol, or a mixture

thereof. Also, preferably, the zinc dialkyl dithiophosphate compound is derived from a mixture of a C_1 to C_8 primary alcohol and a C_1 to C_8 secondary alcohol.

[0053] The zinc content contributed by the zinc-containing compound or antiwear agent in the lubricating oil ranges from 500 ppm to 2000 ppm, preferably from 600 ppm to 900 ppm

[0054] The phosphorus content contributed by the zinc-containing compound or antiwear agent in the lubricating oil ranges from 400 ppm to 2000 ppm, preferably from 500 ppm to 900 ppm. The phosphorus derived from the secondary ZDDP is preferably from 0 to 900 ppm and more preferably from 400 to 900 ppm.

[0055] The zinc to phosphorus ratio in the lubricating oil ranges from 1.0 to 2.0, preferably from 1.1 to 1.9.

[0056] The ratio of total metals provided by the detergent to total metals provided by the zinc-containing compound and antiwear agent is from 0.8 to 4.8, preferably from 1.4 to 4.0, and more preferably from 1.5 to 3.7.

[0057] Illustrative zinc-containing compounds useful in this disclosure include, for example, zinc carboxylates, zinc sulfonates, zinc acetates, zinc napthenates, zinc alkenyl succinates, zinc acid phosphate salts, zinc phenates, zinc salicylates, and the like.

[0058] In accordance with this disclosure, an engine exhibits greater than 20%, preferably greater than 25%, and more preferably greater than 30%, reduced low speed pre-ignition, based on normalized low speed pre-ignition (LSPI) counts per 25,000 engine cycles, engine operation at 2000 revolutions per minute (RPM) and brake mean effective pressure (BMEP) at 18 bar, as compared to low speed pre-ignition performance achieved in an engine using a lubricating oil containing a minor component other than the at least one zinc-containing compound or at least one antiwear agent, and in an amount other than the amount of the at least one zinc-containing compound or at least one antiwear agent, in the lubricating oil. Similar or even greater reduced low speed pre-ignition can be attained using mixtures of the at least one zinc-containing compound or at least one antiwear agent with at least one boron-containing compound and/or with at least one detergent, as described herein.

[0059] Preferably, the zinc dialkyl dithiophosphate compounds having the R^1 and R^2 primary or secondary alkyl groups, in which the R^1 and R^2 primary or secondary alkyl groups are derived from 2-propanol (C3), 2-butanol (2-C4), 1-isobutanol (1-i-C4), or n-pentanol (n-C5), are present in an amount of from 0.1 weight percent to 5.0 weight percent, preferably from 0.1 to 1.2 weight percent, and more preferably from 0.2 to 0.8 weight percent, based on the total weight of the lubricating oil.

[0060] The zinc-containing compound or antiwear agent concentration in the lubricating oils of this disclosure can range from 0.1 to 5.0 weight percent, preferably 0.2 to 2.0 weight percent, and more preferably from 0.2 weight percent to 1.0 weight percent, based on the total weight of the lubricating oil. In the presence of magnesium detergents and boron containing additives, only small amounts of ZDDP are needed to give exceptionally low LSPI counts. In such presence of magnesium and boron containing compounds as little as 0.1% to 1.0 wt.% ZDDP (100 ppm P to 1000 ppm P phosphorus in the formulated engine oil) will provide unexpected improvements in LSPI performance. At higher ash levels and higher TBN levels, ZDDP levels of 1.1 to 4.0 wt.% can provide unexpected improvements in LSPI performance. For SAE xW-40 and xW-50 oils (x = 0, 5, 10, 15), ZDDP levels of 1.1 to 4.0 wt.% are especially useful to provide unexpected improvements in LSPI performance.

Dispersants

[0061] During engine operation, oil-insoluble oxidation byproducts are produced. Dispersants help keep these byproducts in solution, thus diminishing their deposition on metal surfaces. Dispersants used in the formulation of the lubricating oil may be ashless or ash-forming in nature. Preferably, the dispersant is ashless. So called ashless dispersants are organic materials that form substantially no ash or little ash upon combustion. For example, non-metal-containing or borated metal-free dispersants are considered ashless. In contrast, metal-containing detergents discussed above form ash upon combustion.

[0062] At least one boron-containing compound is used in this disclosure. The boron-containing compound comprises at least one borated dispersant, or a mixture of a boron-containing compound and a non-borated dispersant. Ranges of Boron in the formulation from the borated dispersant or other boron containing additive(s) are 30 ppm to 1500 ppm, or more a preferred range of 60 ppm to 1000ppm, or a most preferred range of 120 ppm to 600 ppm.

[0063] Preferably, the boron-containing compound includes, for example, a borated succinimide, a borated succinate ester, a borated succinate ester amide, a borated Mannich base, and mixtures thereof.

[0064] The non-borated dispersant includes, for example, a hydrocarbyl succinic anhydride derived succinimide or succinate ester with a coupling agent, wherein the coupling agent comprises a boron-containing compound.

[0065] Preferably, boron is provided to the lubricating oil by a mixture of an organic or inorganic boron-containing compound and a borated succinimide, a borated succinate ester, a borated succinate ester amide, a Mannich base ester, or mixtures thereof. The borated succinimide is preferably a mono succinimide, bis-succinimide, or a mixture thereof. Effective boron containing compounds include borated hydrocarbyl succinimides, including those derived for hydrocarbyl sources where number average molecular weight (M_n) is between 50 and 5000 Daltons, borated hydrocarbyl

succinates, borated hydrocarbyl substituted Mannich bases, borated alcohols, borated alkoxylated alcohols, borated hydrocarbyl diols, borated hydrocarbyl amines, borated hydrocarbyl diamines, borated hydrocarbyl triamines, borated alkoxylated hydrocarbyl amines, borated alkoxylated hydrocarbyl amides, borated hydrocarbyl containing hydroxyl esters, borated hydrocarbyl substituted oxazolines, borated hydrocarbyl substituted imidazolones, and the like and mixtures of organic borates. Borates of -N-H, and/or -OH derived moieties can also be used. These borates can be inorganic, or organic moiety derived borates. Borates can be prepared using boric acid, borated alcohols and the like. These borates can be used at concentrations to provide 60-1200 ppm boron in the engine oil formulations, 60-240 ppm boron, 240-1200 ppm boron, 240-500 ppm boron, or 60-120 ppm boron to produce unexpected surprising improvement in LSPI performance, as desired.

[0066] The ratio of total zinc from the zinc-containing compound and antiwear agent plus total alkaline earth metal from the detergent divided by the total boron from the boron-containing compound and borated dispersant, in the lubricating oil, is from about 9.2 to 45, preferably from about 11 to 15.

[0067] Suitable dispersants typically contain a polar group attached to a relatively high molecular weight hydrocarbon chain. The polar group typically contains at least one element of nitrogen, oxygen, or phosphorus. Typical hydrocarbon chains contain 50 to 400 carbon atoms. In some exemplifications, the hydrocarbon chain can range from 6 to 50 carbon atoms.

[0068] Chemically, many dispersants may be characterized as phenates, sulfonates, sulfurized phenates, salicylates, naphthenates, stearates, carbamates, thiocarbamates, phosphorus derivatives. A particularly useful class of dispersants are the alkenylsuccinic derivatives, typically produced by the reaction of a long chain hydrocarbyl substituted succinic compound, usually a hydrocarbyl substituted succinic anhydride, with a polyhydroxy or polyamino compound. The long chain hydrocarbyl group constituting the oleophilic portion of the molecule which confers solubility in the oil, is normally a polyisobutylene group. Many examples of this type of dispersant are well known commercially and in the literature. Exemplary U.S. patents describing such dispersants are U.S. Patent Nos. 3,172,892; 3,2145,707; 3,219,666; 3,316,177; 3,341,542; 3,444,170; 3,454,607; 3,541,012; 3,630,904; 3,632,511; 3,787,374 and 4,234,435. Other types of dispersant are described in U.S. Patent Nos. 3,036,003; 3,200,107; 3,254,025; 3,275,554; 3,438,757; 3,454,555; 3,565,804; 3,413,347; 3,697,574; 3,725,277; 3,725,480; 3,726,882; 4,454,059; 3,329,658; 3,449,250; 3,519,565; 3,666,730; 3,687,849; 3,702,300; 4,100,082; 5,705,458. A further description of dispersants may be found, for example, in European Patent Application No. 471 071, to which reference is made for this purpose.

[0069] Hydrocarbyl-substituted succinic acid and hydrocarbyl-substituted succinic anhydride derivatives are useful dispersants. In particular, succinimide, succinate esters, or succinate ester amides prepared by the reaction of a hydrocarbon-substituted succinic acid compound preferably having at least 50 carbon atoms in the hydrocarbon substituent, with at least one equivalent of an alkylene amine are particularly useful, although on occasion, having a hydrocarbon substituent between 20-50 carbon atoms can be useful.

[0070] Succinimides are formed by the condensation reaction between hydrocarbyl substituted succinic anhydrides and amines. Molar ratios can vary depending on the polyamine. For example, the molar ratio of hydrocarbyl substituted succinic anhydride to ethylene amines (e.g., Diethylene triamine, triethylene tetraamine, tetraethylene pentaamine, hexaethylene heptamine, heptaethylene octaamine, and the like) Polyethylene amines containing Tetraethylene Pentaamine (TEPA) are often preferred. High molecular weight polyethylene amine bottoms comprising hexaethylene heptamine, and heptaethylene octaamine can also be used. The ratio of hydrocarbyl substituted succinic anhydride to polyethylene amines can vary from about 1:1 to about 5:1. Representative examples are shown in U.S. Patent Nos. 3,087,936; 3,172,892; 3,219,666; 3,272,746; 3,322,670; and 3,652,616, 3,948,800; and Canada Patent No. 1,094,044.

[0071] Succinate esters are formed by the condensation reaction between hydrocarbyl substituted succinic anhydrides and alcohols or polyols. Molar ratios can vary depending on the alcohol or polyol used. For example, the condensation product of a hydrocarbyl substituted succinic anhydride and pentaerythritol is a useful dispersant.

[0072] Succinate ester amides are formed by condensation reaction between hydrocarbyl substituted succinic anhydrides and alkanol amines. For example, suitable alkanol amines include ethoxylated polyalkylpolyamines, propoxylated polyalkylpolyamines and polyalkenylpolyamines such as polyethylene polyamines. One example is propoxylated hexamethylenediamine. Representative examples are shown in U.S. Patent No. 4,426,305.

[0073] The molecular weight of the hydrocarbyl substituted succinic anhydrides used in the preceding paragraphs will typically range between 800 and 2,500 Daltons or more. The above products can be post-reacted with various reagents such as sulfur, oxygen, formaldehyde, carboxylic acids such as oleic acid. The above products can also be post reacted with boron compounds such as boric acid, borate esters or highly borated dispersants, to form borated dispersants generally having from about 0.1 to about 5 moles of boron per mole of dispersant reaction product.

[0074] Mannich base dispersants are made from the reaction of alkylphenols, formaldehyde, and amines. See U.S. Patent No. 4,767,551. Process aids and catalysts, such as oleic acid and sulfonic acids, can also be part of the reaction mixture. Molecular weights of the alkylphenols range from 800 to 2,500. Representative examples are shown in U.S. Patent Nos. 3,697,574; 3,703,536; 3,704,308; 3,751,365; 3,756,953; 3,798,165; and 3,803,039.

[0075] Typical high molecular weight aliphatic acid modified Mannich condensation products useful in this disclosure

can be prepared from high molecular weight alkyl-substituted hydroxyaromatics or HN®$_2$ group-containing reactants.

[0076] Hydrocarbyl substituted amine ashless dispersant additives are well known to one skilled in the art; see, for example, U.S. Patent Nos. 3,275,554; 3,438,757; 3,565,804; 3,755,433, 3,822,209, and 5,084,197.

[0077] Preferred dispersants include borated succinimides, including those derivatives from mono-succinimides, bis-succinimides, and/or mixtures of mono- and bis-succinimides, wherein the hydrocarbyl succinimide is derived from a hydrocarbylene group such as polyisobutylene having a M_n of from about 500 to about 5000 Daltons, or from about 1000 to about 3000 Daltons, or about 1000 to about 2000 Daltons, or a mixture of such hydrocarbylene groups, often with high terminal vinylic groups. Preferred dispersants useful in this disclosure are characterized having a M_n of about 800 to 1700 Daltons for low molecular weight, and a M_n of about 1700 to about 5000 Daltons or greater for high molecular weight. Other preferred dispersants include succinic acid-esters and amides, alkylphenol-polyamine-coupled Mannich adducts, their capped derivatives, and other related components. Such additives may be used in an amount of about 0.1 to 20 weight percent, preferably about 0.5 to 8 weight percent, or more preferably 0.5 to 4 weight percent. The hydrocarbon portion of the dispersant atoms can range from C_{60} to C_{400}, or from C_{70} to C_{300}, or from C_{70} to C_{200}. These dispersants may contain both neutral and basic nitrogen, and mixtures of both.

[0078] The ratio of basic to non-basic nitrogen in the dispersant can range from 1 to 5, to 5 to 1 or more preferably from 1 to 2, to 2 to 1. Dispersants can be endcapped by borates and/or cyclic carbonates and or any carboxylic acid such as hydrocarbyl carboxylic acids or hydrocarbyl carboxylic acid anhydrides.

[0079] For lubricating oil formulations containing at least one boron-containing compound and at least one zinc-containing compound or antiwear agent in accordance with this disclosure, an engine exhibits greater than about 20%, preferably greater than 25%, and more preferably greater than 30%, reduced low speed pre-ignition, based on normalized low speed pre-ignition (LSPI) counts per 25,000 engine cycles, engine operation at 2000 revolutions per minute (RPM) and brake mean effective pressure (BMEP) at 18 bar, as compared to low speed pre-ignition performance achieved in an engine using a lubricating oil containing a minor component other than the at least one boron-containing compound and at least one zinc-containing compound or antiwear agent, and in an amount other than the amount of the at least one boron-containing compound and at least one zinc-containing compound or antiwear agent, in the lubricating oil.

[0080] As used herein, the dispersant concentrations are given on an "as delivered" basis. Typically, the active dispersant is delivered with a process oil. The "as delivered" dispersant typically contains from 20 weight percent to 80 weight percent, or from 40 weight percent to about 60 weight percent, of active dispersant in the "as delivered" dispersant product.

Detergents

[0081] Illustrative detergents include, for example, alkaline earth metal detergents, or mixtures of alkaline earth metal detergents. A typical alkaline earth metal detergent is an anionic material that contains a long chain hydrophobic portion of the molecule and a smaller anionic or oleophobic hydrophilic portion of the molecule. The anionic portion of the detergent is derived from an organic acid such as a sulfur acid, carboxylic acid, phosphorous acid, phenol, or mixtures thereof. The counterion is an alkaline earth metal. According to this invention, the detergent comprises at least one magnesium salt of an organic acid.

[0082] Preferred detergents useful in the lubricating oils of this disclosure are selected from the group consisting of an alkaline earth metal sulfonate, an alkaline earth metal carboxylate (e.g., salicylate), an alkaline earth metal phenate, an alkaline earth metal phosphate, and mixtures thereof. The alkaline earth metal sulfonate, alkaline earth metal carboxylate, alkaline earth metal phenate, alkaline earth metal phosphate, and mixtures thereof, and the amount of the alkaline earth metal sulfonate, alkaline earth metal carboxylate, alkaline earth metal phenate, alkaline earth metal phosphate, and mixtures thereof in the lubricating oil, are sufficient for the engine to exhibit reduced low speed pre-ignition, as compared to low speed pre-ignition performance achieved in an engine using a lubricating oil containing a detergent other than the alkaline earth metal sulfonate, alkaline earth metal carboxylate, alkaline earth metal phenate, alkaline earth metal phosphate, and mixtures thereof, and in an amount other than the amount of the alkaline earth metal sulfonate, alkaline earth metal carboxylate, alkaline earth metal phenate, alkaline earth metal phosphate, and mixtures thereof, in the lubricating oil.

[0083] The alkaline earth metal detergents useful in this disclosure can be prepared by convention methods known in the art.

[0084] Alkaline earth metal sulfonates are a preferred class of detergents. Sulfur acids useful in preparing the alkaline earth metal sulfonates include sulfonic acids, thiosulfonic, sulfinic, sulfenic, partial ester sulfuric, sulfurous and thiosulfuric acids. Sulfonic acids are preferred.

[0085] The sulfonic acids are generally petroleum sulfonic acids or synthetically prepared alkaryl sulfonic acids. Among the petroleum sulfonic acids, the most useful products are those prepared by the sulfonation of suitable petroleum fractions with a subsequent removal of acid sludge, and purification. Synthetic alkaryl sulfonic acids are prepared usually from alkylated benzenes such as the Friedel-Crafts reaction products of benzene and polymers such as tetrapropylene.

The following are specific examples of sulfonic acids useful in preparing the alkaline earth metal sulfonate detergents useful in this disclosure. It is to be understood that such examples serve also to illustrate the alkaline earth metal salts of such sulfonic acids. In other words, for every sulfonic acid enumerated, it is intended that the corresponding basic alkaline earth metal salts thereof are also understood to be illustrated.

[0086] Such sulfonic acids include mahogany sulfonic acids, bright stock sulfonic acids, petrolatum sulfonic acids, mono- and polywax-substituted naphthalene sulfonic acids, cetylchlorobenzene sulfonic acids, cetylphenol sulfonic acids, cetylphenol disulfide sulfonic acids, cetoxycapryl benzene sulfonic acids, dicetyl thianthrene sulfonic acids, dilauryl beta-naphthol sulfonic acids, dicapryl nitronaphthalene sulfonic acids, saturated paraffin wax sulfonic acids, unsaturated paraffin wax sulfonic acids, hydroxy-substituted paraffin wax sulfonic acids, tetra-isobutylene sulfonic acids, tetra-amylene sulfonic acids, chloro-substituted paraffin wax sulfonic acids, nitroso-substituted paraffin wax sulfonic acids, petroleum naphthene sulfonic acids, cetylcyclopentyl sulfonic acids, lauryl cyclohexyl sulfonic acids, mono- and polywax-substituted cyclohexyl sulfonic acids, dodecylbenzene sulfonic acids, "dimer alkylate" sulfonic acids, and the like.

[0087] Alkyl-substituted benzene sulfonic acids wherein the alkyl group contains at least 8 carbon atoms including dodecyl benzene "bottoms" sulfonic acids are useful in this disclosure. The latter are acids derived from benzene which has been alkylated with propylene tetramers or isobutene trimers to introduce 1, 2, 3, or more branched-chain C_{12} substituents on the benzene ring. Dodecyl benzene bottoms, principally mixtures of mono- and di-dodecyl benzenes, are available as by-products from the manufacture of household detergents.

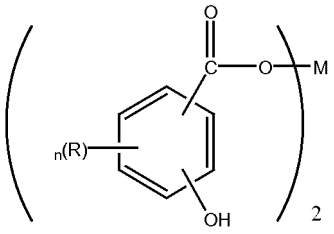
[0088] Preferred alkaline earth metal sulfonates include magnesium sulfonate, calcium sulfonate, and mixtures thereof.

[0089] Alkaline earth phenates are a useful class of detergents. These detergents can be made by reacting alkaline earth metal hydroxide or oxide (CaO, $Ca(OH)_2$, BaO, $Ba(OH)_2$, MgO, $Mg(OH)_2$, for example) with an alkyl phenol or sulfurized alkylphenol. Useful alkyl groups include straight chain or branched C_1-C_{30} alkyl groups, preferably, C_4-C_{20} or mixtures thereof. Examples of suitable phenols include isobutylphenol, 2-ethylhexylphenol, nonylphenol, dodecyl phenol, and the like. It should be noted that starting alkylphenols may contain more than one alkyl substituent that are each independently straight chain or branched and can be used from 0.5 to 6 weight percent. When a non-sulfurized alkylphenol is used, the sulfurized product may be obtained by methods well known in the art. These methods include heating a mixture of alkylphenol and sulfurizing agent (including elemental sulfur, sulfur halides such as sulfur dichloride, and the like) and then reacting the sulfurized phenol with an alkaline earth metal base.

[0090] Preferred phenate compounds include, for example, magnesium phenate, calcium phenate, an overbased phenate compound, a sulfurized/carbonated calcium phenate compound, and mixtures thereof.

[0091] Alkaline earth metal salts of carboxylic acids are also useful as detergents. These carboxylic acid detergents may be prepared by reacting a basic alkaline earth metal compound with at least one carboxylic acid and removing free water from the reaction product. These compounds may be overbased to produce the desired TBN level.

[0092] Detergents made from salicylic acid are one preferred class of detergents derived from carboxylic acids. Useful salicylates include long chain alkyl salicylates. One useful family of compositions is of the formula



where R is an alkyl group having 1 to about 30 carbon atoms, n is an integer from 1 to 4, and M is an alkaline earth metal. Preferred R groups are alkyl chains of at least C_{11}, preferably C_{13} or greater. R may be optionally substituted with substituents that do not interfere with the detergent's function. M is preferably, calcium, magnesium, or barium. More preferably, M is calcium or magnesium.

[0093] Hydrocarbyl-substituted salicylic acids may be prepared from phenols by the Kolbe reaction (see U.S. Patent No. 3,595,791). The alkaline earth metal salts of the hydrocarbyl-substituted salicylic acids may be prepared by double decomposition of an alkaline earth metal salt in a polar solvent such as water or alcohol.

[0094] Preferred carboxylate compounds comprise a noncarbonated magnesium salicylate (carboxylate); a carbonated magnesium salicylate (carboxylate); a noncarbonated calcium salicylate (carboxylate); a carbonated calcium salicylate (carboxylate); and mixtures thereof.

[0095] Salts that contain a substantially stoichiometric amount of the alkaline earth metal are described as neutral salts and have a total base number (TBN, as measured by ASTM D2896) of from 0 to 100. Many compositions are overbased, containing large amounts of a metal base that is achieved by reacting an excess of an alkaline earth metal compound with an acidic gas (such as carbon dioxide). Useful detergents can be neutral, mildly overbased, or highly

overbased. These detergents can be used in mixtures of neutral, overbased, highly overbased magnesium salicylate, sulfonates, phenates and/or calcium salicylate, sulfonates, and phenates. The TBN ranges can vary from low TBN of about 0 to 100, medium TBN of about 100 to 200, and high TBN of about 200 to as high as 600, including as low as 0 to as high as 600. Mixtures of low, medium, high TBN can be used, along with mixtures of calcium and magnesium metal based detergents, and including sulfonates, phenates, salicylates, and carboxylates. Further examples of mixed TBN detergents can be found as described in U.S. Patent No. 7,704,930. A detergent mixture with a metal ratio of 1, in conjunction of a detergent with a metal ratio of 2, and as high as a detergent with a metal ratio of 5 or 10 or 15, can be used. Borated detergents can also be used.

[0096] Alkaline earth metal phosphates may also be used as detergents and are known in the art.

[0097] Detergents may be simple detergents or what is known as hybrid or complex detergents. The latter detergents can provide the properties of two detergents without the need to blend separate materials. See U.S. Patent No. 6,034,039.

[0098] Suitable detergents include magnesium sulfonates, calcium sulfonates, calcium phenates, magnesium phenates, calcium salicylates, magnesium salicylates, and other related components (including borated detergents), and mixtures thereof. Preferred detergents include magnesium sulfonate, calcium sulfonate, magnesium phenate, calcium phenate, magnesium salicylate, calcium salicylate, and mixtures thereof.

[0099] Other illustrative detergents that may be used in combination with the alkaline earth metal detergents include, for example, alkali metal detergents, or mixtures of alkali metal detergents.

[0100] In a detergent comprising a mixture of a magnesium salt of an organic acid and a calcium salt of an organic acid, the detergent ratio of magnesium metal to calcium metal ranges from 1:0 to 1:10, preferably from 1:0 to 1:4.

[0101] The magnesium and alkaline earth metal contributed by the detergent is present in the lubricating oil in an amount from 500 ppm to 5000 ppm, preferably from 1000 ppm to 2500 ppm. The magnesium contributed by the detergent is present in the lubricating oil in an amount from 100 ppm to 3000 ppm, preferably from 300 ppm to 2500 ppm, and more preferably from 750 ppm to 2000 ppm.

[0102] The total base number (TBN), as measured by ASTM D2896, contributed by the detergent ranges from 2 mg KOH/g to 17 mg KOH/g, preferably from 4 mg KOH/g to 14 mg KOH/g. The TBN contributed by the magnesium detergent ranges from 2 mg KOH/g to 17 mg KOH/g, preferably from 3 mg KOH/g to 14 mg KOH/g

[0103] The sulfated ash contributed by the detergent ranges from 0.4 to about 1.7 wt%, preferably from 0.5 to 1.6 wt%, and more preferably from 0.6 to 1.0 wt%. The sulfated ash contributed by the magnesium detergent ranges from 0.3 to 1.8 wt%, preferably from 0.4 to 1.6 wt%, and more preferably from 0.6 to 1.0 wt%. The lubricating engine oil of this disclosure preferably contains less than 1.6 percent by weight sulfated ash and/or more preferably contains less than 4000 ppm of magnesium. At higher engine oil sulfated ash at or above 1.2% ash (with the use of a magnesium detergent) greater than a 95% reduction in LSPI counts is achieved. At sulfated ash levels <1.2% with the use of a magnesium detergent, LSPI can be entirely eliminated.

[0104] For lubricating oil formulations containing at least one zinc-containing compound or antiwear agent and at least one detergent in accordance with this disclosure, an engine exhibits greater than 50%, preferably greater than 75%, and more preferably greater than 95%, reduced low speed pre-ignition, based on normalized low speed pre-ignition (LSPI) counts per 25,000 engine cycles, engine operation at 2000 revolutions per minute (RPM) and brake mean effective pressure (BMEP) at 18 bar, as compared to low speed pre-ignition performance achieved in an engine using a lubricating oil containing a minor component other than the at least one zinc-containing compound or antiwear agent and at least one detergent, and in an amount other than the amount of the at least one zinc-containing compound or antiwear agent and at least one detergent, in the lubricating oil.

[0105] Also, for lubricating oil formulations containing at least one zinc-containing compound or antiwear agent, at least one boron-containing compound, and at least one detergent in accordance with this disclosure, an engine exhibits greater than about 50%, preferably greater than about 75%, and more preferably greater than about 95%, reduced low speed pre-ignition, based on normalized low speed pre-ignition (LSPI) counts per 25,000 engine cycles, engine operation at 2000 revolutions per minute (RPM) and brake mean effective pressure (BMEP) at 18 bar, as compared to low speed pre-ignition performance achieved in an engine using a lubricating oil containing a minor component other than the at least one zinc-containing compound or antiwear agent, at least one boron-containing compound, and at least one detergent, and in an amount other than the amount of the at least one zinc-containing compound or antiwear agent, at least one boron-containing compound, and at least one detergent, in the lubricating oil.

[0106] The detergent concentration in the lubricating oils of this disclosure ranges from 1.0 to 6.0 weight percent, preferably 2.0 to 5.0 weight percent, and more preferably from 2.0 weight percent to 4.0 weight percent, based on the total weight of the lubricating oil. In the lubricating oils of this disclosure, the amount of alkaline earth metal sulfonate preferably can range from 0.5 to 2.5 weight percent, preferably from 0.5 to 2.0 weight percent, and more preferably from 0.5 to 1.5 weight percent, based on the total weight of the lubricating oil. In the lubricating oils of this disclosure, the amount of alkaline earth metal phenate preferably can range from 0.5 to 2.5 weight percent, preferably from 0.5 to 2.0 weight percent, and more preferably from 0.5 to 1.5 weight percent, based on the total weight of the lubricating oil. In the lubricating oils of this disclosure, the amount of alkaline earth metal carboxylate can range from 1.0 to 4.0 weight

percent, preferably from 1.0 to 3.0 weight percent, and more preferably from 1.5 to 2.5 weight percent, based on the total weight of the lubricating oil. In the lubricating oils of this disclosure, the amount of alkaline earth metal phosphate can range from 1.0 to 4.0 weight percent, preferably from 1.0 to 3.0 weight percent, and more preferably from 1.5 to 2.5 weight percent, based on the total weight of the lubricating oil.

[0107] As used herein, the detergent concentrations are given on an "as delivered" basis. Typically, the active detergent is delivered with a process oil. The "as delivered" detergent typically contains from about 20 weight percent to about 80 weight percent, or from about 40 weight percent to about 60 weight percent, of active detergent in the "as delivered" detergent product.

Other Additives

[0108] The formulated lubricating oil useful in the present disclosure may additionally contain one or more of the other commonly used lubricating oil performance additives including but not limited to other antiwear agents, other dispersants, other detergents, corrosion inhibitors, rust inhibitors, metal deactivators, extreme pressure additives, anti-seizure agents, wax modifiers, viscosity index improvers, viscosity modifiers, fluid-loss additives, seal compatibility agents, friction modifiers, lubricity agents, anti-staining agents, chromophoric agents, defoamants, demulsifiers, emulsifiers, densifiers, wetting agents, gelling agents, tackiness agents, colorants, and others. For a review of many commonly used additives, see Klamann in Lubricants and Related Products, Verlag Chemie, Deerfield Beach, FL; ISBN 0-89573-177-0. Reference is also made to "Lubricant Additives" by M. W. Ranney, published by Noyes Data Corporation of Parkridge, NJ (1973); see also U.S. Patent No. 7,704,930. These additives are commonly delivered with varying amounts of diluent oil, that may range from 5 weight percent to 50 weight percent.

[0109] The types and quantities of performance additives used in combination with the instant disclosure in lubricant compositions are not limited by the examples shown herein as illustrations.

Viscosity Index Improvers

[0110] Viscosity index improvers (also known as VI improvers, viscosity modifiers, and viscosity improvers) can be included in the lubricant compositions of this disclosure.

[0111] Viscosity index improvers provide lubricants with high and low temperature operability. These additives impart shear stability at elevated temperatures and acceptable viscosity at low temperatures.

[0112] Suitable viscosity index improvers include high molecular weight hydrocarbons, polyesters and viscosity index improver dispersants that function as both a viscosity index improver and a dispersant. Typical molecular weights of these polymers are between about 10,000 to 1,500,000, more typically about 20,000 to 1,200,000, and even more typically between about 50,000 and 1,000,000.

[0113] Examples of suitable viscosity index improvers are linear or star-shaped polymers and copolymers of methacrylate, butadiene, olefins, or alkylated styrenes. Polyisobutylene is a commonly used viscosity index improver. Another suitable viscosity index improver is polymethacrylate (copolymers of various chain length alkyl methacrylates, for example), some formulations of which also serve as pour point depressants. Other suitable viscosity index improvers include copolymers of ethylene and propylene, hydrogenated block copolymers of styrene and isoprene, and polyacrylates (copolymers of various chain length acrylates, for example). Specific examples include styrene-isoprene or styrene-butadiene based polymers of 50,000 to 200,000 molecular weight.

[0114] Olefin copolymers, are commercially available from Chevron Oronite Company LLC under the trade designation "PARATONE®" (such as "PARATONE® 8921" and "PARATONE® 8941"); from Afton Chemical Corporation under the trade designation "HiTEC®" (such as "HiTEC® 5850B"; and from The Lubrizol Corporation under the trade designation "Lubrizol® 7067C". Polyisoprene polymers are commercially available from Infineum International Limited, e.g. under the trade designation "SV200"; diene-styrene copolymers are commercially available from Infineum International Limited, e.g. under the trade designation "SV 260".

[0115] In an embodiment of this disclosure, the viscosity index improvers may be used in an amount of less than about 2.0 weight percent, preferably less than about 1.0 weight percent, and more preferably less than about 0.5 weight percent, based on the total weight of the formulated oil or lubricating engine oil. Viscosity improvers are typically added as concentrates, in large amounts of diluent oil.

[0116] In another embodiment of this disclosure, the viscosity index improvers may be used in an amount of from 0.25 to about 2.0 weight percent, preferably 0.15 to about 1.0 weight percent, and more preferably 0.05 to about 0.5 weight percent, based on the total weight of the formulated oil or lubricating engine oil.

Antioxidants

[0117] Antioxidants retard the oxidative degradation of base oils during service. Such degradation may result in deposits

on metal surfaces, the presence of sludge, or a viscosity increase in the lubricant. One skilled in the art knows a wide variety of oxidation inhibitors that are useful in lubricating oil compositions. See, Klamann in Lubricants and Related Products, op cite, and U.S. Patent Nos. 4,798,684 and 5,084,197, for example.

[0118] Useful antioxidants include hindered phenols. These phenolic antioxidants may be ashless (metal-free) phenolic compounds or neutral or basic metal salts of certain phenolic compounds. Typical phenolic antioxidant compounds are the hindered phenolics which are the ones which contain a sterically hindered hydroxyl group, and these include those derivatives of dihydroxy aryl compounds in which the hydroxyl groups are in the o- or p-position to each other. Typical phenolic antioxidants include the hindered phenols substituted with C_6+ alkyl groups and the alkylene coupled derivatives of these hindered phenols. Examples of phenolic materials of this type 2-t-butyl-4-heptyl phenol; 2-t-butyl-4-octyl phenol; 2-t-butyl-4-dodecyl phenol; 2,6-di-t-butyl-4-heptyl phenol; 2,6-di-t-butyl-4-dodecyl phenol; 2-methyl-6-t-butyl-4-heptyl phenol; and 2-methyl-6-t-butyl-4-dodecyl phenol. Other useful hindered mono-phenolic antioxidants may include for example hindered 2,6-di-alkyl-phenolic propionic ester derivatives. Bis-phenolic antioxidants may also be advantageously used in combination with the instant disclosure. Examples of ortho-coupled phenols include: 2,2'-bis(4-heptyl-6-t-butyl-phenol); 2,2'-bis(4-octyl-6-t-butyl-phenol); and 2,2'-bis(4-dodecyl-6-t-butyl-phenol). Para-coupled bisphenols include for example 4,4'-bis(2,6-di-t-butyl phenol) and 4,4'-methylene-bis(2,6-di-t-butyl phenol).

[0119] Effective amounts of one or more catalytic antioxidants may also be used. The catalytic antioxidants comprise an effective amount of a) one or more oil soluble polymetal organic compounds; and, effective amounts of b) one or more substituted N,N'-diaryl-o-phenylenediamine compounds or c) one or more hindered phenol compounds; or a combination of both b) and c). Catalytic antioxidants are more fully described in U.S. Patent No. 8,048,833.

[0120] Non-phenolic oxidation inhibitors which may be used include aromatic amine antioxidants and these may be used either as such or in combination with phenolics. Typical examples of non-phenolic antioxidants include: alkylated and non-alkylated aromatic amines such as aromatic monoamines of the formula $R^8R^9R^{10}N$ where R^8 is an aliphatic, aromatic or substituted aromatic group, R^9 is an aromatic or a substituted aromatic group, and R^{10} is H, alkyl, aryl or $R^{11}S(O)_XR^{12}$ where R^{11} is an alkylene, alkenylene, or aralkylene group, R^{12} is a higher alkyl group, or an alkenyl, aryl, or alkaryl group, and x is 0, 1 or 2. The aliphatic group R^8 may contain from 1 to 20 carbon atoms, and preferably contains from 6 to 12 carbon atoms. The aliphatic group is a saturated aliphatic group. Preferably, both R^8 and R^9 are aromatic or substituted aromatic groups, and the aromatic group may be a fused ring aromatic group such as naphthyl. Aromatic groups R^8 and R^9 may be joined together with other groups such as S.

[0121] Typical aromatic amines antioxidants have alkyl substituent groups of at least 6 carbon atoms. Examples of aliphatic groups include hexyl, heptyl, octyl, nonyl, and decyl. Generally, the aliphatic groups will not contain more than 14 carbon atoms. The general types of amine antioxidants useful in the present compositions include diphenylamines, phenyl naphthylamines, phenothiazines, imidodibenzyls and diphenyl phenylene diamines. Mixtures of two or more aromatic amines are also useful. Polymeric amine antioxidants can also be used. Particular examples of aromatic amine antioxidants useful in the present disclosure include: p,p'-dioctyldiphenylamine; t-octylphenyl-alphanaphthylamine; phenyl-alphanaphthylamine; and p-octylphenyl-alphanaphthylamine.

[0122] Sulfurized alkyl phenols and alkali or alkaline earth metal salts thereof also are useful antioxidants.

[0123] Preferred antioxidants include hindered phenols, arylamines. These antioxidants may be used individually by type or in combination with one another. Such additives may be used in an amount of 0.01 to 5 weight percent, preferably 0.01 to 2 weight percent, more preferably zero to about 1.5 weight percent, more preferably zero to less than 1 weight percent.

Pour Point Depressants (PPDs)

[0124] Conventional pour point depressants (also known as lube oil flow improvers) may be added to the compositions of the present disclosure if desired. These pour point depressant may be added to lubricating compositions of the present disclosure to lower the minimum temperature at which the fluid will flow or can be poured. Examples of suitable pour point depressants include polymethacrylates, polyacrylates, polyarylamides, condensation products of haloparaffin waxes and aromatic compounds, vinyl carboxylate polymers, and terpolymers of dialkylfumarates, vinyl esters of fatty acids and allyl vinyl ethers. U.S. Patent Nos. 1,815,022; 2,015,748; 2,191,498; 2,387,501; 2,655, 479; 2,666,746; 2,721,877; 2,721,878; and 3,250,715 describe useful pour point depressants and/or the preparation thereof. Such additives may be used in an amount of about 0.01 to 5 weight percent, preferably about 0.01 to 1.5 weight percent.

Seal Compatibility Agents

[0125] Seal compatibility agents help to swell elastomeric seals by causing a chemical reaction in the fluid or physical change in the elastomer. Suitable seal compatibility agents for lubricating oils include organic phosphates, alkoxysulfolanes, aromatic esters, aromatic hydrocarbons, esters (butylbenzyl phthalate, for example), and polybutenyl succinic anhydride. Such additives may be used in an amount of about 0.01 to 3 weight percent, preferably about 0.01 to 2 weight

percent.

Antifoam Agents

[0126] Anti-foam agents may advantageously be added to lubricant compositions. These agents retard the formation of stable foams. Silicones and organic polymers are typical anti-foam agents. For example, polysiloxanes, such as silicon oil or polydimethyl siloxane, provide antifoam properties. Anti-foam agents are commercially available and may be used in conventional minor amounts along with other additives such as demulsifiers; usually the amount of these additives combined is less than 1 weight percent and often less than 0.1 weight percent.

Inhibitors and Antirust Additives

[0127] Antirust additives (or corrosion inhibitors) are additives that protect lubricated metal surfaces against chemical attack by water or other contaminants. A wide variety of these are commercially available.

[0128] One type of antirust additive is a polar compound that wets the metal surface preferentially, protecting it with a film of oil. Another type of antirust additive absorbs water by incorporating it in a water-in-oil emulsion so that only the oil touches the metal surface. Yet another type of antirust additive chemically adheres to the metal to produce a non-reactive surface. Examples of suitable additives include zinc dithiophosphates, metal phenolates, basic metal sulfonates, fatty acids and amines. Such additives may be used in an amount of about 0.01 to 5 weight percent, preferably about 0.01 to 1.5 weight percent.

Friction Modifiers

[0129] A friction modifier is any material or materials that can alter the coefficient of friction of a surface lubricated by any lubricant or fluid containing such material(s). Friction modifiers, also known as friction reducers, or lubricity agents or oiliness agents, and other such agents that change the ability of base oils, formulated lubricant compositions, or functional fluids, to modify the coefficient of friction of a lubricated surface may be effectively used in combination with the base oils or lubricant compositions of the present disclosure if desired. Friction modifiers that lower the coefficient of friction are particularly advantageous in combination with the base oils and lube compositions of this disclosure.

[0130] Illustrative friction modifiers may include, for example, organometallic compounds or materials, or mixtures thereof. Illustrative organometallic friction modifiers useful in the lubricating engine oil formulations of this disclosure include, for example, molybdenum amine, molybdenum diamine, an organotungstenate, a molybdenum dithiocarbamate, molybdenum dithiophosphates, molybdenum amine complexes, molybdenum carboxylates, and the like, and mixtures thereof. Similar tungsten based compounds may be preferable.

[0131] Other illustrative friction modifiers useful in the lubricating engine oil formulations of this disclosure include, for example, alkoxylated fatty acid esters, alkanolamides, polyol fatty acid esters, borated glycerol fatty acid esters, fatty alcohol ethers, and mixtures thereof.

[0132] Illustrative alkoxylated fatty acid esters include, for example, polyoxyethylene stearate, fatty acid polyglycol ester, and the like. These can include polyoxypropylene stearate, polyoxybutylene stearate, polyoxyethylene isosterate, polyoxypropylene isostearate, polyoxyethylene palmitate, and the like.

[0133] Illustrative alkanolamides include, for example, lauric acid diethylalkanolamide, palmic acid diethylalkanolamide, and the like. These can include oleic acid diethyalkanolamide, stearic acid diethylalkanolamide, oleic acid diethylalkanolamide, polyethoxylated hydrocarbylamides, polypropoxylated hydrocarbylamides, and the like.

[0134] Illustrative polyol fatty acid esters include, for example, glycerol mono-oleate, saturated mono-, di-, and tri-glyceride esters, glycerol monostearate, and the like. These can include polyol esters, hydroxyl-containing polyol esters, and the like.

[0135] Illustrative borated glycerol fatty acid esters include, for example, borated glycerol mono-oleate, borated saturated mono-, di-, and tri-glyceride esters, borated glycerol mono-sterate, and the like. In addition to glycerol polyols, these can include trimethylolpropane, pentaerythritol, sorbitan, and the like. These esters can be polyol monocarboxylate esters, polyol dicarboxylate esters, and on occasion polyoltricarboxylate esters. Preferred can be the glycerol mono-oleates, glycerol dioleates, glycerol trioleates, glycerol monostearates, glycerol distearates, and glycerol tristearates and the corresponding glycerol monopalmitates, glycerol dipalmitates, and glycerol tripalmitates, and the respective isostearates, linoleates, and the like. On occasion the glycerol esters can be preferred as well as mixtures containing any of these. Ethoxylated, propoxylated, butoxylated fatty acid esters of polyols, especially using glycerol as underlying polyol can be preferred.

[0136] Illustrative fatty alcohol ethers include, for example, stearyl ether, myristyl ether, and the like. Alcohols, including those that have carbon numbers from C_3 to C_{50}, can be ethoxylated, propoxylated, or butoxylated to form the corresponding fatty alkyl ethers. The underlying alcohol portion can preferably be stearyl, myristyl, C_{11} - C_{13} hydrocarbon,

oleyl, isosteryl, and the like.

[0137] Useful concentrations of friction modifiers may range from 0.01 weight percent to 5 weight percent, or about 0.1 weight percent to about 2.5 weight percent, or about 0.1 weight percent to about 1.5 weight percent, or about 0.1 weight percent to about 1 weight percent. Concentrations of molybdenum-containing materials are often described in terms of Mo metal concentration. Advantageous concentrations of Mo may range from 25 ppm to 700 ppm or more, and often with a preferred range of 50-200 ppm. Friction modifiers of all types may be used alone or in mixtures with the materials of this disclosure. Often mixtures of two or more friction modifiers, or mixtures of friction modifier(s) with alternate surface active material(s), are also desirable.

[0138] When lubricating oil compositions contain one or more of the additives discussed above, the additive(s) are blended into the composition in an amount sufficient for it to perform its intended function. Typical amounts of such additives useful in the present disclosure are shown in Table 1 below.

[0139] It is noted that many of the additives are shipped from the additive manufacturer as a concentrate, containing one or more additives together, with a certain amount of base oil diluents. Accordingly, the weight amounts in the table below, as well as other amounts mentioned herein, are directed to the amount of active ingredient (that is the non-diluent portion of the ingredient). The weight percent (wt%) indicated below is based on the total weight of the lubricating oil composition.

Table 2. Typical Amounts of Other Lubricating Oil Components

Compound	Approximate wt% (Useful)	Approximate wt% (Preferred)
Dispersant	0.1-20	0.1-8
Detergent	0.1-20	0.1-8
Friction Modifier	0.01-5	0.01-1.5
Antioxidant	0.1-5	0.1-1.5
Pour Point Depressant (PPD)	0.0-5	0.01-1.5
Anti-foam Agent	0.001-3	0.001-0.15
Viscosity Index Improver (solid polymer basis)	0.1-2	0.1-1
Antiwear	0.1-2	0.5-1
Inhibitor and Antirust	0.01-5	0.01-1.5

[0140] The foregoing additives are all commercially available materials. These additives may be added independently but are usually precombined in packages which can be obtained from suppliers of lubricant oil additives. Additive packages with a variety of ingredients, proportions and characteristics are available and selection of the appropriate package will take the requisite use of the ultimate composition into account.

[0141] Formulated engine oils of the instant disclosure exhibit substantial elimination of LSPI. Substantial elimination of LSPI means greater than about 95%, or greater than about 97%, or greater than about 99% reduced low speed pre-ignition, based on normalized low speed pre-ignition (LSPI) counts per 25,000 engine cycles, engine operation at 2000 revolutions per minute (RPM) and brake mean effective pressure (BMEP) at 18 bar.

[0142] Formulated engine oils with higher ash levels of 1.2 to 1.6% or more in conjunction with the other components disclosed in this disclosure can significantly reduce the number of LSPI events by 96% or more. Formulated engine oils with lower ash levels of 0.2 to 1.2% in conjunction with the other components disclosed in this disclosure can reduce the number of LSPI events entirely.

[0143] Engines that are highly susceptible to Low speed pre-ignition (LSPI) are those which operate at high brake mean effective pressure (BMEP) and low engine speed (RPM). This includes internal combustion engines using a variety of fuels, including natural gas, gasoline, diesel, biofuels, and the like. Downsized, downspeeded, forced-induction (eg. Turbocharged) engines are most susceptible to operating under these engine conditions and are thus more susceptible to LSPI. Non-limiting examples of engines possessing these characteristics include the GM Ecotec and Ford EcoBoost family of engines as well as other high BMEP (capable of >10 bar) engines with displacements ranging from about 1 L to about 6 L as well as engines possessing between 2-10 combustion cylinders in geometric configurations including inline, flat (Boxer), and "V" (eg "V8", "in-line 3", "in-line 4", "flat 4" etc.). Furthermore the calibration and operational setpoints of the engine may significantly influence both the frequency and severity of LSPI events.

[0144] The following non-limiting examples are provided to illustrate the disclosure.

EXAMPLES

Example A

[0145] Formulations were prepared as described in Fig. 1. All of the ingredients used herein are commercially available. Group III, IV and V base stocks were used in the formulations.

[0146] The antiwear agents used in the formulations were ZDDP derived from a secondary alcohol (which contained 10% by weight Phosphorus and was prepared from mixed C3 and C6 secondary alcohols) and ZDDP derived from a primary alcohol (which contained 7% by weight Phosphorus and was prepared from C8 primary alcohols). In addition, zinc only and phosphorus only antiwear additives were used in the formulations.

[0147] The remaining ingredients used in the formulations were one or more of a viscosity index improver, antioxidant, dispersant, antiwear agent, pour point depressant, corrosion inhibitor, metal deactivator, seal compatibility additive, anti-foam agent, inhibitor, anti-rust additive, and friction modifier.

[0148] Testing was conducted for formulations described in Fig. 1. The results are set forth in Fig. 1. Sulfated ash testing was determined in accordance with ASTM D874. Zinc and phosphorus content were determined in accordance with ASTM D6443.

[0149] It has been documented that different engine hardware and control schemes can significantly influence the occurrence of LSPI. See, for example, U.S. Patent Application Publication Nos. 2012/1866225 and 2003/0908070, and also SAE 2012-02-1148, SAE 2011-01-0340, and SAE 2011-01-0343. Furthermore, Fig. 12 shows drive cycle data obtained from a taxi cab field trial. Two different 2.0L L4 TGDI engine types, from different Original Equipment Manufacturers were driven in a typical taxi cab city drive cycle for 2 weeks. Engine performance data was collected using the vehicles' OBD-II data ports and mapped onto the published engine torque maps for the respective engines. As published in SAE 2011-01-0339, engines are specifically prone to LSPI when they operate in a region above 10 bar BMEP and below 3000 rpm engine speed. Therefore, any region of the torque maps for these engines which is bounded by these operating conditions is potentially prone to LSPI. Based on the measured data for the OBD-II data loggers, it can be shown that engines with different calibrations can exhibit different LSPI behavior based on how they are tuned. Fig. 12 shows approximately 1.2 million data points summarizing the operation of two different engine types in a typical taxi cab city driving cycle over a 2 week period. Several taxi cabs using each engine type were observed in this manner. Engine Make 1 spends on average 1.67% of its operating time in the LSPI "danger zone" while Engine Make 2 only spends on average 0.17% in a typical taxi cab city drive cycle, even though both engines are 2.0 L inline 4-cylinder TGDI engines. Furthermore, Engine Make 2 has exhibited zero LSPI related field failures, while Engine Make 1 has exhibited multiple failures related to LSPI. This further illustrates the different responsiveness of different engine platforms to LSPI.

[0150] For the purposes of this disclosure, a 2.0 L, 4-cylinder TGDI GM Ecotec engine was used for LSPI testing. A six segment test procedure was used to determine the number of LSPI events that occurred at two different specified engine load and speed conditions. Each segment of the test procedure comprised 25,000 engine cycles, where one cycle corresponds to 720 degrees of crank shaft rotation. The first set of conditions was 2000 RPM and 18 bar BMEP, hereafter referred to as "High Load". The second set of conditions was 1500 RPM and 12.5 bar BMEP, hereafter referred to as "Low Load". The test procedure comprised two segments of High Load, followed by two segments of Low Load, followed by two segments of High Load. A 30 minute warm up at 2000 RPM and 4 bar BMEP was also conducted prior to commencing the test procedure. This test procedure was repeated four times for each of the lubricants tested. LSPI events were counted during the High Load segments only, using pressure transducers placed in each of the 4 cylinders to monitor the peak cylinder pressure. Peak pressures in the cylinder that were greater than 4.7 standard deviations above the mean peak cylinder pressure, or more than 4.7 standard deviations below the mean peak cylinder pressure were counted as an LSPI event. The results of such LSPI testing are set forth in Fig. 1.

[0151] The testing evaluated the impact of ZDDP on LSPI. As shown in Fig. 1, the use of secondary alcohol derived ZDDP is more preferable than the use of primary alcohol derived ZDDP, to reduce LSPI count. Example 1 shows that a secondary ZDDP can be used to obtain approximately 27 LSPI events, while Comparative Example 1, at an equivalent zinc and phosphorus content, shows that a primary ZDDP has unexpectedly higher LSPI counts at 34 counts per 25,000 engine cycles. Thus, the formulation with a secondary alcohol derived ZDDP exhibits an unexpected reduction in LSPI of 20%. This novel finding to reduce the LSPI count by the use of secondary ZDDP, or mostly secondary ZDDP, can be very beneficial to lubricant formulations. Example 2 presents a case where the ZDDP treat rate is taken to a very high level and shows that by increasing the amount of ZDDP within the formulation, the LSPI counts can be reduced, almost eliminated. Finally Comparative Examples 2 and 3 look further into the benefits of ZDDP by examining the impact of zinc and phosphorus separately. Comparative Example 2 uses a zinc only antiwear agent, at an equivalent treat rate to Example 1 and Comparative Example 1, to yield 36 LSPI counts. Comparative Example 3 on the other hand uses a phosphorus only antiwear agent, at an equivalent treat rate to Example 1 and Comparative Example 1, to yield 55 LSPI events. Comparing Comparative Example 2 with Comparative Example 3, the unique benefits of the zinc compound in controlling LSPI counts are clearly seen. At the same time, the detrimental effects of using a phosphorus only antiwear

agent can also be seen.

Example B

[0152] Formulations were prepared as described in Fig. 2. All of the ingredients used herein are commercially available. Group III, IV and V base stocks were used in the formulations.

[0153] The antiwear agents used in the formulations were ZDDP derived from a secondary alcohol and ZDDP derived from a primary alcohol.

[0154] The dispersants used in the formulations were a borated succinimide (which comprised a borated polyisobutenyl succinimede with a B/N ratio equal to about 0.5), a high molecular weight succinimide (High MW Succinimide Dispersant 1 which comprised an ethylene carbonate-capped bis-polyisobutenyl succinimide dispersant with about 1% total nitrogen) and a high molecular weight succinimide (High MW Succinimide Dispersant 2 which comprised a bis-polyisobutenyl succinimde with about 1.2% total nitrogen).

[0155] The remaining ingredients used in the formulations were one or more of a viscosity index improver, antioxidant, dispersant, antiwear agent, pour point depressant, corrosion inhibitor, metal deactivator, seal compatibility additive, anti-foam agent, inhibitor, anti-rust additive, and friction modifier.

[0156] Testing was conducted for formulations described in Fig. 2. The results are set forth in Fig. 3. Sulfated ash testing was determined in accordance with ASTM D874. Boron, zinc and phosphorus content were determined in accordance with ASTM D6443. Nitrogen content was determined in accordance with ASTM D3228. LSPI testing was conducted for formulations in accordance with the procedures described in Example 1 using the 2.0 L, 4-cylinder TGDI GM Ecotec engine.

[0157] The testing evaluated the impact of borated dispersants and ZDDP derived from secondary alcohols on LSPI. As shown in Fig. 3, the use of a borated dispersant and secondary ZDDP is unexpectedly beneficial to LSPI performance. Example 1, Comparative Example 4, Comparative Example 5, and Example 3 all use secondary ZDDP antiwear agent at the same treat rate while the dispersant is being varied. As indicated by the boron content in these blends, as the boron content increases, the LSPI count unexpectedly reduces. Specifically, Example 3 which has about 507 ppm of boron has only 24 LSPI events, while Comparative Examples 4 and 5 which have no boron present, have 46 and 43 LSPI events, respectively. Going from no boron, to 240 ppm boron, to 507 ppm boron, reduces LSPI count from 46, to 27, to 24, respectively. That is a 40% LSPI reduction with 240 ppm of boron and a 48% LSPI reduction with about 507 ppm of boron. The LSPI reduction is expected to continue as the boron level is increased. The benefits of using a borated dispersant with a secondary ZDDP are clearly seen. Comparative Example 1 further demonstrates the unique and unexpected benefits of a borated dispersant and a secondary ZDDP by showing the disadvantages of a borated dispersant and a primary ZDDP. When compared with Example 1, which has the same level of boron as Comparative Example 1, Comparative Example 1 shows an increase in LSPI count from 27 to 34 when the secondary ZDDP is switched out for a primary ZDDP.

[0158] Comparative Example 8 shows an example in which no dispersants are used, and had an LSPI count of 22. While this is virtually the same as the blends which contained a boarated disperant, this further demonstrates the utility of borated dispersants for reducing LSPI for oils used in commercial applications. Typically dispersants are required to be used to disperse sludge and other particulate matter which may be generated during normal operation. Comparing Comparative Example 4 with Comparative Example 4 shows that non-borated disperants can cause an increase in LSPI by almost 100 %, while using borated dispersant alone or in combination with other non-borated dispersants reduces LSPI frequency.

Example C

[0159] Formulations were prepared as described in Fig. 4. All of the ingredients used herein are commercially available. Group III, IV and V base stocks were used in the formulations.

[0160] The detergents used in the formulations were a medium TBN calcium alkyl salicylate (Calcium Salicylate 1 which contains 7.3 % Ca and has a TBN of about 200), a low TBN calcium alkyl salicylate (Calcium Salicylate 2 which contains 2.3% Ca and about 65 TBN), a high TBN calcium alkyl sulfonate (Calcium Sulfonate 1 which contains 11.6% Ca and about 300 TBN), a low TBN calcium alkyl sulfonate (Calcium Sulfonate 2 which contains 2.0% Ca and about 8 TBN), and a high TBN magnesium alkyl sulfonate (Magnesium Sulfonate 1 which contains 9.1% Mg and about 400 TBN). The TBN ranges are defined as: low TBN of about 0 to 100, medium TBN of about 100 to 200, and high TBN of about 200 to as high as 600.

[0161] The dispersants used in the formulations were a borated succinimide and a high molecular weight succinimide.

[0162] The antiwear agents used in the formulations were ZDDP derived from a secondary alcohol and ZDDP derived from a primary alcohol.

[0163] The remaining ingredients used in the formulations were one or more of a viscosity index improver, antioxidant,

dispersant, antiwear agent, pour point depressant, corrosion inhibitor, metal deactivator, seal compatibility additive, anti-foam agent, inhibitor, anti-rust additive, and friction modifier.

[0164] Testing was conducted for formulations described in Fig. 4. The results are set forth in Fig. 5. Sulfated ash testing was determined in accordance with ASTM D874. Calcium, magnesium, boron, zinc and phosphorus content were determined in accordance with ASTM D6443. Nitrogen content was determined in accordance with ASTM D3228. LSPI testing was conducted for formulations in accordance with the procedures described in Example 1 using the 2.0 L, 4-cylinder TGDI GM Ecotec engine.

[0165] The testing evaluated the impact of a three additive system (i.e., detergent, dispersant and antiwear agent) on LSPI. As shown in Fig. 5, where LSPI is measured for formulations containing a non-borated dispersant and for formulations containing a mixture of non-borated dispersant and borated dispersant, the use of a borated succinimide dispersant has unique LSPI benefits over high molecular weight succinimide dispersant. Comparative Example 6, Example 4 and Example 8 show the impact of increasing boron content on LSPI performance. As the boron content increases from 0, to 240, to 507 ppm, the LSPI count decreases from 46, to 27, to 24. The benefit of boron in reducing LSPI frequency represents a significant and unexpected finding presented in Figs. 4 and 5. Example 6 and Example 7 showcase the unique combination of a magnesium sulfonate detergent with a dual dispersant system and a secondary alcohol derived ZDDP. The dual dispersant system contains a boron source. The uniqueness of this combination is shown by comparing to Comparative Example 6, which uses a different calcium salicylate based detergent system and has the worst LSPI counts. The use of magnesium sulfonate detergent, with a secondary alcohol derived ZDDP, and a borated dispersant is shown to unexpectedly and significantly reduce, if not eliminate, LSPI. The desirable ratio of the total concentration of ([Mg] + [Ca] + [Zn] + [P]) / ([B] + $[N]_{dispersant}$) is about 2.5 to 7, more preferably from about 3.3 to 5. Comparing Example 4 with Example 10 further demonstrates the utility of this approach incorporating a borated dispersant with a secondary alcohol derived ZDDP and a combination of a magnesium sulfonate detergent with a calcium salicylate detergent. Example 10 shows a reduction in LSPI by 98% compared to Comparative Example 6.

Example D

[0166] The lubricating engine oil formulations in Figs. 6 and 7 are combinations of additives and base stocks and are anticipated to have kinematic viscosity at 100°C around 7.5-8.5 cSt and high temperature high shear (10^{-6} s^{-1}) viscosity at 150°C around 2.5 to 2.9 cP. The lubricating engine oil formulations of Examples P1, P2, P3 are expected to have boron to dispersant nitrogen ratios of 0.05, 0.15, and 0.51, respectively. The total boron content in these formulations is expected to range from 50 ppm to 800 ppm. The ([Mg]+[Ca])/([B] + $[N]_{dispersant}$) ratio is expected to range from 1.28 for Example P3 to 2.91 for Example P1. Similarly, the ([Zn] + [P])/([B] + $[N]_{dispersant}$) ratio is expected to range from 0.71 for Example P3 and 1.62 for Example P1. Finally, the ([Mg]+[Ca]+[Zn]+[P])/([B]+$[N]_{dispersant}$) ratio of Examples P1, P2 and P3, is expected to be between 1.99 and 4.53. The lubricating engine oil formulations of Examples P4 and P5 are expected to have magnesium content of 300 ppm to 600 ppm. Similarly the lubricating engine oil formulations of Examples P6, P7, and P8 are expected to have magnesium content of about 300 ppm to 900 ppm and a magnesium to calcium ratio of about 0.12 for Example P6 to 1.21 for Example P8. At the same time, the TBN of these examples is varying from 6.8 for Examples P8, to P9 for Example P6. Similarly the sulfated ash content in Example P4, P5, and P6 is varying from 0.3 wt% to 1.2 wt% ash. The other ratios identified in Figs. 6 and 7 are also changing as indicated therein. The lubricating engine oil formulations of Examples P9 and P10 are expected to have magnesium to calcium ratio of about 0.06 and 3, respectively, at a constant TBN. The lubricating engine oil formulations of Examples P11, P12 and P13 are expected to have zinc content ranging from about 96 ppm for Example P13 to about 635 ppm for Example P11. The lubricating engine oil formulations of Examples P11, P12 and P13 are expected to have phosphorus content ranging from about 87 ppm for Example P13 to about 570 ppm for Example P11. The ([Mg]+[Ca])/([Zn]+[P]) ratio ranges from about 2.5 for Example P11 to 16.5 for Example P13. The ([Zn]+[P])/([B]+$[N]_{dispersant}$) ratio ranges from about 1 for Example P11 to 0.15 for Example P13. The ([Mg]+[Ca]+[Zn]+[P])/([B]+$[N]_{dispersant}$) ratio ranges from about 3.4 for c Example P11 to 2.6 for c Example P13.

Example E

[0167] The lubricating engine oil formulations in Figs. 8 and 9 are combinations of additives and base stocks and are anticipated to have kinematic viscosity at 100°C around 5.5-7.5 cSt and high temperature high shear (10^{-6} s^{-1}) viscosity at 150°C around 2 to 2.5 cP. The lubricating engine oil formulations of Examples P14, P15 and P16 are expected to have boron to dispersant nitrogen ratios of 0.05, 0.15, and 0.51, respectively. The total boron content in these formulations is expected to range from 50 ppm to 800 ppm. The ([Mg]+[Ca])/([B] + $[N]_{dispersant}$) ratio is expected to range from 1.28 for Example P16 to 2.91 for Example P14. Similarly, the ([Zn] + [P])/([B] + [N] dispersant) ratio is expected to range from 0.71 for Example P16 and 1.62 for Example P14. Finally, the ([Mg]+[Ca]+[Zn]+[P])/([B]+$[N]_{dispersant}$) ratio of Examples P14, P15 and P16, is expected to be between 1.99 and 4.53. The lubricating engine oil formulations of Examples P17

and P18 are expected to have magnesium content of 300 ppm to 600 ppm. Similarly the lubricating engine oil formulations of Examples P19, P20, and P21 are expected to have magnesium content of about 300 ppm to 900 ppm and a magnesium to calcium ratio of about 0.12 for Example P19 to 1.21 for Example P21. At the same time, the TBN of these examples is varying from 6.8 for Example P21, to 9 for Example P19. Similarly the sulfated ash content in Example P17, P18, and P19 is varying from 0.3 wt% to 1.2 wt% ash. The other ratios identified in Figs. 8 and 9 are also changing as indicated therein. The lubricating engine oil formulations of Examples P22 and P23 are expected to have magnesium to calcium ratio of about 0.06 and 3, respectively, at a constant TBN. The lubricating engine oil formulations of Examples P24, P25, and P26 are expected to have zinc content ranging from about 96 ppm for Example P26 to about 635 ppm for Example P24. The lubricating engine oil formulations of Examples P24, P25, and P26 are expected to have phosphorus content ranging from about 87 ppm for Example P26 to about 570 ppm for Example P24. The ([Mg]+[Ca])/([Zn]+[P]) ratio ranges from about 2.5 for Example P24 to 16.5 for Example P26. The ([Zn]+[P])/([B]+$[N]_{dispersant}$) ratio ranges from about 1 for Example P24 to 0.15 for Example P26. The ([Mg]+[Ca]+[Zn]+[P])/([B]+$[N]_{dispersant}$) ratio ranges from about 3.4 for Example P24 to 2.6 for Example P26.

Example F

[0168] The lubricating engine oil formulations in Figs. 10 and 11 are combinations of additives and base stocks and are anticipated to have kinematic viscosity at 100°C around 9-11 cSt and high temperature high shear (10^{-6} s^{-1}) viscosity at 150°C around 2.9 to 3.4 cP. The lubricating engine oil formulations of Examples P27, P28, and P29 are expected to have boron to dispersant nitrogen ratios of 0.05, 0.15, and 0.51, respectively. The total boron content in these formulations is expected to range from 50 ppm to 800 ppm. The ([Mg]+[Ca])/([B] + $[N]_{dispersant}$) ratio is expected to range from 1.28 for Example P29 to 2.91 for Example P27. Similarly, the ([Zn] + [P])/([B] + $[N]_{dispersant}$) ratio is expected to range from 0.71 for Example P29 and 1.62 for Example P27. Finally, the ([Mg]+[Ca]+[Zn]+[P])/([B]+$[N]_{dispersant}$) ratio of Examples P27, P28, and P29, is expected to be between 1.99 and 4.53. The lubricating engine oil formulations of Examples P30 and P31 are expected to have magnesium content of 300 ppm to 600 ppm. Similarly the lubricating engine oil formulations of Examples P32, P33, and P34 are expected to have magnesium content of about 300 ppm to 900 ppm and magnesium to calcium ratio of about 0.12 for Example P32 to 1.21 for Example P34. At the same time, the TBN of these examples is varying from 6.8 for Example P34, to 9 for Example P32. Similarly the sulfated ash content in Example P30, P31, P32 is varying from 0.3 wt% to 1.2 wt% ash. The other ratios identified in Figs. 10 and 11 are also changing as indicated therein. The lubricating engine oil formulations of Examples P35 and P36 are expected to have magnesium to calcium ratio of about 0.06 and 3, respectively, at a constant TBN. The lubricating engine oil formulations of Examples P37, P38, and P39 are expected to have zinc content ranging from about 96 ppm for Example P39 to about 635 ppm for Example P37. The lubricating engine oil formulations of Examples P37, P38, and P39 are expected to have phosphorus content ranging from about 87 ppm for Example P39 to about 570 ppm for Example P37. The ([Mg]+[Ca])/([Zn]+[P]) ratio ranges from about 2.5 for Example P37 to 16.5 for Example P39. The ([Zn]+[P])/([B]+$[N]_{dispersant}$) ratio ranges from about 1 for Example P37 to 0.15 for Example P39. The ([Mg]+[Ca]+[Zn]+[P])/([B]+$[N]_{dispersant}$) ratio ranges from about 3.4 for Example P37 to 2.6 for Example P39.

[0169] Examples 1, 2, 3, 4, 5, 8, 9, P1, P2, P3,P11, P12, P13, P14, P15, P16, P24, P25, P26, P27, P28, P29,P37, P38, P39 are reference examples.

Claims

1. Use of a formulated oil as lubricating oil for preventing or reducing low speed pre-ignition in an internal combustion engine lubricated with the lubricating oil, wherein
the formulated oil has a composition comprising a lubricating oil base stock as a major component; and as a minor component at least one zinc-containing compound or at least one antiwear agent in an amount of from 0.1 to 5.0 wt% based on the total weight of the lubricating oil,
the at least one antiwear agent comprises at least one zinc dialkyl dithiophosphate compound derived from a secondary alcohol in an amount of from 0.4 to 1.2 wt% based on the total weight of the lubricating oil;
the minor component further comprises at least one boron-containing compound in an amount of from 30 to 1500 ppm of boron based on the total weight of the lubricating oil and from 1.0 to 6.0 wt% based on the total weight of the lubricating oil of at least one detergent,
the boron-containing compound comprises at least one borated dispersant or a mixture of a boron-containing compound and a non-borated dispersant, and
the detergent comprises at least one magnesium salt of an organic acid in an amount of 100 to 3000 ppm of magnesium based on the total weight of the lubricating oil,
and wherein the engine exhibits greater than 20% reduced low speed pre-ignition, based on normalized low speed

pre-ignition (LSPI) counts per 25,000 engine cycles, engine operation at 2000 revolutions per minute (RPM) and brake mean effective pressure (BMEP) at 18 bar, as compared to low speed pre-ignition performance achieved in an engine using a lubricating oil that does not comprise at least one zinc-containing compound or antiwear agent.

2. The use of claim 1, wherein the lubricating oil base stock comprises a Group I, Group II, Group III, Group IV, or Group V base oil; wherein the Group V base oil comprises an ester base oil having a kinematic viscosity at 100°C of 2 cSt to 8 cSt at a concentration of 2% to 20%, and the Group III base oil comprises a GTL base oil.

3. The use of claims 1-2, wherein the zinc-containing compound is selected from the group consisting of zinc sulfonate, zinc acetate, zinc napthenate, zinc alkenyl succinate, zinc acid phosphate salt, zinc phenate, and zinc salicylate.

4. The use of claims 1-3, wherein the zinc dialkyl dithiophosphate compound is represented by the formula

$$Zn[SP(S)(OR^1)(OR^2)]_2$$

wherein R^1 and R^2 are independently primary or secondary C_1 to C_8 alkyl groups, provided at least one of R^1 and R^2 is a secondary C_1 to C_8 alkyl group.

5. The use of claims 1-4, wherein the zinc dialkyl dithiophosphate compound is derived from (i) a C_3 to C_8 secondary alcohol, or a mixture thereof; or (ii) a mixture of a C_1 to C_8 primary alcohol and a C_1 to C_8 secondary alcohol.

6. The use of claims 1-5, wherein the boron-containing compound or borated dispersant is selected from the group consisting of a borated succinimide, a borated succinate ester, a borated succinate ester amide, a borated Mannich base, and mixtures thereof; and the non-borated dispersant comprises a succinic anhydride derived succinimide or succinate ester with a coupling agent, wherein the coupling agent comprises a boron-containing compound.

7. The use of claims 1-6, wherein the detergent comprises (i) at least one of magnesium sulfonate, magnesium phenate, and magnesium salicylate, and mixtures thereof, and optionally at least one of calcium sulfonate, calcium phenate, and calcium salicylate, and mixtures thereof; (ii) at least one magnesium salt of an organic acid which is selected from magnesium sulfonate, magnesium carboxylate, magnesium phenate, magnesium phosphate, and mixtures thereof; or (iii) magnesium sulfonate, a mixture of magnesium sulfonate and magnesium salicylate, a mixture of magnesium sulfonate and magnesium phenate, or a mixture of magnesium sulfonate and magnesium carboxylate.

8. The use of claims 1-7, wherein (i) magnesium and alkaline earth metal contributed by the detergent is present in the lubricating oil in an amount from 500 ppm to 5000 ppm; (ii) total base number (TBN), as measured by ASTM D2896, contributed by the detergent ranges from 2 mg KOH/g to 17 mg KOH/g; or (iii) sulfated ash contributed by the detergent ranges from 0.4 to 1.7 wt%.

Patentansprüche

1. Verwendung von formuliertem Öl als Schmieröl zum Verhindern oder Verringern von Frühzündung bei niedriger Drehzahl in einem Verbrennungsmotor, der mit dem Schmieröl geschmiert wird,
wobei das formulierte Öl eine Zusammensetzung aufweist, die als Hauptkomponente Basisschmieröl und als Nebenkomponente mindestens eine zinkhaltige Verbindung oder mindestens ein Antiverschleißmittel in einer Menge von 0,1 bis 5,0 Gew.-%, bezogen auf das Gesamtgewicht des Schmieröls, umfasst,
wobei das mindestens eine Antiverschleißmittel mindestens eine von einem sekundären Alkohol abgeleitete Zinkdialkyldithiophosphatverbindung in einer Menge von 0,4 bis 1,2 Gew.-%, bezogen auf das Gesamtgewicht des Schmieröls, umfasst,
wobei die Nebenkomponente ferner mindestens eine borhaltige Verbindung in einer Menge von 30 bis 1500 ppm Bor, bezogen auf das Gesamtgewicht des Schmieröls, und von 1,0 bis 6,0 Gew.-%, bezogen auf das Gesamtgewicht des Schmieröls, mindestens eines Detergens umfasst,
wobei die borhaltige Verbindung mindestens ein boriertes Dispergiermittel oder eine Mischung aus borhaltiger Verbindung und nicht-boriertem Dispergiermittel umfasst und
wobei das Detergens mindestens ein Magnesiumsalz einer organischen Säure in einer Menge von 100 bis 3000 ppm Magnesium, bezogen auf das Gesamtgewicht des Schmieröls, umfasst,
und wobei der Motor eine um mehr als 20 % verringerte Frühzündung bei niedriger Drehzahl aufweist, bezogen auf normierte Frühzündungsereignisse bei niedriger Drehzahl (LSPI) pro 25.000 Motorzyklen, Motorbetrieb bei 2000

Umdrehungen pro Minute (U/min) und effektivem Mitteldruck (BMEP) bei 18 bar, im Vergleich zur Frühzündungsleistung bei niedriger Drehzahl, die in einem Motor unter Verwendung eines Schmieröls erreicht wird, das nicht mindestens eine zinkhaltige Verbindung oder Antiverschleißmittel umfasst.

2. Verwendung nach Anspruch 1, wobei das Basisschmieröl Basisöl der Gruppe I, Gruppe II, Gruppe III, Gruppe IV oder Gruppe V umfasst, wobei das Basisöl der Gruppe V Esterbasisöl umfasst, das eine kinematische Viskosität bei 100 °C von 2 cSt bis 8 cSt bei einer Konzentration von 2% bis 20% aufweist, und das Basisöl der Gruppe III GTL-Basisöl umfasst.

3. Verwendung nach einem der Ansprüche 1 bis 2, wobei die zinkhaltige Verbindung ausgewählt ist aus der Gruppe bestehend aus Zinksulfonat, Zinkacetat, Zinknaphtenat, Zinkalkenylsuccinat, saures Zinkphosphatsalz, Zinkphenolat und Zinksalicylat.

4. Verwendung nach einem der Ansprüche 1 bis 3, wobei die Zinkdialkyldithiophosphatverbindung durch die Formel wiedergegeben ist

$$Zn[SP(S)(OR^1)(OR^2)]_2,$$

in der R^1 und R^2 unabhängig primäre oder sekundäre C_1- bis C_8-Alkylgruppen sind, vorausgesetzt, dass mindestens eines von R^1 und R^2 eine sekundäre C_1- bis C_8-Alkylgruppe ist.

5. Verwendung nach einem der Ansprüche 1 bis 4, wobei die Zinkdialkyldithiophosphatverbindung von (i) einem sekundären C_3- bis C_8-Alkohol oder Mischungen davon oder (ii) einer Mischung aus primärem C_1- bis C_8-Alkohol und sekundärem C_1- bis C_8-Alkohol abgeleitet ist.

6. Verwendung nach einem der Ansprüche 1 bis 5, wobei die borhaltige Verbindung oder das borierte Dispergiermittel ausgewählt ist aus der Gruppe bestehend aus boriertem Bersteinsäureimid, boriertem Bersteinsäureester, boriertem Bersteinsäureesteramid, borierter Mannichbase und Mischungen davon, und wobei das nicht-borierte Dispergiermittel Bernsteinsäureanhydrid umfasst, das von Bersteinsäureimid oder Bernsteinsäureester mit einem Kupplungsmittel abgeleitet ist, wobei das Kupplungsmittel borhaltige Verbindung umfasst.

7. Verwendung nach einem der Ansprüche 1 bis 6, wobei das Detergens (i) mindestens eines von Magnesiumsulfonat, Magnesiumphenolat und Magnesiumsalicylat und Mischungen davon und wahlweise mindestens eines von Calciumsulfonat, Calciumphenolat und Calciumsalicylat und Mischungen davon, (ii) mindestens ein Magnesiumsalz einer organischen Säure, das ausgewählt ist aus Magnesiumsulfonat, Magnesiumcarboxylat, Magnesiumphenolat, Magnesiumphosphat und Mischungen davon oder (iii) Magnesiumsulfonat, eine Mischung von Magnesiumsulfonat und Magnesiumsalicylat oder eine Mischung von Magnesiumsulfonat und Magnesiumcarboxylat umfasst.

8. Verwendung nach einem der Ansprüche 1 bis 7, wobei (i) Magnesium und Erdalkalimetall, das vom Detergens beigesteuert wird, im Schmieröl in einer Menge von 500 ppm bis 5000 ppm vorhanden ist, (ii) die Gesamtbasenzahl (TBN), die durch das Detergens beigesteuert wird, wie gemäß ASTM D2896 gemessen, im Bereich von 2 mg KOH/g bis 17 mg KOH/g liegt, oder (iii) Sulfatasche, die durch das Detergens beigesteuert wird, im Bereich von 0,4 bis 1,7 Gew.-% liegt.

Revendications

1. Utilisation d'une huile formulée comme huile lubrifiante pour empêcher ou réduire le préallumage à basse vitesse dans un moteur à combustion interne lubrifié avec l'huile lubrifiante, dans laquelle
l'huile formulée a une composition comprenant une huile de base lubrifiante comme principal constituant ;
et comme constituant secondaire, au moins un composé contenant du zinc ou au moins un agent antiusure dans une quantité de 0,1 à 5,0 % en poids, rapporté au poids total de l'huile lubrifiante ;
l'au moins un agent antiusure comprend au moins un composé dialkyldithiophosphate de zinc dérivé d'un alcool secondaire dans une quantité de 0,4 à 1,2 % en poids, rapporté au poids total de l'huile lubrifiante ;
le constituant secondaire comprend en outre au moins un composé contenant du bore dans une quantité de 30 à 1500 ppm de bore, rapporté au poids total de l'huile lubrifiante, et de 1,0 à 6,0 % en poids, rapporté au poids total de l'huile lubrifiante, d'au moins un détergent,
le composé contenant du bore comprend au moins un dispersant boré ou un mélange d'un composé contenant du

bore et d'un dispersant non boré, et
le détergent comprend au moins un sel de magnésium d'un acide organique dans une quantité de 100 à 3000 ppm de magnésium, rapporté au poids total de l'huile lubrifiante,
et dans laquelle le moteur présente un préallumage à basse vitesse réduit de plus de 20 %, sur la base d'un nombre de préallumages à basse vitesse normalisés (LSPI) pour 25 000 cycles moteurs, d'un fonctionnement du moteur à 2000 tours par minute (tr/min) et d'une pression de freinage effective moyenne (BMEP) à 18 bar, tel que comparé à des performances de préallumage à basse vitesse obtenues dans un moteur utilisant une huile lubrifiante qui ne comprend pas au moins un composé contenant du zinc ou agent antiusure.

2. Utilisation de la revendication 1, dans laquelle l'huile de base lubrifiante comprend une huile de base du groupe I, du groupe II, du groupe III, du groupe IV ou du groupe V ; dans laquelle l'huile de base du groupe V comprend une huile de base estérifiée ayant de viscosité cinématique à 100 °C de 2 cSt à 8 cSt à une concentration de 2 % à 20 %, et l'huile de base du groupe III comprend une huile de base GTL.

3. Utilisation des revendications 1 et 2, dans laquelle le composé contenant du zinc est choisi dans le groupe constitué par le sulfonate de zinc, l'acétate de zinc, le naphténate de zinc, un alcénylsuccinate de zinc, un sel de phosphate acide de zinc, le phénate de zinc, et le salicylate de zinc.

4. Utilisation des revendications 1 à 3, dans laquelle le composé dialkyldithiophosphate de zinc est représenté par la formule

$$Zn[SP(S)(OR^1)(OR^2)]_2$$

dans laquelle R^1 et R2 sont indépendamment des groupes alkyle primaires ou secondaires en C_1 à C_8, à condition qu'au moins un de R^1 et R^2 soit un groupe alkyle secondaire en C_1 à C_8.

5. Utilisation des revendications 1 à 4, dans laquelle le composé dialkyldithiophosphate de zinc est dérivé de (i) un alcool secondaire en C_3 à C_8, ou un mélange de ceux-ci ; ou (ii) un mélange d'un alcool primaire en C_1 à C_8 et d'un alcool secondaire en C_1 à C_8.

6. Utilisation des revendications 1 à 5, dans laquelle le composé contenant du bore ou dispersant boré est choisi dans le groupe constitué par un succinimide boré, un ester de succinate boré, un amide d'ester de succinate boré, une base de Mannich borée, et les mélanges de ceux-ci ; et le dispersant non boré comprend un succinimide ou ester de succinate dérivé de l'anhydride succinique avec un agent de couplage, l'agent de couplage comprenant un composé contenant du bore.

7. Utilisation des revendications 1 à 6, dans laquelle le détergent comprend (i) au moins un composé parmi le sulfonate de magnésium, le phénate de magnésium et le salicylate de magnésium, et les mélanges de ceux-ci, et éventuellement au moins un composé parmi le sulfonate de calcium, le phénate de calcium et le salicylate de calcium, et les mélanges de ceux-ci ; (ii) au moins un sel de magnésium d'un acide organique qui est choisi parmi le sulfonate de magnésium, le carboxylate de magnésium, le phénate de magnésium, le phosphate de magnésium, et les mélanges de ceux-ci ; ou (iii) du sulfonate de magnésium, un mélange de sulfonate de magnésium et de salicylate de magnésium, un mélange de sulfonate de magnésium et de phénate de magnésium, ou un mélange de sulfonate de magnésium et de carboxylate de magnésium.

8. Utilisation des revendications 1 à 7, dans laquelle (i) le magnésium et le métal alcalino-terreux apportés par le détergent sont présents dans l'huile lubrifiante dans une quantité de 500 ppm à 5000 ppm ; (ii) l'indice de basicité totale (TBN), tel que mesuré par la méthode ASTM D2896, apporté par le détergent va de 2 mg KOH/g à 17 mg KOH/g ; ou (iii) les cendres sulfatées apportées par le détergent vont de 0,4 à 1,7 % en poids.

Fig. 1

	Example 1	Example 2	Comparative Example 1	Comparative Example 2	Comparative Example 3
Group III 1, wt%	48.84	48.84	48.84	48.84	48.84
Group IV 1, wt %	23.62	20.67	23.28	21.32	23.45
Group V 1, wt%	5	5	5	5	5
2° ZDDP 1, wt %	0.8	3.75			
1° ZDDP, wt %			1.14		
Zn only AW, wt %				3.1	
P only AW, wt %					0.97
Rest of formulation, wt %	21.74	21.74	21.74	21.74	21.74
Sulfated Ash, wt %	1.2	1.6	1.2	1.2	1.1
Zinc, ppm	884	4150	890	893	
Phosphorus, ppm	800	3750	798		805
[Zn] /([Zn] + [P])	0.5	0.5	0.5	1.0	0.0
Normalized LSPI Counts per 25,000 Engine Cycles	**27**	**1**	**34**	**36**	**55**

Fig. 2

	Example 1	Comparitive Example 4	Comparitive Example 5	Example 3	Example 2	Comparitive Example 1	Comparitive Example 8	Example 9
Group III 1, wt%	48.84	48.84	48.84	48.84	48.84	48.84	48.84	48.84
Group IV 1, wt %	23.62	21.69	23.34	25.77	20.67	23.28	27.59	15.867
Group V 1, wt%	5	5	5	5	5	5	5	5
Viscosity Index Improver	2	2	2	2	2	2	6	2
Borated Succinimide Dispersant, wt %	2.77			5.823	2.77	2.77	0	5.823
High MW Succinimide Dispersant 1, wt %	5.2	9.9			5.2	5.2	0	9.9
High MW Succinimide Dispersant 2, wt %			8.25					
2° ZDDP 1, wt %	0.8	0.8	0.8	0.8	3.75		0.8	0.8
1° ZDDP, wt %						1.14		
Rest of formulation, wt %	11.77	11.77	11.77	11.77	11.77	11.77	11.77	11.77

Fig. 3

	Example 1	Comparative Example 4	Comparative Example 5	Example 3	Example 2	Comparative Example 1	Comparative Example 6	Example 4
Sulfated Ash, wt %	1.2	1.2	1.2	1.2	1.6	1.2	1.2	1.2
Dispersant Nitrogen, ppm	990	990	990	990	990	990		1980
Boron, ppm	240			507	240	240		507
Zinc, ppm	884	884	884	884	4150	890	884	884
Phosphorus, ppm	800	800	800	800	3750	798	800	800
([Zn] + [P]) / ([B] + $[N]_{dispersant}$)	1.4	1.7	1.7	1.1	6.4	1.4		0.7
Normalized LSPI Counts per 25,000 Engine Cycles	**27**	**46**	**43**	**24**	**1**	**34**	22	36

Fig. 4

	Example 4	Example 5	Example 6	Example 7	Comparative Example 6	Example 8	Comparative Example 7
Group III 1, wt%	48.8	48.8	48.8	48.8	48.8	48.8	48.8
Group IV 1, wt %	23.6	25.4	25.6	27.6	21.7	25.8	23.3
Group V 1, wt%	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Viscosity Index Improver	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Calcium Salicylate 1, wt %	3.5				3.5	3.5	3.5
Calcium Salicylate 2, wt %	2.0				2.0	2.0	2.0
Calcium Sulfonate 1, wt %		2.5					
Calcium Sulfonate 2, wt %		1.3					
Magnesium Sulfonate, wt %			3.5	1.5			
Borated Succinimide Dispersant, wt %	2.8	2.8	2.8	2.8		5.8	2.8
High MW Succinimide Dispersant 1, wt %	5.2	5.2	5.2	5.2	9.9		5.2
2° ZDDP, wt %	0.8	0.8	0.8	0.8	0.8	0.8	
1° ZDDP, wt %							1.1
Rest of formulation, wt %	6.3	6.3	6.3	6.3	6.3	6.3	6.3

Fig. 4 (Cont.)

	Example 10	Example 11	Comparative Example 8	Example 9
Group III 1, wt%	48.8	48.8	48.8	48.8
Group IV 1, wt %	25.5	23.8	27.6	15.9
Group V 1, wt%	5.0	5.0	5.0	5.0
Viscosity Index Improver	2.0	2.0	2.0	2.0
Calcium Salicylate 1, wt %	1.4	2.1	1.5	1.5
Calcium Salicylate 2, wt %	0.8	1.2	2.0	2.0
Calcium Sulfonate 1, wt %				
Calcium Sulfonate 2, wt %				
Magnesium Sulfonate, wt %	1.4	2.2		
Borated Succinimide Dispersant, wt %	2.8	2.8	0.0	5.8
High MW Succinimide Dispersant 1, wt %	5.2	5.2	0.0	9.9
2° ZDDP, wt %	0.8	0.8	0.8	0.8
1 ° ZDDP, wt %				
Rest of formulation, wt %	6.3	6.3	6.3	6.3

Fig. 5

	Example 4	Example 5	Example 6	Example 7	Comparative Example 6	Example 8	Comparative Example 7
Sulfated Ash, wt %	1.2	1.2	1.6	0.8	1.2	1.2	1.2
Dispersant Nitrogen, ppm	990	990	990	990	990	990	990
Calcium, ppm	3015	3102			3015	3015	3015
Magnesium, ppm			3185	1365			
Boron, ppm	240	240	240	240		507	240
Zinc, ppm	884	884	884	884	884	884	890
Phosphorus, ppm	800	800	800	800	800	800	798
$([Mg]+[Ca]+[Zn]+[P]) / ([B]+[N]_{dispersant})$	3.8	3.9	4.0	2.5	4.7	3.1	3.8
Normalized LSPI Counts per 25,000 Engine Cycles	**27**	**21**	**2**	**0**	**46**	**24**	**34**

Fig. 5 (Cont.)

	Example 10	Example 11	Comparative Example 8	Example 9
Sulfated Ash, wt %	1.2	1.6	1.2	1.2
Dispersant Nitrogen, ppm	990	990	0	1980
Calcium, ppm	1206	1809	2010	2010
Magnesium, ppm	1206	1809	2010	2010
Boron, ppm	240	240	0	507
Zinc, ppm	884	884	884	884
Phosphorus, ppm	800	800	800	800
$([Mg]+[Ca]+[Zn]+[P]) / ([B]+[N]_{dispersant})$	3.3	4.3		1.9
Normalized LSPI Counts per 25,000 Engine Cycles	1	13	22	36

Fig. 6

Component Description	Example P1	Example P2	Example P3
Group IV base stock(s)	22.12	22.94	22.39
Group III base stock(s)	48.84	48.84	48.84
Group III+ base stock(s)			
Group V base stock(s)	5	5	5
Mg and/or Ca Salicylates	5.50	5.50	5.50
Mg and/or Ca Sulfonates			
Borated and/or non-borated succinimides	9.47	8.65	9.2
Zinc dialkyl dithiophosphate (primary, secondary, and/or mixed)	0.8	0.8	0.8
Rest of Formulation	8.27	8.27	8.27
Total	100	100	100

Fig. 6 (Cont.)

Component Description	Example P4	Example P5	Example P6
Group IV base stock(s)	28.79	28.46	24.25
Group III base stock(s)	48.84	48.84	48.84
Group III+ base stock(s)			
Group V base stock(s)	5	5	5
Mg and/or Ca Salicylates	0.00	0.00	4.54
Mg and/or Ca Sulfonates	0.33	0.66	0.33
Borated and/or non-borated succinimides	7.97	7.97	7.97
Zinc dialkyl dithiophosphate (primary, secondary, and/or mixed)	0.8	0.8	0.8
Rest of Formulation	8.27	8.27	8.27
Total	100	100	100

Fig. 6 (Cont.)

Component Description	Example P7	Example P8	Example P9
Group IV base stock(s)	24.80	26.75	26.27
Group III base stock(s)	48.84	48.84	48.84
Group III+ base stock(s)			
Group V base stock(s)	5	5	5
Mg and/or Ca Salicylates	3.66	1.38	2.75
Mg and/or Ca Sulfonates	0.66	1.00	0.10
Borated and/or non-borated succinimides	7.97	7.97	7.97
Zinc dialkyl dithiophosphate (primary, secondary, and/or mixed)	0.8	0.8	0.8
Rest of Formulation	8.27	8.27	8.27
Total	100	100	100

Fig. 6 (Cont.)

Component Description	Example P10	Example P11	Example P12
Group IV base stock(s)	27.57	23.61	23.42
Group III base stock(s)	48.84	48.84	48.84
Group III+ base stock(s)			
Group V base stock(s)	5	5	5
Mg and/or Ca Salicylates	0.55	5.50	5.50
Mg and/or Ca Sulfonates	1.00		
Borated and/or non-borated succinimides	7.97	7.97	7.97
Zinc dialkyl dithiophosphate (primary, secondary, and/or mixed)	0.8	0.81	1
Rest of Formulation	8.27	8.27	8.27
Total	100	100	100

Fig. 6 (Cont.)

Component Description	Example P13
Group IV base stock(s)	24.33
Group III base stock(s)	48.84
Group III+ base stock(s)	
Group V base stock(s)	5
Mg and/or Ca Salicylates	5.50
Mg and/or Ca Sulfonates	
Borated and/or non-borated succinimides	7.97
Zinc dialkyl dithiophosphate (primary, secondary, and/or mixed)	0.09
Rest of Formulation	8.27
Total	100

Fig. 7

Testing Description	Example P1	Example P2	Example P3
KV100	8.47	8.28	8.98
HTHS	2.86	2.76	2.66
Ash	1.2	1.2	1.3
Ca	3015	3015	3015
Mg	0	0	0
Zn	884	884	884
P	800	800	800
B	50	152	800
Ndisp	987	988	1564
TBN	9.6	9.4	8.5
B/Ndisp	0.05	0.15	0.51
2 °/ 1 °	-	-	-
Mg/Ca	0.00	0.00	0.00
(Mg+Ca) / (B + Ndisp)	2.91	2.65	1.28
(Mg + Ca)/ (Zn + P)	1.79	1.79	1.79
(Zn + P) / (B + Ndisp)	1.62	1.48	0.71
(Mg+Ca+Zn+P)/ (B + Ndisp)	4.53	4.12	1.99

Fig. 7 (Cont.)

Testing Description	Example P4	Example P5	Example P6
KV100	7.41	7.50	8.07
HTHS	2.47	2.49	2.66
Ash	0.3	0.5	1.2
Ca	0	0	2487
Mg	300	601	300
Zn	884	884	884
P	800	800	800
B	241	241	241
Ndisp	991	991	991
TBN	2.0	3.3	9.0
B/Ndisp	0.24	0.24	0.24
2 °/ 1 °	-	-	-
Mg/Ca	-	-	0.12
(Mg+Ca) / (B + Ndisp)	0.24	0.49	2.26
(Mg + Ca)/ (Zn + P)	0.18	0.36	1.66
(Zn + P) / (B + Ndisp)	1.37	1.37	1.37
(Mg+Ca+Zn+P)/ (B + Ndisp)	1.61	1.85	3.63

Fig. 7 (Cont.)

Testing Description	Example P7	Example P8	Example P9
KV100	8.03	7.78	7.74
HTHS	2.65	2.57	2.57
Ash	1.1	0.9	0.7
Ca	2005	754	1508
Mg	601	910	91
Zn	884	884	884
P	800	800	800
B	241	241	241
Ndisp	991	991	991
TBN	9.0	6.8	5.3
B/Ndisp	0.24	0.24	0.24
2 °/ 1 °	-	-	-
Mg/Ca	0.30	1.21	0.06
(Mg+Ca) / (B + Ndisp)	2.12	1.35	1.30
(Mg + Ca)/ (Zn + P)	1.55	0.99	0.95
(Zn + P) / (B + Ndisp)	1.37	1.37	1.37
(Mg+Ca+Zn+P)/ (B + Ndisp)	3.48	2.72	2.66

Fig. 7 (Cont.)

Testing Description	Example P10	Example P11	Example P12
KV100	7.66	8.13	8.14
HTHS	2.54	2.53	2.62
Ash	0.7	1.2	1.2
Ca	302	3015	3015
Mg	910	0	0
Zn	884	635	943
P	800	570	850
B	241	241	241
Ndisp	991	991	991
TBN	5.6	9.1	9.1
B/Ndisp	0.24	0.24	0.24
2 °/ 1 °	-	0.01	1.00
Mg/Ca	3.02	0.00	0.00
(Mg+Ca) / (B + Ndisp)	0.98	2.45	2.45
(Mg + Ca)/ (Zn + P)	0.72	2.50	1.68
(Zn + P) / (B + Ndisp)	1.37	0.98	1.46
(Mg+Ca+Zn+P)/ (B + Ndisp)	2.35	3.43	3.90

Fig. 7 (Cont.)

Testing Description	Example P13
KV100	8.06
HTHS	2.57
Ash	1.1
Ca	3015
Mg	0
Zn	96
P	87
B	241
Ndisp	991
TBN	9.1
B/Ndisp	0.24
2 °/ 1 °	8.00
Mg/Ca	0.00
(Mg+Ca) / (B + Ndisp)	2.45
(Mg + Ca)/ (Zn + P)	16.46
(Zn + P) / (B + Ndisp)	0.15
(Mg+Ca+Zn+P)/ (B + Ndisp)	2.60

Fig. 8

Component Description	Example P14	Example P15	Example P16
Group IV base stock(s)	22.12	22.94	22.39
Group III base stock(s)	48.84	48.84	48.84
Group III+ base stock(s)			
Group V base stock(s)	5	5	5
Mg and/or Ca Salicylates	5.50	5.50	5.50
Mg and/or Ca Sulfonates			
Borated and/or non-borated succinimides	9.47	8.65	9.2
Zinc dialkyl dithiophosphate (primary, secondary, and/or mixed)	0.8	0.8	0.8
Rest of Formulation	8.27	8.27	8.27
Total	100	100	100

Fig. 8 (Cont.)

Component Description	Example P17	Example P18	Example P19
Group IV base stock(s)	28.79	28.46	24.25
Group III base stock(s)	48.84	48.84	48.84
Group III+ base stock(s)			
Group V base stock(s)	5	5	5
Mg and/or Ca Salicylates	0.00	0.00	4.54
Mg and/or Ca Sulfonates	0.33	0.66	0.33
Borated and/or non-borated succinimides	7.97	7.97	7.97
Zinc dialkyl dithiophosphate (primary, secondary, and/or mixed)	0.8	0.8	0.8
Rest of Formulation	8.27	8.27	8.27
Total	100	100	100

Fig. 8 (Cont.)

Component Description	Example P20	Example P21	Example P22
Group IV base stock(s)	24.80	26.75	26.27
Group III base stock(s)	48.84	48.84	48.84
Group III+ base stock(s)			
Group V base stock(s)	5	5	5
Mg and/or Ca Salicylates	3.66	1.38	2.75
Mg and/or Ca Sulfonates	0.66	1.00	0.10
Borated and/or non-borated succinimides	7.97	7.97	7.97
Zinc dialkyl dithiophosphate (primary, secondary, and/or mixed)	0.8	0.8	0.8
Rest of Formulation	8.27	8.27	8.27
Total	100	100	100

Fig. 8 (Cont.)

Component Description	Example P23	Example P24	Example P25
Group IV base stock(s)	27.57	23.61	23.42
Group III base stock(s)	48.84	48.84	48.84
Group III+ base stock(s)			
Group V base stock(s)	5	5	5
Mg and/or Ca Salicylates	0.55	5.50	5.50
Mg and/or Ca Sulfonates	1.00		
Borated and/or non-borated succinimides	7.97	7.97	7.97
Zinc dialkyl dithiophosphate (primary, secondary, and/or mixed)	0.8	0.81	1
Rest of Formulation	8.27	8.27	8.27
Total	100	100	100

Fig. 8 (Cont.)

Component Description	Example P26
Group IV base stock(s)	24.33
Group III base stock(s)	48.84
Group III+ base stock(s)	
Group V base stock(s)	5
Mg and/or Ca Salicylates	5.50
Mg and/or Ca Sulfonates	
Borated and/or non-borated succinimides	7.97
Zinc dialkyl dithiophosphate (primary, secondary, and/or mixed)	0.09
Rest of Formulation	8.27
Total	100

Fig. 9

Testing Description	Example P14	Example P15	Example P16
KV100	6.97	6.76	7.37
HTHS	2.43	2.33	2.26
Ash	1.2	1.2	1.3
Ca	3015	3015	3015
Mg	0	0	0
Zn	884	884	884
P	800	800	800
B	50	152	800
Ndisp	987	988	1564
TBN	9.6	9.4	8.5
B/Ndisp	0.05	0.15	0.51
2 °/ 1 °	-	-	-
Mg/Ca	0.00	0.00	0.00
(Mg+Ca) / (B + Ndisp)	2.91	2.65	1.28
(Mg + Ca)/ (Zn + P)	1.79	1.79	1.79
(Zn + P) / (B + Ndisp)	1.62	1.48	0.71
(Mg+Ca+Zn+P)/ (B + Ndisp)	4.53	4.12	1.99

Fig. 9 (Cont.)

Testing Description	Example P17	Example P18	Example P19
KV100	5.75	5.83	6.52
HTHS	2.00	2.02	2.23
Ash	0.3	0.5	1.2
Ca	0	0	2487
Mg	300	601	300
Zn	884	884	884
P	800	800	800
B	241	241	241
Ndisp	991	991	991
TBN	2.0	3.3	9.0
B/Ndisp	0.24	0.24	0.24
2 °/ 1 °	-	-	-
Mg/Ca	-	-	0.12
(Mg+Ca) / (B + Ndisp)	0.24	0.49	2.26
(Mg + Ca)/ (Zn + P)	0.18	0.36	1.66
(Zn + P) / (B + Ndisp)	1.37	1.37	1.37
(Mg+Ca+Zn+P)/ (B + Ndisp)	1.61	1.85	3.63

Fig. 9 (Cont.)

Testing Description	Example P20	Example P21	Example P22
KV100	6.45	6.15	6.14
HTHS	2.21	2.11	2.12
Ash	1.1	0.9	0.7
Ca	2005	754	1508
Mg	601	910	91
Zn	884	884	884
P	800	800	800
B	241	241	241
Ndisp	991	991	991
TBN	9.0	6.8	5.3
B/Ndisp	0.24	0.24	0.24
2 °/ 1 °	-	-	-
Mg/Ca	0.30	1.21	0.06
(Mg+Ca) / (B + Ndisp)	2.12	1.35	1.30
(Mg + Ca)/ (Zn + P)	1.55	0.99	0.95
(Zn + P) / (B + Ndisp)	1.37	1.37	1.37
(Mg+Ca+Zn+P)/ (B + Ndisp)	3.48	2.72	2.66

Fig. 9 (Cont.)

Testing Description	Example P23	Example P24	Example P25
KV100	6.01	6.60	6.63
HTHS	2.07	2.13	2.20
Ash	0.7	1.2	1.2
Ca	302	3015	3015
Mg	910	0	0
Zn	884	635	943
P	800	570	850
B	241	241	241
Ndisp	991	991	991
TBN	5.6	9.1	9.1
B/Ndisp	0.24	0.24	0.24
2 °/ 1 °	-	0.01	1.00
Mg/Ca	3.02	0.00	0.00
(Mg+Ca) / (B + Ndisp)	0.98	2.45	2.45
(Mg + Ca)/ (Zn + P)	0.72	2.50	1.68
(Zn + P) / (B + Ndisp)	1.37	0.98	1.46
(Mg+Ca+Zn+P)/ (B + Ndisp)	2.35	3.43	3.90

Fig. 9 (Cont.)

Testing Description	Example P26
KV100	6.51
HTHS	2.15
Ash	1.1
Ca	3015
Mg	0
Zn	96
P	87
B	241
Ndisp	991
TBN	9.1
B/Ndisp	0.24
2 °/ 1 °	8.00
Mg/Ca	0.00
(Mg+Ca) / (B + Ndisp)	2.45
(Mg + Ca)/ (Zn + P)	16.46
(Zn + P) / (B + Ndisp)	0.15
(Mg+Ca+Zn+P)/ (B + Ndisp)	2.60

Fig. 10

Component Description	Example P27	Example P28	Example P29
Group IV base stock(s)			
Group III base stock(s)	40.96	41.78	41.23
Group III+ base stock(s)	30	30	30
Group V base stock(s)	5	5	5
Mg and/or Ca Salicylates	5.50	5.50	5.50
Mg and/or Ca Sulfonates			
Borated and/or non-borated succinimides	9.47	8.65	9.2
Zinc dialkyl dithiophosphate (primary, secondary, and/or mixed)	0.8	0.8	0.8
Rest of Formulation	8.27	8.27	8.27
Total	100	100	100

Fig. 10 (Cont.)

Component Description	Example P30	Example P31	Example P32
Group IV base stock(s)			
Group III base stock(s)	47.63	47.30	43.09
Group III+ base stock(s)	30	30	30
Group V base stock(s)	5	5	5
Mg and/or Ca Salicylates	0.00	0.00	4.54
Mg and/or Ca Sulfonates	0.33	0.66	0.33
Borated and/or non-borated succinimides	7.97	7.97	7.97
Zinc dialkyl dithiophosphate (primary, secondary, and/or mixed)	0.8	0.8	0.8
Rest of Formulation	8.27	8.27	8.27
Total	100	100	100

Fig. 10 (Cont.)

Component Description	Example P33	Example P34	Example P35
Group IV base stock(s)			
Group III base stock(s)	43.64	45.59	45.11
Group III+ base stock(s)	30	30	30
Group V base stock(s)	5	5	5
Mg and/or Ca Salicylates	3.66	1.38	2.75
Mg and/or Ca Sulfonates	0.66	1.00	0.10
Borated and/or non-borated succinimides	7.97	7.97	7.97
Zinc dialkyl dithiophosphate (primary, secondary, and/or mixed)	0.8	0.8	0.8
Rest of Formulation	8.27	8.27	8.27
Total	100	100	100

Fig. 10 (Cont.)

Component Description	Example P36	Example P37	Example P38
Group IV base stock(s)			
Group III base stock(s)	46.41	42.45	42.26
Group III+ base stock(s)	30	30	30
Group V base stock(s)	5	5	5
Mg and/or Ca Salicylates	0.55	5.50	5.50
Mg and/or Ca Sulfonates	1.00		
Borated and/or non-borated succinimides	7.97	7.97	7.97
Zinc dialkyl dithiophosphate (primary, secondary, and/or mixed)	0.8	0.81	1
Rest of Formulation	8.27	8.27	8.27
Total	100	100	100

Fig. 10 (Cont.)

Component Description	Example P39
Group IV base stock(s)	
Group III base stock(s)	43.17
Group III+ base stock(s)	30
Group V base stock(s)	5
Mg and/or Ca Salicylates	5.50
Mg and/or Ca Sulfonates	
Borated and/or non-borated succinimides	7.97
Zinc dialkyl dithiophosphate (primary, secondary, and/or mixed)	0.09
Rest of Formulation	8.27
Total	100

Fig. 11

Testing Description	Example P27	Example P28	Example P29
KV100	10.23	9.99	10.85
HTHS	3.36	3.24	3.13
Ash	1.2	1.2	1.3
Ca	3015	3015	3015
Mg	0	0	0
Zn	884	884	884
P	800	800	800
B	50	152	800
Ndisp	987	988	1564
TBN	9.6	9.4	8.5
B/Ndisp	0.05	0.15	0.51
2 °/ 1 °	-	-	-
Mg/Ca	0.00	0.00	0.00
(Mg+Ca) / (B + Ndisp)	2.91	2.65	1.28
(Mg + Ca)/ (Zn + P)	1.79	1.79	1.79
(Zn + P) / (B + Ndisp)	1.62	1.48	0.71
(Mg+Ca+Zn+P)/ (B + Ndisp)	4.53	4.12	1.99

Fig. 11 (Cont.)

Testing Description	Example P30	Example P31	Example P32
KV100	8.93	9.03	9.74
HTHS	2.90	2.93	3.13
Ash	0.3	0.5	1.2
Ca	0	0	2487
Mg	300	601	300
Zn	884	884	884
P	800	800	800
B	241	241	241
Ndisp	991	991	991
TBN	2.0	3.3	9.0
B/Ndisp	0.24	0.24	0.24
2 °/ 1 °	-	-	-
Mg/Ca	-	-	0.12
(Mg+Ca) / (B + Ndisp)	0.24	0.49	2.26
(Mg + Ca)/ (Zn + P)	0.18	0.36	1.66
(Zn + P) / (B + Ndisp)	1.37	1.37	1.37
(Mg+Ca+Zn+P)/ (B + Ndisp)	1.61	1.85	3.63

Fig. 11 (Cont.)

Testing Description	Example P33	Example P34	Example P35
KV100	9.68	9.38	9.34
HTHS	3.11	3.02	3.02
Ash	1.1	0.9	0.7
Ca	2005	754	1508
Mg	601	910	91
Zn	884	884	884
P	800	800	800
B	241	241	241
Ndisp	991	991	991
TBN	9.0	6.8	5.3
B/Ndisp	0.24	0.24	0.24
2 °/ 1 °	-	-	-
Mg/Ca	0.30	1.21	0.06
(Mg+Ca) / (B + Ndisp)	2.12	1.35	1.30
(Mg + Ca)/ (Zn + P)	1.55	0.99	0.95
(Zn + P) / (B + Ndisp)	1.37	1.37	1.37
(Mg+Ca+Zn+P)/ (B + Ndisp)	3.48	2.72	2.66

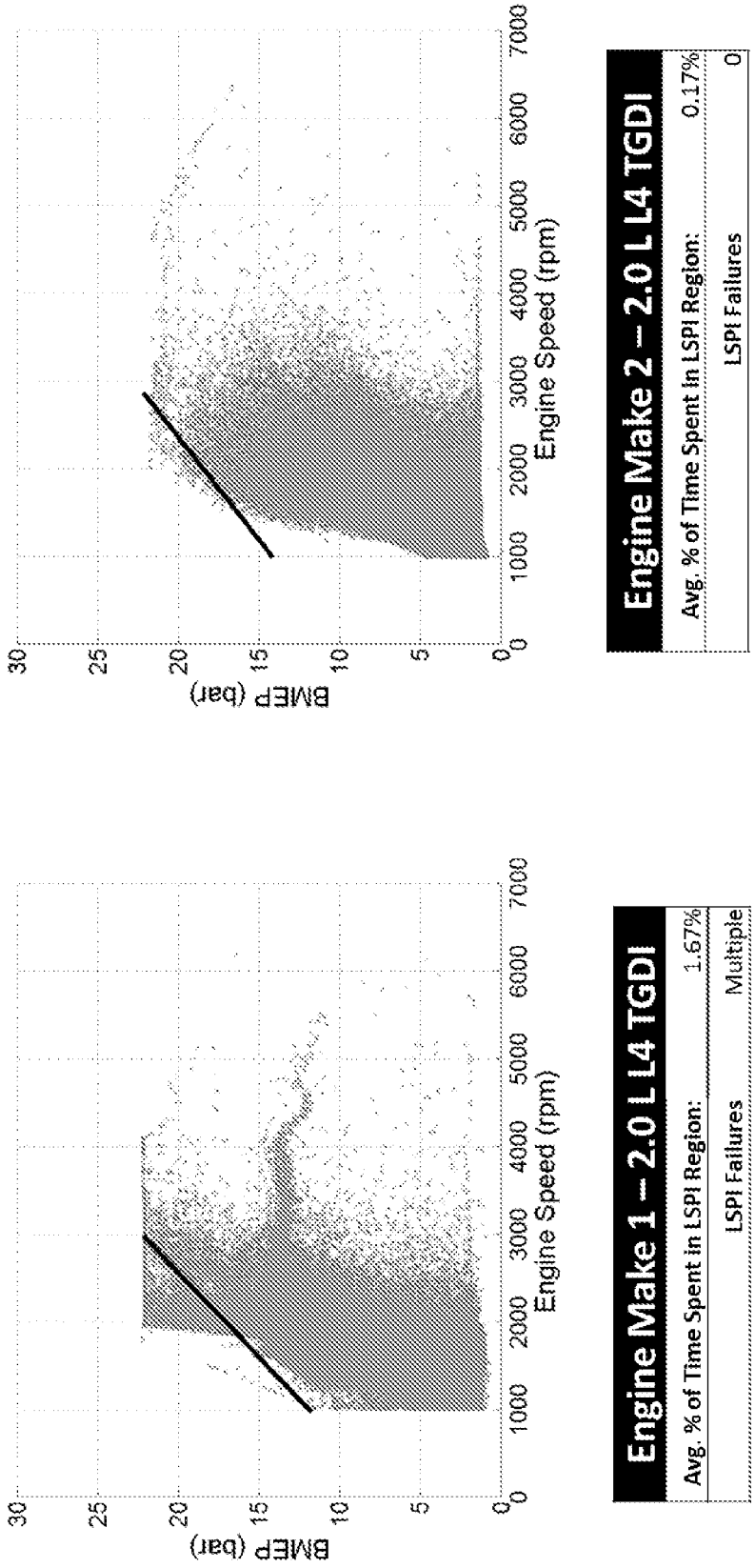
Fig. 11 (Cont.)

Testing Description	Example P36	Example P37	Example P38
KV100	9.23	9.81	9.83
HTHS	2.98	2.97	3.07
Ash	0.7	1.2	1.2
Ca	302	3015	3015
Mg	910	0	0
Zn	884	635	943
P	800	570	850
B	241	241	241
Ndisp	991	991	991
TBN	5.6	9.1	9.1
B/Ndisp	0.24	0.24	0.24
2 °/ 1 °	-	0.01	1.00
Mg/Ca	3.02	0.00	0.00
(Mg+Ca) / (B + Ndisp)	0.98	2.45	2.45
(Mg + Ca)/ (Zn + P)	0.72	2.50	1.68
(Zn + P) / (B + Ndisp)	1.37	0.98	1.46
(Mg+Ca+Zn+P)/ (B + Ndisp)	2.35	3.43	3.90

Fig. 11 (Cont.)

Testing Description	Example P39
KV100	9.73
HTHS	3.02
Ash	1.1
Ca	3015
Mg	0
Zn	96
P	87
B	241
Ndisp	991
TBN	9.1
B/Ndisp	0.24
2 °/ 1 °	8.00
Mg/Ca	0.00
(Mg+Ca) / (B + Ndisp)	2.45
(Mg + Ca)/ (Zn + P)	16.46
(Zn + P) / (B + Ndisp)	0.15
(Mg+Ca+Zn+P)/ (B + Ndisp)	2.60

Fig. 12


BMEP (bar)
Engine Speed (rpm)
0
5
10
15
20
25
30
1000
2000
3000
4000
5000
6000
7000
Engine Make 1 – 2.0 L L4 TGDI
Avg. % of Time Spent in LSPI Region: 1.67%
LSPI Failures Multiple
Engine Make 2 – 2.0 L L4 TGDI
Avg. % of Time Spent in LSPI Region: 0.17%
LSPI Failures 0

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- US 20090082233 A **[0006]**
- US 4956122 A **[0023] [0025]**
- US 4827064 A **[0023]**
- US 4827073 A **[0023]**
- US 4149178 A **[0025]**
- US 3382291 A **[0025]**
- US 3742082 A **[0025]**
- US 3769363 A **[0025]**
- US 3876720 A **[0025]**
- US 4239930 A **[0025]**
- US 4367352 A **[0025]**
- US 4413156 A **[0025]**
- US 4434408 A **[0025]**
- US 4910355 A **[0025]**
- US 5068487 A **[0025]**
- US 4218330 A **[0025]**
- US 5075269 A **[0026]**
- US 2817693 A **[0026]**
- US 4975177 A **[0026]**
- US 4921594 A **[0026]**
- US 4897178 A **[0026]**
- GB 1429494 A **[0026]**
- GB 1350257 A **[0026]**
- GB 1440230 A **[0026]**
- GB 1390359 A **[0026]**
- EP 464546 A **[0026]**
- EP 464547 A **[0026]**
- US 4594172 A **[0026]**
- US 4943672 A **[0026]**
- US 6080301 A **[0027]**
- US 6090989 A **[0027]**
- US 6165949 A **[0027]**
- US 3172892 A **[0068] [0070]**
- US 32145707 B **[0068]**
- US 3219666 A **[0068] [0070]**
- US 3316177 A **[0068]**
- US 3341542 A **[0068]**
- US 3444170 A **[0068]**
- US 3454607 A **[0068]**
- US 3541012 A **[0068]**
- US 3630904 A **[0068]**
- US 3632511 A **[0068]**
- US 3787374 A **[0068]**
- US 4234435 A **[0068]**
- US 3036003 A **[0068]**
- US 3200107 A **[0068]**
- US 3254025 A **[0068]**
- US 3275554 A **[0068] [0076]**
- US 3438757 A **[0068] [0076]**
- US 3454555 A **[0068]**
- US 3565804 A **[0068] [0076]**
- US 3413347 A **[0068]**
- US 3697574 A **[0068] [0074]**
- US 3725277 A **[0068]**
- US 3725480 A **[0068]**
- US 3726882 A **[0068]**
- US 4454059 A **[0068]**
- US 3329658 A **[0068]**
- US 3449250 A **[0068]**
- US 3519565 A **[0068]**
- US 3666730 A **[0068]**
- US 3687849 A **[0068]**
- US 3702300 A **[0068]**
- US 4100082 A **[0068]**
- US 5705458 A **[0068]**
- EP 471071 A **[0068]**
- US 3087936 A **[0070]**
- US 3272746 A **[0070]**
- US 3322670 A **[0070]**
- US 3652616 A **[0070]**
- US 3948800 A **[0070]**
- CA 1094044 **[0070]**
- US 4426305 A **[0072]**
- US 4767551 A **[0074]**
- US 3703536 A **[0074]**
- US 3704308 A **[0074]**
- US 3751365 A **[0074]**
- US 3756953 A **[0074]**
- US 3798165 A **[0074]**
- US 3803039 A **[0074]**
- US 3755433 A **[0076]**
- US 3822209 A **[0076]**
- US 5084197 A **[0076] [0117]**
- US 3595791 A **[0093]**
- US 7704930 B **[0095] [0108]**
- US 6034039 A **[0097]**
- US 4798684 A **[0117]**
- US 8048833 B **[0119]**
- US 1815022 A **[0124]**
- US 2015748 A **[0124]**
- US 2191498 A **[0124]**
- US 2387501 A **[0124]**
- US 2655 A **[0124]**
- US 479 A **[0124]**
- US 2666746 A **[0124]**
- US 2721877 A **[0124]**
- US 2721878 A **[0124]**
- US 3250715 A **[0124]**

- US 20121866225 A **[0149]**
- US 20030908070 A **[0149]**

Non-patent literature cited in the description

- SAE International Journal of Fuels and Lubricants. LSPI, vol. 5, 1017-1024 **[0005]**
- *SAE International Journal of Engines,* vol. 4 (1), 246-273 **[0005]**
- Friedel-Crafts and Related Reactions. Interscience Publishers, 1963 **[0029]**
- Friedel-Crafts and Related Reactions. vol. 2 **[0029]**
- **KLAMANN.** Lubricants and Related Products. Verlag Chemie **[0108]**
- **M. W. RANNEY.** Lubricant Additives. Noyes Data Corporation of Parkridge, 1973 **[0108]**