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(54) **LUBRICATING OIL COMPOSITIONS**

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(57) **ABSTRACT**

The present invention relates to a method of lubricating a passenger car motor vehicle engine having a rotating tappet, comprising lubricating the engine with a lubricating oil composition having up to 0.09 wt % phosphorus, 0.4 wt % sulphur and 1.0 wt % sulphated ash, and being substantially free of friction-modifier.

Fig. 1

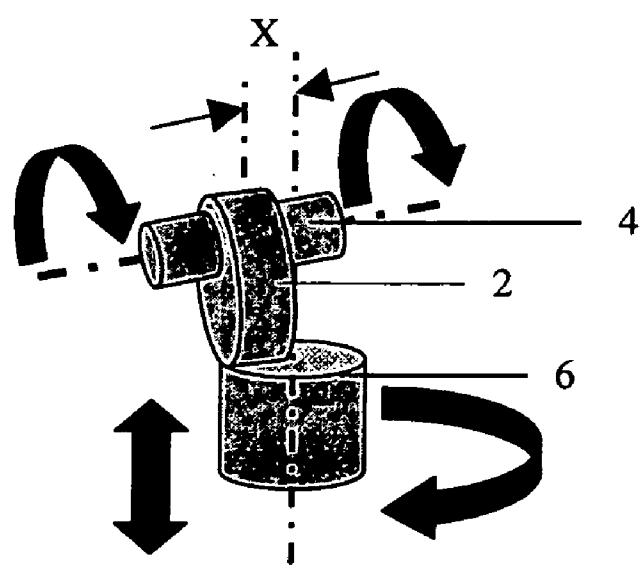
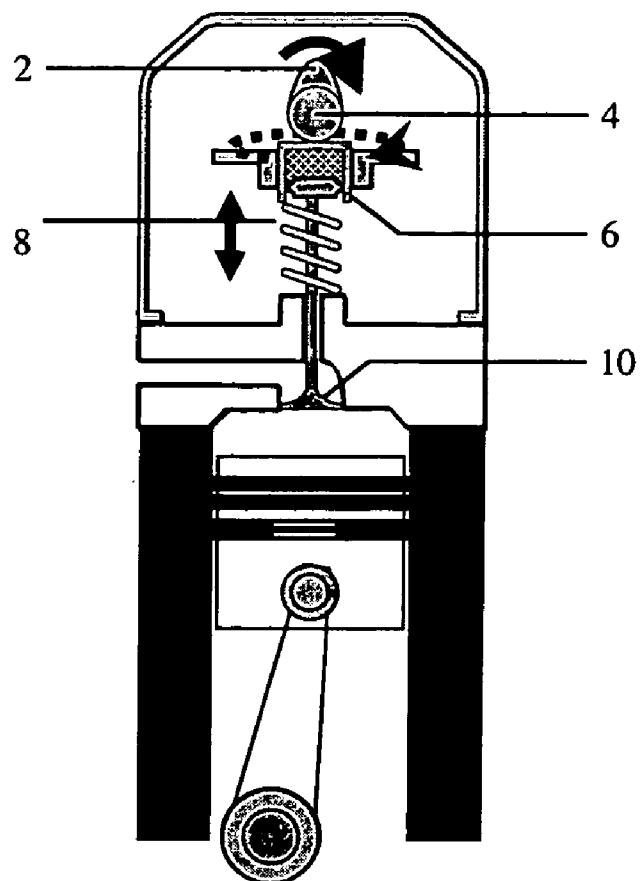


Fig. 2

LUBRICATING OIL COMPOSITIONS

[0001] The present invention relates to passenger car motor vehicle lubricating oil compositions. In particular, although not exclusively, the present invention relates to passenger car motor vehicle lubricating oil compositions which exhibit improved wear performance.

BACKGROUND OF THE INVENTION

[0002] Lubricating oil compositions used to lubricate internal combustion engines comprise a base oil of lubricating viscosity, or a mixture of such oils, and additives used to improve the performance characteristics of the oil. For example, additives are used to improve detergency, to reduce engine wear, to provide stability against oxidation, to reduce friction loss, to increase fuel economy and to inhibit corrosion. Some additives provide multiple benefits, such as dispersant-viscosity modifiers. Other additives, whilst improving one characteristic of the lubricating oil, are detrimental to another characteristic.

[0003] It has long been known to use friction modifiers, such as molybdenum-containing compounds, and/or organic friction modifiers, such as glycerol mono-oleate, in passenger car motor vehicles to reduce friction between moving engine parts and to improve fuel economy.

[0004] For example, U.S. Pat. Nos. 4,164,473 and 4,479,883, EP Patent No. 13 469 and UK Patent No. 2 068 380 disclose various oil-soluble molybdenum containing compounds suitable as friction reducing additives for use in passenger car motor vehicles. U.S. Pat. No. 6,723,685 discloses a composition comprising a molybdenum additive and an organic friction modifier, in an amount sufficient to pass a Sequence VIB fuel economy test.

[0005] In addition, International patent application number WO-A-03/064568 discloses use of friction modifiers as additives in lubricating oil compositions to reduce wear in internal combustion engines.

[0006] In addition, as the permitted levels of sulphated ash, phosphorus and sulphur (SAPS) emissions from passenger car motor vehicles decrease the levels of additives such as metal dialkyldithiophosphates that can be used are decreased. This leads to an imbalance in the additive combinations conventionally used in passenger car motor vehicles and leads the formulator to consider new additive combinations in order to meet the requirements of vehicle manufacturers.

[0007] Passenger car motor vehicle internal combustion engines have many different conformations that have different lubrication requirements. One problem associated with lower SAPS lubricants is increased engine wear due to reduced phosphorus levels limiting the amount of conventional anti-wear additives that can be used. This problem is particularly evident for rotating tappets in the valve train, which can stall when lubricated with lower SAPS lubricants and exhibit unacceptable wear.

[0008] US 2003/0148895 A discloses lubricating oil compositions intended to reduce wear in the Peugeot TU3M Scuffing Test. This test is intended to investigate wear on the cam and tappets of an internal combustion engine. The disclosures of this document show that relatively high levels of boron (derived from borated dispersant) and preferably

augmented with significant amount of molybdenum (derived from, e.g., a trinuclear molybdenum additive) are required to reduce cam and tappet wear to acceptable levels.

[0009] WO 03/064568 A2 discloses lubricating oil compositions for use with low sulfur fuels in internal combustion engines. The lubricating oils, when tested in a Sequence IVA test, result in increased wear (cam nose wear and total wear) as the molybdenum and boron concentrations thereof are reduced. Other disadvantageous effects are also apparent.

[0010] Preferred embodiments of the present invention seek to provide a method of lubricating an engine comprising a rotating tappet to provide improved wear performance, particularly in lower SAPS formulations.

SUMMARY OF THE INVENTION

[0011] The present invention provides a method of lubricating an internal combustion engine having a cam and a rotating tappet associated with the said cam, the said method being defined by claim 1 of the set of claims following the description of the invention. Preferred and optional features of the invention are the subjects of the claims which are directly or indirectly appended to claim 1.

[0012] The present invention, in another aspect, provides a combination comprising an internal combustion engine having a rotating tappet and a lubricating composition, wherein the lubricating composition has the characteristics specified for the lubricating composition of claim 1.

[0013] In yet another aspect, the invention provides the use of a lubricating oil composition to pass the 650 hour Volkswagen (trade mark) RNT test (PV1473 Draft), and optionally the VW (trade mark) PV1451 FE test, wherein the said lubricating oil composition has the formulation specified for the lubricating oil of claim 1, and optionally, one or more of the features of the claims which are appended, directly and/or indirectly, to claim 1.

[0014] The present invention provides in a first further aspect, a method of lubricating a passenger car motor vehicle engine having a rotating tappet, by lubricating the engine with a lubricating oil composition having up to 0.09 wt % phosphorus, 0.4 wt % of sulphur and 1.0 wt % sulphated ash, based on the total weight of the composition, the lubricating oil composition comprising an oil of lubricating viscosity and being substantially free of friction-modifier.

[0015] In a second further aspect, the present invention provides a method of reducing wear in a passenger car motor vehicle engine having a rotating tappet, comprising lubricating the engine with a lubricating oil composition having up to 0.09 wt % phosphorus, 0.4 wt % of sulphur and 1.0 wt % sulphated ash, based on the total weight of the composition, comprising an oil of lubricating viscosity and being substantially free of friction-modifier.

[0016] In a third further aspect, the present invention provides a method of reducing wear and in an engine having a rotating tappet whilst maintaining fuel economy performance, comprising lubricating the engine with a lubricating oil composition having up to 0.09 wt % phosphorus, 0.4 wt % of sulphur and 1.0 wt % sulphated ash, based on the total weight of the composition, comprising an oil of lubricating viscosity and being substantially free of friction-modifier.

[0017] In a fourth further aspect, the present invention provides a combination of an engine having a rotating tappet and a lubricating oil composition having up to 0.09 wt % phosphorus, 0.4 wt % of sulphur and 1.0 wt % sulphated ash, based on the total weight of the composition, comprising an oil of lubricating viscosity and being substantially free of friction-modifier.

[0018] In a fifth further aspect, the present invention provides the use of a lubricating oil composition having up to 0.09 wt % phosphorus, 0.4 wt % of sulphur and 1.0 wt % sulphated ash, based on the total weight of the composition, comprising an oil of lubricating viscosity and being substantially free of friction-modifier to pass the 650 hour VW RNT engine test (PV1473 Draft).

[0019] In a sixth further aspect, the present invention provides the use of a lubricating oil composition according having up to 0.09 wt % phosphorus, 0.4 wt % of sulphur and 1.0 wt % sulphated ash, based on the total weight of the composition, comprising an oil of lubricating viscosity and being substantially free of friction-modifier to pass both the VW PV 1451 FE test and the 650 hour VW RNT test (PV1473 Draft).

BRIEF DESCRIPTION OF THE FIGURES

[0020] **FIG. 1** is a schematic representation of a section of a valve train of an engine, and

[0021] **FIG. 2** is a schematic representation of the cam and tappet action of the valve train section of **FIG. 1**.

DETAILED DESCRIPTION OF THE INVENTION

[0022] The engine of the present invention is an internal combustion engine, such as a passenger car motor vehicle engine. The engine may be a spark-ignited engine or a compression-ignited engine.

[0023] The oil of lubricating viscosity useful in the practice of the invention may have a viscosity from about 2 mm²/sec (centistokes) to about 40 mm²/sec, especially from about 3 mm²/sec to about 20 mm²/sec, most preferably from about 5 mm²/sec to about 15 mm²/sec, as measured at 100° C.

[0024] Natural oils include animal oils and vegetable oils (e.g., castor oil, lard oil); liquid petroleum oils and hydro-refined, solvent-treated or acid-treated mineral oils of the paraffinic, naphthenic and mixed paraffinic-naphthenic types. Oils of lubricating viscosity derived from coal or shale also serve as useful base oils.

[0025] Synthetic lubricating oils include hydrocarbon oils and halo-substituted hydrocarbon oils such as polymerized and interpolymerized olefins (e.g., polybutylenes, polypropylenes, propylene-isobutylene copolymers, chlorinated polybutylenes, poly(1-hexenes), poly(1-octenes), poly(1-decenes)); alkylbenzenes (e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di(2-ethylhexyl)benzenes); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenols); and alkylated diphenyl ethers and alkylated diphenyl sulfides and derivative, analogs and homologs thereof.

[0026] Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc., consti-

tute another class of known synthetic lubricating oils. These are exemplified by polyoxyalkylene polymers prepared by polymerization of ethylene oxide or propylene oxide, and the alkyl and aryl ethers of polyoxyalkylene polymers (e.g., methyl-polyiso-propylene glycol ether having a molecular weight of 1000 or diphenyl ether of poly-ethylene glycol having a molecular weight of 1000 to 1500); and mono- and polycarboxylic esters thereof, for example, the acetic acid esters, mixed C₃-C₈ fatty acid esters and C₁₃ Oxo acid diester of tetraethylene glycol.

[0027] Another suitable class of synthetic lubricating oils comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids and alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebasic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkylmalonic acids, alkenyl malonic acids) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol). Specific examples of such esters includes dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid.

[0028] Esters useful as synthetic oils also include those made from C₅ to C₁₂ monocarboxylic acids and polyols and polyol esters such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol and tripentaerythritol.

[0029] Silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy- or polyaryloxy silicone oils and silicate oils comprise another useful class of synthetic lubricants; such oils include tetraethyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl) silicate, tetra-(4-methyl-2-ethylhexyl) silicate, tetra-(p-tert-butyl-phenyl) silicate, hexa-(4-methyl-2-ethylhexyl) disiloxane, poly(methyl)siloxanes and poly(methylphenyl)siloxanes. Other synthetic lubricating oils include liquid esters of phosphorous-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, diethyl ester of decylphosphonic acid) and polymeric tetrahydrofurans.

[0030] Other examples of base oil are gas-to-liquid ("GTL") base oils, i.e. the base oil may be oil derived from Fischer-Tropsch-synthesised hydrocarbons made from synthesis gas containing hydrogen and carbon monoxide using a Fischer-Tropsch catalyst. These hydrocarbons typically require further processing in order to be useful as base oil. For example, they may, by methods known in the art, be hydroisomerized; hydrocracked and hydroisomerized; dewaxed; or hydroisomerized and dewaxed.

[0031] Definitions for the base stocks and base oils in this invention are the same as those found in the American Petroleum Institute (API) publication 1509 "Engine Oil Licensing and Certification System", Fifteenth Edition, April 2002, Appendix E, November 2004. Said publication categorizes base stocks as follows:

[0032] a) Group I base stocks contain less than 90 percent saturates and/or greater than 0.03 wt % sulphur and have a viscosity index greater than or equal to 80 and less than 120 using the test methods specified in Table 1.

[0033] b) Group II base stocks contain greater than or equal to 90 percent saturates and less than or equal to 0.03

wt % sulphur and have a viscosity index greater than or equal to 80 and less than 120 using the test methods specified in Table 1.

[0034] c) Group III base stocks contain greater than or equal to 90 percent saturates and less than or equal to 0.03 wt % sulphur and have a viscosity index greater than or equal to 120 using the test methods specified in Table 1.

[0035] d) Group IV base stocks are polyalphaolefins (PAO).

[0036] e) Group V base stocks include all other base stocks not included in Group I, II, III, or IV.

TABLE 1

Analytical Methods for Base Stock	
Property	Test Method
Saturates	ASTM D 2007
Viscosity Index	ASTM D 2270
Sulphur	ASTM D 2622
	ASTM D 4294
	ASTM D 4927
	ASTM D1552
	ASTM D 3120

[0037] The oil of lubricating viscosity of the present invention may comprise a Group I, Group II, Group III, Group IV or Group V base stock or base oil blends of the aforementioned base stocks.

[0038] Preferably, an oil of lubricating viscosity of the present invention comprises a proportion at least of one or more Group IV basestock. Suitably, a lubricating oil composition according to the present invention comprises at least 25 wt %, preferably at least 35 wt % and more preferably at least 40 wt % of a Group IV base stock, based on the total weight of the composition. Suitably, a lubricating oil composition according to the present invention comprises less than 85 wt %, preferably less than 75 wt %, more preferably less than 60 wt % and especially less than 55 wt % of a Group IV base stock, based on the total weight of the composition.

[0039] Preferably, an oil of lubricating viscosity according to the present invention comprises a proportion at least of one or more Group III basestock. Suitably, a lubricating oil composition according to the present invention comprises at least 15 wt %, preferably at least 20 wt % and more preferably, at least 25 wt % Group III basestock, based on the total weight of the composition. Suitably, a lubricating oil composition according to the present invention comprises less than 80 wt %, preferably less than 60 wt % and, most preferably, less than 50 wt % of Group III basestock, based on the total weight of the composition.

[0040] A lubricating composition according to the present invention may comprise one or more Group V ester base stock. Suitably, the lubricating composition comprises less than 25 wt %, preferably less than 10 wt % and more preferably 5 wt % or less of an ester base stock based on the total weight of the composition. Suitably, a lubricating oil composition according to the present invention comprises at least 1 wt %, preferably at least 1.5 wt % and more preferably at least 3 wt % of an ester basestock.

[0041] It should be noted that any of the basestocks mentioned above may be provided to the composition as a separate component for blending. Alternatively, all or a proportion of any of the basestocks may be provided to the composition as a diluent for another component of the lubricating oil composition.

[0042] It should be noted that substantially free of friction modifier is defined herein as meaning the lubricating oil composition comprises less than 0.1 wt %, suitably less than 0.05 wt % (e.g., 0 to 0.4 wt %), preferably less than 0.01 wt %, such as 0 to 0.0075 wt % and most preferable no (0 wt %) friction modifier.

[0043] By friction modifier it is meant boundary lubricant additives that lower friction coefficients and hence improve fuel economy and includes, but is not necessarily limited to the following types of compounds.

[0044] (1) Organic, ashless (metal-free), nitrogen-free organic friction modifiers include esters formed by reacting carboxylic acids and anhydrides with alkanols. Such friction modifiers include, aliphatic carboxylic acids, aliphatic carboxylic esters of polyols, such as glycerol esters of fatty acids, for example, glycerol oleate, boric esters of glycerol fatty acid monoesters, esters of long chain polycarboxylic acids with diols, for example, the butane diol ester of a dimerized unsaturated fatty acid, aliphatic phosphonates, aliphatic phosphates, aliphatic thiophosphates, aliphatic thiophosphonates, aliphatic thiophosphates and oxazoline compounds. The aliphatic group usually contains at least eight carbon atoms so as to render the compound suitably oil soluble. Esters of carboxylic acids and anhydrides with alkanols are described in U.S. Pat. No. 4,702,850. Examples of other conventional organic friction modifiers are described by M. Belzer in the "Journal of Tribology" (1992), Vol. 114, pp. 675-682 and M. Belzer and S. Jahanmir in "Lubrication Science" (1988), Vol. 1, pp. 3-26.

[0045] (2) Ashless aminic friction modifiers include oil-soluble aliphatic amines, alkoxyated mono- and di-amines and aliphatic fatty acids amides. One common class of such metal free, nitrogen-containing friction modifier comprises ethoxylated amines. These amines may, for example, be in the form of an adduct or reaction product with a boron compound such as a boric oxide, boron halide, metaborate, boric acid or a mono-, di- or tri-alkyl borate. Other aminic friction modifiers include, alkoxyated alkyl-substituted mono-amines, diamines and alkyl ether amines, for example, ethoxylated tallow amine and ethoxylated tallow ether amine and aliphatic carboxylic ester-amides. Examples of fatty acid esters and amides as friction modifiers are disclosed in U.S. Pat. No. 3,933,659.

[0046] (3) Additives which deposit molybdenum disulfide. Such molybdenum compounds include sulphur-containing, organo-molybdenum compounds, such as, dithiocarbamates, dithiophosphates, dithiophosphinates, xanthates, thioxanthates, alkylthioxanthates and sulfides. Such molybdenum compounds also include acidic molybdenum compounds that react with basic nitrogen as measured by ASTM test D-664 or D-2896 titration procedure and are typically hexavalent. Such compounds include molybdic acid, ammonium molybdate, sodium molybdate, potassium molybdate, and other alkaline earth metal molybdates and other molybdenum salts, e.g., hydrogen sodium molybdate, MoOCl_4 , MoO_2Br_2 , $\text{Mo}_2\text{O}_3\text{Cl}_6$, molybdenum trioxide and similar molybdenum compounds.

[0047] A lubricating oil composition according to the present invention suitably comprises less than 1.0 wt % sulphated ash, preferably, less than 0.9 wt %, more preferably less than 0.8 wt % and particularly less than 0.7 wt % sulphated ash, based on the total weight of the composition. Advantageously, a lubricating oil composition according to the present invention comprises 0.6 wt % or less sulphated ash measured using ASTM D874.

[0048] A lubricating oil composition according to the present invention suitably comprises less than 0.09 wt %, preferably less than 0.08 wt % and more preferably less than 0.07 wt % phosphorus, based on the total weight of the composition. Advantageously, a lubricating oil composition according to the present invention comprises 0.06 wt % of less phosphorus, based on the total weight of the composition, measured using ASTM D4951.

[0049] A lubricating oil composition according to the present invention suitably comprises less than 0.4 wt %, preferably less than 0.3 wt % and more preferably less than 0.2 wt % sulphur, based on the total weight of the composition, as measured using ASTM 5185 or ASTM 2622.

[0050] A lubricating oil composition according to the present invention suitably has a total base number (TBN) of 13 or less, preferably less than 10 and more preferably between 4 and 9, as measured using ASTM D2986.

[0051] A lubricating oil composition according to the present invention may comprise additional conventional additives. Examples of suitable additional additives are set out in the following pages.

[0052] Metal-containing or ash-forming detergents function as both detergents to reduce or remove deposits and as acid neutralizers or rust inhibitors, thereby reducing wear and corrosion and extending engine life. Detergents generally comprise a polar head with a long hydrophobic tail. The polar head comprises a metal salt of an acidic organic compound. The salts may contain a substantially stoichiometric amount of the metal in which case they are usually described as normal or neutral salts, and would typically have a total base number or TBN (as can be measured by ASTM D2896) of from 0 to 80. A large amount of a metal base may be incorporated by reacting excess metal compound (e.g., an oxide or hydroxide) with an acidic gas (e.g., carbon dioxide). The resulting overbased detergent comprises neutralized detergent as the outer layer of a metal base (e.g., carbonate) micelle. Such overbased detergents may have a TBN of 150 or greater, and typically will have a TBN of from 250 to 450 or more.

[0053] Detergents that may be used in a lubricating oil composition according to the present invention include oil-soluble neutral and overbased sulfonates, phenates, sulphurized phenates, thiophosphonates, salicylates, and naphthenates and other oil-soluble carboxylates of a metal, particularly the alkali or alkaline earth metals, e.g., barium, sodium, potassium, lithium, calcium, and magnesium. The most commonly used metals are calcium and magnesium, which may both be present, and mixtures of calcium and/or magnesium with sodium. Particularly convenient metal detergents are neutral and overbased calcium or magnesium sulfonates having TBN of from 20 to 450, neutral and overbased calcium or magnesium phenates and sulphurized phenates having TBN of from 50 to 450 and neutral and

overbased magnesium or calcium salicylates having a TBN of from 20 to 450. Combinations of detergents, whether overbased or neutral or both, may be used. Detergents generally useful in the formulation of lubricating oil compositions also include "hybrid" detergents formed with mixed surfactant systems, e.g., phenate/salicylates, sulfonate/phenates, sulfonate/salicylates, sulfonates/phenates/salicylates, as described, for example, in U.S. Pat. Nos. 6,153,565; 6,281,179; 6,429,178; and 6,429,179.

[0054] The detergent may be present in any suitable amount, within the limits provided by the maximum sulphated ash and sulphur levels of the lubricating oil composition of the present invention. A detergent may be used in an amount providing the lubricating oil composition with from about 0.05 to about 0.30 wt %, such as from about 0.07 to about 0.25 wt %, more preferably from about 0.8 to about 0.22 wt % of calcium, measured as sulfated ash (SASH) content.

[0055] Ashless dispersants comprise an oil soluble polymeric hydrocarbon backbone bearing one or more functional groups that are capable of associating with particles to be dispersed. Typically, the polymer backbone is functionalized by amine, alcohol, amide, or ester polar moieties, often via a bridging group. The ashless dispersant may be, for example, selected from oil soluble salts, esters, amino-esters, amides, imides, and oxazolines of long chain hydrocarbon substituted mono and dicarboxylic acids or their anhydrides; thiocarboxylate derivatives of long chain hydrocarbons; long chain aliphatic hydrocarbons having a polyamine attached directly thereto; and Mannich condensation products formed by condensing a long chain substituted phenol with formaldehyde and polyalkylene polyamine.

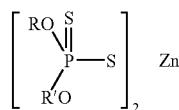
[0056] The oil soluble polymeric hydrocarbon backbone of these dispersants is typically derived from an olefin polymer or polyene, especially polymers comprising a major molar amount (i.e., greater than 50 mole %) of a C₂ to C₁₈ olefin (e.g., ethylene, propylene, butylene, isobutylene, pentene, octene-1, styrene), and typically a C₂ to C₅ olefin. The oil soluble polymeric hydrocarbon backbone may be a homopolymer (e.g., polypropylene or polyisobutylene) or a copolymer of two or more of such olefins (e.g., copolymers of ethylene and an alpha-olefin such as propylene or butylene, or copolymers of two different alpha-olefins). Other copolymers include those in which a minor molar amount of the copolymer monomers, for example, 1 to 10 mole %, is an α,ω -diene, such as a C₃ to C₂₂ non-conjugated diolefin (for example, a copolymer of isobutylene and butadiene, or a copolymer of ethylene, propylene and 1,4-hexadiene or 5-ethylidene-2-norbornene). Preferred are polyisobutylene (Mn 400-2500, preferably 950-2200) succinimide dispersants. Preferably, a lubricating oil composition according to the present invention comprises from 0.005 to 0.08 wt %, preferably from 0.01 to 0.08 wt %, most, preferably from about 0.05 to 0.08 wt % of total nitrogen. Suitably, substantially all of the nitrogen in the lubricating oil composition is provided by the dispersant.

[0057] A lubricating oil composition according to the present invention, may comprise one or more borated dispersant. Such dispersants can be borated by conventional means, as generally taught in U.S. Pat. Nos. 3,087,936; 3,254,025 and 5,430,105. Boration of the dispersant is

readily accomplished by treating an acyl nitrogen-containing dispersant with a boron compound such as boron oxide, boron halide boron acids, and esters of boron acids, in an amount sufficient to provide from about 0.1 to about 20 atomic proportions of boron for each mole of acylated nitrogen composition. Preferably, lubricating oil compositions of the present invention contain less than 100 ppm of boron, such as less than 90 ppm of boron, more preferably, less than 80 ppm, such as less than 70 ppm of boron.

[0058] Dihydrocarbyl dithiophosphate metal salts are frequently used as antiwear and antioxidant agents. The metal may be an alkali or alkaline earth metal, or aluminum, lead, tin, molybdenum, manganese, nickel or copper. The zinc salts are most commonly used in lubricating oil in amounts of 0.1 to 10 wt %, preferably 0.2 to 2 wt %, based upon the total weight of the lubricating oil composition. They may be prepared in accordance with known techniques by first forming a dihydrocarbyl dithiophosphoric acid (DDPA), usually by reaction of one or more alcohol or a phenol with P_2S_5 and then neutralizing the formed DDPA with a zinc compound. For example, a dithiophosphoric acid may be made by reacting mixtures of primary and secondary alcohols. Alternatively, multiple dithiophosphoric acids can be prepared where the hydrocarbyl groups on one are entirely secondary in character and the hydrocarbyl groups on the others are entirely primary in character. To make the zinc salt, any basic or neutral zinc compound could be used but the oxides, hydroxides and carbonates are most generally employed. Commercial additives frequently contain an excess of zinc due to the use of an excess of the basic zinc compound in the neutralization reaction.

[0059] The preferred zinc dihydrocarbyl dithiophosphates are oil soluble salts of dihydrocarbyl dithiophosphoric acids and may be represented by the following formula:



wherein R and R' may be the same or different hydrocarbyl radicals containing from 1 to 18, preferably 2 to 12, carbon atoms and including radicals such as alkyl, alkenyl, aryl, arylalkyl, alkaryl and cycloaliphatic radicals. Particularly preferred as R and R' groups are alkyl groups of 2 to 8 carbon atoms. Thus, the radicals may, for example, be ethyl, n-propyl, i-propyl, n-butyl, i-butyl, sec-butyl, amyl, n-hexyl, i-hexyl, n-octyl, decyl, dodecyl, octadecyl, 2-ethylhexyl, phenyl, butylphenyl, cyclohexyl, methylcyclopentyl, propenyl, butenyl. In order to obtain oil solubility, the total number of carbon atoms (i.e. R and R') in the dithiophosphoric acid will generally be about 5 or greater. The zinc dihydrocarbyl dithiophosphate (ZDDP) can therefore comprise zinc dialkyl dithiophosphates. Although the lubricating oil compositions of the present invention are capable of providing excellent performance in the presence of amounts of ZDDP providing greater amounts of phosphorus, the improved performance of the inventive lubricating oil compositions are particularly apparent in lower SAPS formulations, which generally have phosphorous levels of no greater than about 0.08 wt % (800 ppm). Therefore, lubricating oil

compositions of the present invention suitably contain less than 800 ppm, preferably less than 700 ppm and more preferably 600 ppm or less of phosphorus. Lubricating oil compositions according to the present invention suitably comprise at least 50 ppm, preferably at least 100 ppm and more preferably at least 200 ppm of phosphorus.

[0060] Oxidation inhibitors or antioxidants reduce the tendency of mineral oils to deteriorate in service. Oxidative deterioration can be evidenced by sludge in the lubricant, varnish-like deposits on the metal surfaces, and by viscosity growth. Such oxidation inhibitors include hindered phenols, alkaline earth metal salts of alkylphenolthioesters having preferably C_5 to C_{12} alkyl side chains, calcium nonylphenol sulfide, oil soluble phenates and sulphurized phenates, phosphosulphurized or sulphurized hydrocarbons or esters, phosphorous esters, ashless and metal-containing thiocarbamates, and oil soluble copper compounds as described in U.S. Pat. No. 4,867,890.

[0061] Aromatic amines having at least two aromatic groups attached directly to the nitrogen constitute another class of compounds that is frequently used for antioxidant. Typical oil soluble aromatic amines having at least two aromatic groups attached directly to one amine nitrogen contain from 6 to 16 carbon atoms. The amines may contain more than two aromatic groups. Compounds having a total of at least three aromatic groups in which two aromatic groups are linked by a covalent bond or by an atom or group (e.g., an oxygen or sulphur atom, or a $—CO—$, $—SO_2—$ or alkylene group) and two are directly attached to one amine nitrogen also considered aromatic amines having at least two aromatic groups attached directly to the nitrogen. The aromatic rings are typically substituted by one or more substituents selected from alkyl, cycloalkyl, alkoxy, aryloxy, acyl, acylamino, hydroxy, and nitro groups. The amount of any such oil soluble aromatic amines having at least two aromatic groups attached directly to one amine nitrogen should preferably not exceed 0.4 wt % active ingredient.

[0062] Preferably, lubricating oil compositions in accordance with the present invention contain from about 0.05 to about 5 wt %, preferably from about 0.10 to about 3 wt %, most preferably from about 0.20 to about 2.5 wt % of phenolic antioxidant, aminic antioxidant, or a combination thereof, based on the total weight of the lubricating oil composition.

[0063] Lubricating oil compositions according to the present invention may optionally comprise a rust or corrosion inhibitor. Any suitable rust or corrosion inhibitor may be used. As rust inhibitors there may be mentioned nonionic polyoxyalkylene polyols and esters thereof, polyoxyalkylene phenols and anionic alkyl sulfonic acids. Preferably, a lubricating oil composition according to the present invention comprises a succinic acid based rust inhibitor and/or an alkyl substituted phenol ethoxylate.

[0064] As copper and lead bearing corrosion inhibitors there may be mentioned the thiadiazole polysulfides containing from 5 to 50 carbon atoms, their derivatives and polymers thereof. Such materials are widely known and disclosed, for example, in U.S. Pat. No. 2,719,125, U.S. Pat. No. 4,097,387 and GB Patent No. 1 560 830.

[0065] If present the rust or corrosion inhibitor is suitably present in an amount not exceeding 1.0 wt %, and preferably not exceeding 0.5 wt %, based on the total weight of the composition.

[0066] Foam control can be provided by an antifoamant of the polysiloxane type, for example, silicone oil or polydimethyl siloxane.

[0067] In the present invention it may be advantageous to include an additive that maintains the stability of the viscosity of the blend. Additives which are effective in controlling this viscosity increase include the long chain hydrocarbons functionalized by reaction with mono- or dicarboxylic acids or anhydrides which are used in the preparation of the ashless dispersants as hereinbefore disclosed. In another preferred embodiment, the lubricating oil compositions of the present invention contain an effective amount of a long chain hydrocarbons functionalized by reaction with mono- or dicarboxylic acids or anhydrides (e.g., polyisobutylene succinic anhydride (PIBSA)).

[0068] The viscosity index of the base stock may be increased, or improved, by incorporating therein certain polymeric materials that function as viscosity modifiers (VM) or viscosity index improvers (VII). Generally, polymeric materials useful as viscosity modifiers are those having number average molecular weights (Mn) of from about 5,000 to about 250,000, preferably from about 15,000 to about 200,000, more preferably from about 20,000 to about 150,000. Polymer molecular weight, specifically Mn, can be determined by various known techniques. One convenient method is gel permeation chromatography (GPC), which additionally provides molecular weight distribution information (see W. W. Yau, J. J. Kirkland and D. D. Bly, "Modern Size Exclusion Liquid Chromatography", John Wiley and Sons, New York, 1979). Another useful method for determining molecular weight, particularly for lower molecular weight polymers, is vapor pressure osmometry (see, e.g., ASTM D3592).

[0069] A viscosity index improver dispersant functions both as a viscosity index improver and as a dispersant. Examples of viscosity index improver dispersants include reaction products of amines, for example polyamines, with a hydrocarbyl-substituted mono- or dicarboxylic acid in which the hydrocarbyl substituent comprises a chain of sufficient length to impart viscosity index improving properties to the compounds. In general, the viscosity index improver dispersant may be, for example, a polymer of a C₄ to C₂₄ unsaturated ester of vinyl alcohol or a C₃ to C₁₀ unsaturated mono-carboxylic acid or a C₄ to C₁₀ di-carboxylic acid with an unsaturated nitrogen-containing monomer having 4 to 20 carbon atoms; a polymer of a C₂ to C₂₀ olefin with an unsaturated C₃ to C₁₀ mono- or di-carboxylic acid neutralised with an amine, hydroxyamine or an alcohol; or a polymer of ethylene with a C₃ to C₂₀ olefin further reacted either by grafting a C₄ to C₂₀ unsaturated nitrogen-containing monomer thereon or by grafting an unsaturated acid onto the polymer backbone and then reacting carboxylic acid groups of the grafted acid with an amine, hydroxy amine or alcohol. A preferred lubricating oil composition contains a dispersant composition of the present invention, base oil, and a viscosity index improver dispersant.

[0070] Pour point depressants (PPD), otherwise known as lube oil flow improvers (LOFIs) lower the temperature. Typical additives that improve the low temperature fluidity of the fluid are C₈ to C₁₈ dialkyl fumarate/vinyl acetate copolymers, and polymethacrylates. Like VM, LOFIs can be grafted with grafting materials such as, for example, maleic

anhydride, and the grafted material can be reacted with, for example, amines, amides, nitrogen-containing heterocyclic compounds or alcohol, to form multifunctional additives.

[0071] Some other of the above-mentioned additives can also provide a multiplicity of effects; thus for example, a single additive may act as a dispersant-oxidation inhibitor. This approach is well known and need not be further elaborated herein.

[0072] When lubricating compositions contain one or more of the above-mentioned additives, each additive is typically blended into the base oil in an amount that enables the additive to provide its desired function. Representative effective amounts of such additives, when used in crankcase lubricants, are listed below.

ADDITIVE	WT % (Broad)	WT % (Preferred)
Dispersant	0.1-20	1-8
Metal Detergents	0.1-15	0.2-9
Corrosion Inhibitor	0-5	0-1.5
Metal Dihydrocarbyl Dithiophosphate	0.1-6	0.1-4
Antioxidant	0-5	0.01-2.5
Pour Point Depressant	0.01-5	0.01-1.5
Antifoaming Agent	0-5	0.001-0.15
Supplemental Antiwear Agents	0-1.0	0-0.5
Viscosity Modifier	0.01-10	0.25-3

[0073] It may be desirable, although not essential to prepare one or more additive concentrates comprising additives (concentrates sometimes being referred to as additive packages) whereby several additives can be added simultaneously to the oil to form the lubricating oil composition.

[0074] The final composition may employ from 5 to 30 wt %, preferably 5 to 25 wt %, typically 10 to 20 wt % of the concentrate, the remainder being oil of lubricating viscosity.

[0075] The terms "oil-soluble" or "dispersible" used herein do not necessarily indicate that the compounds or additives are soluble, dissolvable, miscible, or capable of being suspended in the oil in all proportions. These do mean, however, that they are, for instance, soluble or stably dispersible in oil to an extent sufficient to exert their intended effect in the environment in which the oil is employed. Moreover, the additional incorporation of other additives may also permit incorporation of higher levels of a particular additive, if desired.

[0076] Throughout this specification reference to quantitative amounts of a component are given on an active ingredient basis. It is common for some additives to be combined with a diluent.

[0077] The present invention advantageously provides a method of reducing wear of the rotating tappets in passenger car motor vehicles engines lubricated with lower SAPS lubricants.

[0078] It is unexpected that removal of conventional friction modifier additives from the lubricating oil used to lubricate an engine comprising a rotating tappet would provide an improvement in wear performance, particularly of the rotating tappet. It is particularly surprising that the present invention also exhibits acceptable fuel economy

performance despite the absence of friction modifier, which is normally thought necessary for acceptable fuel economy performance.

[0079] The invention will be further described, by way of example only, with reference to **FIG. 1** and **FIG. 2**.

[0080] **FIG. 1**, shows part of an engine valve train comprising a rotating tappet **6**. It can be seen from **FIG. 1** that a cam lobe **2**, supported on camshaft **4**, contacts the end face of the rotating tappet **6**, which is connected to the valve **10**.

[0081] In use, the cam lobe **2** is rotated by rotation of the cam shaft **4** on which it is mounted. There is a point of contact between the cam lobe **2** and the face of the rotating tappet **6**. The action of the eccentric shape cam effects linear reciprocating motion of the tappet **6**. In moving to the distal extreme of this linear reciprocating motion (not shown) the tappet **6** actuates the valve **10** and compresses the valve spring **8**. As the camshaft **4** continues to rotate and the cam lobe **2** releases the tappet **6**, the tappet moves back to the proximate extreme of this linear motion (as illustrated in **FIG. 1**) by relaxation of the valve spring the valve **10** closes.

[0082] During operation of the engine at operating temperature and oil pressure, the cam surface, of which the cam lobe **2** is part, remains in continuous contact with the face of the tappet **6**. As shown in **FIG. 2**, the point of contact between the cam **2** and tappet **6** is off-set from the axis of linear reciprocating motion by distance **X**. Consequently in addition to the linear reciprocating motion, the rotational motion of the camshaft **4** also translates into rotational motion of the tappet **6** about the axis of linear motion. This motion is clearly illustrated in **FIG. 2**.

[0083] As the cam lobe **2** rotates there is a sliding contact between the surface of the cam lobe **2** and the face of the tappet **6**. The rotational movement of the tappet **6** means that the point of contact between cam lobe **2** and tappet **6** varies. Thus any mechanical stress, deformation or wear of the tappet **6** by the impact of the cam lobe **2** is evenly distributed over the working face of the tappet **6**, rather than being concentrated within a fixed or restricted area.

[0084] The present invention advantageously facilitates rotation of the tappet and reduces stalling of the tappet, thus effecting improved wear performance.

[0085] This invention will be further understood by reference to the following examples, which include preferred embodiments of the invention. Compositions described as "comprising" a plurality of defined components are to be construed as including compositions formed by admixing the plurality of defined components.

EXAMPLES

Example 1

[0086] The VW RNT test (Draft PV 1473) is one test used to evaluate cam and tappet wear. The test uses a 1.91 TDI PD, 85 kW VW diesel engine on a static engine bench test. This engine has a rotating tappet and cam design. The test is a continuous test of 650 hour duration. Prior to the test the exhaust cam and tappet (number **1**) are irradiated and the wear is monitored on-line using a radio nucleide tracer technique.

[0087] Four oils were blended and tested in the 650 hour VW RNT test (PV1473 Draft). Oils 1 and 2 are lubricating oil compositions in accordance with the present invention, and comprise no friction modifier. Oils A and B are comparative examples and comprise glycerol monooleate and oleamide friction modifiers.

[0088] Each of oils 1, 2, A and B had a sulphated ash content of 0.6 wt %, a phosphorus content of 0.06 wt % and a sulphur content of around 0.22 wt %. Each of the exemplified oils was blended to a viscosity grade of 5W-30, according to SAE J300 May 2004.

[0089] The test results are set out below in Table 2.

TABLE 2

Measure	Oil 1	Oil 2	Oil A	Oil B
Radiated Cam Wear (nm)	2182	1157	12006	4296
Radiated Tappet Wear (nm)	4194	1375	8957	8479
Radiated cam and tappet (Cam Limit = 4000) (Tappet Limit = 5000)	Pass	Pass	Fail	Fail

[0090] The above results demonstrate that the lubricants containing no friction modifier performed better in the 650 hour VW RNT test (PV 1473 Draft) than comparable formulations with friction modifier, showing reduced wear on the rotating tappet. In fact, Oils 1 and 2 in accordance with the present invention passed the test as defined by the radiated cam and tappet limit, whereas the comparative Oils A and B failed.

[0091] It is unexpected that removal of a friction modifier from a passenger car motor vehicle lubricating oil composition would provide improved wear resistance of the rotating tappet.

Example 2

[0092] The VW PV 1451 FE test measures fuel economy. It involves comparison of candidate oils against a specified reference oil (CEC RL 191).

[0093] Oil 2, as above, and Oil C were tested in the VW FE PV1451 test. Oil C corresponds essentially with Oil B of example 1, except that Oil C contained only glycerol monooleate friction modifier. Each of Oils 2 and C and reference oil CEC RL 191 were run in the test and the fuel saving of Oils 2 and C was measured relative to the reference oil.

[0094] The test results are set out in Table 3 below.

TABLE 3

Measure	Oil 2	Oil C
Fuel savings (%)	2.03	2.04
Result (Pass $\geq 2.0\%$)	Pass	Pass

[0095] It can be seen from Table 3 that both Oils 2 and C pass the VW PV P1451 FE test for fuel economy. It can therefore be seen that a lubricating oil according to the present invention not only passes the 650 hour VW RNT test (PV 1473 Draft), but also passes the VW PV 1451 FE test, and thus provides a combination of acceptable wear resis-

tance and fuel economy. It is unexpected that a lubricating oil composition for a passenger car motor vehicle being substantially free of friction modifier would pass both industry wear and fuel economy tests. This is particularly unexpected in a lower SAPS oil composition, which is inherently limited as to the amount of metal dihydrocarbyl dithiophosphate anti-wear additive that can be used in the composition.

1. A method of lubricating an internal combustion engine having a cam and a rotating tappet, the method comprising employing as the lubricant for the engine a lubricating composition comprising a base oil of lubricating viscosity, phosphorus in an amount of from 50 to 900 ppm by mass, sulfur in an amount of from 1500 to 3000 ppm by mass, boron in an amount of from 0.0 to 100 ppm, sulphated ash in an amount not exceeding 1.0 mass %, and friction modifier in an amount of from 0.0 to 0.1 mass %, said amounts being based on the mass of fully formulated lubricating oil composition.

2. The method of claim 1 wherein the lubricating oil composition comprises less than 0.05 mass % friction modifier, based on the mass of fully formulated oil composition.

3. The method of claim 1, wherein any friction modifier in the lubricating compositions is selected from one or more of the following: glycerol esters of fatty acids, nitrogen-containing friction modifiers and molybdenum compounds.

4. The method of claim 1, wherein sulphated ash of the lubricating oil composition amounts to less than 0.7 mass %.

5. The method of claim 1, wherein the phosphorus content of the lubricating oil composition is 0.06 mass % or less, based on the mass of the fully formulated composition.

6. The method of claim 1, wherein the boron content of the composition is less than 90 ppm by mass.

7. The method of claim 1, wherein the lubricating oil composition comprises one or more additives selected from: metal-containing or ash-forming detergents; ashless dispersants; borated ashless dispersants; dihydrocarbyl dithiophosphate metal salts as antiwear and antioxidant agents; oxidation inhibitors or antioxidants; rust or corrosion inhibitors; foam control agents; viscosity stabilizing agents; viscosity modifying agents; pour point depressants; and supplemental antiwear agents.

8. The method of claim 1, wherein the lubricating oil composition comprises one or more nitrogen-containing dispersants, which dispersant(s) provide said composition with from 0.005 to 0.08 mass % of nitrogen.

9. An internal combustion engine having a rotating tappet lubricated with a lubricating oil composition comprising a base oil of lubricating viscosity; phosphorus in an amount of from 50 to 90 ppm by mass; sulfur in an amount of from 1500 to 3000 ppm by mass; boron in an amount of from 0.0 to 0.1 mass %, sulphated ash in an amount not exceeding 1.0 mass %; and friction modifier in an amount of from 0.0 to 0.1 mass %, said amounts being based on the mass of fully formulated lubricating oil composition.

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