

IMPROVEMENTS IN AND RELATING TO LUBRICATING COMPOSITIONS

Field of the Invention

The present invention concerns a method of reducing low-speed pre-ignition (LSPI) events in a direct-injection spark-ignition combustion engine comprising lubricating the crankcase of the engine with a lubricating composition comprising a combination of a molybdenum-containing additive and a boron-containing additive.

Background of the Invention

Market demand, as well as governmental legislation, has led automotive manufacturers to continuously improve fuel economy and reduce CO₂ emissions across engine families, while simultaneously maintaining performance (horsepower). Using smaller engines providing higher power densities, increasing boost pressure, by using turbochargers or superchargers to increase specific output and down-speeding the engine by using higher transmission gear ratios allowed by higher torque generation at lower engine speeds have allowed engine manufacturers to provide excellent performance while reducing frictional and pumping losses. However, higher torque at lower engine speeds has been found to cause random pre-ignition in engines at low speeds, a phenomenon known as Low Speed Pre-Ignition, or LSPI, resulting in extremely high cylinder peak pressures, which can lead to catastrophic engine failure. The possibility of LSPI prevents engine manufacturers from fully optimizing engine torque at lower engine speed in such smaller, high-output engines.

While not wishing to be bound by any specific theory, it is believed that LSPI may be caused, at least in part, by auto-ignition of droplets, e.g. comprising engine oil, or a mixture of engine oil, fuel and/or deposits, that enter the engine combustion chamber from the piston crevice (space between the piston ring pack and cylinder liner) under high pressure, during periods in which the engine is operating at low speeds, and compression stroke time is longest (*e.g.*, an engine having a 7.5 msec compression stroke at 4000 rpm may have a 24 msec compression stroke when operating at 1250 rpm). Therefore, it would be advantageous to identify and provide

lubricating oil compositions that are resistant to auto-ignition and therefore prevent or ameliorate the occurrence of LSPI.

Some attempts have been made in the art to address this problem. For example, SAE 2013-01-2569 (“Investigation of Engine Oil Effect on Abnormal Combustion in Turbocharged Direct Injection-Spark Ignition Engines (Part 2)”, Hirano *et al.*) concludes that increasing calcium concentration leads to greater LSPI frequency. It is also concluded that increasing zinc dihydrocarbyl dithiophosphate (ZDDP) concentration can reduce LSPI frequency. SAE 2014-01-2785 (“Engine Oil Development for Preventing Pre-Ignition in Turbocharged Gasoline Engine”, Fujimoto *et al.*) concludes that reducing the amount of calcium detergent in a lubricating oil formulation is the most effective approach at reducing LSPI events. It is also concluded that increasing the amount of ZDDP can be effective in reducing LSPI frequency. SAE 2015-01-2027 (“Engine Oil Formulation Technology to Prevent Pre-Ignition in Turbocharged Direct Injection Spark Ignition Engines”, Onodera *et al.*) concludes that (a) reducing calcium content together with increasing molybdenum content in engine oil formulations, and (b) substitution of calcium with magnesium in detergents for engine oil formulations, were both effective in reducing the frequency of LSPI events. A method of reducing LSPI frequency by using a lubricating oil having a reduced sodium content and containing certain molybdenum-containing compounds is disclosed in WO2017/011683. WO2015/171980 discloses a method of reducing LSPI frequency by including in a lubricating oil formulation at least one boron-containing compound, such as a borated dispersant or a mixture of a boron-containing compound and a dispersant. However, according to the examples disclosed in WO2015/171980, it was necessary to replace a substantial amount, or even all of, the calcium detergent with a magnesium detergent in order to obtain significant improvements in LSPI frequency.

The prior art has further recognised that reducing the calcium content, and/or increasing the ZDDP content, of a lubricating oil formulation can lead to a reduction in LSPI events. However, detergents are often considered to be necessary additives for maintaining basic engine oils performance. Thus, recent efforts in providing lubricating oil formulations that reduce LSPI events have focused on replacing calcium detergents with alternative detergents. However, alternative detergents capable of providing appropriate detergent activity and adequate total base number

(TBN) can be challenging to develop. Furthermore, increased ZDDP contents in lubricating oil formulations can lead to other, less desirable, effects. In particular, increasing ZDDP concentration often leads to an increase in ash formation and can lead to damage of catalysts in engine exhaust systems. EP 3 101 095 discloses a lubricating oil composition for reducing LSPI frequency, the composition comprising a compound containing calcium and/or magnesium, a compound containing molybdenum and/or phosphorus, and an ashless dispersion containing nitrogen. According to the disclosure of EP 3 101 095, LSPI event frequency can be reduced by controlling the relative amounts of calcium, magnesium, molybdenum and phosphorus in the lubricating oil composition.

Thus, there remains a need for a lubricating oil composition suitable for use in modern direct injection-spark ignition engines that reduces occurrences of LSPI events.

Summary of the Invention

The present inventors have surprisingly found that the use of both molybdenum-containing and boron-containing additives in a lubricating oil composition significantly reduces in the frequency of LSPI events in direct injection-spark ignition internal combustion engines when the crankcase of the engine is lubricated with said lubricating oil composition. More particularly, the present inventors have surprisingly found a synergistic improvement in LSPI reduction when using such a lubricating composition as compared to using a lubricating oil composition comprising only molybdenum-containing additives and not boron-containing additives, and *vice versa*.

Thus, the present invention provides, according to a first aspect, a method of reducing LSPI events in a direct-injection spark-ignition internal combustion engine comprising lubricating the crankcase of the engine with a lubricating oil composition, the composition comprising a boron-containing additive and a molybdenum-containing additive, having a molybdenum content of at least 150 ppm by weight, based on the weight of the lubricating oil composition, and having a boron content of at least 150 ppm by weight, based on the weight of the lubricating oil composition.

According to a second aspect, the present invention provides the use of a combination of the composition a boron-containing additive and a molybdenum-containing additive in a lubricating oil composition to reduce LSPI events, when the composition lubricates the crankcase of a direct injection-spark ignition internal combustion engine, wherein, the molybdenum-containing additive provides the lubricating oil composition with a molybdenum content of at least 150 ppm by weight, based on the weight of the lubricating oil composition, and the boron-containing additive provides the lubricating oil composition with a boron content of at least 150 ppm by weight, based on the weight of the lubricating oil composition.

In this specification, the following words and expressions, if and when used, have the meanings ascribed below:

“hydrocarbyl” means a chemical group of a compound that normally contains only hydrogen and carbon atoms and that is bonded to the remainder of the compound directly via a carbon atom but that may contain hetero atoms provided that they do not detract from the essentially hydrocarbyl nature of the group;

“oil-soluble” or “oil-dispersible”, or cognate terms, do not necessarily indicate that the compounds or additives are soluble, dissolvable, miscible, or are capable of being suspended in the oil in all proportions. These do mean, however, that they are, for example, 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 other additives may also permit incorporation of higher levels of a particular additive, if desired;

“major amount” mean in excess of 50 mass % of a composition;

“minor amount” means 50 mass % or less of a composition;

“antifoam” is a chemical additive that reduces and hinders the formation of foam in the lubricating oil composition, examples of commonly used antifoams are polydimethylsiloxanes and other silicones, certain alcohols, stearates and glycols;

“TBN” means total base number as measured by ASTM D2896 in units of mg KOH g^{-1} ;

“phosphorus content” is measured by ASTM D5185;

“molybdenum content” is measured by ASTM D5185;

“boron content” is measured by ASTM D5185;

“sulfur content” is measured by ASTM D2622; and,
“sulphated ash content” is measured by ASTM D874.

Also, it will be understood that various components used, essential as well as optimal and customary, may react under conditions of formulation, storage or use and that the invention includes the use of the product obtainable or obtained as a result of any such reaction. Further, it is understood that any upper and lower quantity, range and ratio limits set forth herein may be independently combined. Furthermore, the constituents of this invention may be isolated or be present within a mixture and remain within the scope of the invention.

It will of course be appreciated that features described in relation to one aspect of the present invention may be incorporated into other aspects of the present invention. For example, the use of the invention may incorporate any of the features described with reference to the method of the invention and *vice versa*.

Brief Description of the Figures

Fig. 1 shows the LSPI test results of Example 3 in matrix format.

Detailed Description

Several terms exist for various forms of abnormal combustion in spark ignited internal combustion engines including knock, extreme knock (sometimes referred to as super-knock or mega-knock), surface ignition, and pre-ignition (ignition occurring prior to spark ignition). Extreme knock occurs in the same manner as traditional knock, but with increased knock amplitude, and can be mitigated using traditional knock control methods. LSPI occurs at low speeds and high loads. In LSPI, initial combustion is relatively slow and similar to normal combustion, followed by a sudden increase in combustion speed. LSPI is not a runaway phenomenon, unlike some other types of abnormal combustion. Occurrences of LSPI are difficult to predict, but are often cyclical in nature.

LSPI is most likely to occur in direct-injected, boosted (turbocharged or supercharged), spark-ignited (gasoline) internal combustion engines that, in operation, generate a brake mean effective pressure level of greater than about 1,500 kPa (15

bar) (peak torque), such as at least about 1,800 kPa (18 bar), particularly at least about 2,000 kPa (20 bar) at engine speeds of from about 1000 to about 2500 rotations per minute (rpm), such as at engine speeds of from about 1000 to about 2000 rpm. As used herein, brake mean effective pressure (BMEP) is the mean effective pressure calculated from measured brake torque. The word "brake" denotes the actual torque or power available at the engine flywheel, as measured on a dynamometer. Thus, BMEP is a measure of the useful power output of the engine. BMEP is defined as the work accomplished during an engine cycle, divided by the engine swept volume; the engine torque normalized by engine displacement and can be calculated using the following formula:

$$\text{BMEP} = 2\pi T n_c / V_d$$

where T is torque (Nm), n_c is the number of revolutions per cycle, V_d is displacement (m^3). For a 4 stroke engine n_c is 2, for a 2 stroke engine n_c is 1.

SAE 2014-01-2785 has concluded that LSPI event frequency is strongly influenced by the calcium content of the lubricating oil composition, and that it is preferable to avoid lubricating composition calcium contents of greater than 0.11 wt.%, based on the weight of the lubricating oil composition, in order to avoid excessive LSPI event frequency.

Surprisingly, the present inventors have found that the presence of a combination of molybdenum and boron in a lubricating oil formulation is effective at reducing the occurrence of LSPI events. Unexpectedly, it has been found that the combination of both molybdenum and boron provides a synergistic improvement in LSPI event reduction, the frequency reduction being greater than expected from analysing the performance of lubricating oil compositions comprising only molybdenum and compositions comprising only boron. It has now been found that the occurrence of LSPI in engines can be reduced by lubricating the crankcase with lubricating oil compositions comprising at least 150 ppm by weight molybdenum and at least 150 ppm by weight boron, based on the weight of the lubricating oil composition, compared to lubricating the crankcase with lubricating oil compositions comprising less than 150 ppm by weight molybdenum and less than 150 ppm by weight boron. Surprisingly, the present inventors have found that the method and use of the first and second aspects of the invention is effective at reducing LSPI event frequency even when the lubricating oil composition comprises a significant amount

of calcium, for example when the lubricating oil composition additionally comprises at least 0.08 wt.% calcium, based on the weight of the lubricating oil composition.

Preferably, the engine of the method of the first aspect of the invention, and/or the use of the second aspect of the invention, is an engine that generates a break mean effective pressure level of greater than 1,500 kPa, optionally greater than 2,000 kPa, at engine speeds of from 1,000 to 2,500 rotations per minute (rpm), optionally from 1,000 to 2,000 rpm.

Optionally, the lubricating oil composition of all aspects of the invention comprises at least 175 ppm molybdenum, preferably at least 300 ppm molybdenum, optionally at least 350 ppm molybdenum, such as at least 500 ppm molybdenum, for example at least 700 ppm molybdenum, by weight, based on the weight of the lubricating oil composition. Optionally, the lubricating oil composition comprises no more than 1500 ppm molybdenum, preferably no more than 1400 ppm molybdenum, such as no more than 1200 ppm molybdenum, for example no more than 1100 ppm molybdenum, optionally no more than 1000 ppm molybdenum, by weight, based on the weight of the lubricating oil composition. Optionally, the lubricating oil composition comprises from 150 to 1500 ppm molybdenum, preferably from 175 to 1500 ppm molybdenum, optionally from 300 to 1400 ppm molybdenum, such as from 350 to 1200 ppm molybdenum, for example from 500 to 1100 ppm molybdenum, optionally from 700 to 1000 ppm molybdenum, by weight, based on the weight of the lubricating oil composition.

Optionally, the lubricating oil composition comprises at least 200 ppm boron, preferably at least 300 ppm boron, such as at least 400 ppm boron, by weight, based on the weight of the lubricating oil composition. Optionally, the lubricating oil composition comprises no more than 1500 ppm boron, preferably no more than 1000 ppm boron, such as no more than 800 ppm boron, by weight, based on the weight of the composition. Optionally, the lubricating oil composition comprises from 150 to 1500 ppm boron, preferably from 200 to 1000 ppm boron, optionally from 400 to 800 ppm boron, by weight, based on the weight of the lubricating oil composition.

It will be understood that the boron-containing additive may be any suitable oil-soluble compound or oil-dispersible compound. Boron-containing additives may be prepared by reacting a boron compound with an oil-soluble or oil-dispersible additive or compound. Boron compounds include boron oxide, boron oxide hydrate,

boron trioxide, boron trifluoride, boron tribromide, boron trichloride, boron acid such as boronic acid, boric acid, tetraboric acid and metaboric acid, boron hydrides, boron amides and various esters of boron acids. For example, the boron-containing additive may be one or more of a borated dispersant; a borated dispersant viscosity index improver; an alkali metal or a mixed alkali metal or an alkaline earth metal borate; a borated overbased metal detergent; a borated epoxide; a borate ester; a sulfurised borate ester; and a borate amide. Preferably, the boron-containing additive is one or more of a borated dispersant, a borate ester or a borated overbased metal detergent. Optionally, the borated overbased metal detergent, if present, is a borated overbased metal detergent having a TBN of at least 150, such as a borated overbased calcium detergent having a TBN of at least 150.

Borated dispersants may be prepared by boration of succinimide, succinic ester, benzylamine and their derivatives, each of which has an alkyl or alkenyl group of molecular weight of 700 to 3000. Processes for manufacture of these additives are known to those skilled in the art. A preferred amount of boron contained in these dispersants is 0.1 to 5 mass % (especially 0.2 to 2 mass %). A particularly preferable borated dispersant is a succinimide derivative of boron, for example borated polyisobutenyl succinimide. An example of a borated dispersant is a borated polyisobutenyl succinimide wherein the average number molecular weight ($\overline{M}_n$) of the polybutenyl backbone is in the range from 700 to 1250. Additionally or alternatively, borated dispersants are made by borating the ashless dispersants described below, using known borating means and techniques.

Ashless dispersants are non-metallic organic materials that form substantially no ash on combustion, in contrast to metal-containing, and hence ash-forming, materials. They comprise a long chain hydrocarbon with a polar head, the polarity being derived from inclusion of, e.g. an O, P or N atom. The hydrocarbon is an oleophilic group that confers oil-solubility, having, for example 40 to 500 carbon atoms. Thus, ashless dispersants may comprise an oil-soluble polymeric hydrocarbon backbone having functional groups that are capable of associating with particles to be dispersed. Typically, dispersants comprise amine, alcohol, amide, or ester polar moieties attached to the polymer backbone often via a bridging group. Ashless dispersants 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 a long chain of 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 alkylene polyamine, such as described in US-A-3, 442, 808. The oil-soluble polymeric hydrocarbon backbone is typically an olefin polymer or polyene, especially a polymer comprising a major molar amount (i.e. greater than 50 mole %) of a C₂ to C₁₈ olefin (e.g. ethylene, propylene, butylenes, isobutylene, pentene, octane-1, styrene), and typically a C₂ to C₅ olefin. The oil-soluble polymeric hydrocarbon backbone may be homopolymeric (e.g. comprising a copolymer of ethylene and an alpha-olefin such as propylene or butylenes, or a copolymer of two different alpha-olefins). A preferred class of olefin polymers comprises polybutenes, specifically polyisobutenes (PIB) or poly-n-butenes, such as may be prepared by polymerization of a C₄ refinery stream. Other classes of olefin polymers include ethylene alpha-olefin (EAO) copolymers and alpha-olefin homo- and copolymers.

Ashless dispersants include, for example, derivatives of long chain hydrocarbon-substituted carboxylic acids, examples being derivatives of high molecular weight hydrocarbyl-substituted succinic acid. A noteworthy group of dispersants are hydrocarbon- substituted succinimides, made, for example, by reacting the above acids (or derivatives) with a nitrogen-containing compound, advantageously a polyalkylene polyamine, such as polyethylene polyamine. Particularly preferred are the reaction products of polyalkylene polyamines with alkenyl succinic anhydrides, such as described in US-A-3, 202, 678; -3, 154, 560; -3, 172,892; -3, 024, 195, -3, 024, 237; -3,219,666; and -3,216,936; and BE-A-66,875. Preferred dispersants are polyalkene-substituted succinimides wherein the polyalkene group has a number-average molecular weight in the range of 900 to 5,000. The number-average molecular weight is measured by gel permeation chromatography (GPC). The polyalkene group may comprise a major molar amount (i.e. greater than 50 mole %) of a C₂ to C₁₈ alkene, e.g. ethene, propene, butene, isobutene, pentene, octane-1 and styrene. Preferably, the alkene is a C₂ to C₅ alkene; more preferably it is butene or isobutene, such as may be prepared by polymerisation of a C₄ refinery stream. Most

preferably, the number average molecular weight of the polyalkene group is in the range of 950 to 2,800.

The above ashless dispersants are post-treated with boron to form a borated dispersant in ways known in the art, such as described in US-A-3,087,936, US-A-3,254,025 and US-A-5,430,105. Boration may for example be accomplished by treating an acyl nitrogen-containing dispersant with a boron compound selected from boron oxide, boron halides, 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 ashless dispersant.

Alkali metal and alkaline earth metal borates are generally hydrated particulate metal borates, which are known in the art. Alkali metal borates include mixed alkali and alkaline earth metal borates. These metal borates are available commercially. Representative patents describing suitable alkali metal and alkaline earth metal borates and their methods of manufacture include U.S. 3,997,454; 3,819,521; 3,853,772; 3,907,601; 3,997,454; and 4,089,790.

Borated amines may be prepared by reacting one or more of the above boron compounds with one or more of fatty amines, e.g., an amine having from four to eighteen carbon atoms. They may be prepared by reacting the amine with the boron compound at a temperature in the range of from 50 to 300°C, preferably from 100 to 250°C, and at a ratio from 3:1 to 1:3 equivalents of amine to equivalents of boron compound.

Borated epoxides are generally the reaction product of one or more of the above boron compounds with at least one epoxide. The epoxide is generally an aliphatic epoxide having from 8 to 30, preferably from 10 to 24, more preferably from 12 to 20, carbon atoms. Examples of useful aliphatic epoxides include heptyl epoxide and octyl epoxide. Mixtures of epoxides may also be used, for instance commercial mixtures of epoxides having from 14 to 16 carbon atoms and from 14 to 18 carbon atoms. The borated fatty epoxides are generally known and are described in U.S. Patent 4,584,115.

Borate esters may be prepared by reacting one or more of the above boron compounds with one or more alcohols of suitable oleophilicity. Typically, the alcohols contain from 6 to 30, or from 8 to 24, carbon atoms. The methods of making such borate esters are known in the art. The borate esters can be borated

phospholipids. Such compounds, and processes for making such compounds, are described in EP-A-0 684 298. Examples of sulfurised borated esters are also known in the art: see EP-A- 0 285 455 and US-B-6,028,210. Alternatively, it may be that a borate ester is substantially absent in the lubricating oil compositions of the method or use of the present invention.

Borated overbased metal detergents are known in the art where the borate substitutes the carbonate in the core either in part or in full. Borated detergents may be prepared by any conventional method, for example, a borated detergent may be prepared by treating a metal detergent with boric acid. Suitable borated detergents and methods of preparing them are disclosed in US 3,480,548, US 3,679,584, US 3,829,381, US 3,909,691 and US 4, 965,004.

Preferably, at least a portion of the boron content of the lubricating oil composition is provided by a boron-containing dispersant additive, such as a major portion. In an embodiment of the invention, 100 wt.% of the boron in the lubricating oil composition, based on the weight of the boron in the lubricating oil composition, is provided by one or more boron-containing dispersant additives.

Alternatively or in addition, at least a portion of the boron content of the lubricating oil composition is provided by a borated detergent.

Additionally or alternatively, at least a portion of the boron content of the lubricating oil composition is provided by a borate ester.

In an embodiment of the invention, at least a portion of the boron content of the lubricating oil composition is provided by a boron-containing compound that is not a dispersant, such as a major portion.

Optionally, 100 wt.% of the boron in the lubricating oil composition, based on the weight of the boron in the lubricating oil composition is provided by one or more non-dispersant boron-containing compounds, such as a borated detergent and/or a borate ester. Optionally, from 20 wt.% to 100 wt.%, preferably from 40 wt.% to 80 wt.%, such as from 50 wt.% to 70 wt.%, of the boron in the lubricating oil composition, based on the weight of the boron in the lubricating oil composition, is provided by one or more borated detergent(s) and/or borate ester(s).

It will be understood that the molybdenum-containing additive may be any suitable oil-soluble or oil-dispersible organo-molybdenum compound. Preferably, 100 wt.% of the molybdenum content of the lubricating oil composition is provided by an

organo-molybdenum compound, based on the weight of the lubricating oil composition. Such molybdenum-containing additives generally exhibit friction modifying properties when present in a lubricating oil composition. Additionally or alternatively, such molybdenum-containing additives may also provide antioxidant and anti-wear credits to a lubricating oil composition.

To enable the molybdenum compound to be oil-soluble or oil-dispersible, one or more ligands are typically bonded to a molybdenum atom in the compound. The bonding of the ligands includes bonding by electrostatic interaction as in the case of a counter-ion and forms of bonding intermediate between covalent and electrostatic bonding. Ligands within the same compound may be differently bonded. For example, a ligand may be covalently bonded and another ligand may be electrostatically bonded. Preferably, the or each ligand is monoanionic and examples of such ligands are dithiophosphates, dithiocarbamates, xanthates, carboxylates, thioxanthates, phosphates and hydrocarbyl, preferably alkyl, derivatives thereof.

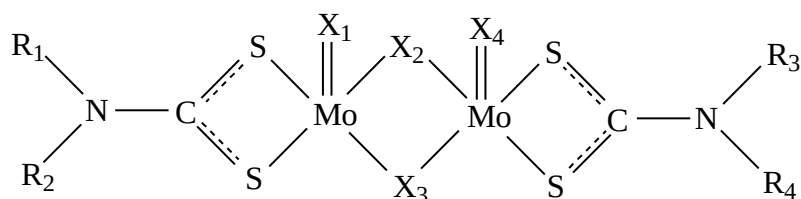
The molybdenum-containing additive may be mono-, di-, tri- or tetra-nuclear. Di-nuclear and tri-nuclear molybdenum compounds are preferred. In the event that the compound is polynuclear, the compound contains a molybdenum core consisting of non-metallic atoms, such as sulfur, oxygen and selenium, preferably consisting essentially of sulfur.

In a preferred embodiment, the molybdenum compound is a molybdenum-sulfur compound. Preferably, the ratio of the number of molybdenum atoms, for example, in the core in the event that the molybdenum-sulfur compound is a polynuclear compound, to the number of monoanionic ligands, which are capable of rendering the compound oil-soluble or oil-dispersible, is greater than 1 to 1, such as at least 3 to 2. The molybdenum-sulfur compound's oil-solubility or oil-dispersibility may be influenced by the total number of carbon atoms present among all of the compound's ligands. The total number of carbon atoms present among all of the hydrocarbyl groups of the compound's ligands typically will be at least 21, e.g. 21 to 800, such as at least 25, at least 30 or at least 35. For example, the number of carbon atoms in each alkyl group will generally range between 1 to 100, preferably 1 to 40, and more preferably between 3 and 20.

Examples of suitable organo-molybdenum compounds include molybdenum dithiocarbamates, molybdenum dithiophosphates, molybdenum dithiophosphinates,

molybdenum xanthates, molybdenum thioxanthates, molybdenum sulfides, and the like, and mixtures thereof. Particularly preferred are molybdenum dithiocarbamates, molybdenum dialkyldithiophosphates, molybdenum alkyl xanthates and molybdenum alkylthioxanthates. An especially preferred organo-molybdenum compound is a molybdenum dithiocarbamate. In an embodiment of the present invention the oil-soluble or oil-dispersible molybdenum compound consists of either a molybdenum dithiocarbamate or a molybdenum dithiophosphate or a mixture thereof, as the sole source of molybdenum atoms in the lubricating oil composition. In an alternative embodiment of the present invention the oil-soluble or oil-dispersible molybdenum compound consists of a molybdenum dithiocarbamate, as the sole source of molybdenum atoms in the lubricating oil composition.

Suitable dinuclear or dimeric molybdenum dialkyldithiocarbamate are represented by the following formula:



R_1 through R_4 independently denote a straight chain, branched chain or aromatic hydrocarbyl group having 1 to 24 carbon atoms; and X_1 through X_4 independently denote an oxygen atom or a sulfur atom. The four hydrocarbyl groups, R_1 through R_4 , may be identical or different from one another.

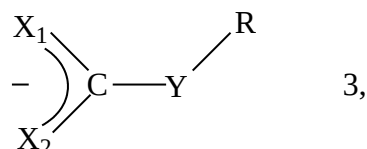
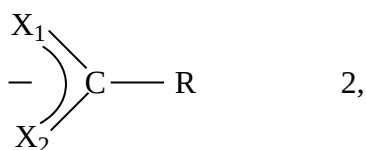
Other molybdenum-containing additives useful in the compositions of this invention are organo-molybdenum compounds of the formulae $\text{Mo}(\text{ROCS}_2)_4$ and $\text{Mo}(\text{RSCS}_2)_4$, wherein R is an organo group selected from the group consisting of alkyl, aryl, aralkyl and alkoxyalkyl, generally of from 1 to 30 carbon atoms, and preferably 2 to 12 carbon atoms and most preferably alkyl of 2 to 12 carbon atoms. Especially preferred are the dialkyldithiocarbamates of molybdenum.

In a preferred embodiment, the molybdenum-containing additive is an oil-soluble or oil-dispersible trinuclear molybdenum-sulfur compound. Examples of trinuclear molybdenum-sulfur compounds are disclosed in WO98/26030, WO99/31113, WO99/66013, EP-A-1 138 752, EP-A-1 138 686 and European patent

application no. 02078011, each of which are incorporated into the present description by reference, particularly with respect to the characteristics of the molybdenum compound or additive disclosed therein.

Suitable tri-nuclear organo-molybdenum compounds include those of the formula $\text{Mo}_3\text{S}_k\text{L}_n\text{Q}_z$ and mixtures thereof wherein L are independently selected ligands having organo groups with a sufficient number of carbon atoms to render the compound soluble or dispersible in the oil, n is from 1 to 4, k varies from 4 through 7, Q is selected from the group of neutral electron donating compounds such as water, amines, alcohols, phosphines, and ethers, and z ranges from 0 to 5 and includes non-stoichiometric values. At least 21 total carbon atoms should be present among all the ligands' organo groups, such as at least 25, at least 30, or at least 35 carbon atoms.

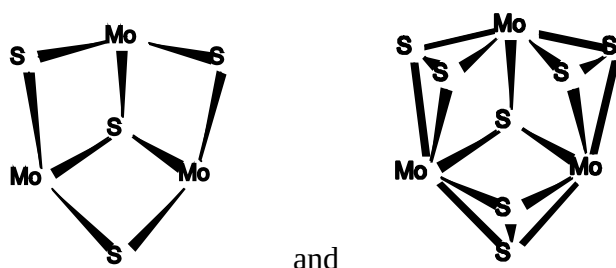
The ligands are independently selected from the group of:



and mixtures thereof, wherein X, X_1 , X_2 , and Y are independently selected from the group of oxygen and sulfur, and wherein R_1 , R_2 , and R are independently selected from hydrogen and organo groups that may be the same or different. Preferably, the organo groups are hydrocarbyl groups such as alkyl (e.g., in which the carbon atom attached to the remainder of the ligand is primary or secondary), aryl, substituted aryl and ether groups. More preferably, each ligand has the same hydrocarbyl group. Importantly, the organo groups of the ligands have a sufficient number of carbon atoms to render the compound soluble or dispersible in the oil. For example, the number of carbon atoms in each group will generally range between about 1 to about 100, preferably from about 1 to about 30, and more preferably between about 4 to about 20. Preferred ligands include dialkyldithiophosphate, alkylxanthate, and dialkyldithiocarbamate, and of these dialkyldithiocarbamate is

more preferred. Organic ligands containing two or more of the above functionalities are also capable of serving as ligands and binding to one or more of the cores. Those skilled in the art will realize that formation of the compounds of the lubricating oil composition of the present invention requires selection of ligands having the appropriate charge to balance the core's charge.

Particularly suitable molybdenum-containing additives include compounds having the formula $\text{Mo}_3\text{S}_k\text{L}_n\text{Q}_z$, having cationic cores surrounded by anionic ligands and being represented by structures such as



and having net charges of +4. Consequently, in order to solubilize these cores the total charge among all the ligands must be -4. Four mono-anionic ligands are preferred. Without wishing to be bound by any theory, it is believed that two or more tri-nuclear cores may be bound or interconnected by means of one or more ligands and the ligands may be multidentate. This includes the case of a multidentate ligand having multiple connections to a single core. It is believed that oxygen and/or selenium may be substituted for sulfur in the core(s).

Additionally or alternatively, particularly suitable trinuclear molybdenum-containing additives may be represented by the formula $\text{Mo}_3\text{S}_k\text{E}_x\text{L}_n\text{A}_p\text{Q}_z$, wherein:

k is an integer of at least 1;

E represents a non-metallic atom selected from oxygen and selenium;

x can be 0 or an integer, and preferably $k + x$ is at least 4, more preferably in the range of 4 to 10, such as 4 to 7, most preferably 4 or 7;

L represents a ligand that confers oil-solubility or oil-dispersibility on the molybdenum-sulfur compound, preferably L is a monoanionic ligand;

n is an integer in the range of 1 to 4;

A represents an anion other than L, if L is an anionic ligand;

p can be 0 or an integer;

Q represents a neutral electron-donating compound; and

z is in the range of 0 to 5 and includes non-stoichiometric values.

Those skilled in the art will realise that formation of the trinuclear molybdenum-sulfur compound will require selection of appropriate ligands (L) and other anions (A), depending on, for example, the number of sulfur and E atoms present in the core, *i.e.* the total anionic charge contributed by sulfur atom(s), E atom(s), if present, L and A, if present, must be -12 . Examples of Q include water, alcohol, amine, ether and phosphine. It is believed that the electron-donating compound, Q, is merely present to fill any vacant coordination sites on the trinuclear molybdenum-sulfur compound. Examples of A can be of any valence, for example, monovalent and divalent and include disulfide, hydroxide, alkoxide, amide and, thiocyanate or derivative thereof; preferably A represents a disulfide ion. Preferably, L is monoanionic ligand, such as dithiophosphates, dithiocarbamates, xanthates, carboxylates, thioxanthates, phosphates and hydrocarbyl, preferably alkyl, derivatives thereof. When n is 2 or more, the ligands can be the same or different. In an embodiment, independently of the other embodiments, k is 4 or 7, n is either 1 or 2, L is a monoanionic ligand, p is an integer to confer electrical neutrality on the compound based on the anionic charge on A and each of x and z is 0.

In a further embodiment, independently of the other embodiments, k is 4 or 7, L is a monoanionic ligand, n is 4 and each of p, x and z is 0.

In another embodiment, the molybdenum-containing additive comprises trinuclear molybdenum core and bonded thereto a ligand, preferably a mono-anionic ligand, such as a dithiocarbamate, capable of rendering the core oil-soluble or oil-dispersible. For the avoidance of doubt, the molybdenum-containing additive may also comprise either negatively charged molybdenum species or positively charged molybdenum species or both negatively and positively charged molybdenum species.

The molybdenum-sulfur cores, for example, the structures depicted in (I) and (II) above, may be interconnected by means of one or more ligands that are multidentate, *i.e.* a ligand having more than one functional group capable of binding to a molybdenum atom, to form oligomers. Molybdenum-sulfur additives comprising such oligomers are considered to fall within the scope of the lubricating oil compositions of this invention.

Oil-soluble or oil-dispersible tri-nuclear molybdenum-containing additives can be prepared by reacting in the appropriate liquid(s)/solvent(s) a molybdenum source

such as $(\text{NH}_4)_2\text{Mo}_3\text{S}_{13}\cdot n(\text{H}_2\text{O})$, where n varies between 0 and 2 and includes non-stoichiometric values, with a suitable ligand source such as a tetralkylthiuram disulfide. Other oil-soluble or dispersible tri-nuclear molybdenum-containing additives can be formed during a reaction in the appropriate solvent(s) of a molybdenum source such as of $(\text{NH}_4)_2\text{Mo}_3\text{S}_{13}\cdot n(\text{H}_2\text{O})$, a ligand source such as tetralkylthiuram disulfide, dialkyldithiocarbamate, or dialkyldithiophosphate, and a sulfur abstracting agent such as cyanide ions, sulfite ions, or substituted phosphines. Alternatively, a tri-nuclear molybdenum-sulfur halide salt such as $[\text{M}']_2[\text{Mo}_3\text{S}_7\text{A}_6]$, where M' is a counter ion, and A is a halogen such as Cl , Br , or I , may be reacted with a ligand source such as a dialkyldithiocarbamate or dialkyldithiophosphate in the appropriate liquid(s)/solvent(s) to form an oil-soluble or dispersible trinuclear molybdenum compound. The appropriate liquid/solvent may be, for example, aqueous or organic.

A compound's oil solubility or dispersibility may be influenced by the number of carbon atoms in the ligand's organo groups. Preferably, at least 21 total carbon atoms should be present among all the ligands' organo groups. Preferably, the ligand source chosen has a sufficient number of carbon atoms in its organo groups to render the compound soluble or dispersible in the lubricating composition.

Other examples of molybdenum compounds include molybdenum carboxylates and molybdenum nitrogen complexes, both of which may be sulfurised.

Alternatively, the molybdenum-containing additive may be an acidic molybdenum compound. These compounds will react with a basic nitrogen compound as measured by ASTM test D-664 or D-2896 titration procedure and are typically hexavalent. Included are molybdic acid, ammonium molybdate, sodium molybdate, potassium molybdate, and other alkaline 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 or similar acidic molybdenum compounds.

Alternatively, the lubricating oil compositions of the present invention can be provided with molybdenum by molybdenum/sulfur complexes of basic nitrogen compounds as described, for example, in U.S. Patent Nos. 4,263,152; 4,285,822; 4,283,295; 4,272,387; 4,265,773; 4,261,843; 4,259,195 and 4,259,194; and WO 94/06897.

Optionally, the lubricating oil composition comprises one or more molybdenum-containing compounds that is not a friction modifier additive (for example that is not used as a friction modifier additive). Optionally, at least a portion of the molybdenum content of the lubricating oil composition is provided by a molybdenum-containing compound that is not a friction modifier, such as a major portion.

Optionally, the lubricating oil composition of all embodiments of the present invention has a calcium content of at least 0.08 wt.%, based on the weight of the lubricating oil composition. The lubricating oil composition of all aspects of the invention may have a calcium content of at least 0.10 wt.%, preferably at least 0.15 wt.%, for example at least 0.18 wt.%, based on the weight of the lubricating oil composition. Optionally, the lubricating oil composition of all aspects of the invention has a calcium content of from 0.08 wt.% to 0.8 wt.%, preferably from 0.10 wt.% to 0.6 wt.%, for example from 0.15 wt.% to 0.5 wt.%, such as from 0.18 wt.% to 0.3 wt.%, based on the weight of the lubricating oil composition. It will be appreciated that it is particularly advantageous to utilise LSPI-reducing additives in lubricating oil compositions containing higher concentrations of calcium.

Optionally, the lubricating oil composition has a magnesium content of no more than 0.12 wt.%, such as no more than 0.6 wt.%, for example no more than 0.03 wt.%, based on the weight of the lubricating oil composition. Optionally, the lubricating oil composition is substantially free from magnesium, for example having a magnesium content of about 0.0 wt.%, based on the weight of the lubricating oil composition.

Lubricating oil compositions suitable for use as passenger car motor oils conventionally comprise a major amount of oil of lubricating viscosity and minor amounts of performance enhancing additives, including detergents. 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 have a total base number or TBN (as can be measured by ASTM D2896) of from 0 to less than

150, such as 0 to about 80 or 100. 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 have a TBN of 150 or greater, and typically will have a TBN of from 250 to 450 or more.

Optionally, the lubricating oil composition comprises a detergent, for example a calcium detergent. Optionally, the detergent is a borated calcium detergent. Examples of suitable borated calcium detergents include, but are not limited to, one or more borated calcium sulfonate detergent, one or more borated calcium salicylate detergent, or a mixture thereof. Preferably, such borated calcium detergents are overbased borated calcium detergents. Such borated calcium detergents may be prepared by any conventional method. For example, it may be that the borated calcium detergent is prepared by treating a calcium detergent with boric acid. Suitable borated calcium detergents and methods of preparing such borated calcium detergents are disclosed in US 3,480,548, US 3,679,584, US 3,829,381, US 3,909,691 and US 4,965,004. Optionally, the detergent is an overbased calcium detergent, for example having a Total Base Number (TBN) of at least 150, preferably at least 200. Preferably, the overbased calcium detergent has a TBN of from 200 to 450. It will be appreciated that the composition optionally includes one or more additional detergents, such as a detergent that is not an overbased calcium detergent having a TBN of at least 150. For example, it may be that the composition comprises a detergent package comprising the overbased calcium detergent. The detergent is preferably used in an amount providing the lubricating oil composition with a TBN of from about 4 to about 10 mg KOH/g, preferably from about 5 to about 8 mg KOH/g. Preferably, overbased detergents based on metals other than calcium are present in amounts contributing no greater than 60%, such as no greater than 50% or no greater than 40% of the TBN of the lubricating oil composition contributed by overbased detergent. Preferably, lubricating oil compositions of the present invention contain non-calcium-based overbased ash-containing detergents in amounts providing no greater than about 40% of the total TBN contributed to the lubricating oil composition by overbased detergent. Combinations of overbased calcium detergents may be used (*e.g.*, comprising two or more of an overbased calcium phenate, an overbased calcium

salicylate and an overbased calcium sulfonate; or comprising two or more calcium detergents each having a different TBN of greater than 150). Preferably, the detergent will have, or have on average, a TBN of at least about 200, such as from about 200 to about 500; preferably at least about 250, such as from about 250 to about 500; more preferably at least about 300, such as from about 300 to about 450.

Calcium detergents that may be used in all aspects of the present invention include, oil-soluble neutral and overbased sulfonates, phenates, sulfurized phenates, thiophosphonates, salicylates, and naphthenates and other oil-soluble carboxylates of calcium. It will be appreciated that suitable calcium detergents may also comprise other metals, particularly alkali or alkaline earth metals, *e.g.*, barium, sodium, potassium, lithium, calcium, and/or magnesium. The most commonly used additional metals are magnesium and sodium, either of which or both may be present in the calcium detergent and/or the borated calcium detergent. The detergent may optionally comprise combinations of detergents, whether overbased or neutral or both.

Sulfonates may be prepared from sulfonic acids which are typically obtained by the sulfonation of alkyl substituted aromatic hydrocarbons such as those obtained from the fractionation of petroleum or by the alkylation of aromatic hydrocarbons. Examples include those obtained by alkylating benzene, toluene, xylene, naphthalene, diphenyl or their halogen derivatives such as chlorobenzene, chlorotoluene and chloronaphthalene. The alkylation may be carried out in the presence of a catalyst with alkylating agents having from about 3 to more than 70 carbon atoms. The alkaryl sulfonates usually contain from about 9 to about 80 or more carbon atoms, preferably from about 16 to about 60 carbon atoms per alkyl substituted aromatic moiety.

The oil soluble sulfonates or alkaryl sulfonic acids may be neutralized with oxides, hydroxides, alkoxides, carbonates, carboxylate, sulfides, hydrosulfides, nitrates, borates and ethers of the metal. The amount of metal compound is chosen having regard to the desired TBN of the final product but typically ranges from about 100 to 220 mass % (preferably at least 125 mass %) of that stoichiometrically required.

Metal salts of phenols and sulfurized phenols are prepared by reaction with an appropriate metal compound such as an oxide or hydroxide and neutral or overbased products may be obtained by methods well known in the art. Sulfurized phenols may be prepared by reacting a phenol with sulfur or a sulfur containing compound such as

hydrogen sulfide, sulfur monohalide or sulfur dihalide, to form products which are generally mixtures of compounds in which 2 or more phenols are bridged by sulfur containing bridges.

Carboxylate detergents, *e.g.*, salicylates, can be prepared by reacting an aromatic carboxylic acid with an appropriate metal compound such as an oxide or hydroxide and neutral or overbased products may be obtained by methods well known in the art. The aromatic moiety of the aromatic carboxylic acid can contain heteroatoms, such as nitrogen and oxygen. Preferably, the moiety contains only carbon atoms; more preferably the moiety contains six or more carbon atoms; for example benzene is a preferred moiety. The aromatic carboxylic acid may contain one or more aromatic moieties, such as one or more benzene rings, either fused or connected *via* alkylene bridges. The carboxylic moiety may be attached directly or indirectly to the aromatic moiety. Preferably the carboxylic acid group is attached directly to a carbon atom on the aromatic moiety, such as a carbon atom on the benzene ring. More preferably, the aromatic moiety also contains a second functional group, such as a hydroxy group or a sulfonate group, which can be attached directly or indirectly to a carbon atom on the aromatic moiety.

Preferred examples of aromatic carboxylic acids are salicylic acids and sulfurized derivatives thereof, such as hydrocarbyl substituted salicylic acid and derivatives thereof. Processes for sulfurizing, for example a hydrocarbyl-substituted salicylic acid, are known to those skilled in the art. Salicylic acids are typically prepared by carboxylation, for example, by the Kolbe-Schmitt process, of phenoxides, and in that case, will generally be obtained, normally in a diluent, in admixture with uncarboxylated phenol.

Preferred substituents in oil-soluble salicylic acids are alkyl substituents. In alkyl-substituted salicylic acids, the alkyl groups advantageously contain 5 to 100, preferably 9 to 30, especially 14 to 20, carbon atoms. Where there is more than one alkyl group, the average number of carbon atoms in all of the alkyl groups is preferably at least 9 to ensure adequate oil solubility.

Detergents generally useful in the formulation of lubricating oil compositions of the invention 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. Patent Nos. 6,153,565; 6,281,179; 6,429,178; and 6,429,178.

Optionally, the detergent comprises a calcium phenate, a calcium sulfonate and/or a calcium salicylate. Optionally, the detergent comprises a borated calcium phenate, a borated calcium sulfonate and/or a borated calcium salicylate, preferably a borated calcium salicylate.

Optionally, the detergent comprises a plurality of calcium detergents. Optionally, each calcium detergent is independently a calcium phenate, a calcium sulfonate or a calcium salicylate. Preferably, the detergent is substantially free from any detergent that is not a calcium detergent. In other words, it may be that the detergent consists of one or more calcium detergents. It will be appreciated that where a detergent is said to be substantially free from anything other than a particular type of detergent, or is said to consist of that particular type of detergent, the detergent may nevertheless comprise trace amounts of another material. For example, it may be that the detergent comprises a trace amount of another material left over from the preparation process used to make the detergent.

Optionally, at least 75 %, for example at least 90 %, such as at least 95 %, of the calcium content of the lubricating oil composition is provided by the detergent. It may be that when the calcium content of the lubricating composition is provided principally by the detergent, the detergent and LSPI characteristics of the composition can be controlled particularly effectively.

Optionally, the composition additionally comprises a further detergent. Preferably, the further detergent is substantially free of calcium. Optionally, the further detergent comprises one or more phenate, sulfonate and/or salicylate detergents. The further detergent may be an overbased or neutral detergent. Optionally, the further detergent comprises one or more neutral metal-containing detergents (having a TBN of less than 150). These neutral metal-based detergents may be magnesium salts or salts of other alkali or alkali earth metals, except calcium. Optionally, 100 % of the metal introduced into the lubricating oil composition by detergent is calcium. The further detergent may also contain ashless (metal-free) detergents such as oil-soluble hydrocarbyl phenol aldehyde condensates described, for example, in US 2005/0277559 A1.

Preferably, detergent in total is used in an amount providing the lubricating oil composition with from 0.2 to 2.0 mass %, such as from 0.35 to 1.5 mass % or from 0.5 to 1.0 mass %, more preferably from about 0.6 to about 0.8 mass % of sulfated ash (SASH).

Optionally, the composition comprises one or more additives from the list consisting of: dispersants, corrosion inhibitors, antioxidants, pour point depressants, antifoaming agents, supplemental anti-wear agents, friction modifiers, and viscosity modifiers.

The oil of lubricating viscosity useful in the formulation of lubricating oil compositions suitable for use in the practice of the invention may range in viscosity from light distillate mineral oils to heavy lubricating oils such as gasoline engine oils, mineral lubricating oils and heavy duty diesel oils. Generally, the viscosity of the oil ranges 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 9 mm²/sec to about 17 mm²/sec, measured at 100°C.

Natural oils include animal oils and vegetable oils (*e.g.*, castor oil, lard oil); liquid petroleum oils and hydrorefined, 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.

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 derivatives, analogs and homologs thereof.

Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, *etc.*, constitute 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.

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, sebacic 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. Also useful are synthetic oils derived from a gas to liquid process from Fischer-Tropsch synthesized hydrocarbons, which are commonly referred to as gas to liquid, or "GTL" base oils.

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.

Silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy- or polyaryloxysilicone 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.

The oil of lubricating viscosity may comprise a Group I, Group II, Group III, Group IV or Group V base stocks or base oil blends of the aforementioned base stocks. Preferably, the oil of lubricating viscosity is a Group II, Group III, Group IV or Group V base stock, or a mixture thereof, or a mixture of a Group I base stock and one or more a Group II, Group III, Group IV or Group V base stock. The base stock,

or base stock blend preferably has a saturate content of at least 65%, more preferably at least 75%, such as at least 85%. Preferably, the base stock or base stock blend is a Group III or higher base stock or mixture thereof, or a mixture of a Group II base stock and a Group III or higher base stock or mixture thereof. Most preferably, the base stock, or base stock blend, has a saturate content of greater than 90 %.

Preferably, the oil or oil blend will have a sulfur content of less than 1 mass %, preferably less than 0.6 mass %, most preferably less than 0.4 mass %, such as less than 0.3 mass %. In one preferred embodiment, at least 30 mass %, preferably at least 50 mass %, more preferably at least 80 mass % of the oil of lubricating viscosity used in lubricating oil compositions of the present invention is Group III base stock, a Group IV base stock, or a mixture of Group II and Group IV base stocks .

Preferably the volatility of the oil or oil blend, as measured by the Noack test (ASTM D5800), is less than or equal to 30 mass %, such as less than about 25 mass %, preferably less than or equal to 20 mass %, more preferably less than or equal to 15 mass %, most preferably less than or equal 13 mass %. Preferably, the viscosity index (VI) of the oil or oil blend is at least 85, preferably at least 100, most preferably from about 105 to 140.

Definitions for the base stocks and base oils in the lubricating oil compositions of this invention are the same as those found in the American Petroleum Institute (API) publication "Engine Oil Licensing and Certification System", Industry Services Department, Fourteenth Edition, December 1996, Addendum 1, December 1998. Said publication categorizes base stocks as follows:

a) Group I base stocks contain less than 90 percent saturates and/or greater than 0.03 percent sulfur and have a viscosity index greater than or equal to 80 and less than 120 using the test methods specified in Table 1;

b) Group II base stocks contain greater than or equal to 90 percent saturates and less than or equal to 0.03 percent sulfur and have a viscosity index greater than or equal to 80 and less than 120 using the test methods specified in Table 1;

c) Group III base stocks contain greater than or equal to 90 percent saturates and less than or equal to 0.03 percent sulfur and have a viscosity index greater than or equal to 120 using the test methods specified in Table 1;

d) Group IV base stocks are polyalphaolefins (PAO); and,

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

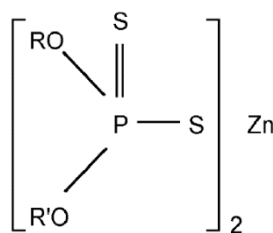
Table 1 - Analytical Methods for Base Stock

Property	Test Method
Saturates	ASTM D 2007
Viscosity Index	ASTM D 2270
Sulfur	ASTM D 2622; ASTM D 4294; ASTM D 4927; ASTM D 3120

The lubricating oil compositions of all aspects of the present invention may further comprise a phosphorus-containing compound.

A suitable phosphorus-containing compound includes dihydrocarbyl dithiophosphate metal salts, which are frequently used as anti-wear 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, preferably 0.2 to 2 mass %, 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.

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) preferably comprises zinc dialkyl dithiophosphates.

Lubricating oil compositions useful in the practice of the present invention will preferably contain a phosphorus-containing compound, in an amount introducing from 0.01 to 0.12 wt.% of phosphorus, such as from 0.04 to 0.10 wt.% of phosphorus, preferably, from 0.05 to 0.08 wt.% of phosphorus, based on the total mass of the lubricating oil composition into the lubricating oil composition. Optionally, the lubricating oil composition has a phosphorus content of no more than 0.1 wt.% (1000ppm), for example no more than 0.09 wt.% (900ppm), preferably no more than 0.08 wt.% (800ppm), based on the weight of the lubricating oil composition. In a preferred embodiment of the present invention, the lubricating oil composition has a phosphorous content of no greater than 0.06 wt.% (600 ppm).

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 C₅ to C₁₂ alkyl side chains, calcium nonylphenol sulfide, oil soluble phenates and sulfurized phenates, phosphosulfurized or sulfurized hydrocarbons or esters, phosphorous esters, metal thiocarbamates, oil

soluble copper compounds as described in U.S. Patent No. 4,867,890, and molybdenum-containing compounds.

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 sulfur atom, or a -CO-, -SO₂- or alkylene group) and two are directly attached to one amine nitrogen are 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 mass %.

Dispersants maintain in suspension materials resulting from oxidation during use that are insoluble in oil, thus preventing sludge flocculation and precipitation, or deposition on metal parts. Optionally, the lubricating oil compositions used according to the present invention comprise at least one dispersant, and may comprise a plurality of dispersants. The dispersant or dispersants are preferably nitrogen-containing dispersants and preferably contribute, in total, from 0.05 to 0.19 mass %, such as from 0.06 to 0.18 mass %, most preferably from 0.07 to 0.16 mass % of nitrogen to the lubricating oil composition.

Dispersants useful in the context of the present invention include the range of nitrogen-containing, ashless (metal-free) dispersants known to be effective to reduce formation of deposits upon use in gasoline and diesel engines, when added to lubricating oils and comprise an oil soluble polymeric long chain backbone having functional groups capable of associating with particles to be dispersed. Typically, such dispersants have amine, amine-alcohol or amide polar moieties attached to the polymer backbone, 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 poly-carboxylic acids or

anhydrides thereof; thiocarboxylate derivatives of long chain hydrocarbons; long chain aliphatic hydrocarbons having polyamine moieties attached directly thereto; and Mannich condensation products formed by condensing a long chain substituted phenol with formaldehyde and polyalkylene polyamine.

Generally, each mono- or di-carboxylic acid-producing moiety will react with a nucleophilic group (amine or amide) and the number of functional groups in the polyalkenyl-substituted carboxylic acylating agent will determine the number of nucleophilic groups in the finished dispersant.

The polyalkenyl moiety of dispersants useful in the present invention has a number average molecular weight of from 700 to 3000, preferably between 950 and 3000, such as between 950 and 2800, more preferably from about 950 to 2500, and most preferably from 950 to 2400. In one embodiment of the invention, the dispersant of the lubricating oil composition comprises a combination of a lower molecular weight dispersant (*e.g.*, having a number average molecular weight of from 700 to 1100) and a high molecular weight dispersant having a number average molecular weight of from at least 1500, preferably between 1800 and 3000, such as between 2000 and 2800, more preferably from 2100 to 2500, and most preferably from 2150 to 2400. The molecular weight of a dispersant is generally expressed in terms of the molecular weight of the polyalkenyl moiety as the precise molecular weight range of the dispersant depends on numerous parameters including the type of polymer used to derive the dispersant, the number of functional groups, and the type of nucleophilic group employed.

The polyalkenyl moiety from which the high molecular weight dispersants are derived preferably have a narrow molecular weight distribution (MWD), also referred to as polydispersity, as determined by the ratio of weight average molecular weight (M_w) to number average molecular weight (M_n). Specifically, polymers from which dispersants useful in the practice of the present invention are derived have a M_w/M_n of from 1.5 to 2.0, preferably from 1.5 to 1.9, most preferably from 1.6 to 1.8.

Suitable hydrocarbons or polymers employed in the formation of dispersants useful in the practice of the present invention include homopolymers, interpolymers or lower molecular weight hydrocarbons. One family of such polymers comprise polymers of ethylene and/or at least one C_3 to C_{28} alpha-olefin having the formula $H_2C=CHR^1$ wherein R^1 is straight or branched chain alkyl radical comprising 1 to 26

carbon atoms and wherein the polymer contains carbon-to-carbon unsaturation, preferably a high degree of terminal ethenylidene unsaturation. Preferably, such polymers comprise interpolymers of ethylene and at least one alpha-olefin of the above formula, wherein R^1 is alkyl of from 1 to 18 carbon atoms, and more preferably is alkyl of from 1 to 8 carbon atoms, and more preferably still of from 1 to 2 carbon atoms. Therefore, useful alpha-olefin monomers and comonomers include, for example, propylene, butene-1, hexene-1, octene-1, 4-methylpentene-1, decene-1, dodecene-1, tridecene-1, tetradecene-1, pentadecene-1, hexadecene-1, heptadecene-1, octadecene-1, nonadecene-1, and mixtures thereof (*e.g.*, mixtures of propylene and butene-1, and the like). Exemplary of such polymers are propylene homopolymers, butene-1 homopolymers, ethylene-propylene copolymers, ethylene-butene-1 copolymers, propylene-butene copolymers and the like, wherein the polymer contains at least some terminal and/or internal unsaturation. Preferred polymers are unsaturated copolymers of ethylene and propylene and ethylene and butene-1. The interpolymers may contain a minor amount, *e.g.* 0.5 to 5 mole % of a C_4 to C_{18} non-conjugated diolefin comonomer. However, it is preferred that the polymers used in the practice of the present invention comprise only alpha-olefin homopolymers, interpolymers of alpha-olefin comonomers and interpolymers of ethylene and alpha-olefin comonomers. The molar ethylene content of the polymers employed in this invention is preferably in the range of 0 to 80 %, and more preferably 0 to 60 %. When propylene and/or butene-1 are employed as comonomer(s) with ethylene, the ethylene content of such copolymers is most preferably between 15 and 50 %, although higher or lower ethylene contents may be present.

These polymers may be prepared by polymerizing alpha-olefin monomer, or mixtures of alpha-olefin monomers, or mixtures comprising ethylene and at least one C_3 to C_{28} alpha-olefin monomer, in the presence of a catalyst system comprising at least one metallocene (*e.g.*, a cyclopentadienyl-transition metal compound) and an alumoxane compound. Using this process, a polymer in which 95 % or more of the polymer chains possess terminal ethenylidene-type unsaturation can be provided. The percentage of polymer chains exhibiting terminal ethenylidene unsaturation may be determined by FTIR spectroscopic analysis, titration, or ^{13}C NMR. Interpolymers of this latter type may be characterized by the formula $POLY-C(R^1)=CH_2$ wherein R^1 is C_1 to C_{26} alkyl, preferably C_1 to C_{18} alkyl, more preferably C_1 to C_8 alkyl, and most

preferably C₁ to C₂ alkyl, (*e.g.*, methyl or ethyl) and wherein POLY represents the polymer chain. The chain length of the R¹ alkyl group will vary depending on the comonomer(s) selected for use in the polymerization. A minor amount of the polymer chains can contain terminal ethenyl, *i.e.*, vinyl, unsaturation, *i.e.*, POLY-CH=CH₂, and a portion of the polymers can contain internal mono-unsaturation, *e.g.*

POLY-CH=CH(R¹), wherein R¹ is as defined above. These terminally unsaturated interpolymers may be prepared by known metallocene chemistry and may also be prepared as described in U.S. Patent Nos. 5,498,809; 5,663,130; 5,705,577; 5,814,715; 6,022,929 and 6,030,930.

Another useful class of polymers is polymers prepared by cationic polymerization of isobutene, styrene, and the like. Common polymers from this class include polyisobutenes obtained by polymerization of a C₄ refinery stream having a butene content of 35 to 75 mass %, and an isobutene content of 30 to 60 mass %, in the presence of a Lewis acid catalyst, such as aluminum trichloride or boron trifluoride. A preferred source of monomer for making poly-*n*-butenes is petroleum feedstreams such as Raffinate II. These feedstocks are disclosed in the art such as in U.S. Patent No. 4,952,739. Polyisobutylene is a most preferred backbone of the polymers useful in the practice of the present invention because it is readily available by cationic polymerization from butene streams (*e.g.*, using AlCl₃ or BF₃ catalysts). Such polyisobutylenes generally contain residual unsaturation in amounts of about one ethylenic double bond per polymer chain, positioned along the chain. A preferred embodiment utilizes polyisobutylene prepared from a pure isobutylene stream or a Raffinate I stream to prepare reactive isobutylene polymers with terminal vinylidene olefins. Preferably, these polymers, referred to as highly reactive polyisobutylene (HR-PIB), have a terminal vinylidene content of at least 65%, *e.g.*, 70%, more preferably at least 80%, most preferably, at least 85%. The preparation of such polymers is described, for example, in U.S. Patent No. 4,152,499. HR-PIB is known and HR-PIB is commercially available under the tradenames Glissopal™ (from BASF).

Polyisobutylene polymers that may be employed are generally based on a hydrocarbon chain of from 700 to 3000. Methods for making polyisobutylene are known. Polyisobutylene can be functionalized by halogenation (*e.g.* chlorination), the

thermal "ene" reaction, or by free radical grafting using a catalyst (*e.g.* peroxide), as described below.

The hydrocarbon or polymer backbone can be functionalized, *e.g.*, with carboxylic acid producing moieties (preferably acid or anhydride moieties) selectively at sites of carbon-to-carbon unsaturation on the polymer or hydrocarbon chains, or randomly along chains using any of the three processes mentioned above or combinations thereof, in any sequence.

Processes for reacting polymeric hydrocarbons with unsaturated carboxylic acids, anhydrides or esters and the preparation of derivatives from such compounds are disclosed in U.S. Patent Nos. 3,087,936; 3,172,892; 3,215,707; 3,231,587; 3,272,746; 3,275,554; 3,381,022; 3,442,808; 3,565,804; 3,912,764; 4,110,349; 4,234,435; 5,777,025; 5,891,953; as well as EP 0 382 450 B1; CA-1,335,895 and GB-A-1,440,219. The polymer or hydrocarbon may be functionalized, for example, with carboxylic acid producing moieties (preferably acid or anhydride) by reacting the polymer or hydrocarbon under conditions that result in the addition of functional moieties or agents, *i.e.*, acid, anhydride, ester moieties, *etc.*, onto the polymer or hydrocarbon chains primarily at sites of carbon-to-carbon unsaturation (also referred to as ethylenic or olefinic unsaturation) using the halogen assisted functionalization (*e.g.* chlorination) process or the thermal "ene" reaction.

Selective functionalization can be accomplished by halogenating, *e.g.*, chlorinating or brominating the unsaturated α -olefin polymer to about 1 to 8 mass %, preferably 3 to 7 mass % chlorine, or bromine, based on the weight of polymer or hydrocarbon, by passing the chlorine or bromine through the polymer at a temperature of 60 to 250°C, preferably 110 to 160°C, *e.g.*, 120 to 140°C, for about 0.5 to 10, preferably 1 to 7 hours. The halogenated polymer or hydrocarbon (hereinafter backbone) is then reacted with sufficient monounsaturated reactant capable of adding the required number of functional moieties to the backbone, *e.g.*, monounsaturated carboxylic reactant, at 100 to 250°C, usually about 180°C to 235°C, for about 0.5 to 10, *e.g.*, 3 to 8 hours, such that the product obtained will contain the desired number of moles of the monounsaturated carboxylic reactant per mole of the halogenated backbones. Alternatively, the backbone and the monounsaturated carboxylic reactant are mixed and heated while adding chlorine to the hot material.

While chlorination normally helps increase the reactivity of starting olefin polymers with monounsaturated functionalizing reactant, it is not necessary with some of the polymers or hydrocarbons contemplated for use in the present invention, particularly those preferred polymers or hydrocarbons which possess a high terminal bond content and reactivity. Preferably, therefore, the backbone and the monounsaturated functionality reactant, *e.g.*, carboxylic reactant, are contacted at elevated temperature to cause an initial thermal "ene" reaction to take place. Ene reactions are known.

The hydrocarbon or polymer backbone can be functionalized by random attachment of functional moieties along the polymer chains by a variety of methods. For example, the polymer, in solution or in solid form, may be grafted with the monounsaturated carboxylic reactant, as described above, in the presence of a free-radical initiator. When performed in solution, the grafting takes place at an elevated temperature in the range of about 100 to 260°C, preferably 120 to 240°C. Preferably, free-radical initiated grafting would be accomplished in a mineral lubricating oil solution containing, *e.g.*, 1 to 50 mass %, preferably 5 to 30 mass % polymer based on the initial total oil solution.

The free-radical initiators that may be used are peroxides, hydroperoxides, and azo compounds, preferably those that have a boiling point greater than about 100°C and decompose thermally within the grafting temperature range to provide free-radicals. Representative of these free-radical initiators are azobutyronitrile, 2,5-dimethylhex-3-ene-2, 5-bis-tertiary-butyl peroxide and dicumene peroxide. The initiator, when used, typically is used in an amount of between 0.005% and 1% by weight based on the weight of the reaction mixture solution. Typically, the aforesaid monounsaturated carboxylic reactant material and free-radical initiator are used in a weight ratio range of from 1.0:1 to 30:1, preferably 3:1 to 6:1. The grafting is preferably carried out in an inert atmosphere, such as under nitrogen blanketing. The resulting grafted polymer is characterized by having carboxylic acid (or ester or anhydride) moieties randomly attached along the polymer chains: it being understood, of course, that some of the polymer chains remain un-grafted. The free radical grafting described above can be used for the other polymers and hydrocarbons useful in the practice of the present invention.

The preferred monounsaturated reactants that are used to functionalize the backbone comprise mono- and di-carboxylic acid material, *i.e.*, acid, anhydride, or acid ester material, including (i) monounsaturated C₄ to C₁₀ dicarboxylic acid wherein (a) the carboxyl groups are vicinyl, (*i.e.*, located on adjacent carbon atoms) and (b) at least one, preferably both, of said adjacent carbon atoms are part of said mono unsaturation; (ii) derivatives of (i) such as anhydrides or C₁ to C₅ alcohol derived mono- or diesters of (i); (iii) monounsaturated C₃ to C₁₀ monocarboxylic acid wherein the carbon-carbon double bond is conjugated with the carboxy group, *i.e.*, of the structure -C=C-CO-; and (iv) derivatives of (iii) such as C₁ to C₅ alcohol derived mono- or diesters of (iii). Mixtures of monounsaturated carboxylic materials (i)-(iv) also may be used. Upon reaction with the backbone, the monounsaturation of the monounsaturated carboxylic reactant becomes saturated. Thus, for example, maleic anhydride becomes backbone-substituted succinic anhydride, and acrylic acid becomes backbone-substituted propionic acid. Exemplary of such monounsaturated carboxylic reactants are fumaric acid, itaconic acid, maleic acid, maleic anhydride, chloromaleic acid, chloromaleic anhydride, acrylic acid, methacrylic acid, crotonic acid, cinnamic acid, and lower alkyl (*e.g.*, C₁ to C₄ alkyl) acid esters of the foregoing, *e.g.*, methyl maleate, ethyl fumarate, and methyl fumarate.

To provide the required functionality, the monounsaturated carboxylic reactant, preferably maleic anhydride, typically will be used in an amount ranging from equimolar amount to about 100 mass % excess, preferably 5 to 50 mass % excess, based on the moles of polymer or hydrocarbon. Unreacted excess monounsaturated carboxylic reactant can be removed from the final dispersant product by, for example, stripping, usually under vacuum, if required.

The functionalized oil-soluble polymeric hydrocarbon backbone is then derivatized with a nitrogen-containing nucleophilic reactant, such as an amine, aminoalcohol, amide, or mixture thereof, to form a corresponding derivative. Amine compounds are preferred. Useful amine compounds for derivatizing functionalized polymers comprise at least one amine and can comprise one or more additional amine or other reactive or polar groups. These amines may be hydrocarbyl amines or may be predominantly hydrocarbyl amines in which the hydrocarbyl group includes other groups, *e.g.*, hydroxy groups, alkoxy groups, amide groups, nitriles, imidazoline groups, and the like. Particularly useful amine compounds include mono- and

polyamines, *e.g.*, polyalkene and polyoxyalkylene polyamines of 2 to 60, such as 2 to 40 (*e.g.*, 3 to 20) total carbon atoms having 1 to 12, such as 3 to 12, preferably 3 to 9, most preferably from 6 to about 7 nitrogen atoms per molecule. Mixtures of amine compounds may advantageously be used, such as those prepared by reaction of alkylene dihalide with ammonia. Preferred amines are aliphatic saturated amines, including, for example, 1,2-diaminoethane; 1,3-diaminopropane; 1,4-diaminobutane; 1,6-diaminohexane; polyethylene amines such as diethylene triamine; triethylene tetramine; tetraethylene pentamine; and polypropyleneamines such as 1,2-propylene diamine; and di-(1,2-propylene)triamine. Such polyamine mixtures, known as PAM, are commercially available. Particularly preferred polyamine mixtures are mixtures derived by distilling the light ends from PAM products. The resulting mixtures, known as "heavy" PAM, or HPAM, are also commercially available. The properties and attributes of both PAM and/or HPAM are described, for example, in U.S. Patent Nos. 4,938,881; 4,927,551; 5,230,714; 5,241,003; 5,565,128; 5,756,431; 5,792,730; and 5,854,186.

Other useful amine compounds include: alicyclic diamines such as 1,4-di(aminomethyl) cyclohexane and heterocyclic nitrogen compounds such as imidazolines. Another useful class of amines is the polyamido and related amido-amines as disclosed in U.S. Patent Nos. 4,857,217; 4,956,107; 4,963,275; and 5,229,022. Also usable is tris(hydroxymethyl)amino methane (TAM) as described in U.S. Patent Nos. 4,102,798; 4,113,639; 4,116,876; and UK Patent No. 989,409. Dendrimers, star-like amines, and comb-structured amines may also be used. Similarly, one may use condensed amines, as described in U.S. Patent No. 5,053,152. The functionalized polymer is reacted with the amine compound using conventional techniques as described, for example, in U.S. Patent Nos. 4,234,435 and 5,229,022, as well as in EP-A-208,560.

A preferred dispersant composition is one comprising at least one polyalkenyl succinimide, which is the reaction product of a polyalkenyl substituted succinic anhydride (*e.g.*, PIBSA) and a polyamine (PAM) that has a coupling ratio of from 0.65 to 1.25, preferably from 0.8 to 1.1, most preferably from 0.9 to 1. In the context of this disclosure, "coupling ratio" may be defined as a ratio of the number of succinyl groups in the PIBSA to the number of primary amine groups in the polyamine reactant.

Another class of high molecular weight ashless dispersants comprises Mannich base condensation products. Generally, these products are prepared by condensing about one mole of a long chain alkyl-substituted mono- or polyhydroxy benzene with about 1 to 2.5 moles of carbonyl compound(s) (*e.g.*, formaldehyde and paraformaldehyde) and about 0.5 to 2 moles of polyalkylene polyamine, as disclosed, for example, in U.S. Patent No. 3,442,808. Such Mannich base condensation products may include a polymer product of a metallocene catalyzed polymerization as a substituent on the benzene group, or may be reacted with a compound containing such a polymer substituted on a succinic anhydride in a manner similar to that described in U.S. Patent No. 3,442,808. Examples of functionalized and/or derivatized olefin polymers synthesized using metallocene catalyst systems are described in the publications identified *supra*.

The dispersant(s) are preferably non-polymeric (*e.g.*, are mono- or bis-succinimides). The dispersant(s), particularly the lower molecular weight dispersants, may optionally be borated. Such dispersants can be borated by conventional means, as generally taught in U.S. Patent 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 0.1 to 20 atomic proportions of boron for each mole of acylated nitrogen composition.

Dispersants derived from highly reactive polyisobutylene have been found to provide lubricating oil compositions with a wear credit relative to a corresponding dispersant derived from conventional polyisobutylene. This wear credit is of particular importance in lubricants containing reduced levels of ash-containing anti-wear agents, such as ZDDP. Thus, in one preferred embodiment, at least one dispersant used in the lubricating oil compositions of the present invention is derived from highly reactive polyisobutylene.

Additional additives may be incorporated into the lubricating oil composition to enable particular performance requirements to be met. Examples of additives which may be included in the lubricating oil compositions of the present invention are metal rust inhibitors, viscosity index improvers, corrosion inhibitors, oxidation inhibitors, friction modifiers, antifoaming agents, anti-wear agents and pour point depressants. Some are discussed in further detail below.

Friction modifiers and fuel economy agents that are compatible with the other ingredients of the final oil may also be included. Examples of such materials include glyceryl monoesters of higher fatty acids, for example, glyceryl mono-oleate; esters of long chain polycarboxylic acids with diols, for example, the butane diol ester of a dimerized unsaturated fatty acid; oxazoline compounds; and alkoxyated alkyl-substituted mono-amines, diamines and alkyl ether amines, for example, ethoxylated tallow amine and ethoxylated tallow ether amine.

The viscosity index of the base stock is 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 (M_n) 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. These viscosity modifiers 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 viscosity modifiers (dispersant-viscosity modifiers). Polymer molecular weight, specifically M_n , 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).

One class of diblock copolymers useful as viscosity modifiers has been found to provide a wear credit relative to, for example, olefin copolymer viscosity modifiers. This wear credit is of particular importance in lubricants containing reduced levels of ash-containing anti-wear agents, such as ZDDP. Thus, in one preferred embodiment, at least one viscosity modifier used in the lubricating oil compositions of the present invention is a linear diblock copolymer comprising one block derived primarily, preferably predominantly, from vinyl aromatic hydrocarbon monomer, and one block derived primarily, preferably predominantly, from diene monomer. Useful vinyl aromatic hydrocarbon monomers include those containing from 8 to about 16 carbon atoms such as aryl-substituted styrenes, alkoxy-substituted styrenes, vinyl

naphthalene, alkyl-substituted vinyl naphthalenes and the like. Dienes, or diolefins, contain two double bonds, commonly located in conjugation in a 1,3 relationship. Olefins containing more than two double bonds, sometimes referred to as polyenes, are also considered within the definition of "diene" as used herein. Useful dienes include those containing from 4 to about 12 carbon atoms, preferably from 8 to about 16 carbon atoms, such as 1,3-butadiene, isoprene, piperylene, methylpentadiene, phenylbutadiene, 3,4-dimethyl-1,3-hexadiene, 4,5-diethyl-1,3-octadiene, with 1,3-butadiene and isoprene being preferred.

As used herein in connection with polymer block composition, "predominantly" means that the specified monomer or monomer type that is the principle component in that polymer block is present in an amount of at least 85 % by weight of the block.

Polymers prepared with diolefins will contain ethylenic unsaturation, and such polymers are preferably hydrogenated. When the polymer is hydrogenated, the hydrogenation may be accomplished using any of the techniques known in the prior art. For example, the hydrogenation may be accomplished such that both ethylenic and aromatic unsaturation is converted (saturated) using methods such as those taught, for example, in U.S. Pat. Nos. 3,113,986 and 3,700,633 or the hydrogenation may be accomplished selectively such that a significant portion of the ethylenic unsaturation is converted while little or no aromatic unsaturation is converted as taught, for example, in U.S. Pat. Nos. 3,634,595; 3,670,054; 3,700,633 and U.S. Re 27,145. Any of these methods can also be used to hydrogenate polymers containing only ethylenic unsaturation and which are free of aromatic unsaturation.

The block copolymers may include mixtures of linear diblock polymers as disclosed above, having different molecular weights and/or different vinyl aromatic contents as well as mixtures of linear block copolymers having different molecular weights and/or different vinyl aromatic contents. The use of two or more different polymers may be preferred to a single polymer depending on the rheological properties the product is intended to impart when used to produce formulated engine oil. Examples of commercially available styrene/hydrogenated isoprene linear diblock copolymers include Infineum SV140™, Infineum SV150™ and Infineum SV160™, available from Infineum USA L.P. and Infineum UK Ltd.; Lubrizol® 7318, available from The Lubrizol Corporation; and Septon 1001™ and Septon 1020™,

available from Septon Company of America (Kuraray Group). Suitable styrene/1, 3-butadiene hydrogenated block copolymers are sold under the tradename Glissoviscal™ by BASF.

Pour point depressants (PPD), otherwise known as lube oil flow improvers (LOFIs) lower the temperature. Compared to VM, LOFIs generally have a lower number average molecular weight. 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.

In the lubricating oil compositions of the present invention it may be necessary to include an additive which maintains the stability of the viscosity of the blend. Thus, although polar group-containing additives achieve a suitably low viscosity in the pre-blending stage it has been observed that some compositions increase in viscosity when stored for prolonged periods. 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.

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. All the values listed (with the exception of detergent values) are stated as mass percent active ingredient (A.I.). As used herein, A.I. refers to additive material that is not diluent or solvent.

ADDITIVE	MASS % (Broad)	MASS % (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 Anti-wear Agents	0 - 1.0	0 - 0.5
Friction Modifier	0 - 5	0 - 1.5
Viscosity Modifier	0.01 - 10	0.25 - 3
Base stock	Balance	Balance

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.

The final composition may employ from 5 to 25 mass %, preferably 5 to 22 mass %, typically 10 to 20 mass % of the concentrate, the remainder being oil of lubricating viscosity.

Preferably, the Noack volatility of the fully formulated lubricating oil composition (oil of lubricating viscosity plus all additives) will be no greater than 20 mass %, such as no greater than 15 mass %, preferably no greater than 13 mass %.

Lubricating oil compositions useful in the practice of the present invention may have an overall sulfated ash content of from 0.3 to 1.2 mass %, such as from 0.4 to 1.1 mass %, preferably from 0.5 to 1.0 mass %.

This invention will be further understood by reference to the following examples, wherein all parts are parts by mass, unless otherwise noted and which include preferred embodiments of the invention.

Description of the Examples

Whilst the present invention has been described and illustrated with reference to particular embodiments, it will be appreciated by those of ordinary skill in the art that the invention lends itself to many different variations not specifically illustrated herein. By way of example only, certain possible variations will now be described.

The amounts of additives provided are additive amounts including diluent oil, amounts unless otherwise indicated.

Example 1

Two SAE 0W-20 grade lubricating oil compositions representing typical European mid-SAPS passenger car motor oils were prepared. The formulation of these compositions is shown in Table 2 below.

Table 2

Constituent Type	Oil 1	Oil 2
Borated Dispersant ¹ (B, mass%)	0.0057	0.0195
Mg Salicylate Detergent ² (Mg, mass%)	0.02	0.02
Ca Salicylate Detergent ³ (Ca, mass%)	0.15	0.15
Molybdenum Compound ⁴ (Mo, mass%)	0	0.0198
Additive Package ⁵ (mass%)	8.053	8.053
SN150 Diluent (mass%)	1.82	1.9
Pour Point Depressant ⁶ (mass%)	0.3	0.3
Viscosity Modifier ⁷ (mass%)	9.5	9.5
Base Stock ⁸ (mass%)	77.5	76
SASH, mass%	0.73	0.75
P %, mass%	0.085	0.085
S %, mass%	0.2	0.2

¹ The borated dispersant was a borated polyisobutenyl succinimide dispersant available from Infineum UK Limited.

² The magnesium detergent was a magnesium salicylate detergent having a total base number of 342 available from Infineum UK Limited.

³ The calcium detergent was the same for each oil and comprised a mixture of a calcium salicylate detergent having a total base number of 225 available from Infineum UK Limited and a calcium salicylate detergent having a total base number of 64 available from Infineum UK Limited.

⁴ The molybdenum dithiocarbamate is a trimeric molybdenum dithiocarbamate available from Infineum UK Limited.

⁵ The additive package was the same for each oil and included non-borated dispersant, zinc dialkyldithiophosphate, aminic antioxidant and silicon antifoam.

⁶ The pour point depressant was Infineum V385 available from Infineum UK Ltd.

⁷ The viscosity modifier was Infineum SV603 available from Infineum UK Ltd.

⁸ The base stock comprised API Group III base oil.

Oil 1, being a comparative example, includes a typical dose of a borated dispersant, the oil composition having a boron content of 57 ppm, and no molybdenum-containing additive. Oil 2, being an example of the invention, includes a higher dose of a borated dispersant, the oil composition having a boron content of 195 ppm, and a molybdenum containing compound providing the oil composition with 198 ppm of molybdenum.

The oils were tested for LSPI event occurrence according to the GM LSPI test for approvals against Dexos™ specifications, the results being presented in Table 3. The test limit for the Dexos test for five runs is 0 0 0 2 2, meaning that a composition achieving zero LSPI events in runs 1, 2 and 3 and two or fewer LSPI events in runs 4 and 5, passes the test, whereas a composition with more than zero LSPI events in runs 1, 2 and/or 3 and/or more than two LSPI events in runs 4 and 5 fails the test.

Table 3

Run	LSPI Events Per Run	
	Oil 1	Oil 2
1	1	0
2	1	0
3	3	0
4	3	0
5	4	1

Across all five runs with each composition, Oil 2 showed a lower LSPI event frequency, passing the Dexos™ test, whereas Oil 1 failed the Dexos™ test. These

results indicate that a combined increase in both boron and molybdenum contents provides a reduction in LSPI event frequency.

Example 2

Two further SAE 0W-20 grade lubricating oil compositions representing typical European mid-SAPS passenger car motor oils with a phosphorous content of 0.09 mass% were prepared. The formulation of these compositions is shown in Table 4 below.

Table 4

Constituent Type	Amount	Oil 3	Oil 4
Borated Dispersant ⁹	B, mass%	0.0037	0.0198
Ca Salicylate Detergent ¹⁰	Ca, mass%	0.18	0.18
Molybdenum compound ¹¹	Mo, mass%	0.0027	0.0330
Additive package ¹²	mass%	8.254	8.254
APP150DIL Diluent	mass%	2.485	2.485
Pour Point Depressant ¹³	mass%	0.300	0.300
Viscosity Modifier ¹⁴	mass%	9.000	9.000
Base Stock ¹⁵	mass%	77.376	75.586

⁹ The borated dispersant was a borated polyisobutenyl succinimide dispersant available from Infineum UK Limited.

¹⁰ The calcium detergent comprised a calcium salicylate detergent having a total base number of 225 available from Infineum UK Limited.

¹¹ The molybdenum dithiocarbamate is a trimeric molybdenum dithiocarbamate available from Infineum UK Limited.

¹² The additive package was the same for each oil and included non-borated dispersant, zinc dialkyldithiophosphate, aminic antioxidant, hindered phenol antioxidant, ashless friction modifier and silicon antifoam.

¹³ The pour point depressant was Infineum V385 available from Infineum UK Ltd.

¹⁴ The viscosity modifier was Infineum SV603 available from Infineum UK Ltd.

¹⁵ The base stock comprised GTL base oil.

It can be seen from Table 4 that Oil 3 has a lower boron content and a lower molybdenum content than Oil 4 composition.

The compositions were tested for LSPI event occurrence according to the ASTM (Ford) LSPI test for applications claiming GF-6 / API SP, the results being presented in Table 6.

Table 5

Run	LSPI Events Per Run	
	Oil 3	Oil 4
1	7	4
2	17	2
3	12	4
4	10	4

Across all four runs with each composition, Oil 4 showed a significantly lower LSPI event frequency than Oil 3, indicating that a increase in both boron and molybdenum content provides a reduction in LSPI event frequency.

Example 3

Five 5W-30 grade lubricating oil representing typical European mid-SAPS passenger car motor oils were prepared. The formulation of these compositions is shown in Table 6 below.

Constituent Type	Amount	Oil 5	Oil 6	Oil 7	Oil 8	Oil 9
Borated Dispersant ¹⁶	B, mass%	0.000	0.000	0.040	0.040	0.020
Non-Borated Dispersant ¹⁷	mass%	2.75	2.75	1.30	1.30	2.00
Ca Sulfonate Detergent ¹⁸	Ca, mass%	0.151	0.151	0.151	0.151	0.151
MgSulfonate Detergent ¹⁹	Mg, mass%	0.030	0.030	0.030	0.030	0.030
Molybdenum Compound ²⁰	Mo, mass%	0.000	0.070	0.000	0.070	0.035
Additive Package ²¹	mass%	3.103	3.103	3.103	3.103	3.103
Group II Diluent	mass%	1.00	1.00	1.00	1.00	1.00
Pour Point Depressant ²²	mass%	0.30	0.30	0.30	0.30	0.30
Viscosity Modifier ²³	mass%	8.20	8.20	8.20	8.20	8.20
Base Stock ³⁴	mass%	balance	balance	balance	balance	balance
SASH	mass%	0.72	0.72	0.75	0.75	0.73
P %	mass%	0.06	0.06	0.06	0.06	0.06
S %	mass%	0.1	0.3	0.1	0.3	0.2

Table 6

- ¹⁶ The borated dispersant was a borated polyisobutenyl succinimide dispersant available from Infineum UK Limited.
- ¹⁷ The non-borated dispersant was a polyisobutylene succinimide dispersant available from Infineum UK Limited. The amount of non-borated dispersant varies in order to balance the varied amount of borated dispersant used to vary the amount of boron present in the oils.
- ¹⁸ The calcium detergent comprised a calcium sulfonate detergent having a total base number of 300 available from Infineum UK Limited.
- ¹⁹ The magnesium detergent is a magnesium sulfonate detergent having a total base number of 400 available from Infineum UK Limited.
- ²⁰ The molybdenum dithiocarbamate is a trimeric molybdenum dithiocarbamate available from Infineum UK Limited.
- ²¹ The additive package was the same for each oil and included zinc dialkyldithiophosphate, aminic antioxidant, hindered phenol antioxidant, ashless friction modifier, diluent oil and silicon antifoam.
- ²² The pour point depressant was Infineum V387 available from Infineum UK Ltd.
- ²³ The viscosity modifier was Paratone 68530 available from Chevron Oronite.
- ²⁴ The base stock comprised an API Group II base stock.

Oils 5 and 6 include no boron (in order to maintain equivalent dispersant functionality in the compositions, boron-free dispersants are included in the compositions). Oils 5 and 7 contain no molybdenum. Thus, Oil 5 contains neither boron nor molybdenum, Oil 6 contains a relatively high molybdenum dose but no boron, and Oil 7 contains a relatively high boron dose but no molybdenum. Oils 8 and 9 include boron and molybdenum. Oil 8 containing the same relatively high boron dose and a relatively high molybdenum dose as Oils 7 and 6, respectively, and Oil 9 including half the amount of boron and molybdenum.

The compositions were tested for LSPI event occurrence according to the ASTM (Ford) LSPI test for applications claiming GF-6 / API SP, the results being presented in Table 7. The tests were run in a matrix fashion in a random order, with a reference oil run every five tests.

Table 7

Average LSPI Event Occurance				
Oil 5	Oil 6	Oil 7	Oil 8	Oil 9
14	8	16	4	6

The LSPI test results set out in Table 7 are also shown in matrix format in Fig.

1. The test results indicate no reduction in LSPI frequency through substantially increasing the boron content of the composition from 0 ppm to 400 ppm in the absence of molybdenum, and a modest reduction in LSPI frequency (43% reduction) through substantially increasing molybdenum content of the composition from 0 ppm to 700 ppm in the absence of boron. In contrast, the test results show a significantly more substantial reduction in LSPI frequency (57% reduction) through only moderately increasing both the boron content and the molybdenum content from 0 ppm to 200 ppm and 350 ppm, respectively. Furthermore, the test results show an even more significant reduction in LSPI frequency (71% reduction) through substantially increasing both the boron content and the molybdenum content from 0 ppm to 400 ppm and 700 ppm, respectively. Surprisingly, the test results of Example 3 show a synergistic effect on LSPI frequency reduction resulting from the combination of both boron and molybdenum in a lubricating oil composition.

Where in the foregoing description, integers or elements are mentioned which have known, obvious or foreseeable equivalents, then such equivalents are herein incorporated as if individually set forth. Reference should be made to the claims for determining the true scope of the present invention, which should be construed so as to encompass any such equivalents. It will also be appreciated by the reader that integers or features of the invention that are described as preferable, advantageous, convenient or the like are optional and do not limit the scope of the independent claims. Moreover, it is to be understood that such optional integers or features, whilst of possible benefit in some embodiments of the invention, may not be desirable, and may therefore be absent, in other embodiments.

CLAIMS

1. A method of reducing low-speed pre-ignition (LSPI) events in a direct-injection spark-ignition internal combustion engine comprising lubricating the crankcase of the engine with a lubricating oil composition, the lubricating oil composition comprising:

a calcium detergent providing the lubricating oil composition with a calcium content of from 0.18 to 0.5 wt.%, based on the weight of the lubricating oil composition,

a boron-containing additive, and

a molybdenum-containing additive,

said lubricating oil composition having:

a molybdenum content of 150 ppm to 1500 ppm by weight, based on the weight of the lubricating oil composition,

a boron content of 150 ppm to 1500 ppm by weight, based on the weight of the lubricating oil composition; a magnesium content of no more than 0.03 wt.%, based on the weight of the lubricating oil composition,

a phosphorus content of 0.01 to 0.12 wt.%, based on the weight of the lubricating oil composition, and

a sulfated ash content of from 0.2 to 2.0 mass%, based on the weight of the lubricating oil composition.

2. The method according to claim 1, wherein, in operation, the engine generates a brake mean effective pressure level of greater than 1,500 kPa, optionally greater than 2,000 kPa, at engine speeds of from 1,000 to 2,500 rotations per minute (rpm), optionally from 1,000 to 2,000 rpm.

3. The method according to claim 1 or claim 2, wherein the lubricating oil composition has a molybdenum content of from 300 to 1500 ppm, such as from 350 to 1000 ppm, by weight, based on the weight of the lubricating oil composition.

4. The method according to claim 1, 2 or 3, wherein the lubricating oil composition has a boron content of from 200 to 1000 ppm, by weight, based on the weight of the lubricating oil composition.

5. The method according to any one of the preceding claims, wherein the lubricating oil composition comprises a calcium detergent providing the lubricating oil composition with a calcium content of from 0.18 to 0.4 wt.%, based on the weight of the lubricating oil composition.

6. The method according to any one of the preceding claims, wherein the lubricating oil composition has a magnesium content of 0.0 wt.%, based on the weight of the lubricating oil composition.

7. The method according to any preceding claim,

wherein the boron-containing additive is one or more of:

a borated dispersant, a borated dispersant viscosity index improver,

an alkali metal or an alkaline earth metal borate,

a borated overbased metal detergent,

a borated epoxide,

a borate ester,

a sulfurised borate ester, or

a borate amide;

optionally wherein the boron-containing additive is one or more of a borated dispersant, a borate ester or a borated overbased metal detergent.

8. The method according to any preceding claim,

wherein the molybdenum-containing additive is an oil-soluble or oil-dispersible organo-molybdenum compound,

optionally wherein the molybdenum-containing additive is one or more of a molybdenum dithiocarbamate, a molybdenum dithiophosphate, a molybdenum dithiophosphinate, a molybdenum xanthate, a molybdenum thioxanthate, or a molybdenum sulfide.