

5 **METHOD FOR PREVENTING OR REDUCING LOW SPEED PRE-IGNITION IN
DIRECT INJECTED SPARK-IGNITED ENGINES WITH MOLYBDENUM-
CONTAINING LUBRICANT COMPOSITIONS**

RELATED APPLICATIONS

The present application claims the benefit of U.S. Provisional Patent Application No.
10 63/378,599 filed October 6, 2022, the entire content of which is incorporated herein by
reference.

FIELD OF THE INVENTION

This disclosure relates to a lubricant composition for a direct injected, boosted, spark-ignited
internal combustion engine that contains molybdenum-containing compounds and calcium
15 detergents. This disclosure also relates to a method for preventing or reducing low speed pre-
ignition in an engine lubricated with a formulated oil.

BACKGROUND OF THE INVENTION

Modern engine designs are being developed to improve fuel economy without sacrificing
performance or durability. Historically, gasoline was port-fuel injected (PFI), that is, injected
20 through the air intake and entering the combustion chamber via the air intake valve. Gasoline
direct injection (GDI) involves direct injection of gasoline into the combustion chamber.

In certain situations, the internal combustion engine may exhibit abnormal combustion.
Abnormal combustion in a spark-initiated internal combustion engine may be understood as an
uncontrolled explosion occurring in the combustion chamber as a result of ignition of
25 combustible elements therein by a source other than the igniter.

Pre-ignition may be understood as an abnormal form of combustion resulting from the ignition
of the air-fuel mixture prior to ignition by the igniter. Anytime the air-fuel mixture in the
combustion chamber is ignited prior to ignition by the igniter, such may be understood as pre-
ignition.

30 Without being bound to a particular theory, traditionally, pre-ignition has occurred during high-
speed operation of an engine when a particular point within the combustion chamber of a

- 5 cylinder may become hot enough during high-speed operation of the engine to effectively function as a glow plug (e.g., overheated spark plug tip, overheated burr of metal) to provide a source of ignition which causes the air-fuel mixture to ignite before ignition by the igniter. Such pre-ignition may be more commonly referred to as hot-spot pre-ignition and may be inhibited by simply locating the hot-spot and eliminating it.
- 10 More recently, vehicle manufacturers have observed intermittent abnormal combustion in their production of turbocharged gasoline engines, particularly at low speeds and medium-to-high loads. More particularly, when operating the engine at speeds less than or equal to 3000 rpm and under a load with a break mean effective pressure (BMEP) of greater than or equal to 10 bars, a condition which may be referred to as low-speed pre-ignition (LSPI) may occur in a
- 15 random and stochastic fashion. Moreover, the propensity at which LSPI occurs has been linked to engine oil formulation, with an increasing number of LSPI events as the engine oil ages.

Although some engine knocking and pre-ignition problems can be and are being resolved through the use of new engine technology, such as electronic controls and knock sensors, and through the optimization of engine operating conditions, there is a role for lubricant

20 compositions which can decrease or prevent the problem.

The presently disclosed engine oil lubricant is suitable for reducing, inhibiting, or even eliminating LSPI events in direct injection engines by operating the engines with a lubricant that contains a molybdenum compound. Typical engine oil designed to reduce LSPI events perform well at the beginning of its use but its performance falls off drastically over time. By

25 distinct contrast, the disclosed engine oil lubricant is particularly suitable for maintaining LSPI reducing capacity during its normal use life.

SUMMARY OF THE INVENTION

In one aspect, the present disclosure provides a method for reducing or preventing low speed pre-ignition (LSPI) in a direct-injected, boosted, spark-ignited, internal combustion engine,

30 said method comprising the step of lubricating the engine with a used or aged lubricant composition comprising:

- (i) one or more oils of lubricating viscosity;

- 5 (ii) one or more molybdenum-containing compounds, in an amount providing the lubricant composition with at least about 100 ppm of molybdenum, based upon the total weight of the composition; and
- (iii) one or more calcium detergents, in an amount providing the lubricant composition with at least about 1000 ppm of calcium, based upon the total weight of the composition;
- 10 wherein the used or aged lubricant composition lubricates the engine in the course of at least one oil change interval.

For example, the molybdenum-containing compounds are oil soluble or oil dispersible molybdenum compounds including molybdenum-amine complexes, molybdenum dithiocarbamates, molybdenum dithiophosphates, and the like, and combinations thereof.

- 15 In certain embodiments, the one or more molybdenum-containing compounds, are in an amount providing the lubricant composition with at least about 850 ppm of molybdenum, based upon the total weight of the composition; and the one or more calcium detergents are in an amount providing the lubricant composition with at least about 1800 ppm of calcium, based upon the total weight of the composition.
- 20 In other embodiments, the one or more molybdenum-containing compounds are in an amount providing the lubricant composition with about 100 ppm to about 850 ppm of molybdenum, based upon the total weight of the composition; and the one or more calcium detergents are in an amount providing the lubricant composition with about 1000 to about 1450 ppm of calcium, based upon the total weight of the composition.

25 **DETAILED DESCRIPTION OF THE INVENTION**

Definitions

- To define more clearly the terms used herein, the following definitions are provided. Unless otherwise indicated, the following definitions are applicable to this disclosure. If a term is used in this disclosure but is not specifically defined herein, the definition from the IUPAC
- 30 Compendium of Chemical Terminology can be applied, as long as that definition does not conflict with any other disclosure or definition applied herein or render indefinite or non-

- 5 enabled any claim to which that definition is applied. To the extent that any definition or usage provided by any document incorporated herein by reference conflicts with the definition or usage provided herein, the definition or usage provided herein controls.

While compositions and methods are described in terms of “comprising” various components or steps, the compositions and methods can also “consist essentially of” or “consist of” the
10 various components or steps, unless stated otherwise.

The terms “a,” “an,” and “the” are intended to include plural alternatives, e.g., at least one. The terms “including,” “with,” and “having,” as used herein, are defined as comprising (i.e., open language), unless specified otherwise.

Various numerical ranges are disclosed herein. When Applicant discloses or claims a range of
15 any type, Applicant's intent is to disclose or claim individually each possible number that such a range could reasonably encompass, including end points of the range as well as any sub-ranges and combinations of sub-ranges encompassed therein, unless otherwise specified. For example, all numerical end points of ranges disclosed herein are approximate, unless excluded by proviso.

- 20 A “major amount” means in excess of 50 wt. % of a composition.

A “minor amount” means less than 50 wt. % of a composition.

As used in connection with metallic detergents, the term “overbased” is used to designate metal salts in which the metal is present in stoichiometrically larger amounts than the organic radical.

As referred to herein, the term “ppm” means parts per million by weight, based on the total
25 weight of the lubricant composition.

The “metal content” of the lubricant composition or the detergent component, for example magnesium content, calcium content or total metal content (i.e., the sum of all individual metal contents), is measured by ASTM D4951.

The term “used” or “aged” with respect to a lubricant composition means that the lubricant is
30 not fresh. Used or aged lubricant composition will generally have oxidation, nitration,

5 neutralization, fuel dilution, soot, and/or wear levels that correspond to the aging of this composition under the actual conditions of use. In certain embodiments, the used lubricant composition is used in the course of at least one oil change interval or over a distance travelled by the vehicle of at least about 3000 miles, 4000 miles, 5000 miles, 6000 miles, 7000 miles, or 8000 miles. In certain embodiments, the used lubricant composition is used over a distance
10 travelled by the vehicle of about 3000 to about 20,000 miles, about 4000 to about 20,000 miles, about 5000 to about 20,000 miles, about 6000 to about 20,000 miles, about 7000 to about 20,000 miles, about 8000 to about 20,000 miles, about 3000 to about 15,000 miles, about 4000 to about 15,000 miles, about 5000 to about 15,000 miles, about 6000 to about 15,000 miles, about 7000 to about 15,000 miles, about 8000 to about 15,000 miles, about 3000 to about
15 10,000 miles, about 4000 to about 10,000 miles, about 5000 to about 10,000 miles, about 6000 to about 10,000 miles, about 7000 to about 10,000 miles, or about 8000 to about 10,000 miles.

In some embodiments, the used or agent lubricant composition has been used or aged for at least 1,000 miles such as for at least 2,000 miles, at least 3,000 miles, at least 4,000 miles, at least 5,000 miles, at least 6,000 miles, at least 7,000 miles, at least 8,000 miles, at least 9,000
20 miles, or at least 10,000.

In certain embodiments, the used or aged properties of a lubricant composition may be simulated for testing purposes, *i.e.*, a lubricant composition may be artificially aged by simulating the conditions of use in an engine. For example, an artificially aged lubricant composition for testing may be produced by iron-catalyzed oxidation at a temperature in the
25 range of about 150°C to 170°C for a period of about 110 to 150 hours, according the GFC Lu-43A-11 method. In certain embodiments, the used or aged properties of a lubricant composition may be simulated, for example as described in Example 6, to provide a lubricant composition comparable to a lubricant composition used over a desired distance travelled, for example 5000 miles, under normal driving conditions.

30 The term “boosting” is used throughout the specification. Boosting refers to running an engine at higher intake pressures than in naturally aspirated engines. A boosted condition can be reached by use of a turbocharger (driven by exhaust) or a supercharger (driven by the engine). Using smaller engines that provide higher power densities has allowed engine manufacturers to provide excellent performance while reducing frictional and pumping losses. This is

5 accomplished by increasing boost pressures with the use of turbochargers or mechanical
superchargers, and by down-speeding the engine by using higher transmission gear ratios
allowed by higher torque generation at lower engine speeds. However, higher torque at lower
engine speeds has been found to cause LSPI events, resulting in extremely high cylinder peak
pressures, which can lead to catastrophic engine failure. The possibility of LSPI prevents
10 engine manufacturers from fully optimizing engine torque at lower engine speed in such
smaller, high-output engines.

The terms “oil soluble” or “oil dispersible” means that an amount needed to provide the desired
level of activity or performance can be incorporated by being dissolved, dispersed or suspended
in an oil of lubricating viscosity. Usually, this means that at least about 0.001% by weight of
15 the material can be incorporated in a lubricant composition. For a further discussion of the
terms oil soluble and dispersible, particularly “stably dispersible”, see U.S. Pat. No. 4,320,019
which is expressly incorporated herein by reference for relevant teachings in this regard.

The term “sulfated ash” as used herein refers to the non-combustible residue resulting from
detergents and metallic additives in lubricant. Sulfated ash may be determined using ASTM
20 Test D874.

The term “Total Base Number” or “TBN” as used herein refers to the amount of base equivalent
to milligrams of KOH in one gram of sample. Thus, higher TBN numbers reflect more alkaline
products, and therefore a greater alkalinity. TBN was determined using ASTM D 2896 test.

Unless otherwise specified, all percentages are in weight percent.

25 The term “alkyl”, as used herein, unless otherwise specified, includes a saturated straight,
branched, cyclic, primary, secondary, or tertiary hydrocarbon of C₁ to C₂₄. The term includes
both substituted and unsubstituted alkyl groups. Moieties with which the alkyl group can be
substituted are selected from the group consisting of hydroxyl, halo (F, Cl, Br, I), amino,
alkylamino, arylamino, alkoxy, aryloxy, nitro, cyano, sulfonic acid, sulfate, phosphonic acid,
30 phosphate, or phosphonate, either unprotected, or protected as necessary, as known to those
skilled in the art, for example, as taught in Greene, et al., Protective Groups in Organic
Synthesis, John Wiley and Sons, Second Edition, 1991, hereby incorporated by reference.
When the alkyl group is said to be substituted with an alkyl group, this is used interchangeably

5 with "branched alkyl group". Specific examples of alkyls and/or substituted alkyls includes, but are not limited to, methyl, ethyl, propyl, isopropyl, n-butyl, iso-butyl, tert-butyl, n-pentyl, iso-pentyl, neopentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, isotridecyl, tetradecyl, hexadecyl, stearyl, icosyl, docosyl, tetracosyl, triacontyl, 2-ethylhexyl, 2-butyloctyl, 2-butyldecyl, 2-hexyloctyl, 2-hexyldecyl, 2-octyldecyl, 2-hexyldodecyl, 2-octyldodecyl, 2-decyltetradecyl, 2-dodecylhexadecyl, 2-hexadecyloctadecyl, 2-tetradecyloctadecyl, myristyl, 10 palmityl and stearyl.

The term "cycloalkyl" or "cyclic alkyl" refers to a species of alkyl containing from 3 to 15 carbon atoms including one or more rings, without alternating or resonating double bonds between carbon atoms. The term includes both substituted and unsubstituted cycloalkyl groups.

15 Moieties with which the cycloalkyl group can be substituted are selected from the group consisting of hydroxyl, halo (F, Cl, Br, I), amino, alkylamino, arylamino, alkoxy, aryloxy, nitro, cyano, sulfonic acid, sulfate, phosphonic acid, phosphate, or phosphonate, either unprotected, or protected as necessary, as known to those skilled in the art, for example, as taught in Greene, et al., *Protective Groups in Organic Synthesis*, John Wiley and Sons, Second

20 Edition, 1991, hereby incorporated by reference. For example, cycloalkyls include but are not limited to cyclopropyl, cyclobutyl, cyclopentyl, and cyclohexyl. In certain embodiments, the cycloalkyl contains from 1 to 4 rings, which can be fused. In certain embodiments, the cycloalkyl group may contain one or more double bonds or triple bonds in one or more rings.

The term "alkenyl" includes a hydrocarbon radical straight, branched or cyclic containing from

25 2 to 10 carbon atoms and at least one carbon to carbon double bond. Examples of alkenyl groups include ethenyl, propenyl, butenyl and cyclohexenyl.

Although any processes and materials similar or equivalent to those described herein can be used in the practice or testing of the invention, the typical processes and materials are herein described.

30 All publications and patents mentioned herein are incorporated herein by reference for the purpose of describing and disclosing, for example, the constructs and methodologies that are described in the publications, which might be used in connection with the presently described invention. The publications discussed throughout the text are provided solely for their disclosure prior to the filing date of the present application. Nothing herein is to be construed

- 5 as an admission that the inventors are not entitled to antedate such disclosure by virtue of prior invention.

Lubricant Compositions and Methods

The present disclosure generally relates to methods for reducing or preventing low speed pre-ignition (LSPI) in a direct-injected, boosted, spark-ignited, internal combustion engine in or
10 during the course of an oil change interval. In another aspect, the present disclosure provides methods for maintain low speed pre-ignition reduction capacity of a used or aged lubricant composition in a direct-injected, boosted, spark-ignited, internal combustion engine. The lubricant compositions for use in the methods according to the invention comprise: (i) one or more oils of lubricating viscosity; (ii) one or more molybdenum-containing compounds, and
15 (iii) one or more calcium detergents. The exemplary lubricant compositions are suitable for reducing, preventing, inhibiting or eliminating LSPI events in direct-injected, boosted, spark-ignited, internal combustion engines with used or aged lubricant compositions.

Lubricant compositions, which provide a reduction in LSPI when they are fresh or newly applied to the crankcase of the engine, can suffer degradation of such properties after use or
20 aging. Preignition can be exacerbated by used or aged lubricant compositions. The Applicants have discovered that the lubricant compositions according to the embodiments retain their LSPI reduction capacity through use or aging, i.e., over the long term. Through the methods according to the invention, the exemplary lubricant compositions can be used to prevent or reduce LSPI in direct-injected, boosted, spark-ignited, internal combustion engines in a
25 prolonged manner in the course of its use without substantial loss of performance. Use of the lubricant compositions according to the invention in place of comparative lubricant compositions, can reduce the need to change the lubricant composition in the engine for the purpose of reducing LSPI.

Low Speed Pre-Ignition is most likely to occur in direct-injected, boosted (turbocharged or
30 supercharged), spark-ignited (gasoline) internal combustion engines that, in operation, generate a brake mean effective pressure (BMEP) level of at least about 15 bar (peak torque), at least about 18 bar, or at least about 20 bar, at engine speeds of from about 1500 to about 2500 rotations per minute (rpm), or from about 1500 to about 2000 rpm. As used herein, “brake mean effective pressure” or “BMEP” is defined as the work accomplished during one engine

5 cycle, divided by the engine swept volume; the engine torque normalized by engine displacement. The word "brake" denotes the actual torque/power available at the engine flywheel, as measured on a dynamometer. Thus, BMEP is a measure of the useful power output of the engine.

In certain embodiments, the engine is operated at speeds between about 500 rpm and about 10 3000 rpm, about 800 rpm to about 2800 rpm, or about 1000 rpm to about 2600 rpm. Additionally, the engine may be operated with a brake mean effective pressure of about 10 bars to about 30 bars, about or about 12 bars to about 30 bars or about 12 bars to about 24 bars.

LSPI events, while comparatively uncommon, may be catastrophic in nature. Hence drastic reduction or even elimination of LSPI events during normal or sustained operation of a direct 15 fuel injection engine is desirable.

In one embodiment, the method of the invention provides a reduction in the number of LSPI events of at least 10 percent, at least 20 percent, at least 30 percent, at least 50 percent, at least 60 percent, at least 70 percent, at least 80 percent, at least 90 percent, or at least 95 percent, compared to an oil or lubricant composition that does not contain the one or more molybdenum 20 compounds and one or more calcium detergents according to the embodiments.

Therefore, in an aspect, the present disclosure provides a method for reducing or preventing LSPI in a direct-injected, boosted, spark-ignited, internal combustion engine, said method comprising the step of lubricating the engine with a used or aged lubricant composition comprising:

- 25 (i) one or more oils of lubricating viscosity;
- (ii) one or more molybdenum-containing compounds, in an amount providing the lubricant composition with at least about 100 ppm of molybdenum, based upon the total weight of the composition; and
- (iii) one or more calcium detergents, in an amount providing the lubricant composition with 30 at least about 1000 ppm of calcium, based upon the total weight of the composition;

- 5 wherein the used or aged lubricant composition lubricates the engine in the course of at least one oil change interval.

In one embodiment, the (ii) one or more molybdenum-containing compounds, are in an amount providing the lubricant composition with at least about 850 ppm of molybdenum, based upon the total weight of the composition; and the (iii) one or more calcium detergents are in an
10 amount providing the lubricant composition with at least about 1800 ppm of calcium, based upon the total weight of the composition.

In another embodiment, wherein the (ii) one or more molybdenum-containing compounds are in an amount providing the lubricant composition with about 100 ppm to about 850 ppm of molybdenum, based upon the total weight of the composition; and the (iii) one or more calcium
15 detergents are in an amount providing the lubricant composition with about 1000 to about 1450 ppm of calcium, based upon the total weight of the composition.

In certain embodiments, the (iii) one or more calcium detergents are in an amount providing the lubricant composition with less than about 3500 ppm, less than about 3000 ppm, less than about 2500 ppm, less than about 2400 ppm, less than about 2300 ppm, less than about 2200
20 ppm, less than about 2100 ppm, less than about 2000 ppm, less than about 1900 ppm, less than about 1800 ppm, less than about 1700 ppm, less than about 1600 ppm, less than about 1500 ppm, or less than about 1450 ppm of calcium, based upon the total weight of the composition.

In certain embodiments, the direct-injected, boosted, spark-ignited, internal combustion engine is a downsized engine or an engine that ranges in size from about 0.5 liters to about 3.6 liters.

- 25 In certain embodiments, the engine is a downsized turbocharged engine.

Certain embodiments provide methods for maintaining LSPI reduction capacity of a used or aged lubricant composition in a direct-injected, boosted, spark-ignited internal combustion engine, wherein the method comprises the step of lubricating the engine with the lubricant composition described herein.

- 30 In one embodiment, the disclosure provides a lubricating engine oil composition comprising a lubricant base stock (often referred to as “base oil”) as a major component and LSPI additives

5 as disclosed herein (e.g., the one or more molybdenum compounds and one or more calcium
detergents) as minor components; and wherein the engine exhibits greater than 50% reduced
LSPI, based on normalized LSPI counts per 100,000 engine cycles, engine operation at
between 500 and 3,000 revolutions per minute and BMEP between 10 and 30 bar, as compared
to LSPI performance achieved in an engine using a lubricant that does not comprise the LSPI
10 additives, wherein the LSPI additives include the one or more molybdenum containing
compounds and the one or more calcium detergents according to the embodiments disclosed
herein.

In one aspect, the disclosure provides a lubricating engine oil composition for use in a down-
sized boosted engine comprising a lubricant base stock as a major component and LSPI
15 additives as disclosed herein, as minor components; where the downsized engine ranges from
about 0.5 to about 3.6 liters, from about 0.5 to about 3.0 liters, from about 0.8 to about 3.0
liters, from about 0.5 to about 2.0 liters, or from about 1.0 to about 2.0 liters. The engine can
have two, three, four, five or six cylinders.

In an aspect, the present disclosure provides the use of a lubricant composition as disclosed
20 herein for preventing or reducing LSPI in a direct injected, boosted, spark ignited internal
combustion engine, particularly in aged or used lubricating engine oil compositions.

The methods disclosed herein can be used to prevent or reduce LSPI events in a direct injected,
boosted, spark ignited internal combustion engine, particularly in aged or used lubricating oil
compositions.

25 LSPI events are determined by monitoring peak cylinder pressure (PP) and mass fraction burn
(MFB) of the fuel charge in the cylinder. PP is typically reported in bars while MFB is typically
reported in crank angle degrees. When either or both criteria are met (i.e., meeting and/or
exceeding PP and/or MFB thresholds), it can be said that an LSPI event has occurred. The
threshold for peak cylinder pressure varies by test, but is typically 4-5 standard deviations
30 above the average cylinder pressure. Likewise, the MFB threshold is typically 4-5 standard
deviations earlier than the average MFB. LSPI events can be reported as average events per
test, events per 100,000 combustion cycles, events per cycle, and/or combustion cycles per
event. In one embodiment, the number of LSPI events is the number of combustion events
wherein MFB02 (MFB at 2%) exceeds ~4.7 standard deviations and Peak Pressure (PP)

5 exceeds 90 bar of pressure, such as 95 bar of pressure, 100 bar of pressure, 105 bar of pressure, 110 bar of pressure, 115 bar of pressure, 120 bar of pressure and so forth. In some embodiments, the number of LSPI events is less than 5 events, less than 4 events, less than 3 events, less than 2 events, or less than 1 event. In one embodiment, the number of LSPI events is zero events, or the LSPI events were completely suppressed.

10 It has now been found that the occurrence of LSPI in engines susceptible to the occurrence of LSPI can be reduced by lubricating such engines with the lubricant compositions disclosed herein, and more particularly, that such reduction in LSPI events is sustained as the lubricant compositions ages.

The disclosure further provides the method described herein in which the engine is fueled with
15 a liquid hydrocarbon fuel, a liquid nonhydrocarbon fuel, or mixtures thereof.

The disclosure further provides the method described herein in which the engine is fueled by natural gas, liquefied petroleum gas (LPG), compressed natural gas (CNG), or mixtures thereof.

Lubricant compositions of the present invention comprise: (i) one or more oils of lubricating
20 viscosity; (ii) one or more molybdenum-containing compounds, in an amount providing the lubricant composition with at least about 100 ppm of molybdenum, based upon the total weight of the composition; and (iii) one or more calcium detergents, in an amount providing the lubricant composition with at least about 1000 ppm of calcium, based upon the total weight of the composition.

25 Generally, the lubricant compositions are for use with lubricating engine oil compositions. The one or more oils of lubricating viscosity comprise the major component of the lubricant compositions.

Molybdenum Compounds

The lubricant compositions according to the embodiments comprise one or more molybdenum-
30 containing compounds. The molybdenum-containing compound can be any oil soluble or oil-

- 5 dispersible molybdenum-containing compound. The molybdenum compound may be mono-, di-, tri- or tetra-nuclear.

Examples of oil soluble or oil dispersible organo-molybdenum compounds include molybdenum-amine complexes, molybdenum dithiocarbamates, molybdenum dithiophosphates, molybdenum dithiophosphinates, molybdenum xanthates, molybdenum
10 thioxanthates, molybdenum carboxylates, molybdenum alkoxides, organo-molybdenum complexes, dispersed hydrated molybdenum compounds, and the like, and combinations thereof.

In one embodiment, the one or more molybdenum-containing compounds comprise or consists of molybdenum-amine complexes, molybdenum dithiocarbamates, and molybdenum
15 dithiophosphates. In one embodiment, the one or more molybdenum-containing compounds comprise or consists of molybdenum-amine complexes and molybdenum dithiophosphates.

In one embodiment, molybdenum-containing compound is a sulfurized oxymolybdenum dithiocarbamate, sulfurized oxymolybdenum dithiophosphate, amine-molybdenum complex compound, oxymolybdenum diethylate amide, and oxymolybdenum monoglyceride.

- 20 In one embodiment, the one or more molybdenum-containing compounds comprises molybdenum-amine complexes. In one embodiment, the molybdenum-amine complex is a molybdenum succinimide complex. In one embodiment, the one or more molybdenum-containing compounds comprises an oxymolybdenum complex of succinimide, particularly a sulfur-containing oxymolybdenum complex of succinimide.

- 25 Molybdenum-amine complexes may be generally characterized as containing a molybdenum or molybdenum/sulfur complex of a basic nitrogen compound. The molybdenum compounds used to prepare the molybdenum-amine complexes are acidic molybdenum compounds (e.g., molybdic acid, ammonium molybdate, sodium molybdate, potassium molybdate and other alkali metal molybdates and other molybdenum salts such as MoOCl_4 , MoO_2Br_2 , $\text{Mo}_2\text{O}_3\text{Cl}_6$,
30 molybdenum trioxide or similar acidic molybdenum compounds). The basic nitrogen compound must have a basic nitrogen content as measured by ASTM D-664 or D-2896. Typical of such compositions are succinimides, carboxylic acid amides, hydrocarbyl monoamines, hydrocarbon polyamines, Mannich bases, phosphonamides,

5 (thio)phosphonamides, and combinations thereof. Examples of succinimides include succinimides having an alkyl or alkenyl group of 8 or more carbon atoms (e.g., 8 to 400 carbon atoms). In certain embodiments, the succinimide has alkyl or alkenyl groups of 8 to 30, 12 to 30, or 8 to 18, carbon atoms.

10 The molybdenum/nitrogen-containing complexes employed herein are well known in the art and are complexes of molybdic acid and an oil-soluble basic nitrogen-containing compound. Generally, the molybdenum/nitrogen-containing complex can be made with an organic solvent comprising a polar promoter during a complexation step and procedures for preparing such complexes are described, for example, in U.S. Pat. Nos. 4,259,194; 4,259,195; 4,261,843; 4,263,152; 4,265,773; 4,283,295; 4,285,822; 4,369,119; 4,370,246; 4,394,279; 4,402,840; 15 6,962,896; 8,022,022; 8,022,023; 8,076,275; 8,183,189; 8,193,131; 8,193,132; 8,426,608; 8,476,460; and 8,980,806; and U.S. Patent Application Publication Nos. 2013/0261313; 2014/0179573; and 2014/0018269. As shown in these references, the molybdenum/nitrogen-containing complex can further be sulfurized.

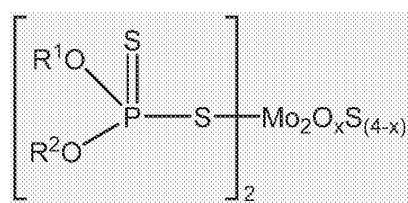
20 The mono and polysuccinimides that can be used to prepare the molybdenum-amine complexes described herein are disclosed in numerous references and are well known in the art. Certain fundamental types of succinimides and the related materials encompassed by the term of art "succinimide" are taught in U.S. Pat. No's. 3,219,666; 3,172,892; and 3,272,746, the disclosures of which are hereby incorporated by reference. The term "succinimide" is understood in the art to include many of the amide, imide, and amidine species which may also 25 be formed. The predominant product however is a succinimide and this term has been generally accepted as meaning the product of a reaction of an alkenyl substituted succinic acid or anhydride with a nitrogen-containing compound. Preferred succinimides, because of their commercial availability, are those succinimides prepared from a hydrocarbyl succinic anhydride, wherein the hydrocarbyl group contains from about 24 to about 350 carbon atoms, 30 and an ethylene amine, said ethylene amines being especially characterized by ethylene diamine, diethylene triamine, triethylene tetramine, and tetraethylene pentamine. Particularly preferred are those succinimides prepared from polyisobutenyl succinic anhydride of 70 to 128 carbon atoms and tetraethylene pentamine or triethylene tetramine or mixtures thereof. Also included within the term "succinimide" are the co-oligomers of a hydrocarbyl succinic acid or 35 anhydride and a poly secondary amine containing at least one tertiary amino nitrogen in

- 5 addition to two or more secondary amino groups. Ordinarily this composition has between 1,500 and 50,000 average molecular weight. A typical compound would be that prepared by reacting polyisobutenyl succinic anhydride and ethylene dipiperazine.

Succinimides having an average molecular weight of 1000 or 1300 or 2300 and mixtures thereof are most preferred.

- 10 In one embodiment, the one or more molybdenum-containing compounds comprises molybdenum dithiophosphates (e.g., molybdenum dialkyldithiophosphates).

One class of molybdenum dithiophosphates useful herein is represented by the following Formula (1):



- 15 Formula (1)

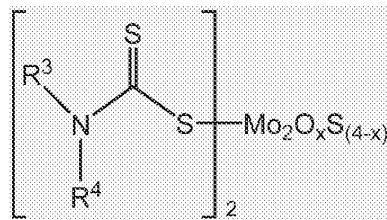
- wherein R^1 and R^2 are independently selected from $\text{C}_4\text{-C}_{30}$ alkyl groups and x is an integer from 0 to 4. Each R^1 and R^2 can be the same or different. Examples of commercially available molybdenum dialkyldithiophosphates include MOLYVAN® L (molybdenum di-(2-ethylhexyl) phosphorodithioate) available from R.T. Vanderbilt Company or the Sakara-lube 300® or Sakura-lube 310G® products available from Adeka.
- 20

In certain embodiments, R^1 and R^2 are independently selected from $\text{C}_4\text{-C}_{24}$ alkyl groups. In certain embodiments, R^1 and R^2 are independently selected from $\text{C}_6\text{-C}_{18}$ alkyl groups.

In certain embodiments, x is 0. In certain embodiments, x is 1. In certain embodiments, x is 2. In certain embodiments, x is 3. In certain embodiments, x is 4.

- 25 In one embodiment, the one or more molybdenum-containing compounds comprises molybdenum dithiocarbamates (e.g., molybdenum dialkyldithiocarbamates).

- 5 One class of molybdenum dithiocarbamates (e.g., dimeric molybdenum dithiocarbamates) useful herein is represented by the following Formula (2):



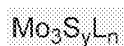
Formula (2)

- wherein R^3 and R^4 are independently selected from $\text{C}_4\text{-C}_{30}$ alkyl groups and x is an integer from 0 to 4. Each R^3 and R^4 can be the same or different. The dimer may be symmetric or asymmetric. Examples of commercially available molybdenum dialkyldithiocarbamates include MOLYVAN® 807, MOLYVAN® 822 and MOLYVAN® 2000 available from R.T. Vanderbilt.

- In certain embodiments, R^3 and R^4 are independently selected from $\text{C}_4\text{-C}_{24}$ alkyl groups. In certain embodiments, R^3 and R^4 are independently selected from $\text{C}_6\text{-C}_{18}$ alkyl groups.

In certain embodiments, x is 0. In certain embodiments, x is 1. In certain embodiments, x is 2. In certain embodiments, x is 3. In certain embodiments, x is 4.

Another class of molybdenum dithiocarbamates (e.g., trimeric molybdenum dithiocarbamates) useful herein is represented by the following Formula (3):



Formula (3)

wherein y is an integer from 4 to 10; n is an integer from 1 to 4; and each L is an alkyl dithiocarbamate group, wherein each alkyl group is selected from $\text{C}_4\text{-C}_{30}$ alkyl groups.

- 5 In one embodiment, y is 4. In one embodiment, y is 5. In one embodiment, y is 6. In one embodiment, y is 7. In one embodiment, y is 8. In one embodiment, y is 9. In one embodiment, y is 10.

In certain embodiments, n is 1. In certain embodiments, n is 2. In certain embodiments, n is 3. In certain embodiments, n is 4.

- 10 In certain embodiments, each L is an alkyl dithiocarbamate group, wherein each alkyl group is selected from C₄-C₂₄ alkyl groups. In certain embodiments, each L is an alkyl dithiocarbamate group, wherein each alkyl group is selected from C₆-C₁₈ alkyl groups.

In certain embodiments, the molybdenum-containing compound is not a molybdenum dithiocarbamate.

- 15 In one embodiment, the one or more molybdenum-containing compounds comprises molybdenum dithiophosphinates.

In one embodiment, the one or more molybdenum-containing compounds comprises molybdenum xanthates, for example a molybdenum-alkyl xanthate such as molybdenum-ethyl xanthate.

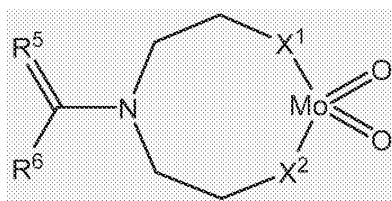
- 20 In one embodiment, the one or more molybdenum-containing compounds comprises molybdenum thioxanthates.

In one embodiment, the one or more molybdenum-containing compounds comprises molybdenum carboxylates.

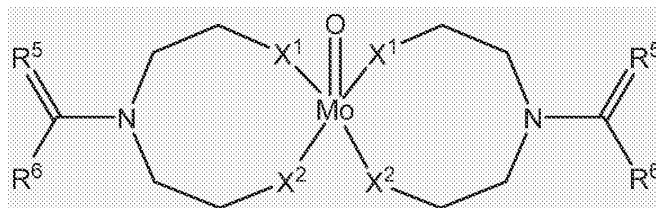
- 25 In one embodiment, the one or more molybdenum-containing compounds comprises molybdenum alkoxides.

In one embodiment, the one or more molybdenum-containing compounds comprises organo-molybdenum complexes.

Two classes of organo-molybdenum complexes useful herein is represented by the following Formula (4a) and Formula (4b):



Formula (4a)



Formula (4b)

wherein R^5 and R^6 are independently selected from C_4 - C_{30} alkyl groups and X^1 and X^2 are
 10 each independently O or NH. R^5 and R^6 can be the same or different. X^1 and X^2 can be the same or different.

In certain embodiments, R^5 and R^6 are independently selected from C_4 - C_{24} alkyl groups. In certain embodiments, R^5 and R^6 are independently selected from C_6 - C_{18} alkyl groups.

In certain embodiments, X^1 is O. In certain embodiments, X^1 is NH. In certain embodiments,
 15 X^2 is O. In certain embodiments, X^2 is NH.

Another class of organo-molybdenum complexes useful herein is represented by the following
 Formula (5):



Formula (5)

20 wherein y is an integer from 4 to 7; n is an integer from 1 to 4; and each L is independently selected ligands having organo groups with a sufficient number of carbon atoms to render the compound soluble or dispersible in oil; and Q is selected from the group of neutral electron-

- 5 donating compounds such as water, amines, alcohols, phosphines, and ethers; and p is an integer from 0 to 5.

In one embodiment, y is 4. In one embodiment, y is 5. In one embodiment, y is 6. In one embodiment, y is 7.

In certain embodiments, n is 1. In certain embodiments, n is 2. In certain embodiments, n is 3.

- 10 In certain embodiments, n is 4.

In certain embodiments, each L comprises at least 5 carbon atoms. In certain embodiments, the total number of carbon atoms included in the among all L groups is at least 21, at least 25, at least 30 or at least 35.

- 15 In certain embodiments the Q is selected from the group consisting of water, hydroxide, alkoxide, oxo, phosphine, phosphite, ammonia, amino, amido, halide, and combinations thereof.

In certain embodiments, p is 0. In certain embodiments, p is 1. In certain embodiments, p is 2. In certain embodiments, p is 3. In certain embodiments, p is 4.

- 20 In one embodiment, the one or more molybdenum-containing compounds comprises dispersed hydrated molybdenum compounds. Examples of dispersed hydrated molybdenum compounds include dispersed hydrated polymolybdates, dispersed hydrated alkali metal polymolybdates and the like and combinations thereof. Suitable dispersed hydrated polymolybdates include those disclosed in, for example, U.S. Pat. No. 7,884,058.

- 25 Generally, the amount of molybdenum increases with the amount of calcium in the lubricant compositions. In certain embodiments, the one or more molybdenum-containing compounds is in an amount to provide the lubricant composition with at least 100 ppm, at least 150 ppm, at least 166 ppm, at least 200 ppm, at least 250 ppm, at least 270 ppm, at least 300 ppm, at least 350 ppm, at least 400 ppm, at least 450 ppm, at least 500 ppm, at least 550 ppm, at least 600 ppm, at least 650 ppm, at least 700 ppm, at least 750 ppm, at least 800 ppm, at least 850 ppm,
30 at least 900 ppm, at least 950 ppm, at least 1000 ppm, at least 1100 ppm, at least 1200 ppm, or at least 1300 ppm of molybdenum, based upon the total weight of the composition.

- 5 In one embodiment, the amount of metal from the molybdenum-containing compound is no more than about 2000 ppm in the lubricant composition.

In certain embodiments, the one or more molybdenum-containing compounds is in an amount to provide the lubricant composition with about 100 ppm to about 2000 ppm, about 150 ppm to about 2000 ppm, about 166 ppm to about 2000 ppm, about 200 ppm to about 2000 ppm, 10 about 250 ppm to about 2000 ppm, about 270 ppm to about 2000 ppm, about 300 ppm to about 2000 ppm, about 350 ppm to about 2000 ppm, about 400 ppm to about 2000 ppm, about 450 ppm to about 2000 ppm, about 500 ppm to about 2000 ppm, about 550 ppm to about 2000 ppm, about 600 ppm to about 2000 ppm, about 650 ppm to about 2000 ppm, about 700 ppm to about 2000 ppm, about 750 ppm to about 2000 ppm, about 800 ppm to about 2000 ppm, about 850 15 ppm to about 2000 ppm, about 900 ppm to about 2000 ppm, about 950 ppm to about 2000 ppm, about 1000 ppm to about 2000 ppm, about 1100 ppm to about 2000 ppm, about 1200 ppm to about 2000 ppm, or about 1300 ppm to about 2000 ppm of molybdenum, based upon the total weight of the composition.

In certain embodiments, the one or more molybdenum-containing compounds is in an amount 20 to provide the lubricant composition with about 100 ppm to about 1200 ppm, about 150 ppm to about 1200 ppm, about 200 ppm to about 1200 ppm, about 250 ppm to about 1200 ppm, about 270 ppm to about 1200 ppm, about 300 ppm to about 1200 ppm, about 350 ppm to about 1200 ppm, about 400 ppm to about 1200 ppm, about 450 ppm to about 1200 ppm, about 500 ppm to about 1200 ppm, about 550 ppm to about 1200 ppm, about 600 ppm to about 1200 ppm, 25 about 650 ppm to about 1200 ppm, about 700 ppm to about 1200 ppm, about 750 ppm to about 1200 ppm, about 800 ppm to about 1200 ppm, about 850 ppm to about 1200 ppm, or about 900 ppm to about 1200 ppm of molybdenum, based upon the total weight of the composition.

In certain embodiments, the one or more molybdenum-containing compounds is in an amount to provide the lubricant composition with about 100 ppm to about 850 ppm, about 150 ppm to 30 about 850 ppm, about 200 ppm to about 850 ppm, about 250 ppm to about 850 ppm, about 270 ppm to about 850 ppm, about 300 ppm to about 850 ppm, about 350 ppm to about 850 ppm, about 400 ppm to about 850 ppm, about 450 ppm to about 850 ppm, about 500 ppm to about 850 ppm, about 550 ppm to about 850 ppm, about 600 ppm to about 850 ppm, about 650 ppm

- 5 to about 850 ppm, or about 700 ppm to about 850 ppm of molybdenum, based upon the total weight of the composition.

In certain embodiments, the one or more molybdenum-containing compounds is in an amount to provide the lubricant composition with about 100 ppm to about 800 ppm, about 150 ppm to about 800 ppm, about 166 ppm to about 800 ppm, about 200 ppm to about 800 ppm, about 250
10 ppm to about 800 ppm, about 270 ppm to about 800 ppm, about 300 ppm to about 800 ppm, about 350 ppm to about 800 ppm, about 400 ppm to about 800 ppm, about 450 ppm to about 800 ppm, about 500 ppm to about 800 ppm, about 550 ppm to about 800 ppm, about 600 ppm to about 800 ppm, about 650 ppm to about 800 ppm, or about 700 ppm to about 800 ppm of molybdenum, based upon the total weight of the composition.

- 15 In certain embodiments, the one or more molybdenum-containing compounds is in an amount to provide the lubricant composition with about 100 ppm to about 400 ppm, about 150 ppm to about 400 ppm, about 166 ppm to about 400 ppm, about 200 ppm to about 400 ppm, about 250 ppm to about 400 ppm, about 270 ppm to about 400 ppm, or about 300 ppm to about 400 ppm of molybdenum, based upon the total weight of the composition.

- 20 In certain embodiments, the one or more molybdenum-containing compounds is in an amount to provide the lubricant composition with about 800 ppm to about 2000 ppm, about 850 ppm to about 2000 ppm, about 900 ppm to about 2000 ppm, about 950 ppm to about 2000 ppm, about 1000 ppm to about 2000 ppm, about 1100 ppm to about 2000 ppm, about 1200 ppm to about 2000 ppm, or about 1300 ppm to about 2000 ppm of molybdenum, based upon the total
25 weight of the composition.

In certain embodiments, the one or more molybdenum-containing compounds is in an amount to provide the lubricant composition with a ratio of about 1:2, about 1:3, about 1:4, about 1:5, about 1:6, about 1:7, about 1:8, about 1:9 or about 1:10 ppm of molybdenum to ppm of calcium, based upon the total weight of the composition.

- 30 In certain embodiment, the amount of molybdenum in lubricant composition is proportional to the amount of calcium in the lubricant composition. In certain embodiments, the one or more molybdenum-containing compounds is in an amount to provide the lubricant composition with a ratio in the range of about 1:2 to about 1:3, about 1:2 to about 1:4, about 1:2 to about 1:5,

- 5 about 1:2 to about 1:6, about 1:2 to about 1:7, about 1:2 to about 1:8, about 1:2 to about 1:9, about 1:2 to about 1:10, about 1:3 to about 1:4, about 1:3 to about 1:5, about 1:3 to about 1:6, about 1:3 to about 1:7, about 1:3 to about 1:8, about 1:3 to about 1:9, about 1:3 to about 1:10, about 1:4 to about 1:5, about 1:4 to about 1:6, about 1:4 to about 1:7, about 1:4 to about 1:8, about 1:4 to about 1:9, about 1:4 to about 1:10, about 1:5 to about 1:6, about 1:5 to about 1:7, about 1:5 to about 1:8, about 1:5 to about 1:9, about 1:5 to about 1:10, about 1:6 to about 1:7, about 1:6 to about 1:8, about 1:6 to about 1:9, about 1:6 to about 1:10, about 1:7 to about 1:8, about 1:7 to about 1:9, about 1:7 to about 1:10, about 1:8 to about 1:9, about 1:8 to about 1:10, about 1:9 to about 1:10 ppm molybdenum to ppm calcium, based upon the total weight of the composition.
- 10
- 15 In certain embodiments, the one or more molybdenum-containing compounds, are in an amount providing the lubricant composition with at least about 850 ppm of molybdenum, based upon the total weight of the composition; and the one or more calcium detergents are in an amount providing the lubricant composition with at least about 1800 ppm of calcium, based upon the total weight of the composition.
- 20 In certain embodiments, the one or more molybdenum-containing compounds, are in an amount providing the lubricant composition with about 100 ppm to about 850 ppm of molybdenum, based upon the total weight of the composition; and the (iii) one or more calcium detergents are in an amount providing the lubricant composition with about 1000 to about 1450 ppm of calcium, based upon the total weight of the composition.

25 ***Calcium Detergent***

Calcium detergents for use in the lubricant compositions of the present disclosure include, but are not limited to, sulfonates, phenates, sulfurized phenates, thiophosphonates, salicylates, and naphthenates and other carboxylates of calcium. In certain embodiments, the calcium detergents are neutral and/or overbased.

- 30 In certain embodiments, the one or more calcium detergents comprise or consist essentially of calcium sulfonate. In certain embodiments, the one or more calcium detergents comprise or consist essentially of calcium phenate. In certain embodiments, the one or more calcium detergents comprise or consist essentially of calcium sulfurized phenate. In certain

5 embodiments, the one or more calcium detergents comprise or consist essentially of calcium thiophosphonates. In certain embodiments, the one or more calcium detergents comprise or consist essentially of calcium salicylate. In certain embodiments, the one or more calcium detergents comprise or consist essentially of calcium naphthenate. In certain embodiments, the one or more calcium detergents comprise or consist essentially of carboxylates of calcium. In
10 certain embodiments, the carboxylate is a salicylate.

In certain embodiments, the lubricant compositions comprise two or more types of calcium detergents.

In certain embodiments, the calcium detergent may be present in an amount to provide from about 600 ppm to about 3500 ppm, or about 600 ppm to about 2400 ppm, about 800 ppm to
15 about 1800, about 1200 ppm to about 1800 ppm, about 1800 ppm to about 2400 ppm, about 1800 ppm to about 3500 ppm of calcium to the lubricant composition.

In certain embodiments, the calcium detergent may be present in an amount to provide at least about 600 ppm, 800 ppm, 1000 ppm, 1200 ppm, 1400 ppm, 1600 ppm, 1800 ppm, 2000 ppm, 2200 ppm, 2400 ppm, 2600 ppm, 2800 ppm, or 3000 ppm of calcium to the lubricant
20 composition.

Oil of Lubricating Viscosity

The oil of lubricating viscosity for use in the lubricant compositions of this disclosure, also referred to as a base oil, is typically present in a major amount, e.g., an amount of greater than about 50 wt. %, greater than about 60 wt. %, greater than about 70 wt. %, greater than about
25 80 wt. %, or from about 60 to about 99.5 wt. %, about 70 to about 99.5 wt. %, about 80 to about 99.5 wt. %, about 85 to about 99.5 wt. %, about 60 to about 98 wt. %, about 70 to about 98 wt. %, about 80 to about 98 wt. %, or about 85 to about 98 wt. %, based on the total weight of the composition. The expression "base oil" as used herein shall be understood to mean a base stock or blend of base stocks that is produced to selected specifications (independent of
30 feed source or manufacturer's location). The base oil for use herein can be any presently known or later-discovered oil of lubricating viscosity used in formulating lubricant compositions for any and all such applications, e.g., engine oils, marine cylinder oils, functional fluids such as hydraulic oils, gear oils, transmission fluids, etc.

- 5 As one skilled in the art would readily appreciate, the viscosity of the base oil is dependent upon the application. Accordingly, the viscosity of a base oil for use herein will ordinarily range from about 2 to about 2000 centistokes (cSt) at 100° Centigrade (C.). Generally, individually the base oils used as engine oils will have a kinematic viscosity range at 100° C. of about 2 cSt to about 30 cSt, preferably about 3 cSt to about 16 cSt, and most preferably
10 about 4 cSt to about 12 cSt and will be selected or blended depending on the desired end use and the additives in the finished oil to give the desired grade of engine oil, e.g., a lubricant composition having an SAE Viscosity Grade of 0W, 0W-8, 0W-12, 0W-16, 0W-20, 0W-26, 0W-30, 0W-40, 0W-50, 0W-60, 5W, 5W-20, 5W-30, 5W-40, 5W-50, 5W-60, 10W, 10W-20, 10W-30, 10W-40, 10W-50, 15W, 15W-20, 15W-30, 15W-40, 30, 40 and the like. In one
15 embodiment, the lubricant composition has an SAE Viscosity Grade of 0W-20 or 0W-40.

Group I base oils generally refer to a petroleum derived lubricating base oil having a saturates content of less than 90 wt. % (as determined by ASTM D 2007) and/or a total sulfur content of greater than 300 ppm (as determined by ASTM D 2622, ASTM D 4294, ASTM D 4297 or ASTM D 3120) and has a viscosity index (VI) of greater than or equal to 80 and less than 120
20 (as determined by ASTM D 2270).

Group II base oils generally refer to a petroleum derived lubricating base oil having a total sulfur content equal to or less than 300 parts per million (ppm) (as determined by ASTM D 2622, ASTM D 4294, ASTM D 4927 or ASTM D 3120), a saturates content equal to or greater than 90 weight percent (as determined by ASTM D 2007), and a viscosity index (VI) of
25 between 80 and 120 (as determined by ASTM D 2270).

Group III base oils generally refer to a petroleum derived lubricating base oil having less than 300 ppm sulfur, a saturates content greater than 90 weight percent, and a VI of 120 or greater.

Group IV base oils are polyalphaolefins (PAOs).

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

- 30 In one embodiment, the lubricant composition comprises one or more Group I base oils. In one embodiment, the lubricant composition comprises one or more Group II base oils. In one embodiment, the lubricant composition comprises one or more Group III base oils. In one

- 5 embodiment, the lubricant composition comprises one or more Group IV base oils. In one embodiment, the lubricant composition comprises one or more Group V base oils. In one embodiment, the lubricant composition comprises one or more Group II or Group III base oils.

The lubricant composition can contain minor amounts of other base oil components. For example, the lubricant composition can contain a minor amount of a base oil derived from
10 natural lubricants, synthetic lubricants or mixtures thereof. Suitable base oil includes base stocks obtained by isomerization of synthetic wax and slack wax, as well as hydrocracked base stocks produced by hydrocracking (rather than solvent extracting) the aromatic and polar components of the crude.

Suitable natural oils include mineral lubricants such as, for example, liquid petroleum oils,
15 solvent-treated or acid-treated mineral lubricants of the paraffinic, naphthenic or mixed paraffinic-naphthenic types, oils derived from coal or shale, animal oils, vegetable oils (e.g., rapeseed oils, castor oils and lard oil), and the like.

Suitable synthetic lubricants include, but are not limited to, hydrocarbon oils and halo-substituted hydrocarbon oils such as polymerized and interpolymerized olefins, e.g.,
20 polybutylenes, polypropylenes, propylene-isobutylene copolymers, chlorinated polybutylenes, poly(1-hexenes), poly(1-octenes), poly(1-decenes), and the like and mixtures thereof; alkylbenzenes such as dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di(2-ethylhexyl)-benzenes, and the like; polyphenyls such as biphenyls, terphenyls, alkylated polyphenyls, and the like; alkylated diphenyl ethers and alkylated diphenyl sulfides and the
25 derivative, analogs and homologs thereof and the like.

Other synthetic lubricants include, but are not limited to, oils made by polymerizing olefins of less than 5 carbon atoms such as ethylene, propylene, butylenes, isobutene, pentene, and mixtures thereof. Methods of preparing such polymer oils are well known to those skilled in the art.

- 30 Additional synthetic hydrocarbon oils include liquid polymers of alpha olefins having the proper viscosity. Especially useful synthetic hydrocarbon oils are the hydrogenated liquid oligomers of C₆ to C₁₂ alpha olefins such as, for example, 1-decene trimer.

5 Another class of synthetic lubricants include, but are not limited to, alkylene oxide polymers, i.e., homopolymers, interpolymers, and derivatives thereof where the terminal hydroxyl groups have been modified by, for example, esterification or etherification. These oils are exemplified by the oils prepared through polymerization of ethylene oxide or propylene oxide, the alkyl and phenyl ethers of these polyoxyalkylene polymers (e.g., methyl poly propylene glycol ether
10 having an average molecular weight of 1,000, diphenyl ether of polyethylene glycol having a molecular weight of 500-1000, diethyl ether of polypropylene glycol having a molecular weight of 1,000-1,500, etc.) or mono- and polycarboxylic esters thereof such as, for example, the acetic esters, mixed C₃-C₈ fatty acid esters, or the C₁₃ oxo acid diester of tetraethylene glycol.

15 Yet another class of synthetic lubricants include, but are not limited to, the esters of dicarboxylic acids e.g., phthalic acid, succinic acid, alkyl succinic acids, alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acids, alkyl malonic acids, alkenyl malonic acids, etc., with a variety of alcohols, e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene
20 glycol, diethylene glycol monoether, propylene glycol, etc. Specific examples of these esters include 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, the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid
25 and the like.

Esters useful as synthetic oils also include, but are not limited to, those made from carboxylic acids having from about 5 to about 12 carbon atoms with alcohols, e.g., methanol, ethanol, etc., polyols and polyol ethers such as neopentyl glycol, trimethylol propane, pentaerythritol, dipentaerythritol, tripentaerythritol, and the like.

30 Silicon-based oils such as, for example, polyalkyl-, polyaryl-, polyalkoxy- or polyaryloxy-siloxane oils and silicate oils, comprise another useful class of synthetic lubricants. Specific examples of these include, but are not limited to, tetraethyl silicate, tetra-isopropyl silicate, tetra-(2-ethylhexyl) silicate, tetra-(4-methyl-hexyl)silicate, tetra-(p-tert-butylphenyl)silicate, hexyl-(4-methyl-2-pentoxy)disiloxane, poly(methyl)siloxanes, poly(methylphenyl)siloxanes,

- 5 and the like. Still yet other useful synthetic lubricants include, but are not limited to, liquid esters of phosphorous containing acids, e.g., tricresyl phosphate, trioctyl phosphate, diethyl ester of decane phosphonic acid, etc., polymeric tetrahydrofurans and the like.

The lubricant may be derived from unrefined, refined and rerefined oils, either natural, synthetic or mixtures of two or more of any of these of the type disclosed hereinabove.

- 10 Unrefined oils are those obtained directly from a natural or synthetic source (e.g., coal, shale, or tar sands bitumen) without further purification or treatment. Examples of unrefined oils include, but are not limited to, a shale oil obtained directly from retorting operations, a petroleum oil obtained directly from distillation or an ester oil obtained directly from an esterification process, each of which is then used without further treatment. Refined oils are
- 15 similar to the unrefined oils except they have been further treated in one or more purification steps to improve one or more properties. These purification techniques are known to those of skill in the art and include, for example, solvent extractions, secondary distillation, acid or base extraction, filtration, percolation, hydrotreating, dewaxing, etc. Rerefined oils are obtained by treating used oils in processes similar to those used to obtain refined oils. Such rerefined oils
- 20 are also known as reclaimed or reprocessed oils and often are additionally processed by techniques directed to removal of spent additives and oil breakdown products.

- Lubricant base stocks derived from the hydroisomerization of wax may also be used, either alone or in combination with the aforesaid natural and/or synthetic base stocks. Such wax isomerate oil is produced by the hydroisomerization of natural or synthetic waxes or mixtures
- 25 thereof over a hydroisomerization catalyst.

Natural waxes are typically the slack waxes recovered by the solvent dewaxing of mineral oils; synthetic waxes are typically the wax produced by the Fischer-Tropsch process.

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

5 *Lubricant Additives*

Generally, the lubricant compositions of the present disclosure may comprise additional lubricant additives. The lubricant compositions may further comprise other conventional additives, such as those that can impart or improve any desirable property of the lubricant composition in which these additives are dispersed or dissolved. Any additive known to a person of ordinary skill in the art may be used in the lubricant compositions disclosed herein. Some suitable additives have been described in Mortier et al., “Chemistry and Technology of Lubricants”, 2nd Edition, London, Springer, (1996); and Leslie R. Rudnick, “Lubricant Additives: Chemistry and Applications”, New York, Marcel Dekker (2003), both of which are incorporated herein by reference. For example, the lubricant compositions can be blended with antioxidants, anti-wear agents, metal detergents, rust inhibitors, dehazing agents, demulsifying agents, metal deactivating agents, friction modifiers, pour point depressants, antifoaming agents, co-solvents, corrosion-inhibitors, ashless dispersants, multifunctional agents, dyes, extreme pressure agents and the like and mixtures thereof. A variety of the additives are known and commercially available. These additives, or their analogous compounds, can be employed for the preparation of the lubricant compositions of the disclosure by the usual blending procedures.

In addition to the calcium detergents, the lubricant composition of the present disclosure can contain one or more non-calcium detergents, for example other metal-containing or ash-forming 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. 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).

Detergents that may be used include oil-soluble neutral and overbased sulfonates, phenates, sulfurized phenates, thiophosphonates, salicylates, and naphthenates and other oil-soluble

- 5 carboxylates of a metal, particularly the alkali or alkaline earth metals, e.g., barium, sodium, potassium, lithium, and magnesium.

In one embodiment, the lubricant composition comprises one or more magnesium detergents. In one embodiment the magnesium detergent(s) can be added in an amount sufficient to provide the lubricant composition from about 100 to about 1000 ppm of magnesium metal, or from
10 about 100 to about 600 ppm, or from about 100 to about 500 ppm, or from about 200 to about 500 ppm of magnesium metal in the lubricant composition. In certain embodiments, the lubricant composition does not contain magnesium detergents, or magnesium-containing compounds.

In one embodiment, the lubricant composition comprises one or more lithium detergents. In
15 one embodiment the lithium detergent(s) can be added in an amount sufficient to provide the lubricant composition from 0 to about 2400 ppm of lithium metal, from 0 to about 2200 ppm of lithium metal, from 100 to about 2000 ppm of lithium metal, from 200 to about 1800 ppm of lithium metal, or from about 100 to about 1800 ppm, or from about 200 to about 1500 ppm, or from about 300 to about 1400 ppm, or from about 400 to about 1400 ppm, of lithium metal
20 in the lubricant composition.

In one embodiment, the lubricant composition comprises one or more sodium detergents. In one embodiment the sodium detergent(s) can be added in an amount sufficient to provide the lubricant composition from 0 to about 2400 ppm of sodium metal, from 0 to about 2200 ppm of sodium metal, from 100 to about 2000 ppm of sodium metal, from 200 to about 1800 ppm
25 of sodium metal, or from about 100 to about 1800 ppm, or from about 200 to about 1500 ppm, or from about 300 to about 1400 ppm, or from about 400 to about 1400 ppm, of sodium metal in the lubricant composition.

In one embodiment, the lubricant composition comprises one or more potassium detergents. In one embodiment the potassium detergent(s) can be added in an amount sufficient to provide
30 the lubricant composition from 0 to about 2400 ppm of potassium metal, from 0 to about 2200 ppm of potassium metal, from 100 to about 2000 ppm of potassium metal, from 200 to about 1800 ppm of potassium metal, or from about 100 to about 1800 ppm, or from about 200 to about 1500 ppm, or from about 300 to about 1400 ppm, or from about 400 to about 1400 ppm, of potassium metal in the lubricant composition.

5 The lubricant composition of the present invention can contain one or more anti-wear agents that can reduce friction and excessive wear. Any anti-wear agent known by a person of ordinary skill in the art may be used in the lubricant composition. Non-limiting examples of suitable anti-wear agents include zinc dithiophosphate, metal (e.g., Pb, Sb, Mo and the like) salts of dithiophosphates, metal (e.g., Zn, Pb, Sb, Mo and the like) salts of dithiocarbamates, 10 metal (e.g., Zn, Pb, Sb and the like) salts of fatty acids, boron compounds, phosphate esters, phosphite esters, amine salts of phosphoric acid esters or thiophosphoric acid esters, reaction products of dicyclopentadiene and thiophosphoric acids and combinations thereof. The amount of the anti-wear agent may vary from about 0.01 wt. % to about 5 wt. %, from about 0.05 wt. % to about 3 wt. %, or from about 0.1 wt. % to about 1 wt. %, based on the total weight of the 15 lubricant composition.

In certain embodiments, the anti-wear agent is or comprises a dihydrocarbyl dithiophosphate metal salt, such as zinc dialkyl dithiophosphate compounds. The metal of the dihydrocarbyl dithiophosphate metal salt may be an alkali or alkaline earth metal, or aluminum, lead, tin, molybdenum, manganese, nickel or copper. In some embodiments, the metal is zinc. In other 20 embodiments, the alkyl group of the dihydrocarbyl dithiophosphate metal salt has from about 3 to about 22 carbon atoms, from about 3 to about 18 carbon atoms, from about 3 to about 12 carbon atoms, or from about 3 to about 8 carbon atoms. In further embodiments, the alkyl group is linear or branched.

The amount of the dihydrocarbyl dithiophosphate metal salt including the zinc dialkyl 25 dithiophosphate salts in the lubricant composition disclosed herein is measured by its phosphorus content. In some embodiments, the phosphorus content of the lubricant composition disclosed herein is from about 0.01 wt. % to about 0.14 wt. %, based on the total weight of the lubricant composition.

The lubricant composition of the present invention can contain one or more friction modifiers 30 that can lower the friction between moving parts. Any friction modifier known by a person of ordinary skill in the art may be used in the lubricant composition. Non-limiting examples of suitable friction modifiers include fatty carboxylic acids; derivatives (e.g., alcohol, esters, borated esters, amides, metal salts and the like) of fatty carboxylic acid; mono-, di- or tri-alkyl substituted phosphoric acids or phosphonic acids; derivatives (e.g., esters, amides, metal salts

5 and the like) of mono-, di- or tri-alkyl substituted phosphoric acids or phosphonic acids; mono-, di- or tri-alkyl substituted amines; mono- or di-alkyl substituted amides and combinations thereof. In some embodiments examples of friction modifiers include, but are not limited to, alkoxyated fatty amines; borated fatty epoxides; fatty phosphites, fatty epoxides, fatty amines, borated alkoxyated fatty amines, metal salts of fatty acids, fatty acid amides, glycerol esters, 10 borated glycerol esters; and fatty imidazolines as disclosed in U.S. Patent No. 6,372,696, the contents of which are incorporated by reference herein; friction modifiers obtained from a reaction product of a C₄ to C₇₅, or a C₆ to C₂₄, or a C₆ to C₂₀, fatty acid ester and a nitrogen-containing compound selected from the group consisting of ammonia, and an alkanolamine and the like and mixtures thereof. The amount of the friction modifier may vary from about 15 0.01 wt. % to about 10 wt. %, from about 0.05 wt. % to about 5 wt. %, or from about 0.1 wt. % to about 3 wt. %, based on the total weight of the lubricant composition.

The lubricant composition of the invention can contain an organic oxidation inhibitor in an amount of 0.01-5 wt. %, preferably 0.1-3 wt. %. The oxidation inhibitor can be a hindered phenol oxidation inhibitor or a diarylamine oxidation inhibitor. The diarylamine oxidation 20 inhibitor is advantageous in giving a base number originating from the nitrogen atoms. The hindered phenol oxidation inhibitor is advantageous in producing no NO_x gas.

Examples of the hindered phenol oxidation inhibitors include 2,6-di-*t*-butyl-*p*-cresol, 4,4'-methylenebis(2,6-di-*t*-butylphenol), 4,4'-methylenebis(6-*t*-butyl-*o*-cresol), 4,4'-isopropylidenebis(2,6-di-*t*-butylphenol), 4,4'-bis(2,6-di-*t*-butylphenol), 2,2'-methylenebis(4- 25 methyl-6-*t*-butylphenol), 4,4'-thiobis(2-methyl-6-*t*-butylphenol), 2,2'-thio-diethylenebis[3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionate], octyl 3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionate, octadecyl 3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionate, and octyl 3-(3,5,4-*t*-butyl-4-hydroxy-3-methylphenyl)propionate, and commercial products such as, but not limited to, Irganox L135® (BASF), Naugalube 531® (Chemtura), and Ethanox 376® (SI 30 Group).

Examples of the diarylamine oxidation inhibitors include alkylldiphenylamine having a mixture of alkyl groups of 4 to 9 carbon atoms, *p,p'*-dioctyldiphenylamine, phenyl-naphthylamine, phenyl-naphthylamine, alkylated-naphthylamine, and alkylated phenyl-naphthylamine.

- 5 Each of the hindered phenol oxidation inhibitor and diarylamine oxidation inhibitor can be employed alone or in combination. If desired, other oil soluble oxidation inhibitors can be employed in combination with the above-mentioned oxidation inhibitor(s).

In certain embodiments, the lubricant composition comprises a sulfur-containing oxymolybdenum complex of succinimide as one of the one or more molybdenum-containing
10 compounds and an additive selected from phenolic or amine oxidation inhibitors.

In the preparation of lubricant formulations, it is common practice to introduce the additives in the form of 10 to 80 wt. % active ingredient concentrates in hydrocarbon oil, e.g., mineral lubricant, or other suitable solvent.

Usually, these concentrates may be diluted with 3 to 100, e.g., 5 to 40, parts by weight of
15 lubricant per part by weight of the additive package in forming finished lubricants, e.g., crankcase motor oils. The purpose of concentrates, of course, is to make the handling of the various materials less difficult and awkward as well as to facilitate solution or dispersion in the final blend.

In general, the level of sulfur in the lubricant compositions of the present invention is less than
20 or equal to about 0.7 wt. %, based on the total weight of the lubricant composition, e.g., a level of sulfur of about 0.01 wt. % to about 0.70 wt. %, 0.01 to 0.6 wt.%, 0.01 to 0.5 wt.%, 0.01 to 0.4 wt.%, 0.01 to 0.3 wt.%, 0.01 to 0.2 wt.%, 0.01 wt. % to 0.10 wt. %. In one embodiment, the level of sulfur in the lubricant compositions of the present invention is less than or equal to about 0.60 wt. %, less than or equal to about 0.50 wt. %, less than or equal to about 0.40 wt.
25 %, less than or equal to about 0.30 wt. %, less than or equal to about 0.20 wt. %, less than or equal to about 0.10 wt. % based on the total weight of the lubricant composition.

In one embodiment, the levels of phosphorus in the lubricant compositions of the present invention is less than or equal to about 0.12 wt. %, based on the total weight of the lubricant composition, e.g., a level of phosphorus of about 0.01 wt. % to about 0.12 wt. %. In one
30 embodiment, the levels of phosphorus in the lubricant compositions of the present invention is less than or equal to about 0.11 wt. %, based on the total weight of the lubricant composition, e.g., a level of phosphorus of about 0.01 wt. % to about 0.11 wt. %. In one embodiment, the levels of phosphorus in the lubricant compositions of the present invention is less than or equal

5 to about 0.10 wt. %, based on the total weight of the lubricant composition, e.g., a level of phosphorus of about 0.01 wt. % to about 0.10 wt. %. In one embodiment, the levels of phosphorus in the lubricant compositions of the present invention is less than or equal to about 0.09 wt. %, based on the total weight of the lubricant composition, e.g., a level of phosphorus of about 0.01 wt. % to about 0.09 wt. %. In one embodiment, the levels of phosphorus in the
10 lubricant compositions of the present invention is less than or equal to about 0.08 wt. %, based on the total weight of the lubricant composition, e.g., a level of phosphorus of about 0.01 wt. % to about 0.08 wt. %. In one embodiment, the levels of phosphorus in the lubricant compositions of the present invention is less than or equal to about 0.07 wt. %, based on the total weight of the lubricant composition, e.g., a level of phosphorus of about 0.01 wt. % to
15 about 0.07 wt. %. In one embodiment, the levels of phosphorus in the lubricant compositions of the present invention is less than or equal to about 0.05 wt. %, based on the total weight of the lubricant composition, e.g., a level of phosphorus of about 0.01 wt. % to about 0.05 wt. %.

In one embodiment, the level of sulfated ash produced by the lubricant compositions of the present invention is less than or equal to about 1.60 wt. % as determined by ASTM D 874, e.g.,
20 a level of sulfated ash of from about 0.10 to about 1.60 wt. % as determined by ASTM D 874. In one embodiment, the level of sulfated ash produced by the lubricant compositions of the present invention is less than or equal to about 1.00 wt. % as determined by ASTM D 874, e.g., a level of sulfated ash of from about 0.10 to about 1.00 wt. % as determined by ASTM D 874. In one embodiment, the level of sulfated ash produced by the lubricant compositions of the
25 present invention is less than or equal to about 0.80 wt. % as determined by ASTM D 874, e.g., a level of sulfated ash of from about 0.10 to about 0.80 wt. % as determined by ASTM D 874. In one embodiment, the level of sulfated ash produced by the lubricant compositions of the present invention is less than or equal to about 0.60 wt. % as determined by ASTM D 874, e.g., a level of sulfated ash of from about 0.10 to about 0.60 wt. % as determined by ASTM D 874.

30 Suitably, the present lubricant composition may have a total base number (TBN) of 4 to 15 mg KOH/g (e.g., 5 to 12 mg KOH/g, 6 to 12 mg KOH/g, or 8 to 12 mg KOH/g).

Processes of Preparing Lubricant Compositions

The lubricant compositions disclosed herein can be prepared by any method known to a person of ordinary skill in the art for making lubricants. In some embodiments, the base oil can be

5 blended or mixed with the one or more molybdenum-containing compounds and one or more calcium detergents described herein. Optionally, one or more additional additives can be mixed or blended. Additional additives include lubricant additives generally known such as anti-wear agents, foam inhibitors, friction modifiers, foam inhibitors, pour point depressants, viscosity index improvers, e.g., polymeric alkylmethacrylates; olefinic copolymers, e.g., an ethylene-
10 propylene copolymer or a styrene-diene copolymer; and the like and mixtures thereof.

The one or more molybdenum-containing compounds and one or more calcium detergents and the optional additives may be blended or mixed separately or simultaneously. In some embodiments, the one or more molybdenum-containing compounds and one or more calcium detergents and the optional additives are blended or mixed separately in one or more additions
15 and the additions may be in any order. In other embodiments, the one or more molybdenum-containing compounds and one or more calcium detergents and the additives are blended or mixed simultaneously, optionally in the form of an additive concentrate. In some embodiments, the solubilizing of the one or more molybdenum-containing compounds, the one or more calcium detergents or any solid additives in the base oil may be assisted by heating the
20 mixture to a temperature from about 25 °C to about 200 °C, from about 50 °C to about 150 °C or from about 75 °C to about 125 °C.

Any mixing or dispersing equipment known to a person of ordinary skill in the art may be used for blending, mixing or solubilizing the ingredients. The blending, mixing or solubilizing may be carried out with a blender, an agitator, a disperser, a mixer (e.g., planetary mixers and double
25 planetary mixers), a homogenizer (e.g., Gaulin homogenizers and Rannie homogenizers), a mill (e.g., colloid mill, ball mill and sand mill) or any other mixing or dispersing equipment known in the art.

Application of the Lubricant Compositions

The lubricant composition disclosed herein may be suitable for use as motor oils (that is, engine
30 oils or crankcase oils), in a spark-ignited internal combustion engine, particularly a direct injected, boosted, engine that is susceptible to low speed pre-ignition.

The following examples are presented to exemplify embodiments of the invention but are not intended to limit the invention to the specific embodiments set forth. Unless indicated to the

- 5 contrary, all parts and percentages are by weight. All numerical values are approximate. When numerical ranges are given, it should be understood that embodiments outside the stated ranges may still fall within the scope of the invention. Specific details described in each example should not be construed as necessary features of the invention.

10

EXAMPLES

The following examples are intended for illustrative purposes only and do not limit in any way the scope of the present invention.

Examples 1-4. Exemplary and Comparative Lubricant Compositions

The exemplary and comparative lubricant compositions formulations contained:

15

a Group II or III base oil,

a mixture of calcium detergents in an amount to provide about 1197 to about 2000 ppm calcium to the lubricant composition,

20

one or more molybdenum compounds, selected from molybdenum-amine complexes and molybdenum dithiocarbamates, in an amount to provide about 166 ppm to about 1000 ppm molybdenum to the lubricant composition,

a mixture of primary and secondary dialkyl zinc dithiophosphates in an amount to provide about 757 to about 890 ppm zinc to the lubricant composition,

a mixture of polyisobutenyl succinimide dispersants (borated and ethylene carbonate post-treated),

25

a foam inhibitor, and

an alkylated diphenylamine antioxidant.

- 5 Example 1 and Comparative Example 1 included salicylate, phenate, and sulfonate calcium detergents as the calcium sources and molybdenum dithiocarbamate as the molybdenum source.

- Examples 2-4 and Comparative Example 2 included phenate, and sulfonate calcium detergents as the calcium sources and molybdenum-amine complexes as the molybdenum
10 source.

Certain lubricant compositions also contained a borated organic friction modifier and/or an olefin copolymer or poly(methyl acrylate) viscosity index improver. The friction modifier was not a Mo-containing compound. Example 1 and Comparative Example 1 contained a poly(methyl acrylate) viscosity index improver.

- 15 Certain lubricant compositions also contained one or more magnesium detergents in an amount to provide about 436 to about 473 magnesium to the composition.

The lubricant compositions were blended to form 0W-20 (Example 1 and Comparative Example 1) or 0W-40 (Examples 2-4 and Comparative 2) viscosity grade oil.

- The amount of the components for each of the exemplary and comparative lubricant
20 compositions, in addition to the base oil, is provided in Table 1.

Table 1.

	Ex. 1	Comp. 1	Ex. 2	Ex. 3	Ex. 4	Comp. 2
Ca content (ppm)	2000	2000	1297	1238	1197	1272
Mo content (ppm)	1000	500	166	270	828	153
Zn content (ppm)	890	890	821	758	757	759
Mg content (ppm)	0	0	473	453	436	436
Dispersant (wt%)	3.4	3.4	3.5	3.3	3.23	4.23
Foam inhibitor (ppm)	5	5	18.43	17	17	20
Antioxidant (wt%)	1	1	1.2	0.8	1.1	1.10
Organic Friction Modifier (wt%)	0	0	0.28	0.3	0.25	0.26
Viscosity Index Improver (wt%)	0	0	16	6.3	6.3	6.1
B (mass %)	0	0	0.0097	0.0105	0.0090	0.0057
P (mass %)	0.077	0.077	0.0713	0.0659	0.0657	0.0658
N (mass %)	n/a	n/a	0.0903	0.0799	0.1164	0.0933
S (mass %)	n/a	n/a	0.1781	0.1723	0.1687	0.1672

5

Example 5. Oil Aging Conditions

The lubricant compositions were aged according to the operating parameters summarized in Table 2. The aging process is a steady state process running for a total of 72 hours. The resulting oil is comparable to oil aged to about 5,000 miles under normal driving conditions.

10 **Table 2.**

Parameter	Units	Conditions
Duration	Hr	72
Engine Speed	r/min	2500 ± 5
Torque	N·M	128 ± 2
Oil Gallery Temperature	°C	100 ± 0.5
Coolant Out Temperature	°C	85 ± 0.5
Coolant Flow	L/min	70 ± 2
Inlet Air Pressure	kPa	0.05 ± 0.02
Coolant Pressure	kPa	70 ± 2
Inlet Air Temperature	°C	32 ± 0.5
Exhaust Back Pressure	kPa	107 ± 2
Air Charge Temperature	°C	30 ± 0.5
AFR	Lambda	1 ± 0.05
Humidity	g/kg	11.4 ± 1.0
Blowby	L/min	65-75
Test Charge	kg	4.5

Example 6. LSPI Testing of Aged Oil Comprising Exemplary or Comparative Lubricant Compositions

15 LSPI events were measured in a Ford 2.0L Ecoboost engine. This engine is a turbocharged gasoline direct injection (GDI) engine.

The Ford Ecoboost engine is operated in four-roughly 4 hours iterations. The engine is operated at 1750 rpm and 1.7 MPa brake mean effective pressure (BMEP) with an oil sump temperature of 95 °C. The engine is run for 175,000 combustion cycles in each stage, and LSPI events are counted.

- 5 LSPI events are determined by monitoring peak cylinder pressure (PP) and mass fraction burn (MFB) of the fuel charge in the cylinder. When either or both criteria are met, it can be said that an LSPI event has occurred. The threshold for peak cylinder pressure varies by test, but is typically 4-5 standard deviations above the average cylinder pressure. Likewise, the MFB threshold is typically 4-5 standard deviations earlier than the average MFB (represented in
- 10 crank angle degrees). LSPI events can be reported as average events per test, events per 100,000 combustion cycles, events per cycle, and/or combustion cycles per event. The results for this test are shown in Table 3.

Table 3. Ford Used Oil LSPI Tests

	Ex. 1	Comp. 1	Ex. 2	Ex. 3	Ex. 4	Comp. 2	Pass Limit**
Ca content (ppm)	2000	2000	1297	1238	1197	1272	-
Mo content (ppm)	1000	500	166	270	828	153	-
Average Counts	3.75	7.75	4.91	1.97	0.44	8.36	<5
Maximum Counts	6	12	6.76	4.96	1.27	9.65	<8

*Counts all cycles of LSPI where both MFB02 and Peak Pressure Requirements are met.

- 15 ** Pass limit values are current standard for GF-6 fresh oil tests.

The Ford Used Oil LSPI results of example 1 versus comparative example 1 show that at high levels of calcium (2000 ppm) increasing the amount of molybdenum decreases the average number of LSPI events from 7.75 to 3.75. Moreover, comparison of example 3 and 4 also shows that increasing the amount of molybdenum decreases the average number of LSPI

20 events.

CLAIMS

What is claimed is:

1. A method for reducing or preventing low speed pre-ignition (LSPI) in a direct-injected, boosted, spark-ignited, internal combustion engine, said method comprising the step of lubricating the engine with a used or aged lubricant composition comprising:
 - (i) one or more oils of lubricating viscosity;
 - (ii) one or more molybdenum-containing compounds, in an amount providing the lubricant composition with at least about 100 ppm of molybdenum, based upon the total weight of the composition; and
 - (iii) one or more calcium detergents, in an amount providing the lubricant composition with at least about 1000 ppm of calcium, based upon the total weight of the composition;wherein the used or aged lubricant composition lubricates the engine in the course of at least one oil change interval.
2. The method of claim 1, wherein the (ii) one or more molybdenum-containing compounds, are in an amount providing the lubricant composition with at least about 850 ppm of molybdenum, based upon the total weight of the composition; and the (iii) one or more calcium detergents are in an amount providing the lubricant composition with at least about 1800 ppm of calcium, based upon the total weight of the composition.
3. The method of claim 1, wherein the (ii) one or more molybdenum-containing compounds are in an amount providing the lubricant composition with about 100 ppm to about 850 ppm of molybdenum, based upon the total weight of the composition; and the (iii) one or more calcium detergents are in an amount providing the lubricant composition with about 1000 to about 1450 ppm of calcium, based upon the total weight of the composition.
4. The method of claim 1, wherein the and the (iii) one or more calcium detergents are in an amount providing the lubricant composition with less than about 2400 ppm, based upon the total weight of the composition.

5. The method of claim 1, wherein the one or more molybdenum-containing compounds are selected from the group consisting of: molybdenum-amine complexes, molybdenum dithiophosphates, and molybdenum dithiocarbamates.
6. The method of claim 1, wherein the one or more molybdenum-containing compounds are selected from the group consisting of: molybdenum-amine complexes and molybdenum dithiophosphates.
7. The method of claim 6, wherein the molybdenum-amine complex is a molybdenum succinimide complex.
8. The method of claim 1, wherein the direct-injected, boosted, spark-ignited, internal combustion engine is a downsized engine or an engine that ranges in size from 0.5 liters to 3.6 liters.
9. The method of claim 1, wherein the direct-injected, boosted, spark-ignited, internal combustion engine is operated at speeds between 500 and 3000 rpm.
10. The method of claim 1, wherein the direct-injected, boosted, spark-ignited, internal combustion engine is operated under a load with a brake mean effective pressure (BMEP) of from about 12 to about 30 bars.
11. The method of claim 1, wherein the LSPI events occurring while the engine is operated are less than 10 per 100,000 combustion events.
12. The method of claim 1, wherein the method provides a reduction in the number of LSPI events of at least 50%.
13. The method of claim 1, wherein the one or more calcium detergents are selected from the group consisting of a carboxylate detergent.
14. The method of claim 1, wherein the one or more calcium detergents are selected from the group consisting of a salicylate, phenate, or sulfonate detergent.
15. The method of claim 1, wherein the lubricant composition further comprises at least one other additive selected from an ashless dispersant, an antioxidant, an anti-wear additive, a friction modifier, and a polymeric viscosity modifier.
16. The method of claim 1, wherein the at least one oil change interval is at least 3000 miles.
17. The method of claim 1, wherein the at least one oil change interval is at least 5000 miles.