LUBRICATING COMPOSITIONS FOR DIESEL PARTICULATE FILTER PERFORMANCE

TECHNICAL FIELD

[0001] The disclosure relates to lubricant compositions exhibiting reduced clogging in diesel engine particulate filters.

BACKGROUND

[0002] Passenger and light-duty vehicles may be equipped with either a compression (diesel) or spark-ignition (gasoline) internal combustion engine. Generally engine oils are specially formulated for use in one or the other. However, it can be beneficial to lubricate a spark-ignition engine with an engine oil formulated for a compression engine. Further, some diesel engine oils are tested to meet both diesel and gasoline engine oil specifications (i.e., mixed specifications), and, thus are recommend for use with either engine-type. Therefore, an oil that meets both diesel engine and gasoline engine specifications and that can handle each of these diverse engine conditions is desirable.

[0003] Vehicles having a compression ignition engine are often equipped with diesel particulate filters. Such filters can become clogged with particulate matter. This particulate matter is caused by the adverse effects of ash, sulphur, and phosphorus. Reducing levels of phosphorus and sulphur can be accomplished by reducing the amount of zinc dithiophosphate and employing low sulphur base oils, for example.

[0004] The major sources of ash in lubricating oil compositions are generally the metal detergents and zinc dithiophosphate anti-wear additives employed therein. To mitigate clogging in the diesel particulate filters, current methods involve reducing the presence of detergents. However, reducing the amount of detergents has an adverse effect on the basicity of the lubricating oil composition which is essential for neutralizing acidic by-products of combustion/oxidation. Therefore, it is desirable to reduce the adverse effects of ash on diesel particulate filters without compromising the basicity of the lubricating oil composition by reducing the amount of detergents.

[0005] Boosted spark-ignited internal combustions engines such as turbocharged or supercharged internal combustion engines may exhibit an abnormal combustion phenomenon known as stochastic pre-ignition or low-speed pre-ignition (or "LSPI"). LSPI is a pre-ignition event that may include very high pressure spikes, early combustion during an inappropriate crank angle, and knock. All of these, individually and in combination, have the potential to cause degradation and/or severe damage to the engine.

[0006] Pre-ignition is a form of combustion that results of ignition of the air-fuel mixture in the combustion chamber prior to the desired ignition of the air-fuel mixture by the igniter. Pre-ignition has typically been a problem during high speed engine operation since heat from operation of the engine may heat a part of the combustion chamber to a sufficient temperature to ignite the air-fuel mixture upon contact. This type of pre-ignition is sometimes referred to as hot-spot pre-ignition.

[0007] More recently, intermittent abnormal combustion has been observed in boosted internal combustion engines at low speeds and medium-to-high loads. For example, during operation of the engine at 3,000 rpm or less, under load, with a brake mean effective pressure (BMEP) of at least 1,000 kPa, low-speed pre-ignition (LSPI) may occur in a random and stochastic fashion. During low speed engine operation, the compression stroke time is longest.

[0008] U.S. Application Publication no. 2007/0129266 A1 relates to a lubricating oil composition comprising a base oil and one or more magnesium detergents for the reduction of clogging in a diesel particulate filter.

[0009] U.S. Application Publication no. 2003/182847 A1 relates to fuel additives, lubricating oil additives for diesel engines having diesel particulate filters, comprising molybdenum compounds with a measured sulfated ash content of 1.0 wt% or less, a sulfur content of 0.3 wt% or less, and a molybdenum content of 100 ppm or more.

SUMMARY AND TERMS

[0009a] In a first aspect, the present disclosure refers to a lubricating oil composition comprising:

a) greater than 50 wt.% of a base oil of lubricating viscosity, based on the total weight of the lubricating oil composition;
b) an amount of one or more calcium-containing detergents to provide less than 1700 ppm calcium, based on a total weight of the lubricating oil composition, and the one or more calcium-containing detergents excludes a calcium salicylate detergent,
c) an amount of one or more magnesium-containing detergents to provide less than 450 ppm magnesium, based on the total weight of the lubricating oil composition;
d) an amount of one or more molybdenum-containing compounds to provide less than 450 ppm molybdenum, based on the total weight of the lubricating oil composition;

e) from 700 ppm to 900 ppm of phosphorus, based on the total weight of the lubricating oil composition; and

f) a total measured sulfated ash content of no greater than 1.0 wt.%, as measured by ASTM D874, based on the total weight of the lubricating oil composition; and
a ratio, in ppm, of calcium from the one or more calcium-containing detergents to magnesium from the one or more magnesium-containing detergents of 1:1 or more, and
wherein the lubricating oil composition contains less than 10 ppm of boron, based on the total weight of the lubricating oil composition.

[0009b] In another aspect, the present disclosure refers to a method for reducing clogging in a diesel particulate filter comprising a step of operating an engine equipped with a diesel particulate filter and lubricated with a lubricating oil composition comprising:

a) greater than 50 wt.% of a base oil of lubricating viscosity, based on the total weight of the lubricating oil composition;

b) an amount of one or more calcium-containing detergents to provide less than 1700 ppm calcium, based on a total weight of the lubricating oil composition, and the one or more calcium-containing detergents excludes a calcium salicylate detergent;

c) an amount of one or more magnesium-containing detergents to provide less than 450 ppm magnesium, based on the total weight of the lubricating oil composition;

d) an amount of one or more molybdenum-containing compounds to provide less than 450 ppm molybdenum, based on the total weight of the lubricating oil composition;

e) from 700 ppm to 900 ppm of phosphorus, based on the total weight of the lubricating oil composition; and

f) a total sulfated ash content of no less than 0.5 wt.% and no greater than 1.0 wt.%, as measured by ASTM D874, based on a total weight of the lubricating oil composition; and

a ratio, in ppm, of calcium from the one or more calcium-containing detergents to magnesium from the one or more magnesium-containing detergents of 1:1 or more, and

wherein the lubricating oil composition contains less than 10 ppm of boron, based on the total weight of the lubricating oil composition.

[0010] The present disclosure relates to a lubricating oil composition including a calcium-containing detergent and a magnesium-containing detergent, and methods for reducing clogging in a diesel particulate filter including a step of operating an engine equipped with a diesel particulate filter and lubricated with the lubricating oil composition including a calcium-containing detergent and a magnesium-containing detergent.

[0011] In a first example, the present disclosure relates to a lubricating oil composition including one or more calcium-containing detergents and one or more magnesium-containing detergents. The lubricating oil composition of the present disclosure includes greater than 50 wt.% of a base oil of lubricating viscosity, an amount of one or more calcium-containing detergents to provide less than 1700 ppm calcium, an amount of one or more magnesium-containing detergents to provide less than 450 ppm magnesium, an amount of one or more molybdenum-containing compounds to provide less than 450 ppm of molybdenum, from about 700 ppm to about 900 ppm of phosphorus, and a total measured sulfated ash content of no greater than 1.0 wt.%, as measured by ASTM D874, all based on the total weight of the

lubricating oil composition, and a ratio, in ppm, of calcium from the one or more calcium-containing detergents to magnesium from the one or more magnesium-containing detergents of 1:1 or more.

[0012] In the foregoing example, the lubricating oil composition may provide a diesel particulate filter delta pressure (ΔP) vs. oil consumption result of 0.6 kPa/kg or less, 0.5 kPa/kg or less or 0.45 kPa/kg or less, as measured in a VW PV 1485 test after 144 hours.

[0013] In each of the foregoing examples, the lubricating oil composition may be effective to reduce low speed pre-ignition events in a boosted internal combustion engine lubricated with the lubricating oil composition relative to a number of low speed pre-ignition events in the same engine lubricated with reference lubricating oil R-1; or the reduction of LSPI events may be 50% or greater reduction and the LSPI events are LSPI counts during 25,000 engine cycles, wherein the engine is operated at 2000 revolutions per minute with brake mean effective pressure of 1,800 kPa.

[0014] In each of the foregoing examples, the one or more magnesium-containing detergents may provide 440 ppm or less of magnesium, or 430 ppm or less of magnesium, or 420 ppm or less of magnesium, or 410 ppm or less of magnesium, based on a total weight of the lubricating oil composition.

[0015] In each of the foregoing examples, the ratio of total calcium from the one or more calcium-containing detergents in ppm to total magnesium from the one or more magnesium-containing detergents may be more than 2.0, or more than 2.5, or more than 3.0, or more than 3.5, or less than 10.0, or less than 9.0, or less than 8.5, or more than 1.0 to less than 10.0.

[0016] In each of the foregoing examples, the one or more calcium-containing detergents may be overbased, having a total base number of greater than 200 mg KOH/g, or greater than 225 mg KOH/g, or greater than 250 mg KOH/g, as measured by the method of ASTM D-2896.

[0017] In each of the foregoing examples, the one or more calcium-containing detergents may be present in an amount sufficient to provide less than 1670 ppm calcium, or less than 1500 ppm calcium, or less than 1400 ppm calcium, or more than 1350 ppm to less than 1700 ppm calcium to the total weight of the lubricating oil composition.

[0018] In each of the foregoing examples, the total measured sulfated ash content may be less than 0.8 wt.%, or more than 0.6 wt.% to less than 1.0 wt.%, or more than 0.6 wt.% to less than 0.8 wt.%, each as measured by ASTM D874.

[0019] In each of the foregoing examples, the lubricating oil composition may provide an amount of one or more calcium-containing detergents having a total base number of up to 175 mg KOH/g as measured by the method of ASTM D-2896, if present, provides less than 50 ppm of calcium, or less than 20 ppm of calcium, or less than 5 ppm of calcium, or about 0 ppm of calcium, to the total weight of the lubricating oil composition.

[0020] In each of the foregoing examples, the lubricating oil composition may contain less than 100 ppm of boron, or less than 75 ppm of boron, or less than 50 ppm of boron, or less than 10 ppm of boron, or about 0 ppm of boron, based on a total weight of the lubricating oil composition.

[0021] In each of the foregoing examples, the lubricating oil composition may have more than 0 ppm of boron and a ratio of total metal in ppm to total boron in ppm of more than 7.5, or more than 50, or more than 75.

[0022] In each of the foregoing examples, the lubricating oil composition may contain 0 ppm to less than 100 ppm of boron, or 0 ppm to less than 75 ppm of boron, or 0 ppm to less than 50 ppm of boron, or 0 ppm to less than 10 ppm of boron.

[0023] In each of the foregoing examples, the one or more magnesium-containing detergents may be overbased having a total base number of greater than 225 mg KOH/g, or greater than 250 mg KOH/g, or greater than 300 mg KOH/g, or greater than 350 mg KOH/g, or greater than 400 mg KOH/g, as measured by the method of ASTM D-2896.

[0024] In each of the foregoing examples, the one or more calcium-containing detergents may optionally exclude a calcium salicylate detergent.

[0025] In each of the foregoing examples, the one or more magnesium-containing detergents may be an overbased magnesium sulfonate detergent having a total base number of greater than 225 mg KOH/g, or greater than 250 mg KOH/g, or greater than 300 mg KOH/g, or greater than 350 mg KOH/g, or greater than 400 mg KOH/g, as measured by the method of ASTM D-2896.

[0026] In each of the foregoing examples, the lubricating oil composition may be an engine oil composition.

[0027] In a second example, the present disclosure relates to a method for reducing clogging in a diesel particulate filter, including a step of operating an engine equipped with a diesel particulate filter and lubricated with a lubricating oil composition comprising greater than 50 wt.% of a base oil of lubricating viscosity, an amount of one or more calcium-containing detergents to provide less than 1700 ppm calcium, an amount of one or more magnesium-containing detergents to provide less than 450 ppm magnesium, an amount of

one or more molybdenum-containing compounds to provide less than 450 ppm of molybdenum, from about 700 ppm to about 900 ppm of phosphorus, and a total measured sulfated ash content of no greater than 1.0 wt.%, as measured by ASTM D874, all based on the total weight of the lubricating oil composition, and a ratio, in ppm, of calcium from the one or more calcium-containing detergents to magnesium from the one or more magnesium-containing detergents of 1:1 or more.

[0028] In this second example, the lubricating oil composition may provide a diesel particulate filter delta pressure (ΔP) vs. oil consumption result of 0.6 kPa/kg or less, 0.5 kPa/kg or less or 0.45 kPa/kg or less, as measured in a VW PV 1485 test after 144 hours.

[0029] In each of the foregoing second examples, the lubricating oil composition may be effective to reduce low speed pre-ignition events in a boosted internal combustion engine lubricated with the lubricating oil composition relative to a number of low speed pre-ignition events in the same engine lubricated with reference lubricating oil R-1; or the reduction of LSPI events may be 50% or greater reduction and the LSPI events are LSPI counts during 25,000 engine cycles, wherein the engine is operated at 2000 revolutions per minute with brake mean effective pressure of 1,800 kPa.

[0030] In each of the foregoing second examples, the one or more magnesium-containing detergents may provide 440 ppm or less of magnesium, or 430 ppm or less of magnesium, or 420 ppm or less of magnesium, or 410 ppm or less of magnesium, based on a total weight of the lubricating oil composition.

[0031] In each of the foregoing second examples, the ratio of total calcium from the one or more calcium-containing detergents in ppm to total magnesium from the one or more magnesium-containing detergents may be more than 2.0, or more than 2.5, or more than 3.0, or more than 3.5, or less than 10.0, or less than 9.0, or less than 8.5, or more than 1.0 to less than 10.0.

[0032] In each of the foregoing second examples, the one or more calcium-containing detergents may be overbased, having a total base number of greater than 200 mg KOH/g, or greater than 225 mg KOH/g, or greater than 250 mg KOH/g, as measured by the method of ASTM D-2896.

[0033] In each of the foregoing second examples, the one or more calcium-containing detergents may be present in an amount sufficient to provide less than 1670 ppm calcium, or less than 1500 ppm calcium, or less than 1400 ppm calcium, or more than 1350 ppm to less than 1700 ppm calcium to the total weight of the lubricating oil composition.

[0034] In each of the foregoing second examples, the total measured sulfated ash content may be less than 0.8 wt.%, or more than 0.6 wt.% to less than 1.0 wt.%, each as measured by ASTM D874.

[0035] In each of the foregoing second examples, the lubricating oil composition may provide an amount of one or more calcium-containing detergents having a total base number of up to 175 mg KOH/g as measured by the method of ASTM D-2896, if present, provides less than 50 ppm of calcium, or less than 20 ppm of calcium, or less than 5 ppm of calcium, or about 0 ppm of calcium, to the total weight of the lubricating oil composition.

[0036] In each of the foregoing second examples, the lubricating oil composition may contain less than 100 ppm of boron, or less than 75 ppm of boron, or less than 50 ppm of boron, or less than 10 ppm of boron, or about 0 ppm of boron, based on a total weight of the lubricating oil composition.

[0037] In each of the foregoing second examples, the lubricating oil composition may have more than 0 ppm of boron and a ratio of total metal in ppm to total boron in ppm of more than 7.5, or more than 50, or more than 500.

[0038] In each of the foregoing examples, the lubricating oil composition may contain 0 ppm to less than 100 ppm of boron, or 0 ppm to less than 75 ppm of boron, or 0 ppm to less than 50 ppm of boron, or 0 ppm to less than 10 ppm of boron.

[0039] In each of the foregoing second examples, the one or more magnesium-containing detergents may be overbased having a total base number of greater than 225 mg KOH/g, or greater than 250 mg KOH/g, or greater than 300 mg KOH/g, or greater than 350 mg KOH/g, or greater than 400 mg KOH/g, as measured by the method of ASTM D-2896.

[0040] In each of the foregoing second examples, the one or more calcium-containing detergents may optionally exclude a calcium salicylate detergent.

[0041] In each of the foregoing second examples, the one or more magnesium-containing detergents may be an overbased magnesium sulfonate detergent having a total base number of greater than 225 mg KOH/g, or greater than 250 mg KOH/g, or greater than 300 mg KOH/g, or greater than 350 mg KOH/g, or greater than 400 mg KOH/g, as measured by the method of ASTM D-2896.

[0042] In each of the foregoing second examples, the lubricating oil composition may be an engine oil composition.

[0043] The following definitions of terms are provided in order to clarify the meanings of certain terms as used herein.

[0044] The terms "oil composition," "lubrication composition," "lubricating oil composition," "lubricating oil," "lubricant composition," "lubricating composition," "fully formulated lubricant composition," "lubricant," "crankcase oil," "crankcase lubricant," "engine oil," "engine lubricant," "motor oil," and "motor lubricant" are considered synonymous, fully interchangeable terminology referring to the finished lubrication product comprising a major amount of a base oil plus a minor amount of an additive composition.

[0045] As used herein, the terms "additive package," "additive concentrate," "additive composition," "engine oil additive package," "engine oil additive concentrate," "crankcase additive package," "crankcase additive concentrate," "motor oil additive package," "motor oil concentrate," are considered synonymous, fully interchangeable terminology referring the portion of the lubricating oil composition excluding the major amount of base oil stock mixture. The additive package may or may not include the viscosity index improver or pour point depressant.

[0046] The term "overbased" relates to metal salts, such as metal salts of sulfonates, carboxylates, salicylates, and/or phenates, wherein the amount of metal present exceeds the stoichiometric amount. Such salts may have a conversion level in excess of 100% (i.e., they may comprise more than 100% of the theoretical amount of metal needed to convert the acid to its "normal," "neutral" salt). The expression "metal ratio," often abbreviated as MR, is used to designate the ratio of total chemical equivalents of metal in the overbased salt to chemical equivalents of the metal in a neutral salt according to known chemical reactivity and stoichiometry. In a normal or neutral salt, the metal ratio is one and in an overbased salt, MR, is greater than one. They are commonly referred to as overbased, hyperbased, or superbased salts and may be salts of organic sulfur acids, carboxylic acids, salicylates, and/or phenols.

[0047] As used herein, the term "hydrocarbyl substituent" or "hydrocarbyl group" is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group having a carbon atom directly attached to the remainder of the molecule and having a predominantly hydrocarbon character. Each hydrocarbyl group is independently selected from hydrocarbon substituents, and substituted hydrocarbon substituents containing one or more of halo groups, hydroxyl groups, alkoxy groups, mercapto groups, nitro groups, nitroso groups, amino groups, pyridyl groups, furyl groups, imidazolyl groups, oxygen and nitrogen, and wherein no more than two non-hydrocarbon substituents are present for every ten carbon atoms in the hydrocarbyl group.

[0048] As used herein, the term "hydrocarbylene substituent" or "hydrocarbylene group" is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group that is directly attached at two locations of the molecule to the remainder of the molecule by a carbon atom and having predominantly hydrocarbon character. Each hydrocarbylene group is independently selected from divalent hydrocarbon substituents, and substituted divalent hydrocarbon substituents containing halo groups, alkyl groups, aryl groups, alkylaryl groups, arylalkyl groups, hydroxyl groups, alkoxy groups, mercapto groups, nitro groups, nitroso groups, amino groups, pyridyl groups, furyl groups, imidazolyl groups, oxygen and nitrogen, and wherein no more than two non-hydrocarbon substituents is present for every ten carbon atoms in the hydrocarbylene group.

[0049] As used herein, the term "percent by weight", unless expressly stated otherwise, means the percentage the recited component represents to the weight of the entire composition.

[0050] The terms “soluble,” "oil-soluble," or "dispersible" used herein may, but does not necessarily, indicate that the compounds or additives are soluble, dissolvable, miscible, or capable of being suspended in the oil in all proportions. The foregoing terms do mean, however, that they are, for instance, soluble, suspendable, dissolvable, or stably dispersible in oil to an extent sufficient to exert their intended effect in the environment in which the oil is employed. Moreover, the additional incorporation of other additives may also permit incorporation of higher levels of a particular additive, if desired.

[0051] The term "TBN" as employed herein is used to denote the Total Base Number in mg KOH/g as measured by the method of ASTM D2896 or ASTM D4739 or DIN 51639-1.

[0052] The term "alkyl" as employed herein refers to straight, branched, cyclic, and/or substituted saturated chain moieties of from about 1 to about 100 carbon atoms.

[0053] The term "alkenyl" as employed herein refers to straight, branched, cyclic, and/or substituted unsaturated chain moieties of from about 3 to about 10 carbon atoms.

[0054] The term “aryl” as employed herein refers to single and multi-ring aromatic compounds that may include alkyl, alkenyl, alkylaryl, amino, hydroxyl, alkoxy, halo substituents, and/or heteroatoms including, but not limited to, nitrogen, oxygen, and sulfur.

[0055] The clogging of diesel particulate filters can be measured by the Volkswagen (VW) diesel particulate filter test (DFT), VW PV 1485. The VW PV 1485 test measures the amount of sulfated ash deposits clogged into the diesel particulate filter of vehicles, thereby reducing filter life, raising back pressure in the vehicle engine and causing increased fuel

consumption. The diesel particulate filter test measures the increase in backpressure versus oil consumption, after 144 hours of an ash loading phase.

[0056] A reduction in low speed pre-ignition events may be expressed as an "LSPI Ratio." The term, "LSPI Ratio" refers to a ratio of the number of low speed pre-ignition events in a boosted internal combustion engine lubricated with the lubricating oil composition of the present disclosure to a number of low speed pre-ignition events in the same boosted internal combustion engine lubricated with reference lubricating oil R-1 described herein. A lubricating oil composition that reduces the LSPI ratio is effective to reduce low speed pre-ignition events in a boosted internal combustion engine lubricated with the lubricating oil composition relative to a number of low speed pre-ignition events in the same engine lubricated with reference lubricating oil R-1.

[0057] Lubricants, combinations of components, or individual components of the present description may be suitable for use in various types of internal combustion engines. Suitable engine types may include, but are not limited to heavy duty diesel, passenger car, light duty diesel, medium speed diesel, or marine engines. An internal combustion engine may be a diesel fueled engine, a gasoline fueled engine, a natural gas fueled engine, a bio-fueled engine, a mixed diesel/biofuel fueled engine, a mixed gasoline/biofuel fueled engine, an alcohol fueled engine, a mixed gasoline/alcohol fueled engine, a compressed natural gas (CNG) fueled engine, or mixtures thereof. A diesel engine may be a compression ignited engine. A gasoline engine may be a spark-ignited engine such as a boosted spark-ignited engine. An internal combustion engine may also be used in combination with an electrical or battery source of power. An engine so configured is commonly known as a hybrid engine. The internal combustion engine may be a 2-stroke, 4-stroke, or rotary engine. Suitable internal combustion engines include marine diesel engines (such as inland marine), aviation piston engines, low-load diesel engines, and motorcycle, automobile, locomotive, and truck engines.

[0058] Passenger and light-duty vehicles may be equipped with either a compression (diesel) or spark-ignition (gasoline) internal combustion engine. Generally engine oils are specially formulated for use in one or the other. However, it can be beneficial to lubricate a spark-ignition engine with an engine oil formulated for a diesel engine. Further, some diesel engine oils are tested to meet both diesel and gasoline engine oil specifications (i.e., mixed specifications), and, thus are recommend for use with either engine-type. Therefore, an oil that meets both diesel engine and gasoline engine specifications and that can handle each of these diverse engine conditions is desirable.

[0059] The internal combustion engine may contain components of one or more of an aluminum-alloy, lead, tin, copper, cast iron, magnesium, ceramics, stainless steel, composites, and/or mixtures thereof. The components may be coated, for example, with a diamond-like carbon coating, a lubrited coating, a phosphorus-containing coating, molybdenum-containing coating, a graphite coating, a nano-particle-containing coating, and/or mixtures thereof. The aluminum-alloy may include aluminum silicates, aluminum oxides, or other ceramic materials. In one example the aluminum-alloy is an aluminum-silicate surface. As used herein, the term "aluminum alloy" is intended to be synonymous with "aluminum composite" and to describe a component or surface comprising aluminum and another component intermixed or reacted on a microscopic or nearly microscopic level, regardless of the detailed structure thereof. This would include any conventional alloys with metals other than aluminum as well as composite or alloy-like structures with non-metallic elements or compounds such with ceramic-like materials.

[0060] The lubricating oil composition for an internal combustion engine may be suitable for any engine lubricant irrespective of the sulfur, phosphorus, or ash (ASTM D-874) content. The sulfur content of the engine oil lubricant may be about 1 wt% or less, or about 0.8 wt% or less, or about 0.5 wt% or less, or about 0.3 wt% or less, or about 0.2 wt% or less. In one example the sulfur content may be in the range of about 0.001 wt% to about 0.5 wt%, or about 0.01 wt% to about 0.3 wt%. The phosphorus content may be from about 700 ppm to about 900 ppm, or from no more than 850 ppm. The total measured sulfated ash content may be no less than 0.5 wt% to no greater than 1.0 wt%,, or less than 0.8 wt%, or more than 0.5 wt% to less than 1.0 wt%, or more than 0.6 wt% to less than 1.0 wt%, as measured by ASTM D874. In another example, the sulfur content may be about 0.4 wt% or less, the phosphorus content may be about 0.08 wt% or less, and the measured sulfated ash is no less than 0.5 wt% to 1 wt% or less. In yet another example the sulfur content may be about 0.3 wt% or less, the phosphorus content is about 0.05 wt% or less, and the measured sulfated ash may be about 0.8 wt% or less.

[0061] In one example the lubricating oil composition is an engine oil, wherein the lubricating oil composition may have (i) a sulfur content of about 0.5 wt% or less, (ii) a phosphorus content of about 0.1 wt% or less, and (iii) a measured sulfated ash content of no less than 0.5 wt% to no greater than 1.0 wt%.

[0062] In one example, the lubricating oil composition contains less than 10 ppm of boron, or less than 50 ppm or boron, or less than 10 ppm or boron, or 0 ppm of boron, based on a total weight of the lubricating oil composition. In another example, the

lubricating oil composition has more than 0 ppm of boron and the ratio of total metal in ppm to total boron in ppm is more than 7.5, or more than 50, or more than 500.

[0063] In one example the lubricating oil composition is suitable for a 2-stroke or a 4-stroke marine diesel internal combustion engine. In one example the marine diesel combustion engine is a 2-stroke engine. In some examples, the lubricating oil composition is not suitable for a 2-stroke or a 4-stroke marine diesel internal combustion engine for one or more reasons, including but not limited to, the high sulfur content of fuel used in powering a marine engine and the high TBN required for a marine-suitable engine oil (e.g., above about 40 TBN in a marine-suitable engine oil).

[0064] In some examples, the lubricating oil composition is suitable for use with engines powered by low sulfur fuels, such as fuels containing about 1 to about 5% sulfur. Highway vehicle fuels contain about 15 ppm sulfur (or about 0.0015% sulfur).

[0065] Low speed diesel typically refers to marine engines, medium speed diesel typically refers to locomotives, and high speed diesel typically refers to highway vehicles. The lubricating oil composition may be suitable for only one of these types or all.

[0066] Further, lubricants of the present description may be suitable to meet one or more industry specification requirements such as ILSAC GF-3, GF-4, GF-5, GF-5+, GF-6, PC-11, CF, CK-4, FA-4, CF-4, CH-4, CI-4, CJ-4, API SG, SJ, SL, SM, SN, SN+, ACEA A1/B1, A2/B2, A3/B3, A3/B4, A5/B5, C1, C2, C3, C4, C5, E4/E6/E7/E9, Euro 5/6,Jaso DL-1, Low SAPS, Mid SAPS, or original equipment manufacturer specifications such as Dexos™ 1, Dexos™ 2, MB-Approval 229.1, 229.3, 229.5, 229.31, 229.51, 229.52, 229.6, 229.71, 226.5, 226.51, 228.0/.1, 228.2/.3, 228.31, 228.5, 228.51, 228.61, VW 501.01, 502.00, 503.00/503.01, 504.00, 505.00, 505.01, 506.00/506.01, 507.00, 508.00, 509.00, 508.88, 509.99, BMW Longlife-01, Longlife-01 FE, Longlife-04, Longlife-12 FE, Longlife-14 FE+, Longlife-17 FE+, Porsche A40, C30, Peugeot Citroën Automobiles B71 2290, B71 2294, B71 2295, B71 2296, B71 2297, B71 2300, B71 2302, B71 2312, B71 2007, B71 2008, Renault RN0700, RN0710, RN0720, Ford WSS-M2C153-H, WSS-M2C930-A, WSS-M2C945-A, WSS-M2C913A, WSS-M2C913-B, WSS-M2C913-C, WSS-M2C913-D, WSS-M2C948-B, WSS-M2C948-A, GM 6094-M, Chrysler MS-6395, Fiat 9.55535 G1, G2, M2, N1, N2, Z2, S1, S2, S3, S4, T2, DS1, DSX, GH2, GS1, GSX, CR1, Jaguar Land Rover STJLR.03.5003, STJLR.03.5004, STJLR.03.5005, STJLR.03.5006, STJLR.03.5007, STJLR.51.5122, or any past or future PCMO or HDD specifications not mentioned herein. In some examples for passenger car motor oil (PCMO) applications, the amount of phosphorus in the finished fluid is 1000 ppm or less or 900 ppm or less or 800 ppm or less.

[0067] Other hardware may not be suitable for use with the disclosed lubricant. A "functional fluid" is a term which encompasses a variety of fluids including but not limited to tractor hydraulic fluids, power transmission fluids including automatic transmission fluids, continuously variable transmission fluids and manual transmission fluids, hydraulic fluids, including tractor hydraulic fluids, some gear oils, power steering fluids, fluids used in wind turbines, compressors, some industrial fluids, and fluids related to power train components. It should be noted that within each of these fluids such as, for example, automatic transmission fluids, there are a variety of different types of fluids due to the various transmissions having different designs which have led to the need for fluids of markedly different functional characteristics. This is contrasted by the term "lubricating fluid" which is not used to generate or transfer power.

[0068] With respect to tractor hydraulic fluids, for example, these fluids are all-purpose products used for all lubricant applications in a tractor except for lubricating the engine. These lubricating applications may include lubrication of gearboxes, power take-off and clutch(es), rear axles, reduction gears, wet brakes, and hydraulic accessories.

[0069] When the functional fluid is an automatic transmission fluid, the automatic transmission fluids must have enough friction for the clutch plates to transfer power. However, the friction coefficient of fluids has a tendency to decline due to the temperature effects as the fluid heats up during operation. It is important that the tractor hydraulic fluid or automatic transmission fluid maintain its high friction coefficient at elevated temperatures, otherwise brake systems or automatic transmissions may fail. This is not a function of an engine oil.

[0070] Tractor fluids, and for example Super Tractor Universal Oils (STUOs) or Universal Tractor Transmission Oils (UTTOs), may combine the performance of engine oils with transmissions, differentials, final-drive planetary gears, wet-brakes, and hydraulic performance. While many of the additives used to formulate a UTTO or a STUO fluid are similar in functionality, they may have deleterious effect if not incorporated properly. For example, some anti-wear and extreme pressure additives used in engine oils can be extremely corrosive to the copper components in hydraulic pumps. Detergents and dispersants used for gasoline or diesel engine performance may be detrimental to wet brake performance. Friction modifiers specific to quiet wet brake noise, may lack the thermal stability required for engine oil performance. Each of these fluids, whether functional, tractor, or lubricating, are designed to meet specific and stringent manufacturer requirements.

[0071] The present disclosure provides novel lubricating oil blends formulated for use as automotive crankcase lubricants. The present disclosure provides novel lubricating oil blends formulated for use as 2T and/or 4T motorcycle crankcase lubricants. Examples of the present disclosure may provide lubricating oils suitable for crankcase applications and having improvements in the following characteristics: air entrainment, alcohol fuel compatibility, antioxidancy, antiwear performance, biofuel compatibility, foam reducing properties, friction reduction, fuel economy, preignition prevention, rust inhibition, sludge and/or soot dispersability, piston cleanliness, deposit formation, and water tolerance.

[0072] Engine oils of the present disclosure may be formulated by the addition of one or more additives, as described in detail below, to an appropriate base oil formulation. The additives may be combined with a base oil in the form of an additive package (or concentrate) or, alternatively, may be combined individually with a base oil (or a mixture of both). The fully formulated engine oil may exhibit improved performance properties, based on the additives added and their respective proportions.

[0073] Additional details and advantages of the present disclosure will be set forth in part in the description which follows, and/or may be learned by practice of the present disclosure. The details and advantages of the present disclosure may be realized and attained by means of the elements and combinations particularly pointed out in the appended claims. It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the present disclosure, as claimed.

DETAILED DESCRIPTION

[0074] Various embodiments of the disclosure provide a lubricating oil composition and methods for reducing clogging in a diesel particulate filter. The lubricating oil composition may be useful in compression (diesel) engines and/or spark-ignited (gasoline) engines. In particular, engines in which the lubricating oil composition may be employed may include boosted internal combustion engines such as turbocharged and supercharged internal combustion engines. The boosted internal combustion engines include spark-ignited, direct injection and/or port-fuel injection engines. Preferably, the boosted internal combustion engine is a spark-ignited internal combustion engine or a direct injection engine.

[0075] In a first aspect, the present disclosure provides a lubricating oil composition that includes greater than 50 wt.% of a base oil of lubricating viscosity, an amount of one or more calcium-containing detergents to provide less than 1700 ppm calcium, an amount of one

or more magnesium-containing detergents to provide less than 450 ppm magnesium, an amount of one or more molybdenum-containing compounds to provide less than 450 ppm molybdenum, from about 700 ppm to about 900 ppm of phosphorus, based on the total weight of the lubricating oil composition, and a total measured sulfated ash content of no greater than 1.0 wt.%, as measured by ASTM D874, all based on the total weight of the lubricating oil composition, and a ratio, in ppm, of calcium from the one or more calcium-containing detergents to magnesium from the one or more magnesium-containing detergents of 1:1 or more.

[0076] In a second aspect, the present invention relates to a method of reducing clogging in a diesel particulate filter, including a step of operating an engine equipped with a diesel particulate filter and lubricated with the lubricating oil composition herein.

[0077] The foregoing lubricating oil compositions and methods may provide a diesel particulate filter delta pressure (ΔP) vs. oil consumption result of 0.6 kPa/kg or less, 0,5 kPa/kg or less, or 0.45 kPa/kg or less, as measured in a VW PV 1485 test after 144 hours.

[0078] Preferably, the lubricating oil compositions and methods are also effective to reduce low speed pre-ignition events in a boosted internal combustion engine lubricated with the lubricating oil composition relative to a number of low speed pre-ignition events in the same engine lubricated with reference lubricating oil R-1; or to provide a reduction of LSPI events is 50% or greater reduction and the LSPI events are LSPI counts during 25,000 engine cycles, wherein the engine is operated at 2000 revolutions per minute with brake mean effective pressure of 1,800 kPa.

[0079] As described in more detail below, the embodiments of the disclosure may provide a significant and unexpected improvement in reducing clogging in a diesel particulate filter and optionally, a significant reduction low speed pre-ignition events while maintaining a relatively high calcium detergent concentration in the lubricating oil composition.

Base Oil

[0080] The base oil used in the lubricating oil compositions may be selected from any of the base oils in Groups I-V as specified in the American Petroleum Institute (API) Base Oil Interchangeability Guidelines. The five base oil groups are as follows:

Base oil Category	Sulfur (%)		Saturates (%)	Viscosity Index
Group I	> 0.03	and/or	<90	80 to 120
Group II	≤0.03	and	≥90	80 to 120
Group III	≤0.03	and	≥90	≥120
Group IV	All polyalphaolefins (PAOs)			
Group V	All others not included in Groups I, II, III, or IV			

[0081] Groups I, II, and III are mineral oil process stocks. Group IV base oils contain true synthetic molecular species, which are produced by polymerization of olefinically unsaturated hydrocarbons. Many Group V base oils are also true synthetic products and may include diesters, polyol esters, polyalkylene glycols, alkylated aromatics, polyphosphate esters, polyvinyl ethers, and/or polyphenyl ethers, and the like, but may also be naturally occurring oils, such as vegetable oils. It should be noted that although Group III base oils are derived from mineral oil, the rigorous processing that these fluids undergo causes their physical properties to be very similar to some true synthetics, such as PAOs. Therefore, oils derived from Group III base oils may be referred to as synthetic fluids in the industry. Group II+ may comprise high viscosity index Group II.

[0082] The base oil used in the disclosed lubricating oil composition may be a mineral oil, animal oil, vegetable oil, synthetic oil, synthetic oil blends, or mixtures thereof. Suitable oils may be derived from hydrocracking, hydrogenation, hydrofinishing, unrefined, refined, and re-refined oils, and mixtures thereof.

[0083] Unrefined oils are those derived from a natural, mineral, or synthetic source without or with little further purification treatment. Refined oils are similar to the unrefined oils except that they have been treated in one or more purification steps, which may result in the improvement of one or more properties. Examples of suitable purification techniques are solvent extraction, secondary distillation, acid or base extraction, filtration, percolation, and the like. Oils refined to the quality of an edible may or may not be useful. Edible oils may also be called white oils. In some embodiments, lubricating oil compositions are free of edible or white oils.

[0084] Re-refined oils are also known as reclaimed or reprocessed oils. These oils are obtained similarly to refined oils using the same or similar processes. Often these oils are

additionally processed by techniques directed to removal of spent additives and oil breakdown products.

[0085] Mineral oils may include oils obtained by drilling or from plants and animals or any mixtures thereof. For example such oils may include, but are not limited to, castor oil, lard oil, olive oil, peanut oil, corn oil, soybean oil, and linseed oil, as well as mineral lubricating oils, such as liquid petroleum oils and solvent-treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic or mixed paraffinic-naphthenic types. Such oils may be partially or fully hydrogenated, if desired. Oils derived from coal or shale may also be useful.

[0086] Useful synthetic lubricating oils may include hydrocarbon oils such as polymerized, oligomerized, or interpolymerized olefins (e.g., polybutylenes, polypropylenes, propyleneisobutylene copolymers); poly(1-hexenes), poly(1-octenes), trimers or oligomers of 1-decene, e.g., poly(1-decenes), such materials being often referred to as α-olefins, and mixtures thereof; alkyl-benzenes (e.g. dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di-(2-ethylhexyl)-benzenes); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenyls); diphenyl alkanes, alkylated diphenyl alkanes, alkylated diphenyl ethers and alkylated diphenyl sulfides and the derivatives, analogs and homologs thereof or mixtures thereof. Polyalphaolefins are typically hydrogenated materials.

[0087] Other synthetic lubricating oils include polyol esters, diesters, liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, and the diethyl ester of decane phosphonic acid), or polymeric tetrahydrofurans. Synthetic oils may be produced by Fischer-Tropsch reactions and typically may be hydroisomerized Fischer-Tropsch hydrocarbons or waxes. In one embodiment oils may be prepared by a Fischer-Tropsch gas-to-liquid synthetic procedure as well as other gas-to-liquid oils.

[0088] The major amount of base oil included in a lubricating composition may be selected from the group consisting of Group I, Group II, a Group III, a Group IV, a Group V, and a combination of two or more of the foregoing, and wherein the major amount of base oil is other than base oils that arise from provision of additive components or viscosity index improvers in the composition. In another embodiment, the major amount of base oil included in a lubricating composition may be selected from the group consisting of Group II, a Group III, a Group IV, a Group V, and a combination of two or more of the foregoing, and wherein the major amount of base oil is other than base oils that arise from provision of additive components or viscosity index improvers in the composition.

[0089] The amount of the oil of lubricating viscosity present may be the balance remaining after subtracting from 100 wt% the sum of the amount of the performance additives inclusive of viscosity index improver(s) and/or pour point depressant(s) and/or other top treat additives. For example, the oil of lubricating viscosity that may be present in a finished fluid may be a major amount, such as greater than about 50 wt%, greater than about 60 wt%, greater than about 70 wt%, greater than about 80 wt%, greater than about 85 wt%, or greater than about 90 wt%.

Detergents

[0090] The lubricating oil composition comprises one or more calcium-containing detergents and optionally one or more magnesium-containing detergents. The one or more calcium-containing detergents and the one or more magnesium-containing detergents may be independently selected from neutral, low based, or overbased detergents, and mixtures thereof. Suitable detergent substrates include phenates, sulfur containing phenates, sulfonates, calixarates, salixarates, salicylates, carboxylic acids, phosphorus acids, mono- and/or di-thiophosphoric acids, alkyl phenols, sulfur coupled alkyl phenol compounds, or methylene bridged phenols. Suitable detergents and their methods of preparation are described in greater detail in numerous patent publications, including US 7,732,390 and references cited therein.

[0091] The detergent substrate may be salted with an alkali or alkaline earth metal such as, but not limited to, calcium, magnesium, potassium, sodium, lithium, barium, or mixtures thereof. In some embodiments, the detergent is free of barium. A suitable detergent may include alkali or alkaline earth metal salts of petroleum sulfonic acids and long chain mono- or di-alkylarylsulfonic acids with the aryl group being benzyl, tolyl, and xylyl. Examples of suitable additional detergents include, but are not limited to, calcium phenates, calcium sulfur containing phenates, calcium sulfonates, calcium calixarates, calcium salixarates, calcium salicylates, calcium carboxylic acids, calcium phosphorus acids, calcium mono- and/or di-thiophosphoric acids, calcium alkyl phenols, calcium sulfur coupled alkyl phenol compounds, calcium methylene bridged phenols, magnesium phenates, magnesium sulfur containing phenates, magnesium sulfonates, magnesium calixarates, magnesium salixarates, magnesium salicylates, magnesium carboxylic acids, magnesium phosphorus acids, magnesium mono- and/or di-thiophosphoric acids, magnesium alkyl phenols, magnesium sulfur coupled alkyl phenol compounds, magnesium methylene bridged phenols, sodium phenates, sodium sulfur containing phenates, sodium sulfonates, sodium calixarates,

sodium salixarates, sodium salicylates, sodium carboxylic acids, sodium phosphorus acids, sodium mono- and/or di-thiophosphoric acids, sodium alkyl phenols, sodium sulfur coupled alkyl phenol compounds, or sodium methylene bridged phenols.

[0092] Overbased detergents are well known in the art and may be alkali or alkaline earth metal overbased detergent additives. Such detergent additives may be prepared by reacting a metal oxide or metal hydroxide with a substrate and carbon dioxide gas. The substrate is typically an acid, for example, an acid such as an aliphatic substituted sulfonic acid, an aliphatic substituted carboxylic acid, or an aliphatic substituted phenol.

[0093] The terminology "overbased" relates to metal salts, such as metal salts of sulfonates, carboxylates, and phenates, wherein the amount of metal present exceeds the stoichiometric amount. Such salts may have a conversion level in excess of 100% (i.e., they may comprise more than 100% of the theoretical amount of metal needed to convert the acid to its "normal," "neutral" salt). The expression "metal ratio," often abbreviated as MR, is used to designate the ratio of total chemical equivalents of metal in the overbased salt to chemical equivalents of the metal in a neutral salt according to known chemical reactivity and stoichiometry. In a normal or neutral salt, the metal ratio is one and in an overbased salt, MR, is greater than one. They are commonly referred to as overbased, hyperbased, or superbased salts and may be salts of organic sulfur acids, carboxylic acids, or phenols.

[0094] An overbased detergent of the lubricating oil composition may have a total base number (TBN) of about 200 mg KOH/gram or greater, or as further examples, about 250 mg KOH/gram or greater, or about 350 mg KOH/gram or greater, or about 375 mg KOH/gram or greater, or about 400 mg KOH/gram or greater.

[0095] Examples of suitable overbased detergents include, but are not limited to, overbased calcium phenates, overbased calcium sulfur containing phenates, overbased calcium sulfonates, overbased calcium calixarates, overbased calcium salixarates, overbased calcium salicylates, overbased calcium carboxylic acids, overbased calcium phosphorus acids, overbased calcium mono- and/or di-thiophosphoric acids, overbased calcium alkyl phenols, overbased calcium sulfur coupled alkyl phenol compounds, overbased calcium methylene bridged phenols, overbased magnesium phenates, overbased magnesium sulfur containing phenates, overbased magnesium sulfonates, overbased magnesium calixarates, overbased magnesium salixarates, overbased magnesium salicylates, overbased magnesium carboxylic acids, overbased magnesium phosphorus acids, overbased magnesium mono- and/or di-thiophosphoric acids, overbased magnesium alkyl phenols, overbased magnesium

sulfur coupled alkyl phenol compounds, or overbased magnesium methylene bridged phenols.

[0096] An overbased calcium detergent may have a total base number of at least 150 mg KOH/g, at least about 225 mg KOH/g, at least 225 mg KOH/g to about 400 mg KOH/g, at least about 225 mg KOH/g to about 350 mg KOH/g or about 230 to about 350 mg KOH/g, all as measured by the method of ASTM D-2896. When such detergent compositions are formed in an inert diluent, e.g. a process oil, usually a mineral oil, the total base number reflects the basicity of the overall composition including diluent, and any other materials (e.g., promoter, etc.) that may be contained in the detergent composition.

[0097] The overbased detergent may have a metal to substrate ratio of from 1.1:1, or from 2:1, or from 4:1, or from 5:1, or from 7:1, or from 10:1.

[0098] In some embodiments, a detergent is effective at reducing or preventing rust in an engine.

[0099] The total detergent may be present up to 10 wt%, or about up to 8 wt%, or about up to 4 wt%, or greater than about 4 wt% to about 8 wt%, based on a total weight of the lubricating oil composition.

[00100] The one or more calcium-containing detergents may be present in an amount to provide less than 1700 ppm calcium, or less than 1670 ppm calcium, or less than 1500 ppm calcium, or less than 1400 ppm calcium; or more than 1350 ppm to less than 1700 ppm calcium, or more than 1350 ppm to less than 1670 ppm calcium, or more than 1350 ppm to less than 1500 ppm calcium, or more than 1350 ppm to less than 1400 ppm calcium based on the total weight of the lubricating oil composition.

[00101] In some embodiments, the one or more calcium-containing detergents is overbased having a total base number of greater than 200 mg KOH/g, greater than 225 mg KOH/g, or greater than 250 mg KOH/g or more, as measured by the method of ASTM D-2896.

[00102] In some embodiments, the one or more calcium-containing detergents excludes calcium salicylate.

[00103] In another embodiment, the lubricating oil composition may include one or more calcium-containing detergents having a total base number of up to 175 mg KOH/g as measured by the method of ASTM D-2896, and provides less than 50 ppm of calcium, or less than 20 ppm of calcium; or less than 5 ppm of calcium, or about 0 ppm of calcium to the total weight of the lubricating oil composition.

[00104] The one or more magnesium-containing detergents may be present in an amount to provide less than 450 ppm magnesium, or 450 ppm or less of magnesium, or 440 ppm or less of magnesium, or 430 ppm or less of magnesium, or 420 ppm or less of magnesium, or 410 ppm or less of magnesium, or less than 400 ppm of magnesium, or less than 350 ppm of magnesium, or less than 300 ppm of magnesium.

[00105] In some embodiments, the one or more magnesium-containing detergents is overbased having a total base number of greater than 225 mg KOH/g, or greater than 250 mg KOH/g, or greater than 300 mg KOH/g, or greater than 350 mg KOH/g, or greater than 400 mg KOH/g, as measured by the method of ASTM D-2896.

[00106] In other embodiments, the one or more magnesium-containing detergents is an overbased magnesium sulfonate detergent having a total base number of greater than 225 mg KOH/g, or greater than 250 mg KOH/g, or greater than 300 mg KOH/g, or greater than 350 mg KOH/g, or greater 400 mg KOH/g, as measured by the method of ASTM D-2896.

[00107] In some embodiments, the ratio, in ppm, of calcium from the one or more calcium-containing detergents to magnesium from the one or more magnesium-containing detergents is 1 or more, or more than 2.0, or more than 2.5, or more than 3.0, or more than 3.5, or less than 10.0, or less than 9.0, or less than 8.5, or more than 1.0 to less than 10.0.

[00108] In an alternative embodiment, the lubricating oil composition optionally contains not more than 15 ppm of magnesium or not more than 10 ppm of magnesium from detergents.

Molybdenum-containing component

[00109] The lubricating oil compositions herein comprises one or more molybdenum-containing compounds. An oil-soluble molybdenum compound may have the functional performance of an antiwear agent, an antioxidant, a friction modifier, or mixtures thereof. An oil-soluble molybdenum compound may include molybdenum dithiocarbamates, molybdenum dialkyldithiophosphates, molybdenum dithiophosphinates, amine salts of molybdenum compounds, molybdenum xanthates, molybdenum thioxanthates, molybdenum sulfides, molybdenum carboxylates, molybdenum alkoxides, a trinuclear organo-molybdenum compound, and/or mixtures thereof. The molybdenum sulfides include molybdenum disulfide. The molybdenum disulfide may be in the form of a stable dispersion. In one embodiment the oil-soluble molybdenum compound may be selected from the group consisting of molybdenum dithiocarbamates, molybdenum dialkyldithiophosphates, amine

salts of molybdenum compounds, and mixtures thereof. In one embodiment the oil-soluble molybdenum compound may be a molybdenum dithiocarbamate.

[00110] Suitable examples of molybdenum compounds which may be used include commercial materials sold under the trade names such as Molyvan 822™, Molyvan™ A, Molyvan 2000™ and Molyvan 855™ from R. T. Vanderbilt Co., Ltd., and Sakura-Lube™ S-165, S-200, S-300, S-310G, S-525, S-600, S-700, and S-710 available from Adeka Corporation, and mixtures thereof. Suitable molybdenum components are described in US 5,650,381; US RE 37,363 E1; US RE 38,929 E1; and US RE 40,595 E1, incorporated herein by reference in their entireties. Preferably, the one or more molybdenum-containing compounds may be the reaction product of a fatty acid ester and molybdenum oxide. Preferably, the fatty acid ester has from 4 to 30 carbon atoms, or from 6 to 20 carbon atoms.

[00111] Additionally, the molybdenum compound may be an acidic molybdenum compound. Included are molybdic acid, ammonium molybdate, sodium molybdate, potassium molybdate, and other alkaline metal molybdates and other molybdenum salts, e.g., hydrogen sodium molybdate, MoOCl4, MoO2Br2, Mo2O3Cl6, molybdenum trioxide or similar acidic molybdenum compounds. Alternatively, the compositions can be provided with molybdenum by molybdenum/sulfur complexes of basic nitrogen compounds as described, for example, in U.S. Pat. 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, incorporated herein by reference in their entireties.

[00112] Another class of suitable organo-molybdenum compounds are trinuclear molybdenum compounds, such as those of the formula Mo3SkLnQz and mixtures thereof, wherein S represents sulfur, L represents 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 may be present among all the ligands' organo groups, such as at least 25, at least 30, or at least 35 carbon atoms. Additional suitable molybdenum compounds are described in U.S. Pat. No. 6,723,685, herein incorporated by reference in its entirety.

[00113] The oil-soluble molybdenum compound may be present in an amount sufficient to provide less than about 450 ppm, or less than about 420 ppm, or less than about 400 ppm, or less than about 390 ppm of molybdenum, or more than 5 ppm of molybdenum, or more than 50 ppm of molybdenum, or more than 80 ppm of molybdenum, or more than

100 ppm of molybdenum, or more than 5 ppm to less than 450 ppm of molybdenum, or more than 50 ppm to less than 420 ppm of molybdenum, or more than 80 ppm to less than 400 ppm of molybdenum, or more than 100 ppm to less than 390 ppm of molybdenum, based on the total weight of the lubricating oil composition.

[00114] The lubricating oil composition may also include one or more optional components selected from the various additives set forth below.

Boron-Containing Compounds

[00115] The lubricating oil compositions herein may optionally contain one or more boron-containing compounds.

[00116] Examples of boron-containing compounds include borate esters, borated fatty amines, borated epoxides, borated detergents, and borated dispersants, such as borated succinimide dispersants, as disclosed in U.S. Patent No. 5,883,057.

[00117] The boron-containing compound, if present, can be used in an amount sufficient to provide up to about 8 wt%, about 0.01 wt% to about 7 wt%, about 0.05 wt% to about 5 wt%, or about 0.1 wt% to about 3 wt% of the lubricating oil composition.

[00118] In some embodiments of the invention, the lubricating oil composition may contain less than 100 ppm of boron, or less than 75 ppm of boron, or less than 50 ppm of boron, or less than 10 ppm of boron, or about 0 ppm of boron, based on a total weight of the lubricating oil composition.

[00119] In some embodiments, the lubricating oil composition may have more than 0 ppm of boron and a ratio of total metal in ppm to total boron in ppm of more than 7.5, or more than 50, or more than 500.

Antioxidants

[00120] The lubricating oil compositions herein also may optionally contain one or more antioxidants. Antioxidant compounds are known and include for example, phenates, phenate sulfides, sulfurized olefins, phosphosulfurized terpenes, sulfurized esters, aromatic amines, alkylated diphenylamines (e.g., nonyl diphenylamine, di-nonyl diphenylamine, octyl diphenylamine, di-octyl diphenylamine), phenyl-alpha-naphthylamines, alkylated phenyl-alpha-naphthylamines, hindered non-aromatic amines, phenols, hindered phenols, oil-soluble molybdenum compounds, macromolecular antioxidants, or mixtures thereof. Antioxidant compounds may be used alone or in combination.

[00121] The hindered phenol antioxidant may contain a secondary butyl and/or a tertiary butyl group as a sterically hindering group. The phenol group may be further substituted with a hydrocarbyl group and/or a bridging group linking to a second aromatic group. Examples of suitable hindered phenol antioxidants include 2,6-di-tert-butylphenol, 4-methyl-2,6-di-tert-butylphenol, 4-ethyl-2,6-di-tert-butylphenol, 4-propyl-2,6-di-tert-butylphenol or 4-butyl-2,6-di-tert-butylphenol, or 4-dodecyl-2,6-di-tert-butylphenol. In one embodiment the hindered phenol antioxidant may be an ester and may include, e.g., Irganox™ L-135 available from BASF or an addition product derived from 2,6-di-tert-butylphenol and an alkyl acrylate, wherein the alkyl group may contain about 1 to about 18, or about 2 to about 12, or about 2 to about 8, or about 2 to about 6, or about 4 carbon atoms. Another commercially available hindered phenol antioxidant may be an ester and may include Ethanox™ 4716 available from Albemarle Corporation.

[00122] Useful antioxidants may include diarylamines and high molecular weight phenols. In an embodiment, the lubricating oil composition may contain a mixture of a diarylamine and a high molecular weight phenol, such that each antioxidant may be present in an amount sufficient to provide up to about 5%, by weight, based upon the final weight of the lubricating oil composition. In an embodiment, the antioxidant may be a mixture of about 0.3 to about 1.5% diarylamine and about 0.4 to about 2.5% high molecular weight phenol, by weight, based upon the final weight of the lubricating oil composition.

[00123] Examples of suitable olefins that may be sulfurized to form a sulfurized olefin include propylene, butylene, isobutylene, polyisobutylene, pentene, hexene, heptene, octene, nonene, decene, undecene, dodecene, tridecene, tetradecene, pentadecene, hexadecene, heptadecene, octadecene, nonadecene, eicosene or mixtures thereof. In one embodiment, hexadecene, heptadecene, octadecene, nonadecene, eicosene or mixtures thereof and their dimers, trimers and tetramers are especially useful olefins. Alternatively, the olefin may be a Diels-Alder adduct of a diene such as 1,3-butadiene and an unsaturated ester, such as, butylacrylate.

[00124] Another class of sulfurized olefin includes sulfurized fatty acids and their esters. The fatty acids are often obtained from vegetable oil or animal oil and typically contain about 4 to about 22 carbon atoms. Examples of suitable fatty acids and their esters include triglycerides, oleic acid, linoleic acid, palmitoleic acid or mixtures thereof. Often, the fatty acids are obtained from lard oil, tall oil, peanut oil, soybean oil, cottonseed oil, sunflower seed oil or mixtures thereof. Fatty acids and/or ester may be mixed with olefins, such as α-olefins.

[00125] In another alternative embodiment the antioxidant composition also contains a molybdenum-containing antioxidant in addition to the phenolic and/or aminic antioxidants discussed above. When a combination of these three antioxidants is used, preferably the ratio of phenolic to aminic to molybdenum-containing is (0 to 2) : (0 to 2) : (0 to 1).

[00126] The one or more antioxidant(s) may be present in ranges about 0 wt% to about 20 wt%, or about 0.1 wt% to about 10 wt%, or about 0.6 wt% to about 5 wt%, or about 1.0 to about 3 wt% of the lubricating oil composition.

Antiwear Agents

[00127] The lubricating oil compositions herein also may optionally contain one or more antiwear agents. Examples of suitable antiwear agents include, but are not limited to, a metal thiophosphate; a metal dialkyldithiophosphate; a phosphoric acid ester or salt thereof; a phosphate ester(s); a phosphite; a phosphorus-containing carboxylic ester, ether, or amide; a sulfurized olefin; thiocarbamate-containing compounds including, thiocarbamate esters, alkylene-coupled thiocarbamates, and bis(S-alkyldithiocarbamyl)disulfides; and mixtures thereof. A suitable antiwear agent may be a molybdenum dithiocarbamate. The phosphorus containing antiwear agents are more fully described in European Patent 612 839. The metal in the dialkyl dithio phosphate salts may be an alkali metal, alkaline earth metal, aluminum, lead, tin, molybdenum, manganese, nickel, copper, titanium, or zinc. A useful antiwear agent may be zinc dialkyldithiophosphate.

[00128] Further examples of suitable antiwear agents include titanium compounds, tartrates, tartrimides, oil soluble amine salts of phosphorus compounds, sulfurized olefins, phosphites (such as dibutyl phosphite), phosphonates, thiocarbamate-containing compounds, such as thiocarbamate esters, thiocarbamate amides, thiocarbamic ethers, alkylene-coupled thiocarbamates, and bis(S-alkyldithiocarbamyl) disulfides. The tartrate or tartrimide may contain alkyl-ester groups, where the sum of carbon atoms on the alkyl groups may be at least 8. The antiwear agent may in one embodiment include a citrate.

[00129] The antiwear agent may be present in ranges including about 0 wt% to about 15 wt%, or about 0.01 wt% to about 10 wt%, or about 0.05 wt% to about 5 wt%, or about 0.1 wt% to about 3 wt% of the lubricating oil composition.

Additional Optional Detergents

[00130] The lubricating oil composition may comprise one or more neutral and/or low based detergents, as well as overbased detergents that do not contain calcium and mixtures

thereof. Suitable detergent substrates include phenates, sulfur containing phenates, sulfonates, calixarates, salixarates, salicylates, carboxylic acids, phosphorus acids, mono- and/or di-thiophosphoric acids, alkyl phenols, sulfur coupled alkyl phenol compounds, or methylene bridged phenols. Suitable detergents and their methods of preparation are described in greater detail in numerous patent publications, including US 7,732,390 and references cited therein. The detergent substrate may be salted with an alkali or alkaline earth metal such as, but not limited to, calcium, magnesium, potassium, sodium, lithium, barium, or mixtures thereof. In some embodiments, the detergent is free of barium. A suitable detergent may include alkali or alkaline earth metal salts of petroleum sulfonic acids and long chain mono- or di-alkylarylsulfonic acids with the aryl group being benzyl, tolyl, and xylyl. Examples of suitable detergents include, but are not limited to, calcium phenates, calcium sulfur containing phenates, calcium sulfonates, calcium calixarates, calcium salixarates, calcium salicylates, calcium carboxylic acids, calcium phosphorus acids, calcium mono- and/or di-thiophosphoric acids, calcium alkyl phenols, calcium sulfur coupled alkyl phenol compounds, calcium methylene bridged phenols, magnesium phenates, magnesium sulfur containing phenates, magnesium sulfonates, magnesium calixarates, magnesium salixarates, magnesium salicylates, magnesium carboxylic acids, magnesium phosphorus acids, magnesium mono- and/or di-thiophosphoric acids, magnesium alkyl phenols, magnesium sulfur coupled alkyl phenol compounds, magnesium methylene bridged phenols, sodium phenates, sodium sulfur containing phenates, sodium sulfonates, sodium calixarates, sodium salixarates, sodium salicylates, sodium carboxylic acids, sodium phosphorus acids, sodium mono- and/or di-thiophosphoric acids, sodium alkyl phenols, sodium sulfur coupled alkyl phenol compounds, or sodium methylene bridged phenols.

[00131] Overbased detergent additives are well known in the art and may be alkali or alkaline earth metal overbased detergent additives. Such detergent additives may be prepared by reacting a metal oxide or metal hydroxide with a substrate and carbon dioxide gas. The substrate is typically an acid, for example, an acid such as an aliphatic substituted sulfonic acid, an aliphatic substituted carboxylic acid, or an aliphatic substituted phenol.

[00132] The terminology "overbased" relates to metal salts, such as metal salts of sulfonates, carboxylates, and phenates, wherein the amount of metal present exceeds the stoichiometric amount. Such salts may have a conversion level in excess of 100% (i.e., they may comprise more than 100% of the theoretical amount of metal needed to convert the acid to its "normal," "neutral" salt). The expression "metal ratio," often abbreviated as MR, is used to designate the ratio of total chemical equivalents of metal in the overbased salt to chemical

equivalents of the metal in a neutral salt according to known chemical reactivity and stoichiometry. In a normal or neutral salt, the metal ratio is one and in an overbased salt, MR, is greater than one. They are commonly referred to as overbased, hyperbased, or superbased salts and may be salts of organic sulfur acids, carboxylic acids, or phenols.

[00133] An overbased detergent of the lubricating oil composition may have a total base number (TBN) of greater than 225 mg KOH/gram, or as further examples, about 250 mg KOH/gram or greater, or about 350 mg KOH/gram or greater, or about 375 mg KOH/gram or greater, or about 400 mg KOH/gram or greater.

[00134] Examples of suitable overbased detergents include, but are not limited to, overbased magnesium phenates, overbased magnesium sulfur containing phenates, overbased magnesium sulfonates, overbased magnesium calixarates, overbased magnesium salixarates, overbased magnesium salicylates, overbased magnesium carboxylic acids, overbased magnesium phosphorus acids, overbased magnesium mono- and/or di-thiophosphoric acids, overbased magnesium alkyl phenols, overbased magnesium sulfur coupled alkyl phenol compounds, or overbased magnesium methylene bridged phenols.

[00135] The overbased detergent may have a metal to substrate ratio of from 1.1:1, or from 2:1, or from 4:1, or from 5:1, or from 7:1, or from 10:1.

[00136] The low-based/neutral detergent has a TBN of up to 175 mg KOH/g, or up to 150 mg KOH/g. The low-based/neutral detergent may include a calcium-containing detergent. The low-based neutral calcium-containing detergent may be selected from a calcium sulfonate detergent, a calcium phenate detergent and a calcium salicylate detergent. In some embodiments, the low-based/neutral detergent is a calcium-containing detergent or a mixture of calcium-containing detergents. In some embodiments, the low-based/neutral detergent is a calcium sulfonate detergent or a calcium phenate detergent.

[00137] The low-based/neutral detergent may comprise at least 2.5 wt.% of the total detergent in the lubricating oil composition. In some embodiments, at least 4 wt.%, or at least 6 wt.%, or at least 8 wt.%, or at least 10 wt.% or at least 12 wt.% or at least 20 wt.% of the total detergent in the lubricating oil composition is a low-based/neutral detergent which may optionally be a low-based/neutral calcium-containing detergent.

[00138] In certain embodiments, the one or more low-based/neutral detergents provide from about 50 to about 1000 ppm calcium by weight to the lubricating oil composition based on a total weight of the lubricating oil composition. In some embodiments, the one or more low-based/neutral calcium-containing detergents provide from 75 to less than 800 ppm, or from

100 to 600 ppm, or from 125 to 500 ppm by weight calcium to the lubricating oil composition based on a total weight of the lubricating oil composition.

[00139] In some embodiments, a detergent is effective at reducing or preventing rust in an engine.

Dispersants

[00140] The lubricating oil composition may optionally further comprise one or more dispersants or mixtures thereof. Dispersants are often known as ashless-type dispersants because, prior to mixing in a lubricating oil composition, they do not contain ash-forming metals and they do not normally contribute any ash when added to a lubricant. Ashless type dispersants are characterized by a polar group attached to a relatively high molecular weight hydrocarbon chain, polymer, or copolymer. Typical ashless dispersants include N-substituted long chain alkenyl succinimides. Examples of N-substituted long chain alkenyl succinimides include polyisobutylene succinimides with a number average molecular weight of the polyisobutylene substituent in the range about 350 to about 50,000, or 350 to about 5,000, or 350 to about 3,000 and polyalphaolefin succinimides with a number average molecular weight of the polyalphaolefin substituent in the range of about 350 to about 10,000, or 350 to about 5,000 or 350 to about 3,000, as measured by gel permeation chromatography (GPC), using polystyrene as a calibration reference. Suitable polyalphaolefins include ethylene-alpha olefin copolymers such as ethylene-propylene copolymers.

[00141] Succinimide dispersants and their preparation are disclosed, for instance in U.S. Pat. No. 7,897,696 or U.S. Pat. No. 4,234,435. The polyolefin may be prepared from polymerizable monomers containing about 2 to about 16, or about 2 to about 8, or about 2 to about 6 carbon atoms. Succinimide dispersants are typically the imide formed from a polyamine, typically a poly(ethyleneamine).

[00142] Preferred amines are selected from polyamines and hydroxyamines. Examples of polyamines that may be used include, but are not limited to, diethylene triamine (DETA), triethylene tetramine (TETA), tetraethylene pentamine (TEPA), and higher homologues such as pentaethylamine hexamine (PEHA), and the like.

[00143] A suitable heavy polyamine is a mixture of polyalkylene-polyamines comprising small amounts of lower polyamine oligomers such as TEPA and PEHA (pentaethylene hexamine) but primarily oligomers with 6 or more nitrogen atoms, 2 or more primary amines per molecule, and more extensive branching than conventional polyamine mixtures. A heavy polyamine preferably includes polyamine oligomers containing 7 or more

nitrogens per molecule and with 2 or more primary amines per molecule. The heavy polyamine comprises more than 28 wt. % (e.g. >32 wt. %) total nitrogen and an equivalent weight of primary amine groups of 120-160 grams per equivalent.

[00144] Suitable polyamines are commonly known as PAM, and contain a mixture of ethylene amines where TEPA and pentaethylene hexamine (PEHA) are the major part of the polyamine, usually less than about 80%.

[00145] Typically PAM has 8.7-8.9 milliequivalents of primary amine per gram (an equivalent weight of 115 to 112 grams per equivalent of primary amine) and a total nitrogen content of about 33-34 wt. %. Heavier cuts of PAM oligomers with practically no TEPA and only very small amounts of PEHA but containing primarily oligomers with more than 6 nitrogens and more extensive branching, may produce dispersants with improved dispersancy.

[00146] In an embodiment the present disclosure further comprises at least one polyisobutylene succinimide dispersant derived from polyisobutylene with number average molecular weight in the range about 350 to about 50,000, or to about 5000, or to about 3000, as measured by gel permeation chromatography (GPC), using polystyrene as a calibration reference. The polyisobutylene succinimide may be used alone or in combination with other dispersants.

[00147] In some embodiments, polyisobutylene, when included, may have greater than 50 mol%, greater than 60 mol%, greater than 70 mol%, greater than 80 mol%, or greater than 90 mol% content of terminal double bonds. Such PIB is also referred to as highly reactive PIB ("HR-PIB"). HR-PIB having a number average molecular weight ranging from about 800 to about 5000 is suitable for use in embodiments of the present disclosure. Conventional PIB typically has less than 50 mol%, less than 40 mol%, less than 30 mol%, less than 20 mol%, or less than 10 mol% content of terminal double bonds.

[00148] An HR-PIB having a number average molecular weight ranging from about 900 to about 3000 may be suitable. Such HR-PIB is commercially available, or can be synthesized by the polymerization of isobutene in the presence of a non-chlorinated catalyst such as boron trifluoride, as described in US Patent No. 4,152,499 to Boerzel, et al. and U.S. Patent No. 5,739,355 to Gateau, et al. When used in the aforementioned thermal ene reaction, HR-PIB may lead to higher conversion rates in the reaction, as well as lower amounts of sediment formation, due to increased reactivity. A suitable method is described in U.S. Patent No. 7,897,696.

[00149] In one embodiment the present disclosure further comprises at least one dispersant derived from polyisobutylene succinic anhydride ("PIBSA"). The PIBSA may have an average of between about 1.0 and about 2.0 succinic acid moieties per polymer.

[00150] The % actives of the alkenyl or alkyl succinic anhydride can be determined using a chromatographic technique. This method is described in column 5 and 6 in U.S. Pat. No. 5,334,321.

[00151] The percent conversion of the polyolefin is calculated from the % actives using the equation in column 5 and 6 in U.S. Pat. No. 5,334,321.

[00152] Unless stated otherwise, all percentages are in weight percent and all molecular weights are number average molecular weights.

[00153] In one embodiment, the dispersant may be derived from a polyalphaolefin (PAO) succinic anhydride.

[00154] In one embodiment, the dispersant may be derived from olefin maleic anhydride copolymer. As an example, the dispersant may be described as a poly-PIBSA.

[00155] In an embodiment, the dispersant may be derived from an anhydride which is grafted to an ethylene-propylene copolymer.

[00156] One class of suitable dispersants may be Mannich bases. Mannich bases are materials that are formed by the condensation of a higher molecular weight, alkyl substituted phenol, a polyalkylene polyamine, and an aldehyde such as formaldehyde. Mannich bases are described in more detail in U.S. Patent No. 3,634,515.

[00157] A suitable class of dispersants may be high molecular weight esters or half ester amides.

[00158] A suitable dispersant may also be post-treated by conventional methods by a reaction with any of a variety of agents. Among these are boron, urea, thiourea, dimercaptothiadiazoles, carbon disulfide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, maleic anhydride, nitriles, epoxides, carbonates, cyclic carbonates, hindered phenolic esters, and phosphorus compounds. US 7,645,726; US 7,214,649; and US 8,048,831 are incorporated herein by reference in their entireties.

[00159] In addition to the carbonate and boric acids post-treatments both the compounds may be post-treated, or further post-treatment, with a variety of post-treatments designed to improve or impart different properties. Such post-treatments include those summarized in columns 27-29 of U.S. Pat. No. 5,241,003, hereby incorporated by reference. Such treatments include, treatment with:

Inorganic phosphorous acids or anhydrates (e.g., U.S. Pat. Nos. 3,403,102 and 4,648,980);

Organic phosphorous compounds (e.g., U.S. Pat. No. 3,502,677);

Phosphorous pentasulfides;

Boron compounds as already noted above (e.g., U.S. Pat. Nos. 3,178,663 and 4,652,387);

Carboxylic acid, polycarboxylic acids, anhydrides and/or acid halides (e.g., U.S. Pat. Nos. 3,708,522 and 4,948,386);

Epoxides polyepoxiates or thioexpoxides (e.g., U.S. Pat. Nos. 3,859,318 and 5,026,495);

Aldehyde or ketone (e.g., U.S. Pat. No. 3,458,530);

Carbon disulfide (e.g., U.S. Pat. No. 3,256,185);

Glycidol (e.g., U.S. Pat. No. 4,617,137);

Urea, thourea or guanidine (e.g., U.S. Pat. Nos. 3,312,619; 3,865,813; and British Patent GB 1,065,595);

Organic sulfonic acid (e.g., U.S. Pat. No. 3,189,544 and British Patent GB 2,140,811);

Alkenyl cyanide (e.g., U.S. Pat. Nos. 3,278,550 and 3,366,569);

Diketene (e.g., U.S. Pat. No. 3,546,243);

A diisocyanate (e.g., U.S. Pat. No. 3,573,205);

Alkane sultone (e.g., U.S. Pat. No. 3,749,695);

1,3-Dicarbonyl Compound (e.g., U.S. Pat. No. 4,579,675);

Sulfate of alkoxylated alcohol or phenol (e.g., U.S. Pat. No. 3,954,639);

Cyclic lactone (e.g., U.S. Pat. Nos. 4,617,138; 4,645,515; 4,668,246; 4,963,275; and 4,971,711);

Cyclic carbonate or thiocarbonate linear monocarbonate or polycarbonate, or chloroformate (e.g., U.S. Pat. Nos. 4,612,132; 4,647,390; 4,648,886; 4,670,170);

Nitrogen-containing carboxylic acid (e.g., U.S. Pat. 4,971,598 and British Patent GB 2,140,811);

Hydroxy-protected chlorodicarbonyloxy compound (e.g., U.S. Pat. No. 4,614,522);

Lactam, thiolactam, thiolactone or ditholactone (e.g., U.S. Pat. Nos. 4,614,603 and 4,666,460);

Cyclic carbonate or thiocarbonate, linear monocarbonate or plycarbonate, or chloroformate (e.g., U.S. Pat. Nos. 4,612,132; 4,647,390; 4,646,860; and 4,670,170);

Nitrogen-containing carboxylic acid (e.g., U.S. Pat. No. 4,971,598 and British Patent GB 2,440,811);

Hydroxy-protected chlorodicarbonyloxy compound (e.g., U.S. Pat. No. 4,614,522);

Lactam, thiolactam, thiolactone or dithiolactone (e.g., U.S. Pat. Nos. 4,614,603, and 4,666,460);

Cyclic carbamate, cyclic thiocarbamate or cyclic dithiocarbamate (e.g., U.S. Pat. Nos. 4,663,062 and 4,666,459);

Hydroxyaliphatic carboxylic acid (e.g., U.S. Pat. Nos. 4,482,464; 4,521,318; 4,713,189);

Oxidizing agent (e.g., U.S. Pat. No. 4,379,064);

Combination of phosphorus pentasulfide and a polyalkylene polyamine (e.g., U.S. Pat. No. 3,185,647);

Combination of carboxylic acid or an aldehyde or ketone and sulfur or sulfur chloride (e.g., U.S. Pat. Nos. 3,390,086; 3,470,098);

Combination of a hydrazine and carbon disulfide (e.g. U.S. Pat. No. 3,519,564);

Combination of an aldehyde and a phenol (e.g., U.S. Pat. Nos. 3,649,229; 5,030,249; 5,039,307);

Combination of an aldehyde and an O-diester of dithiophosphoric acid (e.g., U.S. Pat. No. 3,865,740);

Combination of a hydroxyaliphatic carboxylic acid and a boric acid (e.g., U.S. Pat. No. 4,554,086);

Combination of a hydroxyaliphatic carboxylic acid, then formaldehyde and a phenol (e.g., U.S. Pat. No. 4,636,322);

Combination of a hydroxyaliphatic carboxylic acid and then an aliphatic dicarboxylic acid (e.g., U.S. Pat. No. 4,663,064);

Combination of formaldehyde and a phenol and then glycolic acid (e.g., U.S. Pat. No. 4,699,724);

Combination of a hydroxyaliphatic carboxylic acid or oxalic acid and then a diisocyanate (e.g. U.S. Pat. No.4,713,191);

Combination of inorganic acid or anhydride of phosphorus or a partial or total sulfur analog thereof and a boron compound (e.g., U.S. Pat. No. 4,857,214);

Combination of an organic diacid then an unsaturated fatty acid and then a nitrosoaromatic amine optionally followed by a boron compound and then a glycolating agent (e.g., U.S. Pat. No. 4,973,412);

Combination of an aldehyde and a triazole (e.g., U.S. Pat. No. 4,963,278);

Combination of an aldehyde and a triazole then a boron compound (e.g., U.S. Pat. No. 4,981,492);

Combination of cyclic lactone and a boron compound (e.g., U.S. Pat. No. 4,963,275 and 4,971,711). The above mentioned patents are herein incorporated in their entireties.

[00160] The TBN of a suitable dispersant may be from about 10 to about 65 on an oil-free basis, which is comparable to about 5 to about 30 TBN if measured on a dispersant sample containing about 50% diluent oil.

The dispersant, if present, can be used in an amount sufficient to provide up to about 20 wt%, based upon the final weight of the lubricating oil composition. Another amount of the dispersant that can be used may be about 0.1 wt% to about 15 wt%, or about 0.1 wt% to about 10 wt%, or about 3 wt% to about 10 wt%, or about 1 wt% to about 6 wt%, or about 7 wt% to about 12 wt%, based upon the final weight of the lubricating oil composition. In some embodiments, the lubricating oil composition utilizes a mixed dispersant system. A single type or a mixture of two or more types of dispersants in any desired ratio may be used.

Friction Modifiers

[00161] The lubricating oil compositions herein also may optionally contain one or more friction modifiers. Suitable friction modifiers may comprise metal containing and metal-free friction modifiers and may include, but are not limited to, imidazolines, amides, amines, succinimides, alkoxylated amines, alkoxylated ether amines, amine oxides, amidoamines, nitriles, betaines, quaternary amines, imines, amine salts, amino guanadine, alkanolamides, phosphonates, metal-containing compounds, glycerol esters, sulfurized fatty compounds and olefins, sunflower oil other naturally occurring plant or animal oils, dicarboxylic acid esters, esters or partial esters of a polyol and one or more aliphatic or aromatic carboxylic acids, and the like.

[00162] Suitable friction modifiers may contain hydrocarbyl groups that are selected from straight chain, branched chain, or aromatic hydrocarbyl groups or mixtures thereof, and may be saturated or unsaturated. The hydrocarbyl groups may be composed of carbon and hydrogen or hetero atoms such as sulfur or oxygen. The hydrocarbyl groups may range from about 12 to about 25 carbon atoms. In some embodiments the friction modifier may be a long chain fatty acid ester. In another embodiment the long chain fatty acid ester may be a mono-ester, or a di-ester, or a (tri)glyceride. The friction modifier may be a long chain fatty amide, a long chain fatty ester, a long chain fatty epoxide derivatives, or a long chain imidazoline.

[00163] Other suitable friction modifiers may include organic, ashless (metal-free), nitrogen-free organic friction modifiers. Such friction modifiers may include esters formed by reacting carboxylic acids and anhydrides with alkanols and generally include a polar terminal group (e.g. carboxyl or hydroxyl) covalently bonded to an oleophilic hydrocarbon

chain. An example of an organic ashless nitrogen-free friction modifier is known generally as glycerol monooleate (GMO) which may contain mono-, di-, and tri-esters of oleic acid. Other suitable friction modifiers are described in U.S. Pat. No. 6,723,685, herein incorporated by reference in its entirety.

[00164] Aminic friction modifiers may include amines or polyamines. Such compounds can have hydrocarbyl groups that are linear, either saturated or unsaturated, or a mixture thereof and may contain from about 12 to about 25 carbon atoms. Further examples of suitable friction modifiers include alkoxylated amines and alkoxylated ether amines. Such compounds may have hydrocarbyl groups that are linear, either saturated, unsaturated, or a mixture thereof. They may contain from about 12 to about 25 carbon atoms. Examples include ethoxylated amines and ethoxylated ether amines.

[00165] The amines and amides may be used as such or in the form of an adduct or reaction product with a boron compound such as a boric oxide, boron halide, metaborate, boric acid or a mono-, di- or tri-alkyl borate. Other suitable friction modifiers are described in U.S. Pat. No. 6,300,291, herein incorporated by reference in its entirety.

[00166] A friction modifier may optionally be present in ranges such as about 0 wt% to about 10 wt%, or about 0.01 wt% to about 8 wt%, or about 0.1 wt% to about 4 wt%.

Additional Molybdenum-containing component

[00167] The lubricating oil compositions herein also may optionally contain additional molybdenum-containing compounds. An oil-soluble molybdenum compound may have the functional performance of an antiwear agent, an antioxidant, a friction modifier, or mixtures thereof. An oil-soluble molybdenum compound may include molybdenum dithiocarbamates, molybdenum dialkyldithiophosphates, molybdenum dithiophosphinates, amine salts of molybdenum compounds, molybdenum xanthates, molybdenum thioxanthates, molybdenum sulfides, molybdenum carboxylates, molybdenum alkoxides, a trinuclear organo-molybdenum compound, and/or mixtures thereof. The molybdenum sulfides include molybdenum disulfide. The molybdenum disulfide may be in the form of a stable dispersion. In one embodiment the oil-soluble molybdenum compound may be selected from the group consisting of molybdenum dithiocarbamates, molybdenum dialkyldithiophosphates, amine salts of molybdenum compounds, and mixtures thereof. In one embodiment the oil-soluble molybdenum compound may be a molybdenum dithiocarbamate.

[00168] Suitable examples of molybdenum compounds which may be used include commercial materials sold under the trade names such as Molyvan 822™, Molyvan™ A,

Molyvan 2000™ and Molyvan 855™ from R. T. Vanderbilt Co., Ltd., and Sakura-Lube™ S-165, S-200, S-300, S-310G, S-525, S-600, S-700, and S-710 available from Adeka Corporation, and mixtures thereof. Suitable molybdenum components are described in US 5,650,381; US RE 37,363 E1; US RE 38,929 E1; and US RE 40,595 E1, incorporated herein by reference in their entireties.

[00169] Additionally, the molybdenum compound may be an acidic molybdenum compound. Included are molybdic acid, ammonium molybdate, sodium molybdate, potassium molybdate, and other alkaline metal molybdates and other molybdenum salts, e.g., hydrogen sodium molybdate, MoOCl4, MoO2Br2, Mo2O3Cl6, molybdenum trioxide or similar acidic molybdenum compounds. Alternatively, the compositions can be provided with molybdenum by molybdenum/sulfur complexes of basic nitrogen compounds as described, for example, in U.S. Pat. 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, incorporated herein by reference in their entireties.

[00170] Another class of suitable organo-molybdenum compounds are trinuclear molybdenum compounds, such as those of the formula Mo3SkLnQz and mixtures thereof, wherein S represents sulfur, L represents 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 may be present among all the ligands' organo groups, such as at least 25, at least 30, or at least 35 carbon atoms. Additional suitable molybdenum compounds are described in U.S. Pat. No. 6,723,685, herein incorporated by reference in its entirety.

[00171] The oil-soluble molybdenum compound may be present in an amount sufficient to provide about 0.5 ppm to about 2000 ppm, about 1 ppm to about 700 ppm, about 1 ppm to about 550 ppm, about 5 ppm to about 300 ppm, or about 20 ppm to about 250 ppm of molybdenum.

Transition Metal-containing compounds

[00172] In another embodiment, the oil-soluble compound may be a transition metal containing compound or a metalloid. The transition metals may include, but are not limited to, titanium, vanadium, copper, zinc, zirconium, molybdenum, tantalum, tungsten, and the

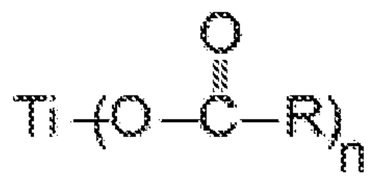
like. Suitable metalloids include, but are not limited to, boron, silicon, antimony, tellurium, and the like.

[00173] In an embodiment, an oil-soluble transition metal-containing compound may function as antiwear agents, friction modifiers, antioxidants, deposit control additives, or more than one of these functions. In an embodiment the oil-soluble transition metal-containing compound may be an oil-soluble titanium compound, such as a titanium (IV) alkoxide. Among the titanium containing compounds that may be used in, or which may be used for preparation of the oils-soluble materials of, the disclosed technology are various Ti (IV) compounds such as titanium (IV) oxide; titanium (IV) sulfide; titanium (IV) nitrate; titanium (IV) alkoxides such as titanium methoxide, titanium ethoxide, titanium propoxide, titanium isopropoxide, titanium butoxide, titanium 2-ethylhexoxide; and other titanium compounds or complexes including but not limited to titanium phenates; titanium carboxylates such as titanium (IV) 2-ethyl-1-3-hexanedioate or titanium citrate or titanium oleate; and titanium (IV) (triethanolaminato)isopropoxide. Other forms of titanium encompassed within the disclosed technology include titanium phosphates such as titanium dithiophosphates (e.g., dialkyldithiophosphates) and titanium sulfonates (e.g., alkylbenzenesulfonates), or, generally, the reaction product of titanium compounds with various acid materials to form salts, such as oil-soluble salts. Titanium compounds can thus be derived from, among others, organic acids, alcohols, and glycols. Ti compounds may also exist in dimeric or oligomeric form, containing Ti–O–Ti structures. Such titanium materials are commercially available or can be readily prepared by appropriate synthesis techniques which will be apparent to the person skilled in the art. They may exist at room temperature as a solid or a liquid, depending on the particular compound. They may also be provided in a solution form in an appropriate inert solvent.

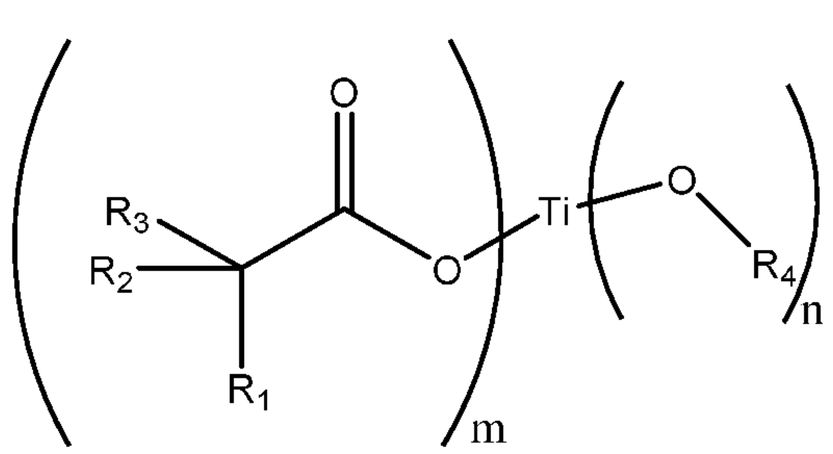
[00174] In one embodiment, the titanium can be supplied as a Ti-modified dispersant, such as a succinimide dispersant. Such materials may be prepared by forming a titanium mixed anhydride between a titanium alkoxide and a hydrocarbyl-substituted succinic anhydride, such as an alkenyl- (or alkyl) succinic anhydride. The resulting titanate-succinate intermediate may be used directly or it may be reacted with any of a number of materials, such as (a) a polyamine-based succinimide/amide dispersant having free, condensable –NH functionality; (b) the components of a polyamine-based succinimide/amide dispersant, i.e., an alkenyl- (or alkyl-) succinic anhydride and a polyamine, (c) a hydroxy-containing polyester dispersant prepared by the reaction of a substituted succinic anhydride with a polyol, aminoalcohol, polyamine, or mixtures thereof. Alternatively, the titanate-succinate intermediate may be reacted with other agents such as alcohols, aminoalcohols, ether alcohols, polyether alcohols or polyols, or fatty

acids, and the product thereof either used directly to impart Ti to a lubricant, or else further reacted with the succinic dispersants as described above. As an example, 1 part (by mole) of tetraisopropyl titanate may be reacted with about 2 parts (by mole) of a polyisobutene-substituted succinic anhydride at 140-150° C for 5 to 6 hours to provide a titanium modified dispersant or intermediate. The resulting material (30 g) may be further reacted with a succinimide dispersant from polyisobutene-substituted succinic anhydride and a polyethylenepolyamine mixture (127 grams + diluent oil) at 150° C for 1.5 hours, to produce a titanium-modified succinimide dispersant.

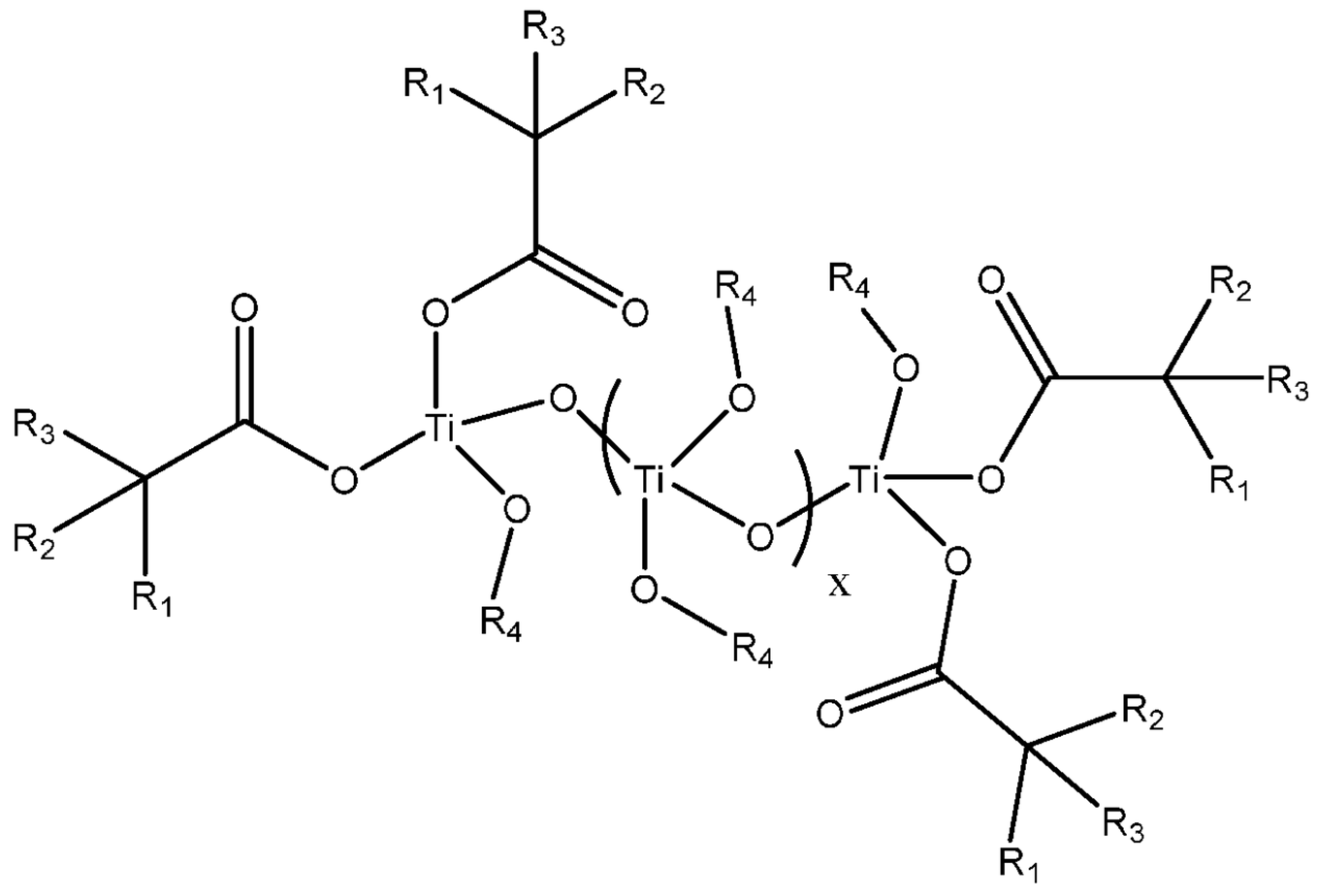
[00175] Another titanium containing compound may be a reaction product of titanium alkoxide and C_6 to C_{25} carboxylic acid. The reaction product may be represented by the following formula:



wherein n is an integer selected from 2, 3 and 4, and R is a hydrocarbyl group containing from about 5 to about 24 carbon atoms, or by the formula:



wherein m + n = 4 and n ranges from 1 to 3, R_4 is an alkyl moiety with carbon atoms ranging from 1-8, R_1 is selected from a hydrocarbyl group containing from about 6 to 25 carbon atoms, and R_2 and R_3 are the same or different and are selected from a hydrocarbyl group containing from about 1 to 6 carbon atoms, or by the formula:



wherein x ranges from 0 to 3, R_1 is selected from a hydrocarbyl group containing from about 6 to 25 carbon atoms, R_2, and R_3 are the same or different and are selected from a hydrocarbyl group containing from about 1 to 6 carbon atoms, and R_4 is selected from a group consisting of either H, or C_6 to C_{25} carboxylic acid moiety.

[00176] Suitable carboxylic acids may include, but are not limited to caproic acid, caprylic acid, lauric acid, myristic acid, palmitic acid, stearic acid, arachidic acid, oleic acid, erucic acid, linoleic acid, linolenic acid, cyclohexanecarboxylic acid, phenylacetic acid, benzoic acid, neodecanoic acid, and the like.

[00177] In an embodiment the oil soluble titanium compound may be present in the lubricating oil composition in an amount to provide from 0 to 3000 ppm titanium by weight or 25 to about 1500 ppm titanium by weight or about 35 ppm to 500 ppm titanium by weight or about 50 ppm to about 300 ppm.

Viscosity Index Improvers

[00178] The lubricating oil compositions herein also may optionally contain one or more viscosity index improvers. Suitable viscosity index improvers may include polyolefins, olefin copolymers, ethylene/propylene copolymers, polyisobutenes, hydrogenated styrene-isoprene polymers, styrene/maleic ester copolymers, hydrogenated styrene/butadiene copolymers, hydrogenated isoprene polymers, alpha-olefin maleic anhydride copolymers, polymethacrylates, polyacrylates, polyalkyl styrenes, hydrogenated alkenyl aryl conjugated diene copolymers, or mixtures thereof. Viscosity index improvers may include star polymers and suitable examples are described in US Publication No. 20120101017A1.

[00179] The lubricating oil compositions herein also may optionally contain one or more dispersant viscosity index improvers in addition to a viscosity index improver or in lieu of a viscosity index improver. Suitable dispersant viscosity index improvers may include functionalized polyolefins, for example, ethylene-propylene copolymers that have been functionalized with the reaction product of an acylating agent (such as maleic anhydride) and an amine; polymethacrylates functionalized with an amine, or esterified maleic anhydride-styrene copolymers reacted with an amine.

[00180] The total amount of viscosity index improver and/or dispersant viscosity index improver may be about 0 wt% to about 20 wt%, about 0.1 wt% to about 15 wt%, about 0.1 wt% to about 12 wt%, or about 0.5 wt% to about 10 wt%, of the lubricating oil composition.

Other Optional Additives

[00181] Other additives may be selected to perform one or more functions required of a lubricating fluid. Further, one or more of the mentioned additives may be multi-functional and provide functions in addition to or other than the function prescribed herein.

[00182] A lubricating oil composition according to the present disclosure may optionally comprise other performance additives. The other performance additives may be in addition to specified additives of the present disclosure and/or may comprise one or more of metal deactivators, viscosity index improvers, detergents, ashless TBN boosters, friction modifiers, antiwear agents, corrosion inhibitors, rust inhibitors, dispersants, dispersant viscosity index improvers, extreme pressure agents, antioxidants, foam inhibitors, demulsifiers, emulsifiers, pour point depressants, seal swelling agents and mixtures thereof. Typically, fully-formulated lubricating oil will contain one or more of these performance additives.

[00183] Suitable metal deactivators may include derivatives of benzotriazoles (typically tolyltriazole), dimercaptothiadiazole derivatives, 1,2,4-triazoles, benzimidazoles, 2-alkyldithiobenzimidazoles, or 2-alkyldithiobenzothiazoles; foam inhibitors including copolymers of ethyl acrylate and 2-ethylhexylacrylate and optionally vinyl acetate; demulsifiers including trialkyl phosphates, polyethylene glycols, polyethylene oxides, polypropylene oxides and (ethylene oxide-propylene oxide) polymers; pour point depressants including esters of maleic anhydride-styrene, polymethacrylates, polyacrylates or polyacrylamides.

[00184] Suitable foam inhibitors include silicon-based compounds, such as siloxane.

[00185] Suitable pour point depressants may include a polymethylmethacrylates or mixtures thereof. Pour point depressants may be present in an amount sufficient to provide from about 0 wt% to about 1 wt%, about 0.01 wt% to about 0.5 wt%, or about 0.02 wt% to about 0.04 wt% based upon the final weight of the lubricating oil composition.

[00186] Suitable rust inhibitors may be a single compound or a mixture of compounds having the property of inhibiting corrosion of ferrous metal surfaces. Non-limiting examples of rust inhibitors useful herein include oil-soluble high molecular weight organic acids, such as 2-ethylhexanoic acid, lauric acid, myristic acid, palmitic acid, oleic acid, linoleic acid, linolenic acid, behenic acid, and cerotic acid, as well as oil-soluble polycarboxylic acids including dimer and trimer acids, such as those produced from tall oil fatty acids, oleic acid, and linoleic acid. Other suitable corrosion inhibitors include long-chain alpha, omega-dicarboxylic acids in the molecular weight range of about 600 to about 3000 and alkenylsuccinic acids in which the alkenyl group contains about 10 or more carbon atoms such as, tetrapropenylsuccinic acid, tetradecenylsuccinic acid, and hexadecenylsuccinic acid. Another useful type of acidic corrosion inhibitors are the half esters of alkenyl succinic acids having about 8 to about 24 carbon atoms in the alkenyl group with alcohols such as the polyglycols. The corresponding half amides of such alkenyl succinic acids are also useful. A useful rust inhibitor is a high molecular weight organic acid. In some embodiments, an engine oil is devoid of a rust inhibitor.

[00187] The rust inhibitor, if present, can be used in an amount sufficient to provide about 0 wt% to about 5 wt%, about 0.01 wt% to about 3 wt%, about 0.1 wt% to about 2 wt%, based upon the final weight of the lubricating oil composition.

[00188] In general terms, a suitable lubricant may include additive components in the ranges listed in the following table.

Table 2

Component	Wt. % (Suitable Embodiments)	Wt. % (Suitable Embodiments)
Dispersant(s)	0.1 – 20.0	1.0 – 10.0
Antioxidant(s)	0.1 – 5.0	0.01 – 3.0
Detergent(s)	0.1 – 15.0	0.2 – 8.0
Ashless TBN booster(s)	0.0 – 1.0	0.01 – 0.5
Corrosion inhibitor(s)	0.0 – 5.0	0.0 – 2.0
Molybdenum containing compound	0.1 – 1.0	0.20 – 0.55
Metal dihydrocarbyldithiophosphate(s)	0.1 – 6.0	0.1 – 4.0
Ash-free phosphorus compound(s)	0.0 – 6.0	0.0 – 4.0
Antifoaming agent(s)	0.0 – 5.0	0.001 – 0.15
Antiwear agent(s)	0.0 - 1.0	0.0 – 0.8
Pour point depressant(s)	0.0 – 5.0	0.01 – 1.5
Viscosity index improver(s) (on a liquid/dilute basis)	0.0 – 25.0	0.1 – 15.0
Dispersant viscosity index improver(s)	0.0 – 10.0	0.0 – 5.0
Friction modifier(s)	0.01 - 5.0	0.05 - 2.0
Base oil(s)	Balance	Balance
Total	**100**	**100**

[00189] The percentages of each component above represent the weight percent of each component, based upon the weight of the final lubricating oil composition. The remainder of the lubricating oil composition consists of one or more base oils.

[00190] Additives used in formulating the compositions described herein may be blended into the base oil individually or in various sub-combinations. However, it may be suitable to blend all of the components concurrently using an additive concentrate (i.e., additives plus a diluent, such as a hydrocarbon solvent).

EXAMPLES

[00191] The following examples are illustrative, but not limiting, of the methods and compositions of the present disclosure. Other suitable modifications and adaptations of the variety of conditions and parameters normally encountered in the field, and which are obvious to those skilled in the art, are within the spirit and scope of the disclosure. All patents and publications cited herein are fully incorporated by reference herein in their entirety.

[00192] A series of tests were carried out to determine the impact of calcium and magnesium detergents and their contributions of ash content on the clogging of diesel particulate filters and to low speed pre-ignition events.

[00193] Each of the lubricating oil compositions contained a major amount of a base oil and a base conventional dispersant inhibitor (DI) package. The DI package contained conventional amounts of dispersant(s), antiwear additive(s), antioxidant(s), friction modifier(s), antifoam agent(s), process oil(s), viscosity index improver(s), and pour point depressant(s), as set forth in Table 3. Specifically, the DI package contained a succinimide dispersant, a molybdenum-containing compound, an antioxidant, and an antifoam agent. The major amount of base oil was a mixture of Group III and Group IV base oils. The components that were varied are specified in the Tables and discussion of the Examples below. All the values listed are states as weight percent of the component in the lubricating oil compositions (i.e., active ingredient plus diluent oil, if any) unless specified otherwise.

Table 3 – DI Package Composition Ranges

Component	**Wt. %**
Antioxidant(s)	0.5 to 2.5
Antiwear agent(s), including any metal dihydrocarbyl dithiophosphate	0.5 to 1.5
Antifoaming agent(s)	0.001 to 0.05
Detergent(s)	1.0-2.0
Dispersant (s)	5.0-9.0
Metal-containing friction modifier(s)	0.03 – 1.5
Metal free friction modifier(s)	0 to 0.5
Pour point depressant(s)	0.05 to 0.5
Process oil	0.25 to 1.0

[00194] Sulfated ash (SASH) was calculated for total of metallic elements that contribute to SASH in the lubricant composition according to the following factors that were multiplied by the amount of each metallic element in the lubricant composition according to: http://konnaris.com/portals/0/search/calculations.htm.

Element	Factor	Element	Factor
Barium	1.70	Magnesium	4.95
Boron	3.22	Manganese	1.291
Calcium	3.40	Molybdenum	1.50
Copper	1.252	Potassium	2.33
Lead	1.464	Sodium	3.09
Lithium	7.92	Zinc	1.50

[00195] The VW PV 1485 test is a diesel particulate filter test used to measure the clogging tendency of diesel particulate filters. The diesel particulate filter test is carried out in a VW 1.9 Liter, 4 cylinder turbocharged direct injection diesel engine. One complete test includes 6 test cycles. The first five stages are run to condition the engine, and the last stage implements the ash loading for 144 hours.

[00196] Improvement in reducing clogging in a diesel particulate filter is recognized when the delta pressure (ΔP) versus oil consumption (OC) is 0.6 kPa/kg or less. A further improvement in clogging is recognized when the ΔP versus OC is 0.5 kPa/kg or less, an even further improvement in clogging is recognized when the ΔP versus OC is 0.45 kPa/kg or less.

[00197] Reference oil R-1 was formulated from about 80.7 wt.% of a Group III base oil, 12.1 wt.% of HiTEC® 11150 PCMO Additive Package available from Afton Chemical Corporation and 7.2 wt.% of a 35 SSI ethylene/propylene copolymer viscosity index improver. HiTEC® 11150 passenger car motor oil additive package is an API SN, ILSAC-GF-5, and ACEA A5/B5 qualified DI package. R-1 also showed the following and properties and partial elemental analysis:

Reference Oil R-1

10.9	Kinematic Viscosity at 100°C, (mm^2/sec)
3.3	TBS, APPARENT_VISCOSITY, cPa
2438	calcium (ppmw)
< 10	magnesium (ppmw)
80	molybdenum (ppmw)
772	phosphorus (ppmw)
855	zinc (ppmw)
9.0	Total Base Number ASTM D-2896 (mg KOH/g)
165	Viscosity Index

[00198] The following examples were evaluated for VW DPF performance.

Table 4

Description	Example 1	Example 2	Example 3	Example 4
Overbased Ca Detergent(s) (ppm Ca)	1365	1378	1638	1638
Overbased Mg Detergent(s) (ppm Mg)	6	367	232	402
Molybdenum containing compound(s) (ppm Mo)	335	319	335	381
Phosphorus content (ppm P)	728	741	759	781
S/ASH content (wt.%)	0.6	0.8	0.8	0.8
Ca/Mg ratio (ppm Ca/ppm Mg)	227.5	3.8	7.1	4.1
VW PV 1485 test (kPa/kg) [a]	0.32 (pass)	0.43 (pass)	0.6 (pass)	0.43 (pass)

[00199] The results shown in inventive examples 2 and 3 indicate that a lower ratio of total Ca ppm from the detergents to the total Mg ppm from the detergents provides a reduction in clogging, when the level of sulfated ash content is held constant.

[00200] Further, the results shown in Table 4 indicate that the VW PV 1485 test does not restrict the formulation to 0.6 % sulfated ash, since inventive examples 2 and 3 pass the VW PV 1485 test with a sulfated ash content of 0.8 %.

[00201] Low Speed Pre-Ignition (LSPI) events were measured in a GM 2.0 Liter, 4 cylinder Ecotec turbocharged gasoline direct injection (TGDi) engine. One complete LSPI fired engine test consisted of 4 test cycles. Within a single test cycle, two operational stages or segments are repeated in order to generate LSPI events. In stage A, when LSPI is most likely to occur, the engine is operated at about 2000 rpm and about 1,800 kPa brake mean effective pressure (BMEP). In stage B, when LSPI is not likely to occur, the engine is operated at about 1500 rpm and about 1,700 kPa BMEP. For each stage, data is collected over 25,000 engine cycles. The structure of a test cycle is as follows: stage A – stage A – stage B – stage B – stage A – stage A. Each stage is separated by an idle period. Because LSPI is statistically significant during stage A, the LSPI event data that was considered in the present examples only included LSPI events generated during stage A operation. Thus, for one complete LSPI fired engine test, data was typically generated over a total of 16 stages and was used to evaluate performance of comparative and inventive oils.

[00202] LSPI events were determined by monitoring peak cylinder pressure (PP) and when 2% of the combustible material in the combustion chamber burns (MFB02). The threshold for peak cylinder pressure is calculated for each cylinder and for each stage and is typically 65,000 to 85,000 kPa. The threshold for MFB02 is calculated for each cylinder and for each stage and typically ranges from about 3.0 to about 7.5 Crank Angle Degree (CAD) After Top Dead Center (ATDC). An LSPI was recorded when both the PP and MFB02 thresholds were exceeded in a single engine cycle. LSPI events can be reported in many ways. In order to remove ambiguity involved with reporting counts per engine cycle, where different fired engine tests can be conducted with a different number of engine cycles, the relative number of LSPI events of comparative and inventive oils were reported as an "LSPI Ratio". In this way improvement relative to some standard response is clearly demonstrated.

[00203] In the following examples, the LSPI Ratio was reported as a ratio of the LSPI events of a test oil relative to the LSPI events of Reference Oil "R-1".

[00204] Considerable improvement in LSPI is recognized when there is greater than 50% reduction in LSPI events relative to R-1 (an LSPI Ratio of less than 0.5). A further

improvement in LSPI is recognized when there is greater than 70% reduction in LSPI events (an LSPI Ratio of less than 0.3), an even further improvement in LSPI is recognized when there is greater than 75% reduction in LSPI events (an LSPI Ratio of less than 0.25), and an even further improvement in LSPI is recognized when there is greater than 80% reduction in LSPI events relative to R-1 (an LSPI Ratio of less than 0.20), and an even further improvement in LSPI is recognized when there is greater than 90% reduction in LSPI events relative to R-1 (an LSPI Ratio of less than 0.1). The LSPI Ratio for R-1 reference oil is thus deemed to be 1.00.

[00205] In the following examples, the LSPI Ratio was reported as a ratio of the LSPI events of a test oil relative to the LSPI events of Reference Oil "R-1".

Table 5

Description	R-1	Example 1	Example 5	Example 6
Overbased Ca Detergent (ppm Ca)		1365	1385	1605
Overbased Mg Detergent (ppm Mg)		6	381	6
Molybdenum containing compound (ppm Mo)		335	334	318
Phosphorus content (ppm P)		728	732	739
S/ASH content (wt.%)		0.62	?	0.7
Ca/Mg ratio (ppm Ca/ppm Mg)		227.5	?	?
VW PV 1485 test (kPa/kg) [a]		0.32 (pass)	Not measured	Not measured
LSPI Ratio	1	0.05	0.15	0.19

[00206] The foregoing examples show that various lubricating oil formulations of the present invention may provide significant reductions in LSPI events. In addition, Example 1 demonstrates that a lubricating oil of the present invention can pass the diesel particulate clogging test and significantly reduce LSPI events. This may be particularly useful in boosted spark-ignited combustion engines equipped with a diesel particulate filter.

[00207] Other embodiments of the present disclosure will be apparent to those skilled in the art from consideration of the specification and practice of the embodiments disclosed herein. As used throughout the specification and claims, "a" and/or "an" may refer to one or more than one. Unless otherwise indicated, all numbers expressing quantities of ingredients, properties such as molecular weight, percent, ratio, reaction conditions, and so forth used in the specification and claims are to be understood as being modified in all instances by the term "about," whether or not the term "about" is present. Accordingly, unless indicated to the contrary, the numerical parameters set forth in the specification and claims are approximations that may vary depending upon the desired properties sought to be obtained by the present disclosure. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques. Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the disclosure are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contains certain errors necessarily resulting from the standard deviation found in their respective testing measurements. It is intended that the specification and examples be considered as exemplary only, with a true scope and spirit of the disclosure being indicated by the following claims.

[00208] The foregoing embodiments are susceptible to considerable variation in practice. Accordingly, the embodiments are not intended to be limited to the specific exemplifications set forth hereinabove. Rather, the foregoing embodiments are within the spirit and scope of the appended claims, including the equivalents thereof available as a matter of law.

[00209] The patentees do not intend to dedicate any disclosed embodiments to the public, and to the extent any disclosed modifications or alterations may not literally fall within the scope of the claims, they are considered to be part hereof under the doctrine of equivalents.

[00210] It is to be understood that each component, compound, substituent or parameter disclosed herein is to be interpreted as being disclosed for use alone or in combination with one or more of each and every other component, compound, substituent or parameter disclosed herein.

[00211] It is also to be understood that each amount/value or range of amounts/values for each component, compound, substituent or parameter disclosed herein is to be interpreted

as also being disclosed in combination with each amount/value or range of amounts/values disclosed for any other component(s), compounds(s), substituent(s) or parameter(s) disclosed herein and that any combination of amounts/values or ranges of amounts/values for two or more component(s), compounds(s), substituent(s) or parameters disclosed herein are thus also disclosed in combination with each other for the purposes of this description.

[00212] It is further understood that each range disclosed herein is to be interpreted as a disclosure of each specific value within the disclosed range that has the same number of significant digits. Thus, a range of from 1-4 is to be interpreted as an express disclosure of the values 1, 2, 3 and 4.

[00213] It is further understood that each lower limit of each range disclosed herein is to be interpreted as disclosed in combination with each upper limit of each range and each specific value within each range disclosed herein for the same component, compounds, substituent or parameter. Thus, this disclosure to be interpreted as a disclosure of all ranges derived by combining each lower limit of each range with each upper limit of each range or with each specific value within each range, or by combining each upper limit of each range with each specific value within each range.

[00214] Furthermore, specific amounts/values of a component, compound, substituent or parameter disclosed in the description or an example is to be interpreted as a disclosure of either a lower or an upper limit of a range and thus can be combined with any other lower or upper limit of a range or specific amount/value for the same component, compound, substituent or parameter disclosed elsewhere in the application to form a range for that component, compound, substituent or parameter.

CLAIMS:

1. A lubricating oil composition comprising:
   a) greater than 50 wt.% of a base oil of lubricating viscosity, based on the total weight of the lubricating oil composition;
   b) an amount of one or more calcium-containing detergents to provide less than 1700 ppm calcium, based on a total weight of the lubricating oil composition, and the one or more calcium-containing detergents excludes a calcium salicylate detergent,
   c) an amount of one or more magnesium-containing detergents to provide less than 450 ppm magnesium, based on the total weight of the lubricating oil composition;
   d) an amount of one or more molybdenum-containing compounds to provide less than 450 ppm molybdenum, based on the total weight of the lubricating oil composition;
   e) from 700 ppm to 900 ppm of phosphorus, based on the total weight of the lubricating oil composition; and
   f) a total measured sulfated ash content of no greater than 1.0 wt.%, as measured by ASTM D874, based on the total weight of the lubricating oil composition; and
   a ratio, in ppm, of calcium from the one or more calcium-containing detergents to magnesium from the one or more magnesium-containing detergents of 1:1 or more, and
   wherein the lubricating oil composition contains less than 10 ppm of boron, based on the total weight of the lubricating oil composition.

2. The lubricating oil composition of claim 1, wherein the lubricating oil composition provides a diesel particulate filter delta pressure (ΔP) vs. oil consumption result of 0.6 kPa/kg or less, 0.5 kPa/kg or less or 0.45 kPa/kg or less, as measured in a VW PV 1485 test after 144 hours.

3. The lubricating oil composition of claim 1, wherein the lubricating oil composition is effective to reduce low speed pre-ignition events in a boosted internal combustion engine lubricated with the lubricating oil composition relative to a number of low speed pre-ignition events in the same engine lubricated with reference lubricating oil R-1; or the reduction of LSPI events is 50% or greater reduction and the LSPI events

are LSPI counts during 25,000 engine cycles, wherein the engine is operated at 2000 revolutions per minute with brake mean effective pressure of 1,800 kPa, wherein R-1 is formulated from 80.7 wt.% of a Group III base oil, 12.1 wt.% of passenger car motor oil additive package and 7.2 wt.% of a 35 SSI ethylene/propylene copolymer viscosity index improver, and R-1 also showed the following properties and partial elemental analysis:

10.9	Kinematic Viscosity at 100°C, (mm^2/sec)
3.3	TBS, APPARENT_VISCOSITY, cPa
2438	calcium (ppmw)
< 10	magnesium (ppmw)
80	molybdenum (ppmw)
772	phosphorus (ppmw)
855	zinc (ppmw)
9.0	Total Base Number ASTM D-2896 (mg KOH/g)
165	Viscosity Index

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4. The lubricating oil composition of any one of claims 1-3, wherein the one or more magnesium-containing detergents provides 410 ppm or less of magnesium, based on a total weight of the lubricating oil composition

5. The lubricating oil composition of any one of claims 1-4, wherein the ratio of total calcium from the one or more calcium-containing detergents in ppm to total magnesium from the one or more magnesium-containing detergents is more than 2.5; or more than 3.5.

6. The lubricating oil composition of any one of claims 1-5, wherein the one or more calcium-containing detergents is overbased having a total base number of greater than 225 mg KOH/g; or 250 mg KOH/g or more as measured by the method of ASTM D-

2896.

7. The lubricating oil composition of any one of claims 1-6, wherein the one or more calcium-containing detergents is present in an amount sufficient to provide less than 1670 ppm calcium; or less than 1500 ppm calcium; or less than 1400 ppm calcium; or more than 1350 ppm to less than 1700 ppm calcium to the total weight of the lubricating oil composition.

8. The lubricating oil composition of any one of claims 1-7, wherein the total sulfated ash content is less than 0.8 wt.%, or more than 0.6 wt.% to less than 1.0 wt.%, each as measured by ASTM D874.

9. The lubricating oil composition of any one of claims 1-8, wherein one or more calcium-containing detergents having a total base number of up to 175 mg KOH/g as measured by the method of ASTM D-2896, if present, provides less than 50 ppm of calcium, or less than 20 ppm of calcium; or less than 5 ppm of calcium; or 0 ppm of calcium to the total weight of the lubricating oil composition.

10. The lubricating oil composition of any one of claims 1-9, wherein the lubricating oil composition contains 0 ppm of boron, based on a total weight of the lubricating oil composition.

11. The lubricating oil composition of any one of claims 1-10, wherein the lubricating oil composition has more than 0 ppm of boron and a ratio of total metal in ppm to total boron in ppm is more than 7.5; or more than 50; or more than 500.

12. The lubricating oil composition of any one of claims 1-11, wherein the one or more magnesium-containing detergents is overbased having a total base number of greater than 225 mg KOH/g; or greater than 250 mg KOH/g or more; or greater than 400 mg KOH/g or more as measured by the method of ASTM D-2896.

13. The lubricating oil composition of any one of claims 1-12, wherein the one or more magnesium-containing detergents is an overbased magnesium sulfonate detergent

having a total base number of greater than 225 mg KOH/g, as measured by the method of ASTM D-2896.

14. The lubricating oil composition, of any one of claims 1-13, wherein the lubricating oil composition is an engine oil composition.

15. A method for reducing clogging in a diesel particulate filter comprising a step of operating an engine equipped with a diesel particulate filter and lubricated with a lubricating oil composition comprising:
    a) greater than 50 wt.% of a base oil of lubricating viscosity, based on the total weight of the lubricating oil composition;
    b) an amount of one or more calcium-containing detergents to provide less than 1700 ppm calcium, based on a total weight of the lubricating oil composition, and the one or more calcium-containing detergents excludes a calcium salicylate detergent;
    c) an amount of one or more magnesium-containing detergents to provide less than 450 ppm magnesium, based on the total weight of the lubricating oil composition;
    d) an amount of one or more molybdenum-containing compounds to provide less than 450 ppm molybdenum, based on the total weight of the lubricating oil composition;
    e) from 700 ppm to 900 ppm of phosphorus, based on the total weight of the lubricating oil composition; and
    f) a total sulfated ash content of no less than 0.5 wt.% and no greater than 1.0 wt.%, as measured by ASTM D874, based on a total weight of the lubricating oil composition; and

    a ratio, in ppm, of calcium from the one or more calcium-containing detergents to magnesium from the one or more magnesium-containing detergents of 1:1 or more, and

    wherein the lubricating oil composition contains less than 10 ppm of boron, based on the total weight of the lubricating oil composition.

16. The method of claim 15, wherein the lubricating oil composition provides a diesel particulate filter delta pressure (ΔP) versus oil consumption result of 0.6 kPa/kg or less, 0.5 kPa/kg or less, or 0.45 kPa/kg or less, as measured in a VW PV 1485 test

after 144 hours.

17. The method of claim 15, wherein the method is effective to reduce low speed pre-ignition events in a boosted internal combustion engine lubricated with the lubricating oil composition relative to a number of low speed pre-ignition events in the same engine lubricated with reference lubricating oil R-1; or the reduction of LSPI events is 50% or greater reduction and the LSPI events are LSPI counts during 25,000 engine cycles, wherein the engine is operated at 2000 revolutions per minute with brake mean effective pressure of 1,800 kPa, wherein R-1 is formulated from 80.7 wt.% of a Group III base oil, 12.1 wt.% of passenger car motor oil additive package and 7.2 wt.% of a 35 SSI ethylene/propylene copolymer viscosity index improver, and R-1 also showed the following properties and partial elemental analysis:

10.9	Kinematic Viscosity at 100°C, (mm^2/sec)
3.3	TBS, APPARENT_VISCOSITY, cPa
2438	calcium (ppmw)
< 10	magnesium (ppmw)
80	molybdenum (ppmw)
772	phosphorus (ppmw)
855	zinc (ppmw)
9.0	Total Base Number ASTM D-2896 (mg KOH/g)
165	Viscosity Index

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18. The method of any one of claims 15-17, wherein the one or more magnesium-containing detergents provides 410 ppm or less of magnesium, based on a total weight of the lubricating oil composition.

19. The method of any one of claims 15-18, wherein the ratio of total calcium from the one or more calcium-containing detergents in ppm to total magnesium from the one or more magnesium-containing detergents is more than 2.5; or more than 3.5.

20. The method of any one of claims 15-19, wherein the one or more calcium-containing detergents is overbased having a total base number of greater than 225 mg KOH/g; or greater than 250 mg KOH/g or more as measured by the method of ASTM D-2896.

21. The method of any one of claims 15-20, wherein the one or more calcium-containing detergents is present in an amount sufficient to provide less than 1670 ppm calcium; or less than 1500 ppm calcium; or less than 1400 ppm calcium; or more than 1350 ppm to less than 1700 ppm calcium to the total weight of the lubricating oil composition.

22. The method of any one of claims 15-21, wherein the total sulfated ash content is less than 0.8 wt.%, or more than 0.5 wt.% to less than 1.0 wt.%, or more than 0.6 wt.% to less than 1.0 wt.%, each as measured by ASTM D874.

23. The method of any one of claims 15-22, wherein one or more calcium-containing detergents having a total base number of up to 175 mg KOH/g as measured by the method of ASTM D-2896, if present, provides less than 50 ppm of calcium, or less than 20 ppm of calcium; or less than 5 ppm of calcium; or 0 ppm of calcium to the total weight of the lubricating oil composition.

24. The method of any one of claims 15-23, wherein the lubricating oil composition contains 0 ppm of boron, based on a total weight of the lubricating oil composition.

25. The method of any one of claims 15-24, wherein the lubricating oil composition has more than 0 ppm of boron and a ratio of total metal in ppm to total boron in ppm is more than 7.5; or more than 50; or more than 500.

26. The method of any one of claims 15-25, wherein the one or more magnesium-containing detergents is overbased having a total base number of greater than 225 mg KOH/g; or greater than 250 mg KOH/g or more; or greater than 400 mg KOH/g or

more as measured by the method of ASTM D-2896.

27. The method of any one of claims 15-26, wherein the one or more magnesium-containing detergents is an overbased magnesium sulfonate detergent having a total base number of greater than 225 mg KOH/g, as measured by the method of ASTM D-2896.

28. The method of any one of claims 15-27, wherein the lubricating oil composition is an engine oil composition.