

- 1 -

LUBRICATING COMPOSITION WITH PHENOLIC ANTIOXIDANT AND LOW ACTIVE SULFUR

FIELD OF THE INVENTION

[0001] The exemplary embodiment relates to lubricating compositions and finds particular application in connection with a lubricating composition containing a phenolic antioxidant and a sulfurized organic compound that is low in active sulfur, which is able to provide both antioxidancy and reduced corrosion.

BACKGROUND OF THE INVENTION

[0002] Ashless additives (additives that produce little or no ash when burnt) are often used in engine oil formulations to provide performance properties, such as antioxidancy. Basic ashless additives, such as amines, are frequently employed as antioxidants. In particular, hydrocarbyl substituted diphenylamines, such as octyl diphenylamine, di-octyl diphenylamine, and dinonyl diphenylamine, have been used. See, for example, U.S. Pat. No. 10,800,992 B2, for LUBRICANT COMPOSITIONS FOR DIRECT INJECTION ENGINE, by Mosier, et al., which describes a lubricant composition which may include a diarylamine antioxidant, such as di-octyl diphenylamine.

[0003] Substituted diphenylamine (SDPA) antioxidants are known for their ability to inhibit oxidation of engine oils. They are widely used in heavy duty engine oil applications, where oxidation stability is key for reducing deposits, sludge, and varnish formation, for controlling viscosity increase and therefore maintaining optimum engine operation. In practice, however, hydrocarbyl substituted diphenylamines can be detrimental for corrosion and deposit testing.

[0004] There have been attempts to replace substituted diphenylamines with similar compounds, such as polymeric diphenylamines. For example, U.S. Pub. No. 20190127526A, for ANTIOXIDANT POLYMERIC DIPHENYLAMINE COMPOSITIONS, by Farnig, et al., describes an antioxidant polymer composition comprising repeat units of diphenylamine

- 2 -

monomers, which may be combined with a base oil and common lubricant additives.

[0005] Others have used combinations of antioxidants. For example, U.S. Pub. No. 20220145204A1, published May 12, 2022, for METHOD OF
5 LUBRICATING AN INTERNAL COMBUSTION ENGINE, by Mayhew, et al., describes a lubricating composition including an antioxidant which includes a mixture of a phenolic antioxidant, an aminic antioxidant, and a sulfurized olefin.

[0006] However, such compositions have often failed to provide good
10 antioxidant properties in combination with reduced corrosion. Achieving corrosion resistance and oxidation control is challenging, particularly when sulfur and amine compounds are used. Further, sulfurized olefins also pose problems. For example, U.S. Patent No. 4,873,006A, issued October 10, 1989, entitled COMPOSITIONS CONTAINING ACTIVE SULFUR, by Vinci, et
15 al., describes using a nitrogen-containing carboxylic compound to reduce the production of hydrogen sulfide from active sulfur-containing compounds.

[0007] There remains a need for a lubricating composition which provides good antioxidant properties while reducing the tendency for corrosion of lubricated devices.

20 BRIEF DESCRIPTION

[0008] In accordance with one aspect of the exemplary embodiment, a lubricating composition includes an oil of lubricating viscosity, a phenolic antioxidant, a sulfurized organic compound with an active sulfur content of no more than 8 wt. %, and optionally, one or more performance additives
25 selected from: a succinimide dispersant, and a detergent.

[0009] The lubricating composition may be at least substantially free of substituted diphenylamine (SDPA) antioxidants. The lubricating composition may be at least substantially free of aminic antioxidants.

[0010] The phenolic antioxidant may be at least 0.1 wt. %, or at least 0.5
30 wt. %, or at least 1 wt. %, or at least 1.5 wt. %, or at least 2 wt. % of the lubricating composition. The phenolic antioxidant may be no more than 8 wt.

- 3 -

% of the lubricating composition, or no more than 6 wt. %, or no more than 5 wt. %, or no more than 4 wt. % or no more than 3 wt. % of the lubricating composition.

[0011] The phenolic antioxidant may be selected from a hindered phenol, a hindered alkyl phenol ester, a hindered alkoxy phenol, a hindered phenol acetate, a hindered bisphenol, a polyphenol, a 4-*tert*-butylphenol-formaldehyde condensate, a 4-*tert*-butylphenol-acetaldehyde condensate, and mixtures thereof. For example, the phenolic antioxidant may be selected from: a mixture of C₇-C₉ branched alkyl esters of 3,5-*bis*(1,1-dimethyl-ethyl)-4-hydroxy-benzenepropanoic acid; a C₄ alkyl ester of 3,5-*bis*(1,1-dimethyl-ethyl)-4-hydroxy-benzenepropanoic acid, and 2,2'-thiodiethylene *bis*[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate].

[0012] The sulfurized organic compound is generally one which is low in active sulfur. A sulfurized organic compound which is low in active sulfur has either a low weight percent of active sulfur or a low weight % active sulfur in the total sulfur in the sulfurized organic compound, or both.

[0013] The sulfurized organic compound may have an active sulfur content of no more than 8 wt. %, or no more than 6 wt. %, or no more than 4.0 wt. %, or no more than 3 wt. %, or no more than 2.5 wt.%, or no more than 2 wt. %. The sulfurized organic compound may have a total sulfur content of at least 0.1 wt. %, or at least 1 wt. %, or at least 1.5 wt. %, or at least 2 wt. %, or no more than 18 wt. %, or no more than 15 wt. %, or no more than 14.0 wt. %, or no more than 12.0 wt. %, or no more than 5 wt. %. The active sulfur may account for no more than 25 wt. %, or no more than 22 wt. %, or no more than 20 wt. %, or no more than 19 wt., or at least 1 wt. %, or at least 1.5 wt. % of the total sulfur in the sulfurized organic compound.

[0014] The sulfurized organic compound may provide at least 0.01 wt.%, or at least 0.03 wt.%, or at least 0.05 wt. %, or up to 0.12 wt.%, or up to 0.09 wt. % sulfur in the lubricating composition. The sulfurized organic compound may provide no more than 0.02 wt. % of active sulfur, or no more than 0.018 wt. %, or no more than 0.015 wt. %, or no more than 0.013 wt. % of active sulfur in the lubricating composition.

- 4 -

[0015] The sulfurized organic compound may be at least 0.1 wt. %, or at least 0.15 wt. % or at least 0.2 wt. % of the lubricating composition. The sulfurized organic compound may be up to 1 wt. %, or up to 0.8 wt. % or up to 0.6 wt. %, or up to 0.5 wt. % of the lubricating composition.

- 5 **[0016]** The sulfurized organic compound may be selected from an oligomeric polysulfide, an alkyl polysulfide, a sulfurized ester, a sulfurized cycloaliphatic dialkylester, a sulfurized cycloaliphatic dialkenyl ester, and mixtures thereof.

- 10 **[0017]** The sulfurized organic compound may be selected from an oligomeric polysulfide of Formula I: $R^1-S_x-[(C(R')_vH_{2-v})_n-S_x]_p-R^2$

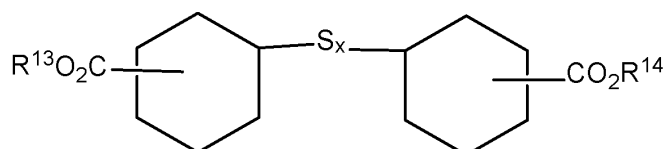
Formula I,

- where R^1 and R^2 are each independently a C2-C20 alkyl, e.g., a C3 or C4 or higher alkyl, or a C16 or lower alkyl; each R' is independently a C1-C20 alkyl, or a C6 or lower alkyl; each n is independently at least 1, or at least 2, or up to 8, e.g., 3-5, such as 3 or 4; p is independently at least 1, or at least 2, or up to 8; each v is from 0-2, e.g., v is 0; and each x is independently at least 1.

- 20 **[0018]** The sulfurized organic compound may include an alkyl polysulfide of Formula II: $R^1-S_x-R^2$, where R^1 and R^2 are each independently a C2-C20 alkyl, or a C3-C8 alkyl, such as a C4 alkyl; and each x is independently at least 1.

- 25 **[0019]** The sulfurized organic compound may include a sulfurized fatty acid ester of an aliphatic alcohol. The sulfurized fatty acid ester of an aliphatic alcohol may include a sulfurized triglyceride.

[0020] The sulfurized organic compound may include at least one of a cycloaliphatic dialkylester and a cycloaliphatic dialkenyl ester of Formula V:



- 5 -

where each of R¹³ and R¹⁴ is independently a C2 or higher alkyl or alkenyl group; and x is at least 1.

[0021] The succinimide dispersant may be at least 0.2 wt. %, or at least 0.5 wt. %, or at least 1.0 wt. %, or up to 7.0 wt. %, or up to 6.0 wt. of the lubricating composition. The succinimide dispersant may provide no more than 0.1 wt. % nitrogen to the lubricating composition.

[0022] The detergent may be at least 0.1 wt. %, or at least 0.2 wt. %, or at least 0.25 wt. %, or at least 0.4 wt. %, or up to 3.0 wt. %, or up to 2.0 wt. %, or up to 1.5 wt. %, or up to 1.25 wt. % of the lubricating composition. The detergent may provide the lubricating composition with at least 0.005 wt. % of boron, or at least 0.03 wt. % boron, or up to 0.06 wt. %, or up to 0.04 wt.% of boron. The detergent may provide the lubricating composition with at least 0.04 wt. %, or at least 0.08 wt. %, or up to 0.4 wt.%, or up to 0.3 wt. % of calcium. The detergent may be selected from an alkaline earth metal sulfonate, an alkaline earth metal salicylate, an alkaline earth metal saligenin, an alkaline earth metal salixarate, an alkaline earth metal hydrocarbyl-substituted hydroxybenzoate, and mixtures thereof.

[0023] The oil of lubricating viscosity may be at least 80 wt. % of the lubricating composition, or up to 94 wt. % of the lubricating composition.

[0024] The lubricating composition may further include at least one of an antiwear agent, a corrosion inhibitor, a viscosity modifier, a pour point depressant, an antifoam agent, an extreme pressure agent, a friction modifier, and combinations thereof. The antiwear agent may provide the lubricating composition with 300 - 850 ppm phosphorus by weight, based upon a total weight of the lubricating composition.

[0025] The viscosity modifier may include a dispersant viscosity modifier which includes at least one of a reaction product of an olefin polymer comprising a carboxylic acid functionality with 3-nitroaniline; and an amine functionalized aromatic maleic anhydride-styrene copolymer. The dispersant viscosity modifier may be at least 0.01 wt. %, or at least 0.1 wt. %, or at least 2 wt. %, or no more than 8 wt. %, or no more than 7 wt. % of the lubricating composition.

- 6 -

[0026] Molybdenum may be less than 800 ppm, or less than 400 ppm, or less than 150 ppm, or less than 100 ppm, or less than 80 ppm, or less than 50 ppm, or less than 20 ppm, based upon a total weight of the lubricating composition.

5 **[0027]** A method for improving oxidative stability of a lubricating oil in an engine may include supplying the lubricating composition described above to the engine. When the engine is a Volvo T-13 engine and is run for 360 hours, the kinematic viscosity at 40°C (KV40) increase from 300 hours to 360 hours may be less than 75 or less than 50. The oxidation at the end of test may be
10 less than 125 A/cm, as measured by the IR peak height.

[0028] The lubricating composition described above may be used for lubricating an engine, such as an internal combustion engine or a heavy duty diesel engine.

[0029] In accordance with another aspect of the exemplary embodiment, a
15 lubricating composition includes a sulfurized organic compound sufficient to provide, in the lubricating composition, at least 0.1 wt. % sulfur; at least 0.1 wt. % of a phenolic antioxidant; at least 0.1 wt. % of a detergent; and at least 2 wt. % of a dispersant. The lubricating composition contains no more than 0.04 wt. % of active sulfur.

20 **[0030]** In the lubricating composition, the detergent may include at least one of a calcium salicylate detergent and a calcium sulfonate detergent sufficient to provide at least 0.1 wt. %, or at least 0.12 wt. % calcium to the lubricating composition; a magnesium sulfonate detergent sufficient to provide at least 0.02 wt. %, or at least 0.04 wt. % magnesium to the lubricating
25 composition.

DETAILED DESCRIPTION

[0031] Aspects of the exemplary embodiment relate to a lubricating composition and to a method of lubricating a mechanical device. The composition provides improved oxidative stability of a lubricating oil in the
30 mechanical device while minimizing corrosion of conductive metals.

- 7 -

[0032] As used herein, TBN is measured according to ASTM D2896-21, "Standard Test Method for Base Number of Petroleum Products by Potentiometric Perchloric Acid Titration," ASTM International, West Conshohocken, PA, 2015, hereinafter, D2896.

- 5 **[0033]** In one embodiment, the lubricating composition has a TBN of at least 5, or at least 7. In another embodiment the lubricating composition has a TBN of no more than 20, or no more than 15, or no more than 12, or no more than 10.

[0034] An exemplary lubricating composition includes:

- 10 a) an oil of lubricating viscosity,
b) a phenolic antioxidant, i.e., one or more phenolic antioxidants,
c) a sulfurized organic compound, i.e., one or more sulfurized organic compounds, the sulfurized organic compound selected to provide the lubricating composition with a low active sulfur content, and
15 d) optionally, one or more performance additives, which may be selected from:
i) a succinimide dispersant, i.e., one or more succinimide dispersants, and
ii) a detergent, i.e., one or more detergents, such an alkaline earth
20 metal salt of an alkyl sulfonate.

[0035] The lubricating composition may further include one or more other performance additives.

- [0036]** The term "active sulfur" of a sulfur-containing compound refers to the relative ability of a sulfur-containing compound to react chemically with a
25 metal surface to form a metal sulfide. As used herein, active sulfur is the weight percent of sulfur which is available for a reaction at 150°C, as determined by ASTM D1662-19, "Standard Test Method for Active Sulfur in Cutting Oils," hereinafter, ASTM D1662. It is to be noted that the active sulfur of a sulfur-containing compound is not merely a function of the mole percent
30 of sulfur that it contains and that two sulfur-containing compounds may have very similar mole % (or weight %) of sulfur but distinctly different weight % of active sulfur. The balance of the sulfur is referred to as inactive sulfur.

- 8 -

- [0037]** In one embodiment, the lubricating composition is free, or substantially free, of substituted diphenylamines. By “substantially free” it is meant that the lubricating composition contains no more than 0.1 wt. %, or no more than 0.01 wt. % of substituted diphenylamines. Substituted
- 5 diphenylamines are defined as phenyl amines having a substituent on one or more of the carbon atoms of the phenyl rings. The substituent(s) can be hydrocarbyl substituent(s) selected from aliphatic substituents (including cycloaliphatic), aromatic substituents, substituents with alkyl and aryl moieties, and mixtures thereof.
- 10 **[0038]** The lubricating composition may have a kinematic viscosity at 100°C (KV₁₀₀) of at least 2 cSt (or mm²/s), or at least 10 cSt, or at least 12 cSt, or up to 25 cSt, or up to 20 cSt, as measured by ASTM D445-21e1, “Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity)”, hereinafter, “D445”. The
- 15 lubricating composition may be liquid, i.e., not a gel or semi-solid, at ambient temperatures (15-30°C).

a) The Oil of Lubricating Viscosity

- [0039]** The lubricating composition comprises an oil of lubricating viscosity. Suitable oils include natural and synthetic oils, oil derived from hydrocracking,
- 20 hydrogenation, and hydrofinishing, unrefined, refined, re-refined oils or mixtures thereof.

- [0040]** Oils of lubricating viscosity may also be defined as specified in April 2008 version of “Appendix E - API Base Oil Interchangeability Guidelines for Passenger Car Motor Oils and Diesel Engine Oils”, section 1.3 Sub-heading
- 25 1.3. “Base Stock Categories”. The API Guidelines are also summarized in U.S. Pat. No. 7,285,516. The five base oil groups are as follows: Group I (sulfur content >0.03 wt. %, and/or <90 wt. % saturates, viscosity index 80-120); Group II (sulfur content ≤0.03 wt. %, and ≥90 wt. % saturates, viscosity index 80-120); Group III (sulfur content ≤0.03 wt. %, and ≥90 wt. % saturates,
- 30 viscosity index ≥120); Group IV (all polyalphaolefins (PAOs)); and Group V (all others not included in Groups I, II, III, or IV). The exemplary oil of

- 9 -

lubricating viscosity includes an API Group I, Group II, Group III, Group IV, Group V oil, or mixtures thereof. In some embodiments, the oil of lubricating viscosity is an API Group I, Group II, Group III, or Group IV oil, or mixtures thereof. In some embodiments, the oil of lubricating viscosity is an API Group I, Group II, or Group III oil, or mixture thereof. In one embodiment the oil of lubricating viscosity may be an API Group II, Group III mineral oil, a Group IV synthetic oil, or mixture thereof. In some embodiments, at least 5 wt. %, or at least 10 wt.%, or at least 20 wt.%, or at least 40 wt. % of the lubricating composition is a polyalphaolefin (Group IV). Other groups (subgroups) have defined, from which the oil of lubricating viscosity may be selected, including API Group II+ base oils, which refers to a Group II base oil having a viscosity index ≥ 110 and less than 120, and API Group III+ base oil, having a viscosity index ≥ 130 , as described in SAE publication "Design Practice: Passenger Car Automatic Transmissions," fourth Edition, AE-29, 2012, pages 12-9. In one embodiment, a Group II and/or Group III base oil is used.

[0041] Unrefined, refined and re-refined oils, and natural and synthetic oils are described, for example, in WO2008/147704 and U.S. Pub. No. 2010/197536. Synthetic oils may also be produced by Fischer-Tropsch reactions and typically may be hydroisomerized Fischer-Tropsch hydrocarbons or waxes. Oils may be prepared by a Fischer-Tropsch gas-to-liquid synthetic procedure as well as other gas-to-liquid procedures.

[0042] Unrefined oils are those obtained directly from a natural or synthetic source generally without (or with little) further purification treatment.

[0043] Refined oils are similar to the unrefined oils except they have been further treated in one or more purification steps to improve one or more properties. Purification techniques are known in the art and include solvent extraction, secondary distillation, acid or base extraction, filtration, percolation and the like.

[0044] Re-refined oils are also known as reclaimed or reprocessed oils and are obtained by processes similar to those used to obtain refined oils and often are additionally processed by techniques directed to removal of spent additives and oil breakdown products.

- 10 -

[0045] Natural oils include animal oils, vegetable oils (e.g., castor oil), 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 and oils derived from coal or shale or mixtures thereof. Example animal and vegetable oils include long chain fatty acid esters, such as linseed oil, sunflower oil, sesame seed oil, beef tallow oil, lard oil, palm oil, castor oil, cottonseed oil, corn oil, peanut oil, soybean oil, olive oil, whale oil, menhaden oil, sardine oil, coconut oil, palm kernel oil, babassu oil, rapeseed oil, and soya oil.

[0046] 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. Exemplary synthetic oils include hydrocarbon oils, such as poly-alpha olefins, synthetic esters and polyesters, poly-acrylates and poly-methacrylates, liquid esters of phosphorus-containing acids, and polymeric tetrahydrofurans.

[0047] Example synthetic esters include esters of a dicarboxylic acid (e.g., selected from phthalic acid, succinic acid, alkyl succinic acids, alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkyl malonic acids, and alkenyl malonic acids) with an alcohol (e.g., selected from butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, and propylene glycol). Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl) sebacate, di-*n*-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid. Esters particularly useful as synthetic oils include those made from C₅ to C₁₂ monocarboxylic acids and polyols and from polyol ethers such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol, and tripentaerythritol. Esters can also be monoesters, such as are available under

- 11 -

the trade name Priolube 1976™ (C₁₈-alkyl-COO-C₂₀ alkyl). Synthetic esters useful herein may have a KV₁₀₀ of 2.5 mm²/s to 30 mm²/s.

[0048] Exemplary synthetic hydrocarbon oils include polymerized and interpolymers of olefins (e.g., polybutylenes, polypropylenes, propylene-isobutylene copolymers); poly(1-hexenes), poly(1-octenes), poly(1-decenes), 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.

[0049] Mixtures of such oils are contemplated, such as a mixture of Group II and Group III base oils, or a mixture of Group III and Group IV base oils.

[0050] The oil of lubricating viscosity may have a kinematic viscosity at 100°C (KV₁₀₀), determined according to D445, of at least 1.8 cSt, or at least 4 cSt, depending on the desired SAE grade of the lubricating composition. This viscosity can be obtained by a mixture of base oils, for example containing mineral bases of Group I such as Neutral Solvent (for example 500 NS or 600 NS) and Bright Stock bases. Any other combination of mineral or synthetic bases or bases of vegetable origin having, in mixture with the additives, a viscosity compatible with the desired SAE grade can be used.

[0051] The amount of the oil of lubricating viscosity present may be typically the balance remaining after subtracting from 100 wt. % the sum of the amount of the additives as described herein above, and any other performance additives.

[0052] The lubricating composition may be in the form of a concentrate and/or a fully formulated lubricant. If the lubricating composition is in the form of a concentrate (which may be combined with additional oil to form, in whole or in part, a finished lubricating composition), a ratio of the components of the lubricating composition (other than the oil of lubricating viscosity) to the oil of lubricating viscosity may be from 20:80 to 90:10 by weight, or from 40:60 to 80:20 by weight. If the lubricating composition is in the form of a finished

- 12 -

lubricating composition, a ratio of the components of the lubricating composition (other than the oil of lubricating viscosity) to the oil of lubricating viscosity may be from 1:99 to 30:70 by weight, or from 5:95 to 20:80 by weight.

[0053] In one embodiment, the oil of lubricating viscosity (including diluent oil and oil present as a result of additives in the composition) is at least 20 wt. %, or at least 40 wt. %, or at least 60 wt. %, or at least 80 wt. %, or at least 82 wt. %, or up to 94 wt. %, or up to 92 wt. %, or up to 90 wt. % of the lubricating composition.

b) The phenolic antioxidant

[0054] The phenolic antioxidant may be present in the lubricating composition at a total concentration of at least 0.1 wt. %, or at least 0.5 wt. %, or at least 1 wt. %, or at least 1.5 wt. %, or at least 2 wt. %, or up to 8 wt. %, or up to 6 wt. %, or up to 5 wt. %, or up to 4 wt. %, or up to 3 wt. % of the lubricating composition.

[0055] Exemplary phenolic antioxidants include hindered phenols, including hindered phenol esters, such as phenol alkyl esters, hindered phenol acetates, hindered phenol alkoxides, bis- and polyphenols, condensates of phenols with formic acid and mixtures thereof. Hindered phenol antioxidants often 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 (typically linear or branched alkyl) and/or a bridging group linking to a second aromatic group.

[0056] Example phenolic antioxidants that may be used include:

- Hindered phenols, such as 2-*tert*-butylphenol, 2-*tert*-butyl-4-methylphenol, 2-*tert*-butyl-5-methylphenol, 2,4-di-*tert*-butylphenol, 2,6-di-*tert*-butylphenol, 2,4-dimethyl-6-*tert*-butylphenol, 2,6-di-*tert*-butyl-4-methylphenol, 2-*tert*-butyl-4-methoxyphenol, 3-*tert*-butyl-4-methoxyphenol, 2,5-di-*tert*-butylhydroquinone, 2,6-di-*tert*-butyl-4-ethylphenol; 4-methyl-2,6-di-*tert*-butylphenol, 4-ethyl-2,6-di-*tert*-butylphenol, 4-propyl-2,6-di-*tert*-butylphenol, 4-butyl-2,6-di-*tert*-butylphenol, and 4-dodecyl-2,6-di-*tert*-butylphenol;

- 13 -

- Hindered alkyl phenol esters, such as C₇-C₉ branched alkyl esters of 3,5-*bis*(1,1-dimethyl-ethyl)-4-hydroxy-benzenepropanoic acid, alkyl-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionates such as n-octadecyl-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate, n-butyl-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate and 2'-ethylhexyl-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate;
- Hindered alkoxy phenols, such as 2,6-di-*tert*-butyl-4-alkoxyphenols, e.g., 2,6-di-*tert*-butyl-4-methoxyphenol and 2,6-di-*tert*-butyl-4-ethoxyphenol;
- Hindered phenol acetates, such as 3,5-di-*tert*-butyl-4-hydroxybenzylmercaptooctylacetate;
- Hindered bisphenols, such as 2,2'-methylene-*bis*(4-alkyl-di-*tert*-butylphenol)s, e.g., 2,2'-methylene-*bis*(4-methyl-di-*tert*-butylphenol), and 2,2'-methylene-*bis*(4-ethyl-di-*tert*-butylphenol), bisphenols, such as 4,4'-butylidene-*bis*(3-methyl-6-*tert*-butylphenol), 4,4'-methylene-*bis*(2,6-di-*tert*-butylphenol), 4,4'-*bis*(2,6-di-*tert*-butylphenol), 2,2-(di-p-hydroxyphenyl)propane, 2,2-*bis*(3,5-di-*tert*-butyl-4-hydroxyphenyl)propane, 4,4'-cyclohexylidene-*bis*(2,6-*tert*-butylphenol), hexamethyleneglycol-*bis*[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate], triethyleneglycol-*bis*[3-(3-*tert*-butyl-4-hydroxy-5-methylphenyl)propionate], 2,2'-thio-[diethyl-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate], 3,9-*bis*{1,1-dimethyl-2-[3-(3-*tert*-butyl-4-hydroxy-5-methylphenyl)propionyloxy]ethyl}2,4,8,10-tetraoxaspiro-[5,5]undecane, 4,4'-thio-*bis*(3-methyl-6-*tert*-butylphenol) and 2,2'-thio-*bis*(4,6-di-*tert*-butylresorcinol);
- Polyphenols such as tetrakis[methylene-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate]methane, 1,1,3-*tris*(2-methyl-4-hydroxy-5-*tert*-butylphenyl)butane, 1,3,5-trimethyl-2,4,6-*tris*(3,5-di-*tert*-butyl-4-hydroxybenzyl)benzene, *bis*-[3,3'-*bis*(4'-hydroxy-3'-*tert*-butylphenyl)butyric acid]glycol ester, 2-(3',5'-di-*tert*-butyl-4-hydroxyphenyl)methyl-4-(2'',4''-di-*tert*-butyl-3''-hydroxyphenyl)methyl-6-*tert*-butylphenol and 2,6-*bis*(2'-hydroxy-3'-*tert*-butyl-5'-methylbenzyl)-4-methylphenol;
- 4-*tert*-butylphenol-formaldehyde condensates and 4-*tert*-butylphenol-acetaldehyde condensates;

- 14 -

- and mixtures thereof.

- [0057]** The hindered phenol antioxidant often contains 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 (typically linear or branched alkyl) 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, 4-butyl-2,6-di-*tert*-butylphenol, and 4-dodecyl-2,6-di-*tert*-butylphenol. In one embodiment the hindered phenol antioxidant is an ester and may include, e.g., Irganox™ L 135 or L 115 from BASF. Irganox™ L 135 is a high molecular weight phenolic antioxidant, specifically, a mixture of C₇-C₉ branched alkyl esters of 3,5-*bis*(1,1-dimethyl-ethyl)-4-hydroxy-benzenepropanoic acid. Irganox™ L 115 is 2,6-di-*tert*-butylphenol. A more detailed description of suitable ester-containing hindered phenol antioxidant chemistry is found in U.S. Pat. No. 6,559,105. In another embodiment, the hindered alkyl phenol is a C₄ alkyl ester of 3,5-*bis*(1,1-dimethyl-ethyl)-4-hydroxy-benzenepropanoic acid. In another embodiment, the hindered alkyl phenol is 2,2'-thiodiethylene *bis*[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate].
- [0058]** Coupled phenols useful herein may contain two alkylphenols coupled with alkylene groups to form bisphenol compounds. Examples of suitable coupled phenol compounds include 4,4'-methylene *bis*(2,6-di-*tert*-butyl phenol); 4-methyl-2,6-di-*tert*-butylphenol; 2,2'-*bis*(6-*tert*-butyl-4-heptylphenol); 4,4'-*bis*(2,6-di-*tert*-butyl phenol); 2,2'-methylene *bis*(4-methyl-6-*tert*-butylphenol), and 2,2'-methylene *bis*(4-ethyl-6-*tert*-butylphenol).
- [0059]** Other phenolic antioxidants may include polyhydric aromatic compounds and their derivatives. Examples of suitable polyhydric aromatic compounds include esters and amides of gallic acid, 2,5-dihydroxybenzoic acid, 2,6-dihydroxybenzoic acid, 1,4-dihydroxy-2-naphthoic acid, 3,5-dihydroxynaphthoic acid, 3,7-dihydroxy naphthoic acid, and mixtures thereof. In one embodiment, the phenolic antioxidant comprises a hindered phenol. In

- 15 -

another embodiment the hindered phenol is derived from 2,6-di-*tert*-butyl phenol.

[0060] In one embodiment, the lubricating composition is free or substantially free of substituted diphenylamine (SDPA) antioxidants. By this it is meant that SDPA antioxidants may be present at no more than 0.1 wt. % of the lubricating composition, or no more than 0.01 wt. % of the lubricating composition, or 0 wt. %.

[0061] Substituted diphenylamines of this type include mono-, di-, tri-, and poly- alkyl, alkenyl, alkynyl, alkoxyalkyl, alkylamino, aryl, alkylaryl, and/or alkoxyaryl-substituted diphenylamines, e.g., C1-C24, particularly C6 and higher, alkyl-substituted diphenylamines, such as mono-octyl diphenylamine, di-octyl diphenylamine, mono-butyl-mono-octyl diphenylamine, nonyl diphenylamine, di-nonyl diphenylamine, tri-nonyl diphenylamine, decyl diphenylamine, and di-decyl diphenylamine, as described, for example, in U.S. Pat. Nos. 2,943,112; 4,824,601; 5,672,752; 6,204,412; 6,315,925; 6,355,839, and U.S. Pub. Nos. 2015/0307803 and 2016/0017252, as well as polymers of such monomers, as described, for example, in U.S. Pub. No. 20190127526A1. Aryl-substituted diphenylamines include phenyl- α -naphthylamine (PANA) and alkylated phenyl naphthylamines.

[0062] Other aminic antioxidants, which may be excluded or substantially free of, include 2,6-di-*tert*-butyl- α -dimethylamino-p-cresol.

[0063] In one embodiment, the lubricating composition is free or substantially free (less than 0.01 wt. %, or less than 0.001 wt. % or 0 wt. %) of all aminic antioxidants.

25 c) The Sulfurized Organic Compound

[0064] The exemplary sulfurized organic compound helps to control wear in a lubricated device, such as an engine, particularly for extreme pressure conditions in automobile, truck and industrial engines. They can also have very good thermal oxidation stability and rust inhibition properties.

[0065] Sulfurized organic compounds include those that are substantially nitrogen-free, that is, do not contain nitrogen functionality. They may be

- 16 -

formed by sulfurizing an organic compound containing at least one olefinic double bond (a non-aromatic double bond), that is, one connecting two aliphatic carbon atoms. The organic compounds to be sulfurized may, in some cases, include metal cations (e.g., from Group I or II, e.g., sodium, potassium, 5 barium, calcium); halogen groups (e.g., chloro, bromo, or iodo); and/or oxygen-containing groups, such as ester groups.

[0066] Example sulfurized organic compounds include dibenzyl mono- and disulfides, sulfurized isobutylene, sulfurized methyl esters of oleic acid, sulfurized alkylphenols, sulfurized dipentene, sulfurized terpenes, and 10 sulfurized Diels-Alder adducts, and phosphosulfurized hydrocarbons such as the reaction product of phosphorus sulfide with turpentine or methyl oleate, and the like.

[0067] The sulfurized organic compound or mixture of compounds particularly useful herein contain(s) little or no active sulfur. Active sulfur 15 compounds include a chain of at least two connected sulfur atoms. The chain of sulfur atoms allows the molecule to break easily between sulfur atoms and the reactive sulfur species formed can cause corrosion of some metals, such as copper. Inactive sulfur compounds contain fewer than two connected sulfur atoms, i.e., each sulfur atom is connected to an atom other than sulfur. Some 20 compounds may include both active sulfur and inactive sulfur, with some of the sulfur content being in a chain of two or more sulfur atoms while the remainder of the sulfur occurs as single sulfur atoms.

[0068] The sulfurized organic compound or mixture of sulfurized organic compounds, where two or more such compounds are used, may have an 25 active sulfur content, as determined at 150°C by ASTM D1662, of no more than 8 wt. %, or no more than 6 wt. %, or no more than 5 wt. %, or no more than 4 wt. %, or no more than 3.5 wt. %, or no more than 3 wt. %, or no more than 2.5 wt. %, or as little as 0 wt. % of active sulfur. In some embodiments, the active sulfur is at least 0.1 wt. %, or at least 0.5 wt. %, or 30 or at least 1.0 wt. %, or at least 1.5 wt. %, or at least 1.8 wt. %, of the sulfurized organic compound or mixture of sulfurized organic compounds. Where two or

- 17 -

more sulfurized organic compound are employed, the active sulfur content is the average (weighted mean) active sulfur content.

[0069] The sulfurized organic compound or mixture of sulfurized organic compounds, where two or more such compounds are used, may have a total sulfur content, as determined in accordance with ASTM D1552-16 (2021),
5 “Standard Test Method for Sulfur in Petroleum Products by High Temperature Combustion and Infrared (IR) Detection or Thermal Conductivity Detection (TCD),” hereinafter D1552, of at least 1 wt. %, or at least 1.5 wt. %, or at least 2 wt. %, or no more than 18 wt. %, or no more than 15 wt. %, or no more than
10 14.0 wt. %, or no more than 12.0 wt. %, or no more than 5 wt. %. Where two or more sulfurized organic compound are employed, the total sulfur content is the average (weighted mean) sulfur content.

[0070] In one embodiment, the percentage, by weight, of the total sulfur (as determined by ASTM D1552) in the sulfurized organic compound that is active sulfur (as determined by ASTM D1662) may be no more than 25 wt. %, or no
15 more than 22 wt. %, or no more than 20 wt. %, or no more than 19 wt. %, and may be as little as 0 wt. %, or in some embodiments, at least 1 wt. %, or at least 1.5 wt. %, or at least 6 wt. %, or at least 10 wt. %, or at least 15 wt. %. Put another way, a ratio by weight of active sulfur to sulfur which is not active
20 sulfur in the sulfurized organic compound may be no more than 25:75, or no more than 22:82, or no more than 20:80.

[0071] The sulfurized organic compound(s) may be present in a sufficient amount to provide the lubricating composition with at least 0.01 wt.%, or at least 0.03 wt.%, or at least 0.05 wt.%, or up to 0.12 wt.%, or up to 0.09 wt. %, or up to 0.07 wt.% sulfur. Other sources of sulfur in the lubricating composition
25 may provide additional amounts of sulfur.

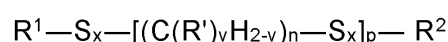
[0072] The sulfurized organic compound(s) may be present in a sufficient amount to provide the lubricating composition with no more than 0.04 wt. % of active sulfur, or no more than 0.03 wt. %, or no more than 0.025 wt. %, or
30 no more than 0.02 wt. %, or no more than 0.015 wt. % of active sulfur and in some embodiments, to provide the lubricating composition with at least 0.005 wt.%, or at least 0.008 wt.%, or at least 0.01 wt. % of active sulfur. In general,

- 18 -

the sulfurized organic compound(s) are the only sources of active sulfur in the lubricating composition.

[0073] The sulfurized organic compound may be selected from oligomeric polysulfides, alkyl polysulfides, sulfurized esters, sulfurized alpha olefins, sulfurized fats, and sulfurized soybean oil.

[0074] Oligomeric polysulfides can be of the general form shown in Formula I:



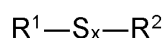
Formula I,

where R^1 and R^2 are each independently a C2-C20 alkyl, e.g., a C3, or C4 or higher alkyl, or a C16 or lower alkyl, each R' is independently a C1-C20 alkyl, or a C6 or lower alkyl; each n is independently at least 1, or at least 2, or up to 8, e.g., 3-5, such as 3 or 4; p is independently at least 1, or at least 2, or up to 8; each v is from 0-2, e.g., v is 0; and each x is independently at least 1, and in some cases may be at least 2, or up to 3, or higher, with the proviso that the limits noted above on active sulfur of the sulfurized organic compound(s) are met.

[0075] In general (e.g., for at least 80% of the S_x groups, or at least 90% of the S_x groups, or in some cases all of the S_x groups) the values of x are no more than 1. The lubricating composition may thus be substantially free of compounds Formula (I) where x is 4 or higher. "Substantially free" in this context, means that x is 4 or higher in no more than 5%, or no more than 2%, or no more than 1%, or no more than 0.5% of the S_x groups. The total sulfur content (ASTM D1552) of such oligomeric polysulfides and mixtures thereof may range from 5-45 wt. %, or at least 10 wt. %. The active sulfur content (ASTM D1662) of such oligomeric polysulfides and mixtures thereof may range from 0.5-10 wt. %, or up to 9 wt. %.

[0076] Alkyl polysulfides can be of the general form shown in Formula II:

- 19 -



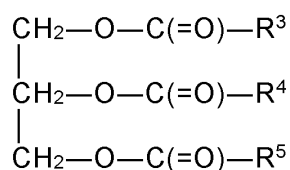
Formula II,

where R^1 and R^2 are each independently a C2-C20 alkyl, e.g., a C3 or higher alkyl, or a C16 or lower alkyl; and

5 each x is independently at least 1, and in some cases may be at least 2, or up to 3, or higher, with the proviso that the limits noted above on active sulfur of the sulfurized organic compound(s) are met. This generally means the value of x is no more than 1.5, or no more than 1.2, on average, and that the
10 lubricating composition is substantially free of compounds of Formula II where x is 4 or higher.

[0077] The total sulfur content (ASTM D1552) of such alkyl polysulfides and mixtures thereof may range from 5-20 wt. %, or at least 10 wt. %. The active sulfur content (ASTM D1662) of such alkyl polysulfides and mixtures thereof
15 may range from 0.5-45 wt. %, or up to 10 wt. %, or up to 9 wt. %, or up to 5 wt. %. The molecular weight may range from 200 to 2000 Dalton.

[0078] Example sulfurized esters include sulfurized fatty acid esters of an aliphatic alcohol, such as glycerol, e.g., monoglycerides, diglycerides, and triglycerides, such as sulfurized triglycerides of the general form shown in
20 Formula III:



Formula III,

where R^3 , R^4 , and R^5 are each independently a C8 or higher alkyl or alkenyl group, or a C10 or higher alkyl or alkenyl group, or up to a C30 or up to a C24 alkyl or alkenyl group; and

wherein at least one of R^3 , R^4 , and R^5 is linked to a sulfur
25 atom of a sulfur-containing moiety, intermediate ends of the alkyl group.

[0079] Example sulfur-containing moieties can be of the general form:

- 20 -

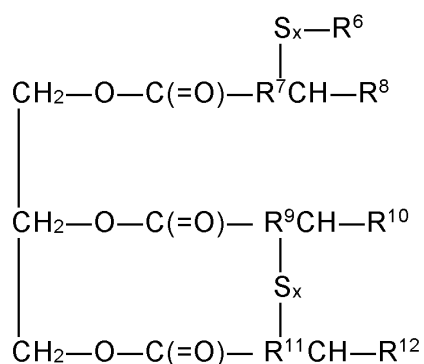
—S_x—, which forms a link between two of R³, R⁴, and R⁵; or

—S_x—R⁶, where R⁶ is a C4 or higher, or a C6, or higher, or a C8 or higher, or a C10 or higher, or up to a C50, linear or branched alkyl or alkenyl group, such as —CH₂CH=CHCH₂(CH₂CH₂)_qCH₃, where q is at least 5, or at least 10, or up to 15;

or mixture thereof;

where each x is independently at least 1, and in some cases may be at least 2, or up to 3, or higher, but substantially free of compounds of Formula II where x is 4 or higher, with the proviso that the limits noted above on active sulfur of the sulfurized organic compound(s) are met.

[0080] One example sulfurized fatty acid ester is a sulfurized triglyceride of the general form shown in Formula IV:



Formula IV,

where R⁶ is as described above, e.g., CH₂CH=CHCH₂(CH₂CH₂)₁₃₋₁₅CH₃;

each of R⁷, R⁸, R⁹, R¹⁰, R¹¹, and R¹² is independently a C2 to C8 alkyl or alkenyl group, e.g., R⁷ is (CH₂)₆, R⁸ is (CH₂)₆CH₃, R⁹ is (CH₂)₇, R¹⁰ is (CH₂)₅CH₃, R¹¹ is (CH₂)₆, and R¹² is (CH₂)₆CH₃;

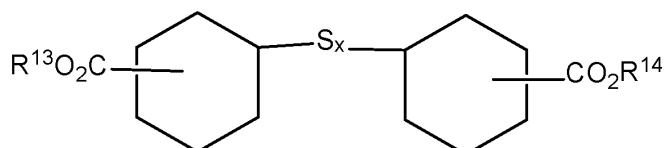
and each x is independently as described above.

[0081] The total sulfur content (ASTM D1552) of the sulfurized triglyceride according to Formula IV may be at least 5 wt. %, or at least 7 wt. %, or up to 15 wt. %, or up to 12 wt. %.

- 21 -

[0082] The active sulfur (ASTM D1662) of the sulfurized esters or mixture thereof may be less than 5 wt. %, e.g., from 3 – 4 wt. %.

[0083] Other sulfurized esters include sulfurized cycloaliphatic dialkylesters and dialkenyl esters of the general form shown in Formula V:



5

Formula V,

where each of R^{13} and R^{14} is independently a C2 or higher alkyl group, such as a C3 or higher, or C4 or higher, or up to C10, or up to C6 alkyl or alkenyl group, e.g., a linear C4 alkyl group; and

10

x is as described above, e.g., x is 1 or 2.

[0084] The sulfur content of the sulfurized cycloaliphatic diester(s) may be at least 5 wt. % or at least 10 wt. % or up to 15 wt. %, such as 10-14 wt. % and the active sulfur may be 1 to 5 wt. %. For example, the active sulfur content of a mixture of sulfurized cycloaliphatic dibutylesters of the form shown in Formula V may be at least 1 wt. % or at least 1.5 wt. % or up to 5 wt. %, such as up to 3 wt. %.

[0085] Example sulfurized organic compounds include sulfurized olefins (sulfurized alkenes), which can be obtained by reacting a sulfurizing agent with an alkene, such as isobutylene, in the presence of a catalyst. Sulfurizing agents include elemental sulfur, hydrogen sulfide, sulfur halide, sodium sulfide, and a mixture of hydrogen sulfide and sulfur or sulfur dioxide. The amount of sulfurizing agent employed may be calculated based on the total olefinic unsaturation of the mixture. For example, 0.5 to 1.2 moles of sulfur are employed per mole of olefinic bonds. The olefinic compound may contain from 2 to 50 carbon atoms.

[0086] Example sulfurized olefins can be obtained from isobutylene, sulfur and hydrogen sulfide, by catalytic processes using solid catalysts such as

- 22 -

those described in U.S. Pat. Nos. 6,472,354B2 and 4,876,389A, by reacting a mercaptan and sulfur in the presence of a basic catalyst. They can also be produced by a two-step process, as described in U.S. Pat. No. 4,937,385A, which includes synthesizing a mercaptan from an alkene and H₂S in the presence of a solid catalyst and then bringing the mercaptan with sulfur and another heterogeneous catalyst together to form the sulfurized olefin.

[0087] A sulfurized olefin as illustrated in Formula IV can be prepared as described in U.S. Pat. No. 4,957,651. The method employs a cosulfurized mixture of two or more reactants selected from (1) at least one fatty acid ester of a polyhydric alcohol, (2) at least one fatty acid, (3) at least one olefin, and (4) at least one fatty acid ester of a monohydric alcohol. Reactant (3), the olefin component, includes at least one olefin. The olefin may be an aliphatic olefin, containing 4 to 40 carbon atoms, such as from 8 to 36 or 12 to 18 carbon atoms. Terminal olefins, or alpha-olefins, are particularly suitable, especially those having from 12 to 20 carbon atoms.

[0088] A sulfurized organic compound as illustrated in Formula V can be the reaction product of a sulfurizing agent and at least one Diels-Alder adduct, in a molar ratio of at least 0.75:1. The molar ratio of sulfur source to Diels-Alder adduct may be from 0.75:1 to 1:1.2. The Diels-Alder adducts can be prepared from dienophiles having at least one carboxylic ester group represented by —C(O)O—R_o, where R_o is the residue of a saturated aliphatic alcohol of up to 40 carbon atoms, the aliphatic alcohol from which —R_o is derived being a mono or polyhydric alcohol, which may be selected from alkylene glycols, alkanols, alkoxy-substituted alkanols, ethanol, ethoxyethanol, propanol, butanol, beta-diethylamino-ethanol, dodecyl alcohol, diethylene glycol, tripropylene glycol, tetrabutylene glycol, hexanol, octanol, isooctyl alcohol and mixtures thereof. Generally, not more than two —C(O)O—R_o groups will be present, and in one embodiment, only one —C(O)O—R_o group. Such materials can also be described as cyclohexene compounds bearing ester substituents. An example sulfurized organic compound of this type is sulfurized 4-carbobutoxy cyclohexene. This and

- 23 -

other sulfurized organic compounds can be further treated with other materials such as an aryl phosphate, e.g., triphenyl phosphite.

[0089] The sulfurization reaction may be affected at an elevated temperature, e.g., 50-350° C or 100-200° C, with efficient agitation and often
5 in an inert atmosphere such as nitrogen, optionally in the presence of an inert solvent.

d) Performance additives

i) Dispersants

[0090] The lubricating composition optionally further includes at least one
10 dispersant. Exemplary dispersants include succinimide dispersants, Mannich dispersants, succinamide dispersants, and polyolefin succinic acid esters, amides, and ester-amides, and mixtures thereof.

[0091] In an exemplary embodiment, the dispersant includes at least one
15 succinimide dispersant. The dispersant may be an N-substituted long chain alkenyl succinimide. An example of an N-substituted long chain alkenyl succinimide is polyisobutylene succinimide. The polyisobutylene from which polyisobutylene succinic anhydride is derived has a number average molecular weight M_n of at least 300, or at least 350, or at least 500, or at least 550, or at least 750, or at least 1000, and can be up to 5000, or up to 3000,
20 or up to 2500. Such succinimides can be formed, for example, from high vinylidene polyisobutylene and maleic anhydride. Succinimide dispersants and their preparation are disclosed, for example, in U.S. Pat. Nos. 3,172,892, 3,219,666, 3,316,177, 3,340,281, 3,351,552, 3,381,022, 3,433,744, 3,444,170, 3,467,668, 3,501,405, 3,542,680, 3,576,743, 3,632,511,
25 4,234,435, Re 26,433, 6,165,235, and 7,238,650 and EP0355895A2.

[0092] In one embodiment, the succinimide dispersant is a polyisobutylene succinimide dispersant derived from an 1800 to 2200 M_n polyisobutylene, which includes 0.80-1.0 wt. % nitrogen.

[0093] In another embodiment, the dispersant may be a polyolefin succinic
30 acid ester, amide, or ester-amide. A polyolefin succinic acid ester-amide may be a polyisobutylene succinic acid reacted with an alcohol (such as

- 24 -

pentaerythritol) and a polyamine. Example polyolefin succinic acid esters include polyisobutylene succinic acid esters of pentaerythritol and mixture thereof.

- [0094]** The exemplary dispersants may also be post-treated by conventional methods by a reaction with any of a variety of agents. Among these are boron compounds (such as boric acid), urea, thiourea, dimercaptothiadiazoles, carbon disulfide, aldehydes, ketones, carboxylic acids, such as terephthalic acid, hydrocarbon-substituted succinic anhydrides, maleic anhydride, nitriles, epoxides, and phosphorus compounds.
- 10 In one embodiment the post-treated dispersant is borated. In one embodiment the post-treated dispersant is reacted with dimercaptothiadiazoles. In one embodiment the post-treated dispersant is reacted with phosphoric or phosphorous acid. In one embodiment the post-treated dispersant is reacted with terephthalic acid and boric acid (as described, for example, in U.S. Pub.
- 15 No. 20090054278A1), which may be derived from an aliphatic polyamine, or mixtures thereof. The aliphatic polyamine may be an ethylenepolyamine, a propylenepolyamine, a butylenepolyamine, or a mixture thereof. In one embodiment the aliphatic polyamine may be an ethylenepolyamine. In one embodiment the aliphatic polyamine may be chosen from ethylenediamine,
- 20 diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, polyamine still bottoms, and mixtures thereof.

[0095] For purposes of expressing the amounts of components in the composition, dispersant viscosity modifiers are classed as viscosity modifiers rather than as dispersants.

- 25 **[0096]** When present, the lubricating composition may include, in total, at least 0.01 wt. %, or at least 0.1 wt. %, or at least 0.2 wt. %, or at least 0.5 wt. %, or at least 1 wt. %, or at least 1.5 wt. %, or at least 2 wt. % or at least 3 wt. % dispersant, and in some embodiments, up to 15 wt. %, or up to 10 wt. %, or up to 8 wt. %, or up to 7 wt. %, or up to 5 wt. % of such dispersants.
- 30 **[0097]** In one embodiment, the lubricating composition includes at least 0.2 wt. %, or at least 0.5 wt. %, or at least 1.0 wt. %, or up to 7.0 wt. %, or up to

- 25 -

6.0 wt. of a succinimide dispersant, which may be borated, or otherwise post-treated.

ii) Detergent

[0098] The lubricating composition optionally further includes at least one
5 detergent. A detergent is an additive that reduces formation of deposits on
lubricated surfaces, for example high-temperature varnish and lacquer
deposits on piston surfaces in engines. Exemplary detergents useful herein
include metal-containing detergents, which may be neutral or overbased.

[0099] The metal of the metal-containing detergent may be zinc, sodium,
10 calcium, barium, or magnesium. The metal-containing detergent may be
chosen from sulfonates, non-sulfur containing phenates, sulfur containing
phenates, salixarates, salicylates, and mixtures thereof, or borated
equivalents thereof. The metal-containing detergent may be borated with a
borating agent such as boric acid.

[0100] The metal-containing detergent may also include "hybrid"
15 detergents formed with mixed surfactant systems including phenate and/or
sulfonate components, e.g., phenate/salicylates, sulfonate/phenates,
sulfonate/salicylates, sulfonates/phenates/salicylates, as described, for
example, in U.S. Pat. Nos. 6,429,178; 6,429,179; 6,153,565; and 6,281,179.
20 Where a hybrid sulfonate/phenate detergent is employed, the hybrid detergent
can be considered equivalent to amounts of distinct phenate and sulfonate
detergents introducing like amounts of phenate and sulfonate soaps,
respectively.

[0101] Example overbased metal-containing detergents include zinc,
25 sodium, calcium, and magnesium salts of sulfonates, phenates (including
sulfur-containing and non-sulfur containing phenates), salixarates, and
hydroxybenzoates, such as salicylates, which may be hydrocarbyl substituted.
Such overbased sulfonates, salixarates, phenates and salicylates may have
a total base number of 120 to 700, or 250 to 600, or 300 to 500 (on an oil free
30 basis).

[0102] Example sulfonate detergents include linear and branched
alkylbenzene sulfonate detergents, and mixtures thereof, which may have a

- 26 -

metal ratio of at least 8, as described, for example, in U.S. Pub. No. 2005065045. Linear alkyl benzenes may have the benzene ring attached anywhere on the linear chain, usually at the 2, 3, or 4 position, or be mixtures thereof. In one embodiment, the alkylbenzene sulfonate detergent may be a
5 branched alkylbenzene sulfonate, a linear alkylbenzene sulfonate, or a mixture thereof. The sulfonate detergent may be a metal salt of one or more oil-soluble alkyl toluene sulfonate compounds, as disclosed in U.S. Pub. No. 20080119378 A1.

[0103] Examples of hydrocarbyl substituted hydroxybenzoate detergents
10 include neutral and overbased alkaline earth metal C10 to C40 hydrocarbyl substituted hydroxybenzoates, in particular C10 to C40 hydrocarbyl substituted salicylates, as described, for example, in U.S. Pub. No. 20100062958A1.

[0104] As an example, the detergent may include at one or more of an
15 overbased calcium hydrocarbyl-substituted hydroxybenzoate detergent (e.g., a calcium salicylate detergent), an overbased calcium sulfonate detergent, and a magnesium sulfonate detergent. The calcium salicylate detergent may be present in sufficient amount to provide the lubricating composition with at least 0.02 wt. % Ca, such at least 0.04 wt. %, or up to 0.3 wt. % or up to 0.2
20 wt.%, or up to 0.15 wt. % Ca. The overbased calcium sulfonate detergent may be present in sufficient amount to provide at least 0.02 wt. % Ca, such at least 0.04 wt. %, or up to 0.2 wt.%, or up to 0.15 wt. % Ca in the lubricating composition. The magnesium sulfonate detergent may neutral or overbased, such as an overbased sulfonate detergent having a metal ratio of 12 to 20, or
25 12 to 18, or 20 to 30, or 22 to 25. The magnesium sulfonate detergent may be present in sufficient amount to provide at least 0.01 wt. % Mg, such at least 0.02 wt. %, or up to 0.1 wt.%, or up to 0.06 wt. % Mg in the lubricating composition. One or more of these detergents may be borated, sufficient to provide at least 0.005 wt. % boron, or at least 0.03 wt. % boron, or up to 0.06
30 wt. %, or up to 0.04 wt.% boron in the lubricating composition.

[0105] In one embodiment, the lubricating composition includes, in total, at least 0.1 wt. %, or at least 0.2 wt. %, or at least 0.25 wt. %, or at least 0.4 wt.

- 27 -

%, or up to 3.0 wt. %, or up to 2.0 wt. %, or up to 1.5 wt. %, or up to 1.25 wt. % of detergent(s).

[0106] The lubricating composition may further include one or more other performance additives, as follows:

5 iii. Anti-wear Agents

[0107] The lubricating composition optionally further includes at least one antiwear agent, other than the sulfurized organic compound. Examples of suitable antiwear agents suitable for use herein include metal dihydrocarbyldithiophosphates (such as zinc dialkyldithiophosphates (ZDDPs)), titanium compounds, tartrates, tartrides, oil soluble amine salts of phosphorus compounds, 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.

15 **[0108]** In one embodiment, the antiwear agent includes a zinc dialkyldithiophosphate. The alkyl groups of the dialkyldithiophosphate may be linear or branched and may contain 2 to 20 carbon atoms, provided that the total number of carbons is sufficient to make the zinc dialkyldithiophosphate oil soluble. Examples of suitable zinc dialkyldithiophosphates (ZDDPs) include zinc di-(2-methylpropyl) dithiophosphate, zinc di-(amyl) dithiophosphate, zinc di-(1,3-dimethylbutyl) dithiophosphate, zinc di-(heptyl) dithiophosphate, zinc di-(octyl) dithiophosphate, zinc di-(2-ethylhexyl) dithiophosphate, zinc di-(nonyl) dithiophosphate, zinc di-(decyl) dithiophosphate, zinc di-(dodecyl) dithiophosphate, zinc di-(dodecylphenyl) dithiophosphate, zinc di-(heptylphenyl) dithiophosphate, and ZDDPs prepared from mixed alcohols such as methylpropyl and amyl alcohols, 2-ethylhexyl and isopropyl alcohols, 4-methyl-2-pentyl and isopropyl alcohols, and mixtures thereof.

25 **[0109]** In one embodiment, the ZDDP is at least 0.1 wt. % or at least 0.25 wt. %, or at least 0.5 wt. %, or up to 5 wt. %, or up to 4 wt. %, or up to 3 wt. % of the lubricating composition.

- 28 -

[0110] In one embodiment, the ZDDP is present in sufficient amount to provide at least 0.03 wt. % or at least 0.06 wt. %, or up to 0.5 wt. % or up to 0.1 wt. % Zn in the lubricating composition.

[0111] The antiwear agent may, in another embodiment, include a tartrate or tartramide, as described in U.S. Pub. Nos. 2006/0079413; 2006/0183647; and 2010/0081592. The tartrate or tartramide may contain alkyl-ester groups, where the sum of carbon atoms on the alkyl groups is at least 8. The antiwear agent may, in one embodiment, include a citrate as disclosed in U.S. Pub. No. 20050198894.

[0112] In one embodiment, the lubricating composition is free or substantially free of metal-containing antiwear agents. In other embodiments, the lubricating composition is free or substantially free of phosphorus-containing antiwear agents. For example, phosphorus-containing antiwear agents are absent or, where present, are in an amount to provide the lubricating composition with no more than 0.8 wt. % phosphorus, or no more than 0.15 wt. % phosphorus. For example, C3/6 mixed secondary ZDDP's may be present at up to 1.2 wt. %, or up to 1 wt. %, or up to 0.5 wt. %.

[0113] When present, the lubricating composition may include at least 0.01 wt. %, or at least 0.1 wt. %, or at least 0.25 wt. %, or at least 0.5 wt. % of antiwear agent(s), and in some embodiments, up to 5 wt. %, or up to 4 wt. %, or up to 3 wt. % antiwear agent.

iv) Extreme Pressure (EP) agents

[0114] The lubricating composition may include an extreme pressure agent in addition to the sulfurized organic compound that is low in active sulfur. Examples of such non-sulfur EP agents include chlorinated wax; phosphorus esters, such as di-hydrocarbon and tri-hydrocarbon phosphites, e.g., dibutyl phosphite, diheptyl phosphite, dicyclohexyl phosphite, pentylphenyl phosphite, dipentylphenyl phosphite, tridecyl phosphite, distearyl phosphite and polypropylene substituted phenol phosphite; and barium heptylphenol diacid; amine salts of alkyl and dialkylphosphoric acids and their derivatives including, for example, the amine salt of a reaction product of a

- 29 -

dialkyldithiophosphoric acid with propylene oxide and subsequently followed by a further reaction with P_2O_5 ; and mixtures thereof. Other useful extreme pressure agents are described in U.S. Pat. No. 3,197,405.

- [0115]** When present, the lubricating composition may include at least 0.01 wt. %, or at least 0.1 wt. %, or at least 0.5 wt. % extreme pressure agent, and in some embodiments, up to 3 wt. %, or up to 1.5 wt. %, or up to 0.9 wt. % of the extreme pressure agent(s).

v. Foam Inhibitors

- [0116]** The lubricating composition may include a foam inhibitor. Foam inhibitors that may be useful in the lubricant composition include polysiloxanes; copolymers of ethyl acrylate and 2-ethylhexylacrylate and optionally vinyl acetate; demulsifiers including fluorinated polysiloxanes, trialkyl phosphates, polyethylene glycols, polyethylene oxides, polypropylene oxides and (ethylene oxide-propylene oxide) polymers.

- [0117]** When present, the lubricating composition may include at least 0.005 wt. %, or at least 0.08 wt. % of foam inhibitor(s), and in some embodiments, up to 3 wt. %, or up to 1.5 wt. %, or up to 0.4 wt. % of the foam inhibitor(s).

vi. Viscosity Modifiers

- [0118]** The lubricating composition may include a viscosity modifier. Viscosity modifiers (also sometimes referred to as viscosity index improvers or viscosity improvers) useful in the lubricant composition are usually polymers, including polyisobutenes, polymethacrylates (PMA) and polymethacrylic acid esters, diene polymers, polyalkylstyrenes, esterified styrene-maleic anhydride copolymers, hydrogenated alkenylarene-conjugated diene copolymers, such as styrene-butadiene copolymer resins (SBRs), and polyolefins also referred to as olefin copolymer or OCP. PMAs are prepared from mixtures of methacrylate monomers having different alkyl groups. The alkyl groups may be either straight chain or branched chain groups containing from 1 to 18 carbon atoms. Most PMAs are viscosity modifiers as well as pour point depressants. In one embodiment, the viscosity

- 30 -

modifier includes a styrene-butadiene resin. In another embodiment, the viscosity modifier includes a polyolefin comprising ethylene and one or more higher olefin, such as propylene.

[0119] In one embodiment, the viscosity modifier includes one or more dispersant viscosity modifiers (DVMs). DVMs provide both dispersancy and viscosity modification. Example DVMs are made from polymers such as an olefin polymer (e.g., ethylene propylene copolymer) and/or vinyl aromatic polymers (e.g., polystyrene) that have been radically grafted with an ethylenically unsaturated carboxylic acid material, such as maleic anhydride, which is functionalized with one or more amines and/ or a pendent functional group which has sulfonate functionality. DVMs of this type are disclosed, for example, in U.S. Pat. Nos. 4,863,623; 5,264,140; 5,409,623; 6,107,257; 6,107,258; 6,117,825; U.S. Pub. Nos. 20120178656A1; 20120178659A1; 20090305923A1, and 20170283733A1.

[0120] When present, the lubricating composition may include at least 0.01 wt. %, or at least 0.1 wt. %, or at least 0.2 wt. %, or at least 0.4 wt. % of viscosity modifier (including dispersant viscosity modifiers) and in some embodiments, up to 10 wt. %, or up 5 wt. %, or up to 4 wt. %, or up to 2 wt. % of such viscosity modifiers. In one embodiment, the lubricating composition includes at least 0.2 wt. %, or at least 0.3 wt. %, or at least 0.5 wt. %, or up to 3.0 wt. %, or up to 2.0 wt. % of a dispersant viscosity modifier, which may be borated, or otherwise post-treated.

[0121] In some embodiments, no viscosity modifiers are used.

vii. Corrosion Inhibitors and Metal Deactivators

[0122] The lubricating composition may include a corrosion inhibitor. Corrosion inhibitors/metal deactivators that may be useful in the exemplary lubricating composition include fatty amines, octylamine octanoate, condensation products of dodecenyl succinic acid or anhydride, and a fatty acid such as oleic acid with a polyamine, derivatives of benzotriazoles (e.g., tolyltriazole), 1,2,4-triazoles, benzimidazoles, 2-alkyldithiobenzimidazoles and 2-alkyldithiobenzothiazoles.

[0123] When present, the lubricating composition may include at least 0.005 wt. %, or at least 0.01 wt. %, or at least 0.015 wt. %, or at least 0.02 wt. % corrosion inhibitor(s), and in some embodiments, up to 5 wt. %, or up to 2.5 wt. %, or up to 0.1 wt. % of corrosion inhibitor(s). In some embodiments, no corrosion inhibitors are used.

viii. Pour Point Depressants

[0124] The lubricating composition may include a pour point depressant. Pour point depressants that may be useful in the exemplary lubricating composition include polyalphaolefins, esters of maleic anhydride-styrene copolymers, polymethacrylates, polyacrylates, and polyacrylamides. In one embodiment, the pour point depressant is a maleic anhydride-styrene copolymer.

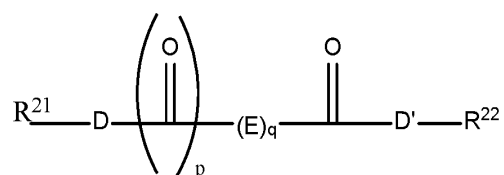
[0125] When present, the lubricating composition may include at least 0.005 wt. %, or at least 0.01 wt. %, or at least 0.1 wt. %, or at least 0.15 wt. % pour point depressant(s), and in some embodiments, up to 5 wt. %, or up to 2 wt. %, or up to 1 wt. % pour point depressant(s). In some embodiments, no pour point depressants are used.

ix. Friction Modifiers

[0126] The lubricating composition may include a friction modifier. Friction modifiers that may be useful in the exemplary lubricating composition include fatty acid derivatives such as amines, esters, epoxides, fatty imidazolines, condensation products of carboxylic acids and polyalkylene-polyamines and amine salts of alkylphosphoric acids. The friction modifier may be an ash-free friction modifier. Such friction modifiers are those which typically do not produce any sulfated ash when subjected to the conditions of ASTM D874-13a (2018). An additive is referred to as "non-metal containing" if it does not contribute metal content to the lubricant composition. As used herein the term "fatty alkyl" or "fatty" in relation to friction modifiers means a carbon chain having 8 to 30 carbon atoms, typically a straight carbon chain.

[0127] In one embodiment, the ash-free friction modifier may be represented by the formula:

- 32 -



where, D and D' are independently selected from -O-, >NH, >NR²³, an imide group formed by taking together both D and D' groups and forming a R²¹-N< group between two >C=O groups; E is selected from -R²⁴-O-R²⁵-, >CH₂, >CHR²⁶, >CR²⁶R²⁷, >C(OH)(CO₂R²²), >C(CO₂R²²)₂, and >CHOR²⁸; where R²⁴ and R²⁵ are independently selected from >CH₂, >CHR²⁶, >CR²⁶R²⁷, >C(OH)(CO₂R²²), and >CHOR²⁸; q is 0 to 10, with the proviso that when q=1, E is not >CH₂, and when n=2, both Es are not >CH₂; p is 0 or 1; R²¹ is independently hydrogen or a hydrocarbyl group, typically containing 1 to 150 carbon atoms, with the proviso that when R²¹ is hydrogen, p is 0, and q is more than or equal to 1; R²² is a hydrocarbyl group, typically containing 1 to 150 carbon atoms; R²³, R²⁴, R²⁵, R²⁶ and R²⁷ are independently hydrocarbyl groups; and R²⁸ is hydrogen or a hydrocarbyl group, typically containing 1 to 150 carbon atoms, or 4 to 32 carbon atoms, or 8 to 24 carbon atoms. In certain embodiments, the hydrocarbyl groups R²³, R²⁴, and R²⁵, may be linear or predominantly linear alkyl groups.

[0128] In certain embodiments, the ash-free friction modifier is a fatty ester, amide, or imide of various hydroxy-carboxylic acids, such as tartaric acid, malic acid lactic acid, glycolic acid, and mandelic acid. Examples of suitable materials include tartaric acid di(2-ethylhexyl) ester (i.e., di(2-ethylhexyl)tartrate), di(C₈-C₁₀)tartrate, di(C₁₂-₁₅)tartrate, dioleyltartrate, oleyl tartramide, and oleyl maleimide.

[0129] In certain embodiments, the ash-free friction modifier may be chosen from long chain fatty acid derivatives of amines, fatty esters, or fatty epoxides; fatty imidazolines such as condensation products of carboxylic acids and polyalkylene-polyamines; amine salts of alkylphosphoric acids; fatty alkyl tartrates; fatty alkyl tartrimides; fatty alkyl tartramides; fatty phosphonates; fatty phosphites; borated phospholipids, borated fatty epoxides; glycerol esters; borated glycerol esters; fatty amines; alkoxylated

- 33 -

fatty amines; borated alkoxyated fatty amines; hydroxyl and polyhydroxy fatty amines including tertiary hydroxy fatty amines; hydroxy alkyl amides; metal salts of fatty acids; metal salts of alkyl salicylates; fatty oxazolines; fatty ethoxylated alcohols; condensation products of carboxylic acids and polyalkylene polyamines; or reaction products from fatty carboxylic acids with

5 guanidine, aminoguanidine, urea, or thiourea and salts thereof.

[0130] Friction modifiers may also encompass materials such as sulfurized fatty compounds and olefins, sunflower oil or soybean oil monoester of a polyol and an aliphatic carboxylic acid.

10 **[0131]** In another embodiment 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 and in another embodiment the long chain fatty acid ester may be a triglyceride.

[0132] The amount of the ash-free friction modifier in a lubricant may be

15 0.1 to 3 percent by weight (or 0.12 to 1.2 or 0.15 to 0.8 percent by weight). The material may also be present in a concentrate, alone or with other additives and with a lesser amount of oil. In a concentrate, the amount of material may be two to ten times the above concentration amounts.

[0133] In some embodiments, the lubricating composition is free or

20 substantially free of friction modifiers, e.g., contains no more than 0.001 wt. % of friction modifiers. In other embodiments, the friction modifier(s) may be at least 0.01%, or at least 0.05 wt. %, or at least 0.1 wt. %, or up to 6 wt. %, or up to 4 wt. %, or up to 2 wt. % of the lubricating composition.

Molybdenum compounds

25 **[0134]** In one embodiment, the lubricating composition contains a molybdenum compound. Molybdenum compounds may serve in various functions in the lubricating composition, such as antiwear agents, friction modifiers, and antioxidants.

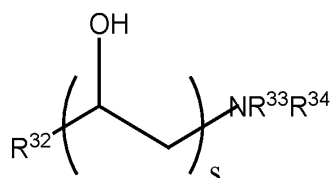
[0135] For ease of description, the amounts of molybdenum compounds

30 are not included in the amounts of antiwear agents, friction modifiers, and antioxidants, described elsewhere.

- 34 -

[0136] Molybdenum-containing antiwear agents and antioxidants include molybdenum hydrocarbyldithiocarbamate, molybdenum hydrocarbyldithiocarbamate dimer complexes, and other compounds containing molybdenum and sulfur, as described, for example, in U.S. Pat. No. 4,285,822. Other molybdenum-containing materials include molybdenum dihydrocarbyldithio-phosphates; molybdenum-amine compounds, as described in U.S. Pat. No. 6,329,327; organomolybdenum compounds made from the reaction of a molybdenum source, fatty oil, and a diamine, as described in U.S. Pat. No. 6,914,037; and trinuclear molybdenum-sulfur complexes, as described in U.S. Pat. No. 6,232,276. Other molybdenum compounds are disclosed in U.S. Pub. No. 20080280795.

[0137] Molybdenum amine compounds may be obtained by reacting a compound containing a hexavalent molybdenum atom with a primary, secondary or tertiary amine represented by the formula $\text{NR}^{29}\text{R}^{30}\text{R}^{31}$, where each of R^{29} , R^{30} and R^{31} is independently hydrogen or a hydrocarbyl group of 1 to 32 carbon atoms and wherein at least one of R^{29} , R^{30} and R^{31} is a hydrocarbyl group of 4 or more carbon atoms or represented by the formula:



where R^{32} represents a chain hydrocarbyl group having 10 or more carbon atoms, s is 0 or 1, R^{33} and/or R^{34} represents a hydrogen atom, a hydrocarbyl group, an alkanol group or an alkyl amino group having 2 to 4 carbon atoms, and when $s = 0$, both R^{33} and R^{34} are not hydrogen atoms or hydrocarbon groups.

[0138] Specific examples of suitable amines include monoalkyl (or alkenyl) amines such as tetradecylamine, stearylamine, oleylamine, beef tallow alkylamine, hardened beef tallow alkylamine, and soybean oil alkylamine; dialkyl(or alkenyl)amines such as N-tetradecylmethylamine, N-pentadecylmethylamine, N-hexadecylmethylamine, N-stearylamine, N-

- 35 -

oleylmethylamine, N-dodecyl(di)methylamine, N-beef tallow alkyl methylamine, N-hardened beef tallow alkyl methylamine, N-soybean oil alkyl methylamine, ditetradecylamine, dipentadecylamine, dihexadecylamine, distearylamine, dioleylamine, N-cocoyl methylamine, di-cocoylamine, *bis*(2-hexyldecyl)amine, *bis*(2-octyldodecyl)amine, *bis*(2-decyltetradecyl)amine, beef tallow dialkylamine, hardened beef tallow dialkylamine, and soybean oil dialkylamine; and trialk(en)ylamines such as tetradecyldimethylamine, hexadecyldimethylamine, octadecyldimethylamine, beef tallow alkyldimethylamine, hardened beef tallow alkyldimethylamine, soybean oil alkyldimethylamine, dioleymethylamine, tritetradecylamine, tristearylamine, and trioleylamine. Suitable secondary amines have two alkyl (or alkenyl) groups with 14 to 18 carbon atoms.

[0139] Examples of the compound containing the hexavalent molybdenum atom include molybdenum trioxides or hydrates thereof ($\text{MoO}_3 \cdot n\text{H}_2\text{O}$), molybdenum acid (H_2MoO_4), alkali metal molybdates (Q_2MoO_4) wherein Q represents an alkali metal such as sodium and potassium, ammonium molybdates (e.g., $(\text{NH}_4)_2\text{MoO}_4$ or heptamolybdate $(\text{NH}_4)_6[\text{Mo}_7\text{O}_{24}] \cdot 4\text{H}_2\text{O}$), MoOCl_4 , MoO_2Cl_2 , MoO_2Br_2 , $\text{Mo}_2\text{O}_3\text{Cl}_6$ and the like. Molybdenum trioxides or hydrates thereof, molybdenum acid, alkali metal molybdates and ammonium molybdates are often suitable because of their availability. In one embodiment, the lubricating composition comprises a molybdenum amine compound.

[0140] Other organomolybdenum compounds may be the reaction products of fatty oils, mono-alkylated alkylene diamines and a molybdenum source. Materials of this sort are generally made in two steps, a first step involving the preparation of an aminoamide/glyceride mixture at high temperature, and a second step involving incorporation of the molybdenum.

[0141] Examples of fatty oils that may be used include cottonseed oil, groundnut oil, coconut oil, linseed oil, palm kernel oil, olive oil, corn oil, palm oil, castor oil, rapeseed oil (low or high erucic acids), soyabean oil, sunflower oil, herring oil, sardine oil, and tallow. These fatty oils are generally known as glyceryl esters of fatty acids, triacylglycerols or triglycerides.

- 36 -

[0142] Examples of mono-alkylated alkylene diamines that may be used include methylaminopropylamine, methylaminoethylamine, butylaminopropylamine, butylaminoethylamine, octylaminopropylamine, octylaminoethylamine, dodecylaminopropylamine, dodecylaminoethylamine, 5 hexadecylaminopropylamine, hexadecylaminoethylamine, octadecylaminopropylamine, octadecylaminoethylamine, isopropoxypropyl-1,3-diaminopropane, and octyloxypropyl-1,3-diaminopropane. Mono-alkylated alkylene diamines derived from fatty acids may also be used. Examples include N-coco alkyl-1,3-propanediamine (Duomeen®C), N-tall oil 10 alkyl-1,3-propanediamine (Duomeen®T) and N-oleyl-1,3-propanediamine (Duomeen®O), all commercially available from Akzo Nobel.

[0143] Sources of molybdenum for incorporation into the fatty oil/diamine complex are generally oxygen-containing molybdenum compounds include, similar to those above, ammonium molybdates, sodium molybdate, 15 molybdenum oxides and mixtures thereof. One suitable molybdenum source comprises molybdenum trioxide (MoO_3).

[0144] Nitrogen-containing molybdenum compounds which are commercially available include, for example, Sakura-lube® 710 available from Adeka which is a molybdenum amine compound, and Molyvan® 855, 20 available from R.T. Vanderbilt.

[0145] The nitrogen-containing molybdenum compound, where used, may be at least 0.001 wt. %, or at least 0.002 wt. % of the lubricating composition or up to 2 wt. %, or up to 1.0 wt. % of the composition. Where present, the molybdenum compound may provide the lubricant composition at least 5 ppm, 25 or at least 10 ppm, 5 ppm, or up to 300 ppm, or up to 800 ppm of molybdenum. In some embodiments, the lubricating composition contains less than 800 ppm molybdenum, or less than 400 ppm, or less than 150 ppm, or less than 100 ppm, or less than 80 ppm, or less than 50 ppm, or less than 20 ppm, or less than 2 ppm, or less than 1 ppm molybdenum, or 0 ppm.

30 **[0146]** In one embodiment, the molybdenum compound does not contain dithiocarbamate moieties or ligands.

- 37 -

[0147] The lubricating composition may include a molybdenum compound in an amount to provide 40 to 1200 parts per million by weight molybdenum to the composition, or at least 50, or at least 60, or at least 100, or at least 300, or up to 1000, or up to 800, or up to 500, or up to 400, or up to 250, or up to 200 parts per million, by weight. The actual amount of the compound will depend in part on the nature and formula weight of the anion or complexing agent associated with the molybdenum, in a way that may be readily calculated. In some embodiments, the molybdenum compound is present in the lubricating composition in an amount of 0 to 1.1 wt. %, or at least 0.01 wt. %, or at least 0.02 wt. %, or at least 0.03 wt. %, or at least 0.04 wt. %, or at least 0.07 wt. %, or up to 0.5 wt. %, or up to 0.35 wt. %, or up to 0.2 wt. %, or up to 0.18 wt. %.

Additional Deposit Control Additives

[0148] The lubricating composition may contain a deposit control additive or additives, which may be selected from an alkylaryl sulfonate, amine oxide, carboxylated alcohol ethoxylate, ethoxylated amine, ethoxylated amide, glycerol ester, glycol ester, imidazoline, lecithin, lecithin derivative, lignin, monoglyceride, monoglyceride derivative, olefin sulfonate, phosphate ester, phosphate ester derivative, propoxylated fatty acid, ethoxylated fatty acid, propoxylated alcohol or alkyl phenol, sucrose ester, sulfonate of dodecyl or tridecyl benzene, naphthalene sulfonate, petroleum sulfonate, tridecyl or dodecyl benzene sulfonic acid, sulfosuccinate, sulfosuccinate derivative, or mixture of two or more thereof, each of these compounds having a hydrocarbon group of at least about 8 carbon atoms.

[0149] For example, alkoxyated hydrocarbyl-substituted phenolic compounds, such as propoxylated polyisobutylene phenol, as described in WO2014/193543A1 may be used.

[0150] Additional deposit control additives, where present, may be at least 0.01%, or at least 0.10 wt. %, or at least 0.5 wt. %, or up to 6 wt. %, or up to 3.0 wt. %.

[0151] In some embodiments, no deposit control additives are used.

Demulsifiers

- [0152]** Demulsifiers useful herein include trialkyl phosphates, and various polymers and copolymers of ethylene glycol, ethylene oxide, propylene oxide, and mixtures thereof. The demulsifier, where present, may be at least 0.001%,
 5 or at least 0.01 wt. %, or up to 0.10 wt. %, of the lubricating composition.

Seal Swell Agents

- [0153]** Seal swell agents useful herein include sulfolene derivatives such as Exxon Necton-37™ (FN 1380) and Exxon Mineral Seal Oil™ (FN 3200).

Example Lubricating Compositions

- 10 **[0154]** An engine lubricant may have a composition as illustrated in Table 1. All additives are expressed on an oil-free basis.

TABLE 1: Example Lubricating Compositions

	A	B	C
Sulfurized organic compound (with low active sulfur)	0.05 - 1.2	0.10 - 1.0	0.15 - 0.8
Phenolic antioxidant	1 - 6	1.5 - 5	2 - 4
Dispersant (e.g., succinimide dispersant, may be borated)	0.2 - 10	1 - 8	2 - 7
Detergent (e.g., one or more of calcium or magnesium sulfonates or salicylates, can be overbased)	0.1 - 2	0.2 - 1.5	0.25 - 1.25
Viscosity Modifier (including Dispersant Viscosity Modifiers)	0 - 5	0.2 - 4.0	0.4 - 2
Antiwear agent, e.g., secondary ZDDP	0.1 - 5	0.25 - 4	0.5 - 3
All other performance additives (e.g., one or more of a corrosion inhibitor, pour point depressant, foam inhibitor, extreme pressure agent, friction modifier, emulsifier)	0 - 10	0.1 - 5	0.2 - 4
Oil of Lubricating Viscosity	Bal. to 100%	Bal. to 100%	Bal. to 100%
Total sulfur in lubricating composition	0.1 - 1	0.15 - 0.5	0.2 - 0.4
Active sulfur in lubricating composition	0.001 - 0.02	0.002 - 0.018	0.005 - 0.015

	A	B	C
Active sulfur as wt. % of total sulfur in sulfurized organic compound *	0.0 - 25	1 - 22	2 - 20
Phosphorus	0 – 0.2	0.01 – 0.12	0.03 – 0.09
Sulfated ash	0.05 - 2	0.2 -1.5	0.3 – 1.2
Boron	0.005 – 0.1	0.01 – 0.08	0.02 - 0.05

Use of the Lubricating Composition

[0155] The end use of the lubricating composition described herein includes use as a cylinder lubricant for an internal combustion engine, e.g., for a passenger car, heavy, medium or light duty diesel vehicle, small engines
5 such as motorcycle and *tert*-stroke oil engines, and 2-stroke marine diesel engines, but may also find use as an engine oil as a driveline lubricant, including gear and automatic transmission oils, and for other industrial oils, such as hydraulic lubricants.

[0156] An exemplary method of lubricating a mechanical device, such as
10 an engine of a car or truck, includes supplying the exemplary lubricating composition to the device.

[0157] Generally, the lubricating composition is added to the lubricating system of an internal combustion engine, which then delivers the lubricating composition to the cylinder of the engine, during its operation, where minor
15 amounts may be combusted with the fuel.

[0158] The internal combustion engine may be a diesel-fueled engine, a gasoline-fueled engine, a natural gas-fueled engine, a mixed gasoline/alcohol-fueled engine, or a biodiesel-fueled engine. The internal combustion engine may be a 2-stroke or 4-stroke engine.

20 **[0159]** In one embodiment, the engine is a heavy-duty diesel engine.

[0160] The lubricating composition may be suitable for use as a cylinder lubricant irrespective of the phosphorus, or sulfated ash (ASTM D874-13a (2018)) content of the fuel.

[0161] Without intending to limit the scope of the exemplary embodiment,
25 the following examples illustrate preparation and evaluation of example lubricating compositions.

- 40 -

Examples

[0162] The following materials were obtained:

[0163] Oils:

5 4-cSt Grp III Base oil, hydrotreated heavy paraffinic petroleum
distillates, sold as Yubase 4, obtained from SK Lubricants Co.,
Ltd.

 6-cSt Grp III Base oil, hydrotreated heavy paraffinic petroleum
distillates, sold as Yubase 6, obtained from SK Lubricants Co.,
Ltd.

10 Diluent Oil, Grp III.

[0164] The following components are expressed on an oil-free basis:

[0165] Antioxidants:

 Hindered Phenolic Antioxidant (HPAO), Irganox™ L 135, obtained from
BASF (3,5-dibutyl-4-hydroxyphenyl) propionate).

15 Substituted Diphenyl Amine (SDPA) antioxidant (nonylated
diphenylamine), obtained from Lubrizol.

[0166] Sulfurized Organic Compounds:

[0167] Sulfurized organic compounds denoted A-F were obtained from The
Lubrizol Corporation, as shown in Table 2. Active Sulfur is determined by
20 ASTM D1662. Total sulfur is determined by ASTM D1552.

TABLE 2: Sulfurized Organic Compounds

Sulfurized olefin	Type	Total Sulfur in compound (wt. %)	Active Sulfur in compound (average wt. %)
A	Mixture of sulfurized cycloaliphatic dibutylesters of the form shown in Formula V, where x is 1 or 2	11.7	2.2
B	Mixture of sulfurized cycloaliphatic dibutylesters of the I form shown in Formula V, where x is 1 or 2	13.9	2.5
C	Mixture of sulfurized fatty acid esters (sulfurized triglycerides) of the form shown in Formula IV, where R ⁶ is —CH ₂ CH=CHCH ₂ (CH ₂ CH ₂) ₁₀₋₁₃ CH ₃ , R ⁷ is C6, R ⁸ is C7, R ⁹ is C7, R ¹⁰ is C6, R ¹¹ is C6, and R ¹² is C7)	10.3	1.6
D	Mixture of sulfurized fatty acid esters (sulfurized triglycerides) of the form shown in Formula IV)	10.5	3.3
E	Alkyl polysulfides of the form shown in Formula II, where R is C4-C16, x=2-8 (high active sulfur)	37.5	37.5
F	Sulfurized fatty acid ester (BECROSAN™ SM 17, from The Lubrizol Corp.)	17.0	10.0

[0168] Dispersants

[0169] Dispersants denoted A-F were obtained from The Lubrizol Corporation, as shown in Table 3.

TABLE 3: Dispersants

Succinimide Dispersant	Type	Nitrogen (wt. %)	TBN
A	Polyisobutylene succinimide dispersant, derived from a ~2000 Mn polyisobutylene	1.16	27
B	Polyisobutylene succinimide dispersant, derived from a ~2000 Mn polyisobutylene	0.75	0.1
C	Polyisobutylene Direct Alkylation succinimide dispersant derived from a ~1500 Mn polyisobutylene	1.0	13
D	Borated polyisobutylene Direct Alkylation succinimide dispersant derived from a ~2000 Mn polyisobutylene	0.84	15
E	Polyisobutylene succinimide dispersant derived from a ~2000 Mn polyisobutylene	0.90	17

5 [0170] Detergents

Overbased Calcium Salicylate Detergent with a TBN of ~ 300, obtained from Wuxi.

Magnesium sulfonate detergent, with a TBN of ~ 690, obtained from The Lubrizol Corporation.

10 Overbased calcium sulfonate detergent, with a TBN of ~170, obtained from The Lubrizol Corporation.

[0171] Viscosity Modifiers

Hydrogenated Styrene-*b*-butadiene copolymer resin viscosity modifier, LZ 7418A, obtained from The Lubrizol Corporation.

15 Olefin copolymer resin viscosity modifier, with an ethylene content of about 50 wt.% obtained from The Lubrizol Corporation.

[0172] Dispersant Viscosity Modifiers

Aromatic dispersant viscosity modifier A (reaction product of an olefin polymer comprising a carboxylic acid functionality with 3-nitroaniline),
20 obtained from The Lubrizol Corporation.

- 43 -

Aromatic dispersant viscosity modifier B (amine functionalized aromatic maleic anhydride-styrene copolymer), obtained from The Lubrizol Corporation.

[0173] Other Additives

5 Secondary ZDDP, a combination of primary and secondary ZDDPs derived from C3 and C6 alcohols.

Pour point depressant: maleic anhydride/styrene copolymer ester, obtained from The Lubrizol Corporation.

Foam inhibitor: mixture of polydimethylsiloxanes.

10 Propoxylated polyisobutylene phenol deposit control agent obtained by reaction of propylene oxide with polyisobutylene phenol and KOH as described in WO2014193543A1.

Triazole derivative corrosion Inhibitor, Irgamet™ 30 (N,N-bis(2-ethylhexyl)-1-triazole-1-methyl amine), obtained from BASF.

15 Preparation of Lubricating Compositions

[0174] SAE-5-W30 viscosity grade engine lubricating formulations suitable for use in a heavy-duty diesel engine were prepared in a Group III base oil of lubricating viscosity containing the sulfurized olefins described herein are prepared according to the formulations shown in Tables 3, 4, and 5.

20 **[0175]** Weight % of all ingredients (except from the oil) are expressed on an actives (oil free) basis.

[0176] In TABLE 4, Example 1 contains both a hindered phenolic antioxidant (HPAO) and a substituted diphenylamine (SDPA) antioxidant, while Example 2 has essentially the same formulation as Example 1, except
25 that only the hindered phenolic antioxidant is used, with the amount being increased to maintain the same total amount of antioxidant.

TABLE 4: Lubricating Composition Formulations

Components	Ex. 1 (with aminic antioxidant)	Ex. 2 (with phenolic antioxidant)
Grp III Base oil, Yubase 4	45.45	45.45
Grp III Base oil, Yubase 6	30.00	30.00
Diluent Oil, Grp III	0.270	0.270
Diluent Oil From Additives	11.478	11.478
Sulfurized Olefin A	0.50	0.50
Hindered Phenol Antioxidant (HPAO)	1.5	3.00
Substituted Diphenyl Amine (SDPA) antioxidant	1.5	-
Polyisobutylene succinimide dispersant A	1.48	1.48
Polyisobutylene succinimide dispersant B	0.75	0.75
Polyisobutylene succinimide dispersant C	2.1	2.1
Borated polyisobutylene succinimide dispersant D	1.14	1.14
Calcium sulfonate detergent (~170 TBN)	0.50	0.50
Overbased calcium salicylate detergent (~300 TBN)	0.90	0.90
Magnesium sulfonate detergent (~690 TBN)	0.38	0.38
Aromatic dispersant viscosity modifier A	0.33	0.33
Aromatic dispersant viscosity modifier B	0.13	0.13
Olefin copolymer, viscosity modifier	0.585	0.585
Maleic anhydride/styrene copolymer, pour point depressant	0.2	0.20
C3/C6 Secondary ZDDP, antiwear agent	0.78	0.76
Polydimethylsiloxanes, foam inhibitor	0.007	0.007
Triazole derivative, corrosion inhibitor	0.020	0.020
Total	100	100
Phosphorus, wt. %	0.076	0.077
Total Sulfur, wt. % *	0.255	0.273
Sulfur, wt. % (from sulfurized organic compound)	0.0585	0.0585
Active Sulfur, wt. % *	0.011	0.011

Components	Ex. 1 (with aminic antioxidant)	Ex. 2 (with phenolic antioxidant)
Active sulfur as wt. % of total sulfur in sulfurized organic compound *	18.8	18.8
% Sulfated Ash, wt. % *	0.87	0.95
Boron, wt. %	0.009	0.010
Calcium, wt. %	0.142	0.150
Magnesium, wt. %	0.041	0.061
Nitrogen Level from Dispersant, wt. % *	0.092	0.092
TBN Lubricating Composition (ASTM D2896- 21)	9.8	7.9

* Theoretical value based on composition

[0177] A series of engine lubricants suitable for use in a heavy duty diesel engine are prepared in a Group III base oil of lubricating viscosity containing sulfurized olefin B, as described above, and aminic free antioxidants as well as polymeric viscosity modifiers, ashless succinimide dispersants, over-based detergents, antioxidants, zinc dialkyldithiophosphate (ZDDP), and other performance additives, as shown in TABLE 5. In these examples, different amounts of the phenolic antioxidant are used.

TABLE 5: Lubricating Composition Formulations

Component	Ex. 3 (SPDA as AO)	Ex. 4 (No AO)	Ex. 5 (2% HPAO)	Ex. 6 (3% HPAO)	Ex. 7 (4% HPAO)
Grp III Base oil, Yubase 4	20	20	20	20	20
Grp III Base oil, Yubase 6	56.41	57.21	55.21	54.21	53.21
Diluent oil, Grp III	0.295	0.295	0.295	0.295	0.295
Diluent oil from additives	13.92	13.12	11.12	10.12	9.12
Sulfurized olefin B	0.5	0.5	0.5	0.5	0.5
Hindered phenolic antioxidant (HPAO)	0	0	2.0	3.0	4.0
Substituted diphenyl amine (SDPA) antioxidant	0.8	0	0	0	0
Polyisobutylene succinimide dispersant E	2.92	2.92	2.92	2.92	2.92

- 46 -

Component	Ex. 3 (SPDA as AO)	Ex. 4 (No AO)	Ex. 5 (2% HPAO)	Ex. 6 (3% HPAO)	Ex. 7 (4% HPAO)
Borated polyisobutylene succinimide dispersant D	0.29	0.29	0.29	0.29	0.29
Overbased calcium salicylate detergent (~300 TBN)	1.1	1.1	1.1	1.1	1.1
Magnesium sulfonate detergent (~690 TBN)	0.29	0.29	0.29	0.29	0.29
Hydrogenated styrene- <i>b</i> -butadiene resin, viscosity modifier	0.536	0.536	0.536	0.536	0.536
Maleic anhydride/styrene copolymer, pour point depressant	0.2	0.2	0.2	0.2	0.2
C3/C6 Secondary ZDDP, antiwear agent	0.73	0.73	0.73	0.73	0.73
Polydimethylsiloxane, foam inhibitor	0.009	0.009	0.009	0.009	0.009
Propoxylated polyisobutylene phenol	2	2	2	2	2
Total	100	100	100	100	100
Phosphorus, wt. %	0.081	0.083	0.078	0.082	0.079*
Boron, wt. %	0.026	0.025	0.023	0.023	0.023*
Calcium, wt. %	0.124	0.130	0.124	0.121	0.124*
Magnesium, wt. %	0.048	0.050	0.045	0.046	0.048*
Total Sulfur, wt. %*	0.246	0.250	0.272	0.246	0.249
Sulfur (from sulfurized organic compound), wt. %*	0.0695	0.0695	0.0695	0.0695	0.0695
Active sulfur, wt. %	0.0125	0.0125	0.0125	0.0125	0.0125
Active sulfur as wt. % of total sulfur in sulfurized organic compound *	18.0	18.0	18.0	18.0	18.0
Sulfated ash, wt. % *	0.863	0.863	0.863	0.863	0.863
Nitrogen from dispersant, wt. % *	0.085	0.085	0.085	0.085	0.085

Component	Ex. 3 (SPDA as AO)	Ex. 4 (No AO)	Ex. 5 (2% HPAO)	Ex. 6 (3% HPAO)	Ex. 7 (4% HPAO)
TBN of Lubricating Composition (ASTM D2896-21)	8.08	6.95	6.96	6.96	6.96

* Theoretical value based on composition

- [0178]** A series of engine lubricants suitable for use in a heavy-duty diesel engine are prepared in a Group III base oil of lubricating viscosity containing various sulfurized olefins are shown in TABLE 6. The amount of sulfurized olefin is adjusted to provide approximately the same total amount of sulfur.

TABLE 6

Component	Ex. 8	Ex. 9	Ex. 10	Ex. 11	Ex. 12	Ex. 13
Grp III Base oil, Yubase 4	20	20	20	20	20	20
Grp III Base oil, Yubase 6	54.21	54.035	54.116	54.08	54.525	54.295
Diluent Oil, Grp III	0.295	0.295	0.295	0.295	0.295	0.295
Diluent Oil From Additives	12.095	12.390	12.099	12.055	12.280	12.510
Sulfurized olefin B	0.50					
Sulfurized olefin C		0.675				
Sulfurized olefin A			0.59			
Sulfurized olefin D				0.66		
Sulfurized olefin E					0.19	
Sulfurized olefin F						0.42
Phenolic antioxidant	3.0	3.0	3.0	3.0	3.0	3.0
Dispersant E	2.92	2.92	2.92	2.92	2.92	2.92
Dispersant D	2.85	2.85	2.85	2.85	2.85	2.85
Overbased calcium salicylate detergent (~300 TBN)	1.1	1.1	1.1	1.1	1.1	1.1
Magnesium Sulfonate Detergent (~690 TBN)	0.29	0.29	0.29	0.29	0.29	0.29

- 48 -

Component	Ex. 8	Ex. 9	Ex. 10	Ex. 11	Ex. 12	Ex. 13
Secondary ZDDPs derived from C3 and C6 alcohols	0.73	0.73	0.73	0.73	0.73	0.73
Polydimethylsiloxanes, foam inhibitor	0.009	0.009	0.009	0.009	0.009	0.009
Propoxylated polyisobutylene phenol	2.0	2.0	2.0	2.0	2.0	2.0
Total	100	100	100	100	100	100
Phosphorus, wt. %	0.078	0.081	0.084	0.079	0.080	0.080
Boron, wt. %	0.022	0.024	0.024	0.023	0.022	0.022
Calcium, wt. %	0.124*	0.126	0.124	0.119	0.128	0.118
Magnesium, wt. %	0.048*	0.049	0.049	0.047	0.048	0.047
Total Sulfur, wt. % *	0.25	0.23	0.22	0.26	0.24	0.26
Sulfur, wt. % * (from sulfurized organic compound)	0.0695	0.0695	0.0695	0.0695	0.0695	0.0705
Active Sulfur, wt. % *	0.0125	0.0108	0.0130	0.0218	0.0695	0.0420
Active sulfur as wt. % of total sulfur in sulfurized organic compound *	18.0	18.5	18.7	31.4	100	59.6
Sulfated Ash, wt. % *	0.86	0.86	0.86	0.86	0.86	0.86
Nitrogen, from Dispersant, wt. % *	0.085	0.085	0.085	0.085	0.085	0.085
TBN Lubricating Composition (ASTM D2896-21)	7.0	7.1	7.1	7.0	7.1	7.1

* Theoretical value based on composition

Evaluation of Lubricating Compositions

[0179] Various tests are performed on the lubricating compositions of the Examples above:

- 5 **[0180]** Total Base Number (TBN): is determined according to ASTM D2896-21.

[0181] Kinematic Viscosity: Kinematic viscosity at 100°C (KV_100) and at 40°C (KV_40) are measured according to ASTM D445-21e1.

[0182] % Sulfated Ash (% SA): determined in accordance with ASTM D874-13a.

- 5 **[0183]** Viscosity Index: is determined according to ASTM D2270-10 (2016), "Standard Practice for Calculating Viscosity Index from Kinematic Viscosity at 40 °C and 100 °C."

[0184] Apparent Viscosity: is determined by the following methods:

- [0185]** 1. The Cold Crank Simulator (CCS) test at -30 °C, according to
10 ASTM D5293-20, "Standard Test Method for Apparent Viscosity of Engine Oils and Base Stocks Between -10 °C and -35 °C Using Cold-Cranking Simulator," in cP.

- [0186]** 2. ASTM D5481-21, "Standard Test Method for Measuring Apparent Viscosity at High-Temperature and High-Shear Rate by Multicell Capillary
15 Viscometer," (HTHS), in cP.

[0187] 3. CEC L-36-90 "High shear high temperature viscosity measurement," 2019, for some examples.

[0188] Antioxidation Properties

- [0189]** Oxidation properties are determined using the Renault Catalyst
20 Oxidation Test (TOC-4) Procedure by Renault (RNES-B-00023). This test method assesses the resistance against oxidation of an engine lubricating oil composition and the method simulates changes in engine oils subjected to harsh conditions of increased load and regime, and hot casing. In the TOC-4 procedure, four tubes each containing 150 g of oil containing anhydrous iron
25 (III) acetylacetonate catalyst (360 ppm iron) are heated in a test cell at 170°C for 168 hours. During this time, air is blown through the oil in the tubes at a rate of 10 liters per hour. Samples of each oil (30 ml) are assessed for oxidative degradation after 24 hours, 120 hours, 136 hours, and 168 hours; the samples after 120 hours providing the average value for the TOC-4
30 procedure. The oxidative degradation of an oil samples is assessed using infra-red spectrometry by measuring the area of the infra-red band between 1800 to 1650 cm⁻¹ (C=O) and comparing the increase in area of this band

- 50 -

with that of the original oil (sample at t=0). A lower peak area increase indicates lower oxidative degradation. To pass the TOC-4 test, a peak area increase after 120 hours must be less than 400.

[0190] Total Acid Number (TAN) at 120hrs (mg KOH/g), according to ASTM D664-18e2, "Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration."

[0191] Oxidation Resistance: determined by the Kinematic Viscosity Change at 170°C for the following:

[0192] 1. Relative Change in KV₄₀ at 120hrs, as compared with fresh lubricating composition, % (≤ 200 to meet the Renault RN-17 Specification).

[0193] 2. Relative Change in KV₁₀₀ at a specified time (e.g., 120 hrs or 260 hrs), as compared with fresh lubricating composition, %.

[0194] Oxidation stability: (Volvo T-13 test) is determined in accordance with ASTM D8048-21ae1, "Standard Test Method for Evaluation of Diesel Engine Oils in T-13 Diesel Engine," using a 2010 Volvo/Mack D13/D8, 505 Brake Horsepower, 13L, in-line 6-cylinder diesel engine with 6 electronic unit injectors, variable geometry turbocharger, with cooled exhaust gas recirculation (EGR). The test is operated for 360 hrs at 1500 RPM steady state conditions at a given fuel flow, producing approximately 2200 N m and 130°C oil temperature with 19-20% EGR to evaluate the oxidative stability of engine oils.

[0195] Oxidation Induction Time (OIT): Thin film antioxidancy is measured as the OIT, in minutes, which is determined according to CEC L-85-99: "Oxidative Stability of Lubricants by PDSC (Pressure Differential Scanning Calorimetry)." This represents the time after which oxygen uptake, as measured by a pressure drop, ceases. The longer the OIT, the better the antioxidancy.

[0196] Deposit Control: Deposit control is evaluated using the MHT TEOST and Komatsu Hot Tube Tests, as follows.

[0197] MHT TEOST: is measured according to ASTM D7097-19, "Standard Test Method for Determination of Moderately High Temperature Piston

Deposits by Thermo-Oxidation Engine Oil Simulation Test—TEOST MHT.”

The total deposits are reported in mg.

- [0198]** Komatsu Hot Tube Test (280°C), KES_07.803: In this test, glass tubes are inserted through and heated by an aluminum heater block. The sample is pumped via a syringe pump through the glass tube for 16 hours, at a flow rate of 0.31 cm³/hr, along with an air flow of 10 cm³/min. At the end of the test the tubes are rinsed and rated visually on a scale of 0 to 10, with 0 being a black tube and 10 being a clean tube.

[0199] Corrosion Properties

- [0200]** Corrosion properties for are evaluated according to ASTM D6594-20e1- “Standard Test Method for Evaluation of Diesel Engine Oil at 135°C” and ASTM D130-19, “Standard Test Method for Corrosiveness to Copper from Petroleum Products by Copper Strip Test.” The ASTM D6594 test method covers testing diesel engine lubricants to determine their tendency to corrode various metals, specifically alloys of lead and copper commonly used in cam followers and bearings.

[0201] TABLE 7 shows results from the Volvo T-13 test for Examples 1 and 2.

TABLE 7: Oxidation Stability

Volvo T-13	API/CK-4 Requirements	Ex. 1	Ex. 2
KV_40 Increase (300-360h), %	75 Max	0	5
IR Peak Height (360hrs), A/cm	125 Max	40	32
Oil Consumption (48-192h), g/h	Report	25	28

- [0202]** This test is a severe heavy duty oxidation engine test. The lubricating composition of Example 2 showed outstanding control of oxidation and viscosity increase, exceeding the required industry limits for this test. The result is unexpected in view of the absence of aminic antioxidant.

[0203] Additional test results for Examples 1-7 are shown in TABLE 8.

TABLE 8: Test Results

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7
TBN	10.1	7.9	8.08	6.96	6.96	6.96	6.96
%SA		0.87	0.863	0.863	0.863	0.863	0.863
KV_40, cSt	69.2	68.7	55.69	54.54	55.14	55.71	56.23
KV_100, cSt	11.5	11.4	9.951	9.828	9.85	9.92	9.967
Viscosity Index	160	160	167	168	166	166	165
CCS @ -30 °C, cP	6250	6438	5370	5100	5410	5600	5830
HTHS, cP	3.5	3.4	3.16	3.14	3.16	3.18	3.2
Oxidation Induction Time, min (CEC L-85-99)			179.9	48.60	123.9	153.4	179.7
Komatsu Hot Tube (280 °C) Tube Rating	7.5	8.0	7.0	0	6.5	7.0	7.0
Total Deposits (MHT TEOST -ASTM D7097B)			31.8	51.0	29.6	23.0	16.4
Renault Catalyzed Oxidation Test:							
TAN at 120hrs (mg KOH/g)			584	*	*	496	450
Peak Area Increase at 120hrs **			470	*	*	751	413

* Too viscous to measure

**A lower peak area increase indicates lower oxidative degradation.

[0204] The results suggest that increases in the amount of phenolic antioxidant leads to improvements in the oxidation resistance (e.g., as oxidation induction time). At 4 wt. % of the phenolic antioxidant, the oxidation resistance is comparable to that of the SDPA-containing composition. Examples 6 and 7 provide excellent oxidative performance and viscosity.

[0205] TABLE 9 shows results of oxidation induction time for Examples 8-13.

TABLE 9: Oxidation Induction Time

	Ex. 8	Ex. 9	Ex. 10	Ex. 11	Ex. 12	Ex. 13
OIT Time, minutes	153.4	141.4	143.5	99.0	81.7	115

[0206] Corrosion test results are shown in TABLE 10.

TABLE 10: Corrosion Test Results

Test	Ex. 9	Ex. 10	Ex. 12	Ex. 13
Copper change, ppm - ASTM D6594	6	7	443	264
Copper Strip -ASTM D130	1A	1A	4C	4A
Lead Change, ppm - ASTM D6594	2	2	5	13

[0207] It can be seen from Tables 9 and 10 that Examples 9 and 10 provide excellent oxidative performance, while also providing reduced corrosion of metals.

- 5 **[0208]** Example 13 uses a sulfurized fatty acid ester of the type described in U.S. Pat. No. 11,136,652 B1. Example 13 did not perform as well as Examples 8, 9, and 10, which exhibit superior oxidative performance. These three samples include active sulfur at less than 0.015 wt. % of the lubricating composition and a sulfurized olefin in which active sulfur amounts to less than
10 20 wt. % of the total sulfur in sulfurized olefin.

[0209] The results show that relatively high levels (2wt. % to 4wt. %) of an SDPA-free phenolic antioxidant can achieve oxidation performance that previously required relying on SDPA phenolic antioxidants and also provide lower corrosion rates.

- 15 **[0210]** Each of the documents referred to above is incorporated herein by reference. Except in the Examples, or where otherwise explicitly indicated, all numerical quantities in this description specifying amounts of materials, reaction conditions, molecular weights, number of carbon atoms, and the like, are to be understood as modified by the word "about." Unless otherwise
20 indicated, each chemical or composition referred to herein should be interpreted as being a commercial grade material which may contain the isomers, by-products, derivatives, and other such materials which are normally understood to be present in the commercial grade. However, the amount of each chemical component is presented exclusive of any solvent or
25 diluent oil, which may be customarily present in the commercial material, unless otherwise indicated. It is to be understood that the upper and lower amount, range, and ratio limits set forth herein may be independently combined. Similarly, the ranges and amounts for each element of the

- 54 -

invention may be used together with ranges or amounts for any of the other elements.

[0211] The singular forms “a,” “an,” and “the” include plural referents unless the context clearly dictates otherwise.

- 5 **[0212]** It will be appreciated that variants of the above-disclosed and other features and functions, or alternatives thereof, may be combined into many other different systems or applications. Various presently unforeseen or unanticipated alternatives, modifications, variations or improvements therein may be subsequently made by those skilled in the art which are also intended
- 10 to be encompassed by the following claims.

- 55 -

WE CLAIM:

1. A lubricating composition comprising:
an oil of lubricating viscosity;
a phenolic antioxidant;
a sulfurized organic compound with an active sulfur content of no more than 8 wt. %;
optionally, one or more performance additives selected from:
a succinimide dispersant, and
a detergent.
2. The lubricating composition according to claim 1, wherein the lubricating composition is at least substantially free of substituted diphenylamine (SDPA) antioxidants.
3. The lubricating composition according to any prior claim, wherein the lubricating composition is at least substantially free of aminic antioxidants.
4. The lubricating composition according to any prior claim, wherein the phenolic antioxidant is at least 0.1 wt. %, or at least 0.5 wt. %, or at least 1 wt. %, or at least 1.5 wt. %, or at least 2 wt. % of the lubricating composition.
5. The lubricating composition according to any prior claim, wherein the phenolic antioxidant is no more than 8 wt. % of the lubricating composition, or no more than 6 wt. %, or no more than 5 wt. %, or no more than 4 wt. %, or no more than 3 wt. % of the lubricating composition.
6. The lubricating composition according to any prior claim, wherein the phenolic antioxidant is selected from the group consisting of a hindered phenol, a hindered alkyl phenol ester, a hindered alkoxy phenol, a hindered phenol acetate, a hindered bisphenol, a polyphenol, a 4-*tert*-butylphenol-

- 56 -

formaldehyde condensate, a 4-*tert*-butylphenol-acetaldehyde condensate, and mixtures thereof.

7. The lubricating composition according to any prior claim, wherein the phenolic antioxidant is selected from the group consisting of:

a mixture of C₇-C₉ branched alkyl esters of 3,5-*bis*(1,1-dimethyl-ethyl)-4-hydroxy-benzenepropanoic acid;

a C₄ alkyl ester of 3,5-*bis*(1,1-dimethyl-ethyl)-4-hydroxy-benzenepropanoic acid, and

2,2'-thiodiethylene *bis*[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate].

8. The lubricating composition according to any prior claim, wherein the sulfurized organic compound has an active sulfur content of no more than 8 wt. %, or no more than 6 wt. %, or no more than 5 wt. %, or no more than 4.0 wt. %, or no more than 3 wt. %, or no more than 2.5 wt. %, or no more than 2 wt. %.

9. The composition according to any prior claim, wherein the sulfurized organic compound has a total sulfur content of at least 1 wt. % or at least 1.5 wt. %, or at least 2 wt. %, or no more than 18 wt. %, or no more than 15 wt. %, or no more than 14.0 wt. %, or no more than 12.0 wt. %, or no more than 5 wt. %.

10. The lubricating composition according to any prior claim, wherein the sulfurized organic compound provides the lubricating composition with at least 0.01 wt. %, or at least 0.03 wt. %, or at least 0.05 wt. %, or up to 0.12 wt. %, or up to 0.09 wt. % sulfur, or up to 0.07 wt. % sulfur.

11. The lubricating composition according to any prior claim, wherein the sulfurized organic compound provides the lubricating composition with no more than 0.04 wt. % of active sulfur, or no more than 0.03 wt. %, or no more than 0.025 wt. %, or no more than 0.02 wt. % of active sulfur.

- 57 -

12. The lubricating composition according to any prior claim, wherein the sulfurized organic compound is at least 0.1 wt. %, or at least 0.15 wt. % or at least 0.2 wt. % of the lubricating composition.

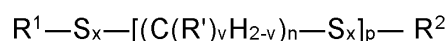
13. The lubricating composition according to any prior claim, wherein the sulfurized organic compound is up to 1 wt. %, or up to 0.8 wt. % or up to 0.7 wt. %, up to 0.6 wt. % or up to 0.5 wt. % of the lubricating composition.

14. The lubricating composition according to any prior claim, wherein active sulfur accounts for no more than 25 wt. %, or no more than 22 wt. %, or no more than 20 wt. %, or no more than 19 wt. % of total sulfur in the sulfurized organic compound, or at least 1 wt. %, or at least 1.5 wt. %, or at least 6 wt. % of the total sulfur in the sulfurized organic compound.

15. The lubricating composition according to any prior claim, wherein the sulfurized organic compound is selected from the group consisting of an oligomeric polysulfide, an alkyl polysulfide, a sulfurized ester, a sulfurized cycloaliphatic dialkylester, a sulfurized cycloaliphatic dialkenyl ester, and mixtures thereof.

16. The lubricating composition according to any prior claim, wherein the sulfurized organic compound comprises an oligomeric polysulfide or a mixture thereof.

17. The lubricating composition according to claim 16, wherein the oligomeric polysulfide or mixture thereof is of Formula I:



Formula I,

where R^1 and R^2 are each independently a C2-C20 alkyl;

each n is independently at least 1;

p is at least 1;

each v is from 0-2; and

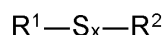
- 58 -

each x is independently at least 1.

18. The lubricating composition according to claim 16, wherein the oligomeric polysulfide or mixture thereof has a total sulfur content of at least 5 wt. % and/or up to 45 wt. % and an active sulfur content of at least 0.5 wt. % and/or up to 10 wt. %.

19. The lubricating composition according to any prior claim, wherein the sulfurized organic compound comprises an alkyl polysulfide or a mixture thereof.

20. The lubricating composition according to claim 19, wherein the alkyl polysulfide or mixture thereof is of Formula II:



Formula II,

where R^1 and R^2 are each independently a C2-C20 alkyl; and
each x is independently at least 1.

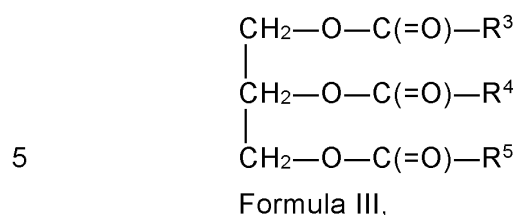
21. The lubricating composition according to claim 19 or 20, wherein the alkyl polysulfide or mixture thereof has a total sulfur content of at least 5 wt. % and/or up to 20 wt. %, and an active sulfur content of at least 0.5 wt. % and/or up to 45 wt. %.

22. The lubricating composition according to any prior claim, wherein the sulfurized organic compound comprises a sulfurized fatty acid ester of an aliphatic alcohol.

23. The lubricating composition according to claim 22, wherein the sulfurized organic compound comprises a sulfurized triglyceride or a mixture thereof.

24. The lubricating composition according to claim 23, wherein the sulfurized triglyceride or mixture thereof is of Formula III:

- 59 -



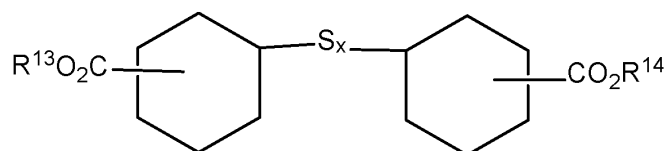
where R^3 , R^4 , and R^5 are each independently a C8 or higher alkyl or alkenyl group, or a C10 or higher alkyl or alkenyl group, or up to a C30 or up to a C24 alkyl or alkenyl group; and

10 wherein at least one of R^3 , R^4 , and R^5 is linked to a sulfur atom of a sulfur-containing moiety, intermediate ends of the alkyl group.

25. The lubricating composition according to claim 23 or 24, wherein the sulfurized triglyceride or mixture thereof has a total sulfur content of at least 5 wt. % and/or up to 15 wt. % and an active sulfur content of less than 5 wt. %.

26. The lubricating composition according to any prior claim, wherein the sulfurized organic compound comprises at least one of a cycloaliphatic dialkylester, a cycloaliphatic dialkenyl ester, and mixtures thereof.

27. The lubricating composition according to claim 26, wherein the at least one of the cycloaliphatic dialkylester, the cycloaliphatic dialkenyl ester, and mixtures thereof is of Formula V:



Formula V,

where each of R^{13} and R^{14} is independently a C2 or higher alkyl or alkenyl group; and
 x is at least 1.

- 60 -

28. The lubricating composition according to claim 26 or 27, wherein the at least one of the cycloaliphatic dialkylester, the cycloaliphatic dialkenyl ester, and mixture thereof has a total sulfur content of at least 5 wt. % and/or up to 15 wt. %, and an active sulfur content of at least 1 wt. % and/or up to 5 wt. %.

29. The lubricating composition according to any prior claim, wherein the succinimide dispersant is at least 0.2 wt. %, or at least 0.5 wt. %, or at least 1.0 wt. %, or up to 7.0 wt. %, or up to 6.0 wt. of the lubricating composition.

30. The lubricating composition according to any prior claim, wherein the succinimide dispersant provides the lubricating composition with no more than 0.1 wt. % nitrogen.

31. The lubricating composition according to any prior claim, wherein the detergent is at least 0.1 wt. %, or at least 0.2 wt. %, or at least 0.25 wt. %, or at least 0.4 wt. %, or up to 3.0 wt. %, or up to 2.0 wt. %, or up to 1.5 wt. %, or up to 1.25 wt. % of the lubricating composition.

32. The lubricating composition according to any prior claim, wherein the detergent provides the lubricating composition with at least 0.005 wt. % of boron, or at least 0.03 wt. % boron, or up to 0.06 wt. %, or up to 0.04 wt.% of boron.

33. The lubricating composition according to any prior claim, wherein the detergent provides the lubricating composition with at least 0.04 wt. %, or at least 0.08 wt. %, or up to 0.4 wt.%, or up to 0.3 wt. % of calcium.

34. The lubricating composition according to any prior claim, wherein the detergent is selected from the group consisting of an alkaline earth metal sulfonate, an alkaline earth metal salicylate, an alkaline earth metal saligenin, an alkaline earth metal salixarate, an alkaline earth metal hydrocarbyl-substituted hydroxybenzoate, and mixtures thereof.

- 61 -

35. The lubricating composition according to any prior claim, wherein the oil of lubricating viscosity is at least 80 wt. % of the lubricating composition, or up to 94 wt. % of the lubricating composition.

36. The lubricating composition according to any prior claim, further comprising at least one of the group consisting of an antiwear agent, a corrosion inhibitor, a viscosity modifier, a pour point depressant, an antifoam agent, an extreme pressure agent, a friction modifier, a viscosity modifier, and combinations thereof.

37. The lubricating composition according to claim 36, wherein the antiwear agent provides the lubricating composition with 300 - 850 ppm phosphorus by weight, based upon a total weight of the lubricating composition.

38. The lubricating composition according to claim 36, wherein the viscosity modifier comprises a dispersant viscosity modifier which comprises at least one of:

a reaction product of an olefin polymer comprising a carboxylic acid functionality with 3-nitroaniline; and

an amine functionalized aromatic maleic anhydride-styrene copolymer.

39. The lubricating composition according to claim 38, wherein the dispersant viscosity modifier is at least 0.01 wt. %, or at least 0.1 wt. %, or at least 2 wt. %, or no more than 8 wt. %, or no more than 7 wt. % of the lubricating composition.

40. The lubricating composition according to claim 36, wherein the viscosity modifier includes at least one of a hydrogenated styrene-*b*-butadiene copolymer resin viscosity modifier and an olefin copolymer resin viscosity modifier.

- 62 -

41. The lubricating composition according to any prior claim, wherein molybdenum is no more than 800 ppm, or no more than 400 ppm, or no more than 150 ppm, or no more than 100 ppm, or no more than 80 ppm, or no more than 50 ppm, or no more than 20 ppm, based upon a total weight of the lubricating composition.

42. A method for improving oxidative stability of a lubricating oil in an engine comprising supplying the lubricating composition according to any prior claim to the engine.

43. The method of claim 42, wherein when the engine is a Volvo T-13 engine and is run for 360 hours, the kinematic viscosity at 40°C (KV₄₀) increase from 300 hours to 360 hours is less than 75 or less than 50 and/or the oxidation at the end of test is less than 125 A/cm, as measured by the IR peak height.

44. Use of the lubricating composition according to any one of claims 1-41 for lubricating an engine.

45. A lubricating composition comprising:
a sulfurized organic compound sufficient to provide, in the lubricating composition, at least 0.1 wt. % sulfur;
at least 0.1 wt. % of a phenolic antioxidant;
at least 0.1 wt. % of a detergent; and
at least 2 wt. % of a dispersant,
wherein the lubricating composition contains no more than 0.04 wt. % of active sulfur.

46. The lubricating composition according to claim 45, wherein the detergent comprises:

- 63 -

at least one of a calcium salicylate detergent and a calcium sulfonate detergent sufficient to provide at least 0.1 wt. %, or at least 0.12 wt. % calcium to the lubricating composition;

a magnesium sulfonate detergent sufficient to provide at least 0.02 wt. %, or at least 0.04 wt. % magnesium to the lubricating composition.