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(54) **LUBRICANT COMPOSITIONS CONTAINING HIGH C9 DISUBSTITUTED DIPHENYLAMINE ANTIOXIDANT CONTENT**

(57) This disclosure relates to the use of di(alkyl substituted phenyl)amine antioxidants as additives in lubricant compositions having good oxidation properties in engine crankcase applications, especially in compression ignited engine and or spark ignited engine applications, where the antioxidant comprises from 0 to 10 mass% mono-C_9-alkyl substituted diphenyl amine, and 90 to 100 mass% di-C_9-alkyl substituted phenyl amines based upon the weight of the mono- and di-C_9-alkyl substituted phenyl amines, preferably where tri-C_9-alkyl substituted phenyl amines are minimized and ortho substituted di-C_9-alkyl substituted phenyl amines are minimized.

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Description

FIELD OF THE INVENTION

[0001] This disclosure relates to the use of di(alkyl-substituted phenyl)amine antioxidants as additives in lubricant compositions having good oxidation properties in engine crankcase applications, especially in compression ignited engine and or spark ignited applications, where certain mono-C_9-alkyl substituted diphenyl amine antioxidants, are absent or present at less than 0.10 mass%.

BACKGROUND OF THE INVENTION

[0002] The present invention relates to lubricating oil compositions which exhibit improved oxidation characteristics. More specifically, the present invention relates to automotive crankcase lubricating oil compositions for use in gasoline (spark-ignited) and diesel (compression-ignited) internal combustion engines, such compositions being referred to as crankcase lubricants; and to the use of additives in such lubricating oil compositions for reducing oxidation in use of such engines and/or improving the viscometric performance of an engine lubricated with the lubricating oil composition.

[0003] Oxidation is a concern for in-service lubricating oils as it can cause thickening of the oil, sludge, varnish, acid number increase and corrosion. These outcomes are generally detrimental to proper operation of automotive engines and limit useful life of the lubricating oil. With continually evolving engine designs, operating conditions and oil performance expectations, oxidation continues to be an important ongoing technical challenge.

[0004] One way to slow down oxidation in engines is to introduce antioxidants to lubricating oils. Additionally, antioxidants can also extend drain intervals, maintain viscosity, reduce deposit, reduce foam formation, protect against corrosion as well as protect lubricating oil against high temperature.

[0005] There are many antioxidants that have varying degrees of effectiveness. Commercial lubricants are usually formulated with one or more antioxidants to protect the fluid under a wide range of conditions (e.g., temperature, time, air mixtures, pressure, etc.).

[0006] Isomer mixtures of alkylated diphenylamines (such as mixture of di(nonylphenyl)amine and (nonyl-phenyl)(phenyl)amine), such as Irganox™ L67, are commonly used as antioxidants in organic fluids such as engine oils, gear oils, hydraulic fluids, compressor oils, turbine oils, and grease. However, these antioxidant isomer blends contribute to viscometric problems (such as kinematic viscosity increase over time), and thus there is a desire to improve the kinematic viscosity increase over time of di(alkylphenyl)amines in organic fluids such as engine oils, gear oils, hydraulic fluids, compressor oils, turbine oils, and grease.

[0007] EP4118170A1 discloses lubricating oil compositions with improved oxidative performance comprising alkylated diphenylamine antioxidant and carboxylate detergents.

[0008] EP4118171A1 discloses lubricating oil compositions with improved oxidative performance comprising alkylated diphenylamine antioxidant and sulfonate detergents.

[0009] US 9,315,760 discloses lubricant compositions with improved antioxidant capability containing an additive composition containing a metal free sulfur-containing compound (such as ashless dithiocarbamates, such as methylenebis(dibutyldithiocarbamate), and sulfurized fatty acids), an aromatic amine, and a hindered amine. (See examples for use of Vanlube™ VL 7723, hindered amine, diaryl amine and dithiocarbamate or sulfated fatty acid methyl ester.)

[0010] US 11,499,117 discloses lubricating oil compositions comprising a base oil and one or more additives, wherein the composition has: a sulfated ash content of 0.4 to 1.0 mass%; a total base number of 4.0 to 12 mg KOH/g; a total aromatics content contributed by the base oil in the range from 1 mass% to 30 mass%; and a sulfur content contributed by the base oil of 0.4 mass% or less; and where the base oil comprises a blend of (i) a first base oil which is a mineral base oil selected from an API Group I mineral base oil and an API Group II mineral base oil, and mixtures thereof, and (ii) a second base oil selected from an API Group II base oil and an API Group III base oil, preferably wherein the first base oil belongs to a different API group to that of the second base oil.

[0011] Other references of interest include: EP 2155657B1; EP0630881; US 5,449,829; US 7,960,322; US 7,145,038 B1; US 8,999,903; US 9,512,380; US 9,315,760; US 11,518,732; WO 2020/194125; WO 2022/108298; WO 2023/133090A1; and WO2024/206388.

[0012] It has now surprisingly been found by the present inventors that purified compositions of di(nonylphenyl)amine (such as di(para-nonylphenyl)amine can be used in a lubricant composition, such as in internal combustion engines, to provide improved viscometric properties, such as reduced kinematic viscosity growth.

SUMMARY OF THE INVENTION

[0013] This disclosure relates to lubricating oil additives that maintain or improve oxidation performance and improve kinematic viscosity growth in lubricating oils.

[0014] This invention further relates to compositions (such as booster packs, concentrates, lubricating oil compositions and the like) comprising: diphenyl amine antioxidant comprising 1) di(C_9-alkyl substituted diphenyl amine (such as 90 mass% or more of di(C_9-alkyl substituted diphenyl) amine) and 2) from 0 to less than 10 mass% of mono-C_9-alkyl substituted diphenyl amine, based upon the weight of the mono- and di-phenyl amines present in the composition.

[0015] This invention further relates to a lubricating oil composition comprising diphenyl amine antioxidant comprising: 1) di(C_9-alkyl substituted diphenyl) amine and 2) from 0 to less than 10 mass% of mono-C_9-alkyl substituted diphenyl amine, based upon the weight of the mono- and di-phenyl amines present in the lubricating oil composition.

[0016] This invention further relates to a lubricating oil composition wherein the diphenyl amine antioxidant comprising 90 mass% or more of di(C_9-alkyl substituted diphenyl) amines, from 0 to less than 10 mass% of mono-C_9-alkyl substituted diphenyl amine, and from 0 to less than 10 mass% of tri-C_9-alkyl substituted diphenyl amine, based upon the weight of the mono-, di-, and tri-phenyl amines present in the lubricating oil composition.

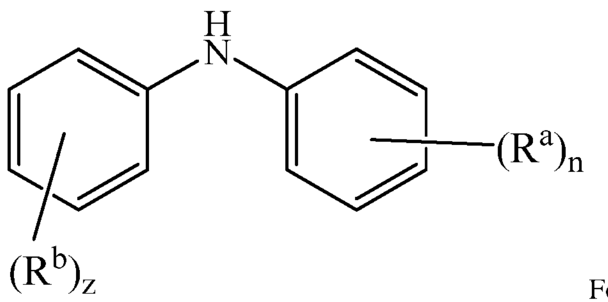
[0017] This invention further relates to a lubricating oil composition comprising or resulting from the admixing of:

(i) at least 50 mass% of one or more base oils, based upon the weight of the lubricating oil composition;
(ii) one or more dispersants;
(iii)one or more detergents; and
(iv)diphenyl amine antioxidant comprising di-C_9-alkyl substituted diphenyl amine and from 0 to less than 10 mass% of mono-C_9-alkyl substituted diphenyl amine, based upon the weight of the mono-C_9-alkyl substituted diphenyl amines and di-C_9-alkyl substituted diphenyl amines present in the lubricating oil composition.

[0018] This invention further relates to a lubricating oil composition comprising or resulting from the admixing of:

(i) at least 50 mass% of one or more base oils, based upon the weight of the lubricating oil composition;
(ii) one or more dispersants;
(iii) one or more detergents; and
(iv) diphenyl amine antioxidant composition comprising:

a) from 0 to less than 10 mass% mono-C_9-alkyl substituted diphenyl amine represented by the Formula (I) where n is 1 and z is 0,
b) 90 mass% or more of di-C_9-alkyl substituted diphenyl amine represented by Formula (I), where n is 1 and z is 1,
c) from 0 to less than 10 mass% tri-C_9-alkyl substituted diphenyl amine represented by Formula (I), where n + z = 3,
d) 1 mass% or less of unsubstituted diphenyl amines represented by Formula (I) where n is 0 and z is 0, based upon the total weight of the diphenyl amines of a), b), c) and d) present in the lubricating oil composition, where Formula (I) is:

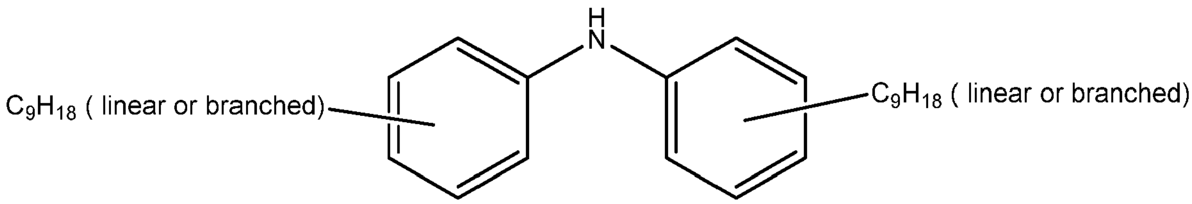


Formula I

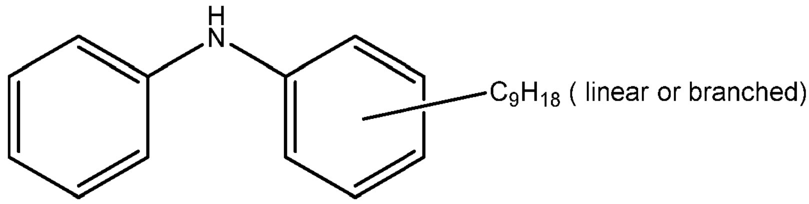
where each R^a and R^b is independently a linear C_9 alkyl or branched C_9 alkyl group, n is 0 or 1 and z is 0, 1 or 2.

[0019] This invention further relates to a lubricating oil composition comprising or resulting from the admixing of:

(i) at least 50 mass% of one or more base oils, based upon the weight of the lubricating oil composition; and
(ii) one or more C_9-alkyl substituted phenyl amine antioxidants, where -mono-C_9-alkyl substituted diphenyl) amines represented by the Formula (B) are absent or present at less than 10 mass%, based upon the weight of the diphenyl amine antioxidants represented by Formulas A and B present in the lubricating oil composition:



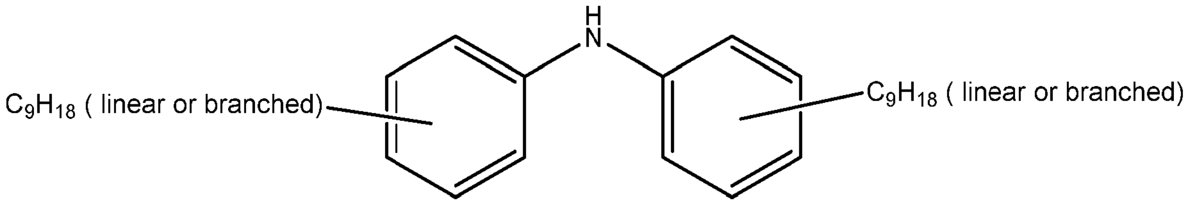
Formula (A),



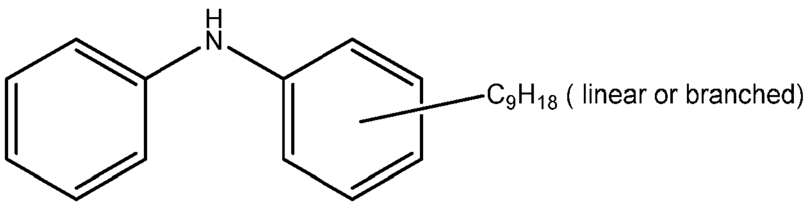
Formula (B),

where the branched C_9H_{18} may be singly, doubly or triply branched at one, two, three, four or more carbons, and may be symmetrically branched or asymmetrically branched.

[0020] This invention further relates to a lubricating oil composition comprising C_9 alkyl substituted phenyl amine antioxidants, where (alkyl substituted diphenyl)amines represented by the Formula (B) are absent or present at less than 15 mass% (such as less than 10 mass%, such as less than 5 mass%, such as less than 1 mass%, such as 0.5 mass%, such as less than 0.05 mass%, such as less than 0.3 mass%, particularly less than 0.1 mass%), and di-alkyl substituted diphenyl amines represented by Formula (A) are present at more than 85 mass% (such as 90 mass% or more), based upon the weight of the phenyl amine antioxidants represented by Formulas A and B present in the lubricating oil composition:



Formula (A), and



Formula (B),

where the branched C_9H_{18} may be singly, doubly or triply branched at one, two, three, four or more carbons, and may be symmetrically branched or asymmetrically branched.

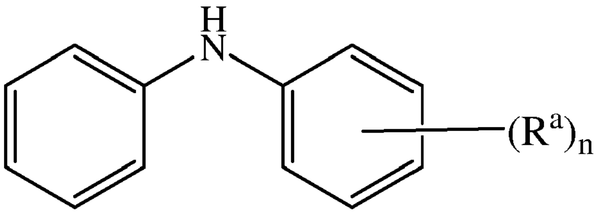
[0021] This invention further relates to a lubricating oil composition comprising one or more (C_9-alkyl substituted phenyl) amines, where (C_9-alkyl substituted diphenyl) amines represented by the Formula (B) are absent or present at less than 5 mass%, and di(C_9-alkyl substituted diphenyl) amines represented by Formula (A) are present at more than 90 mass%, based upon the weight of the phenyl amine antioxidants represented by Formulas A and B present in the lubricating oil composition.

[0022] This invention further relates to a lubricating oil composition where di-C_9-alkyl substituted diphenyl amine represented by Formula (I), where n is 1 and z is 1, is present in the lubricating oil composition at 1.0 mass% or more, based upon the mass of the lubricating composition.

[0023] This invention further relates to a lubricating oil composition comprising or made by admixing:

(i) at least 50 mass% of one or more base oils, based upon the weight of the lubricating oil composition;
(ii) one or more dispersants;
(iii) one or more detergents (such as carboxylate detergent) providing from 1 to 30 mmol/kg soap;
(iv) optionally, one or more hindered phenolic antioxidants;
(v) optionally one or more Mo containing compounds; and
(vi) optionally one or more fatty acid esters, such as sulfated fatty acid methyl esters and or glycerol-based friction modifier, such as glycerol mono-oleate;

where alkyl substituted diphenylamine(s) represented by the Formula (II) are absent or present at less than 0.30 mass% (such as less than 0.10 mass%, such as less than 0.1 mass%), based upon the weight of the lubricating oil composition:



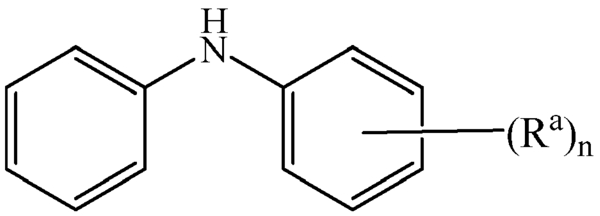
Formula (II)

where each R^a is independently linear C_9 alkyl or branched C_9 alkyl group and n is 1.

[0024] This invention further relates to a lubricating oil composition comprising or made by admixing:

(i) at least 50 mass% of one or more base oils, based upon the weight of the lubricating oil composition;
(ii) one or more dispersants;
(iii) one or more detergents (such as carboxylate detergent) providing from 1 to 30 mmol/kg soap;
(iv) optionally, one or more hindered phenolic antioxidants;
(v) optionally one or more Mo containing compounds;
(vi) optionally one or more fatty acid esters, such as sulfated fatty acid methyl esters and or glycerol-based friction modifier, such as glycerol mono-oleate; and
(vii) optionally one or more organic friction modifier, such as glycerol mono-oleate;

where alkyl substituted diphenylamine(s) represented by the Formula (II) are absent or present at less than 0.30 mass% (such as less than 0.10 mass%, such as less than 0.1 mass%), based upon the weight of the lubricating oil composition:



Formula (II)

where each R^a is independently linear C_9 alkyl or branched C_9 alkyl group and n is 1.

[0025] In a further aspect, there is provided a method of improving (i.e., reducing) viscometric growth of a lubricating oil, the method comprising: supplying to an engine a lubricating oil composition comprising diphenyl amine antioxidant comprising at least 90 mass% (such as 92 mass% or more, such as 94 mass% or more, such as 95 mass% or more, such as 97 mass% or more, such as 98 mass% or more, such as 99 mass% or more, such as 100 mass%) of one or more compounds represented by Formula (I), where n is 1 and z is 1, and less than 10 mass% (such as a 8 mass% or less, such as 6 mass% or less, such as 5 mass% or less, such as 3 mass% or less, such as 2 mass% or less, such as 1 mass% or less, such as 0 mass%) diphenyl amine antioxidant represented by Formula (I), where n is 1 and z is zero, based upon the weight of the diphenyl amine antioxidant represented by Formula (I), as described herein.

[0026] According to another aspect of the present invention, there is provided the use of the lubricating oil composition described above for lubrication of an engine.

[0027] This invention also relates to the use of diphenyl amine antioxidant comprising 1) di(C_9-alkyl substituted diphenyl) amine and 2) from 0 to less than 10 mass% of mono-C_9-alkyl substituted diphenyl amine to reduce piston deposits and or friction and or wear and or viscometric growth in a lubricating oil composition lubricating an internal combustion engine, comprising providing a lubricating oil comprising 1) di(C_9-alkyl substituted diphenyl) amine and 2) from 0 to less than 10 mass% of mono-C_9-alkyl substituted diphenyl amine to the internal combustion engine.

[0028] This invention also relates to the use of diphenyl amine antioxidant comprising 1) di(C_9-alkyl substituted

diphenyl) amine and 2) from 0 to less than 10 mass% of mono-C_9-alkyl substituted diphenyl amine to reduce: piston deposits (Sequence IIIH), and or rod deposits (MHT4 TEOST), and or friction (such as HFRR friction coefficient at 140°C, and or MTM friction coefficient, 135°C, 0.02 m/s, and or MTM-R: Traction Coefficient at 100°C), and or wear (such as HFRR: wear scar diameter and or MTM-R: wear scar volume), and or viscometric growth (CEC-L109-14), (where the tests above are as described in the Experimental section below) in a lubricating oil composition lubricating internal combustion engine, comprising providing the lubricating oil comprising 1) di(C_9-alkyl substituted diphenyl) amine and 2) from 0 to less than 10 mass% of mono-C_9-alkyl substituted diphenyl amine to the internal combustion engine, such as to the crankcase or sump of an internal combustion engine, where the lubricating oil composition optionally further comprises:
one, two, three, four, five, six or more additives selected from the group consisting of:

1) glycerol-based friction modifiers,
2) sulfonate-based detergents,
3) organomolybdenum-based friction modifiers,
4) magnesium-based detergents providing 400 ppm or more of Mg to the composition,
5) salicylate based detergents,
6) zinc-based antiwear agents (such as derived ZDDP from primary alcohol). and/or
7) base oil comprising a combination of refined and renewable base oils, optionally combined with a Group IV base oil, and or a combination of Group III and Group II base oils (such as refined Group II and III base oils), optionally combined with a group IV base oil.

[0029] In a further aspect, this invention relates to a composition, comprising,

a) 0.1 to 99.9 mass %, such as 1 to 99 mass%, based on total weight of the composition, of diphenyl amine antioxidant comprising 90 mass% or more of bis(nonylphenyl)amine and 10 mass% or less of (nonylphenyl)(phenyl)amine based on the weight of the bis(nonylphenyl)amine and (nonylphenyl)(phenyl)amine, and
b) 99.9 to 0.1 mass%, such as 99 to 1 mass%, based on total weight of the composition, of one, two, three, four, five, six or more additives selected from the group consisting of: glycerol-based friction modifiers, sulfonate-based detergents, organomolybdenum-based friction modifiers, magnesium-based detergents providing 400 ppm or more of Mg to the composition, salicylate based detergents, zinc-based antiwear agents, dispersants derived from polymer having an Mn of 1600 g/mol or less, and combinations thereof, and variants thereof.

[0030] In a further aspect, this invention relates to a composition (such as a booster pack, a concentrate, and or a lubricating oil composition), comprising,

a) 0.1 to 99.9 mass%, such as 1 to 99 mass%, based on total weight of the composition, of diphenyl amine antioxidant comprising 90 mass% or more of bis(nonylphenyl)amine and 10 mass% or less of (nonylphenyl)(phenyl)amine based on the weight of the bis(nonylphenyl)amine and (nonylphenyl)(phenyl)amine,
b) 0.1 to 99.9 mass%, such as 99 to 1 mass%, based on total weight of the composition, of base oil, such as base oil comprising one or more Group IV base oil(s), refined and or renewable Group III base oil(s), refined and or renewable Group II base oil(s), or combinations thereof,
c) from 0 to 99.8 mass%, based on total weight of the composition, of one, two, three, four, five, six or more additives selected from the group consisting of: glycerol-based friction modifiers; sulfonate-based detergents; organomolybdenum-based friction modifiers; magnesium-based detergents providing 400 ppm or more of Mg to the composition; salicylate based detergents; zinc-based antiwear agents; dispersants derived from polymer having an Mn of less than 1600 g/mol, such as PIBSA-PAM; base oil comprising a combination of 1) refined and renewable base oils, optionally a containing a Group IV base oil, and or 2) a combination of Group III and Group II base oils, optionally a containing a Group IV base oil;
and combinations and variants thereof.

[0031] In a further aspect, this invention relates to a lubricating oil composition comprising the composition(s) described herein.
[0032] In a further aspect, this invention relates to a lubricating oil composition, comprising:

a) 0.1 to 20 mass%, such as 1 to 10 mass%, based on total weight of the lubricating oil composition, of diphenylamine antioxidant comprising 90 mass% or more of bis(nonylphenyl)amine and 10 mass% or less of (nonylphenyl)(phenyl) amine based on the weight of the bis(nonylphenyl)amine and (nonylphenyl)(phenyl)amine,
b) 50 mass% or more, based on total weight of the lubricating oil composition, of base oil, such as base oil comprising

one or more Group IV base oil(s), refined and or renewable Group III base oil(s), refined and or renewable Group II base oil(s), or combinations thereof (such as base oil comprising a combination of refined and renewable base oils and or a combination of Group III and Group II base oils),

c) from 1 to less than 50 mass%, such as 1 to 20 mass% based on total weight of the lubricating oil composition, of one, two, three, four, five, six or more additives selected from the group consisting of: glycerol-based friction modifiers, sulfonate-based detergents, organomolybdenum-based friction modifiers, magnesium-based detergents providing 400 ppm or more of Mg to the composition, salicylate based detergents (such as calcium salicylate detergents), zinc-based antiwear agents, dispersants derived from polymer having an Mn of less than 1600 g/mol (Such as PIBSA-PAM), and combinations thereof, and variants thereof.

[0033] In a further aspect, this invention relates to a diphenyl amine antioxidant comprising:

a) less than 0.50 mass% of mono-C_9-alkyl substituted diphenyl amines,

b) greater than 99.50 mass% di-C_9-alkyl substituted diphenyl amines,

based upon the total weight of mono-C_9-alkyl substituted diphenyl amines and the di-C_9-alkyl substituted diphenyl amines.

BRIEF DESCRIPTION OF THE DRAWINGS

[0034]

Figure 1 (Fig. 1) shows typical alkylated phenyl amine isomers produced using C_9 alkyl (such as propylene trimer), where R is a C_9 alkyl radical.

Figure 2 (Fig. 2) is a graph of percent viscometric growth as a function of the amount of glycerol-based friction modifier added to an otherwise identical lubricating oil composition except the change from baseline (Component 2) to enhanced aminic antioxidant (Component 1, Batch 5) (measured at 216 hours at a temperature of 150°C).

Figure 3 (Fig. 3) is a graph of percent viscometric growth as a function of the amount of magnesium from magnesium detergent added to an otherwise identical lubricating oil composition except the change from baseline (Component 2) to enhanced aminic antioxidant (Component 1, Batch 5) (measured at 216 hours at a temperature of 150°C).

Figure 4 (Fig. 4) is a graph of CEC L109-14 percent viscometric growth comparing compositions containing Component 1, Batch 5 to compositions containing Component 2.

DEFINITIONS

[0035] For purposes of this specification and all claims to this invention, the following words and expressions, if and when used, have the meanings ascribed below.

[0036] For purposes herein, the new numbering scheme for the Periodic Table of the Elements is used as set out in CHEMICAL AND ENGINEERING NEWS, 63(5), 27 (1985), *i.e.,* **Alkali metals** are group 1 metals (*e.g.,* Li, Na, K, etc.) and **Alkaline earth metals** are group 2 metals (*e.g.*, Mg, Ca, Ba, etc.).

[0037] The term "**comprising**" or any cognate word specifies the presence of stated features, steps, or integers or components, but does not preclude the presence or addition of one or more other features, steps, integers, components or groups thereof. The expressions "**consists of**" or **bconsists essentially of**" or cognates may be embraced within "comprises" or cognates, wherein "consists essentially of" permits inclusion of substances not materially affecting the characteristics of the composition to which it applies.

[0038] The term "**LOC**" means lubricating oil composition.

[0039] The term "**major amount**" means more than 50 mass% of a composition, such as more than 60 mass% of a composition, such as more than 70 mass% of a composition, such as from 80 to 99.009 mass% of a composition, such as from 80 to 99.9 from 80 to 99.009 mass% of a composition, of a composition based upon the mass of the composition.

[0040] The term "**minor amount**" means 50 mass% or less of a composition; such as 40 mass% or less of a composition; such as 30 mass% or less of a composition, such as from 20 to 0.001 mass%, such as from 20 to 0.1 mass%, based upon the mass of the composition.

[0041] The term "**mass%**" means mass percent of a component, based upon the mass of the composition as measured in grams, unless otherwise indicated, and is alternately referred to as weight percent ("weight %", "mass%", or "% w/w").

[0042] The term "**active ingredient**" (also referred to as "ai", "a.i.", or "A.I.") refers to additive material that is neither diluent nor solvent. Unless otherwise indicated, amounts herein are described as active ingredient.

[0043] The terms "**oil-soluble**" and "**oil-dispersible**", or cognate terms, used herein do not necessarily indicate that the compounds or additives are soluble, dissolvable, miscible, or are capable of being suspended in the oil in all proportions. These do mean, however, that they are, for example, soluble or stably dispersible in oil to an extent sufficient to exert their intended effect in the environment in which the oil is employed. Moreover, the additional incorporation of other additives may also permit incorporation of higher levels of a particular additive, if desired.

[0044] The terms "**group**" and "**radical**" are used interchangeably herein.

[0045] The term "**hydrocarbon**" means a compound of hydrogen and carbon atoms. A "heteroatom" is an atom other than carbon or hydrogen. When referred to as "hydrocarbons", particularly as "refined hydrocarbons", the hydrocarbons may also contain one or more heteroatoms or heteroatom-containing groups (such as halo, especially chloro and fluoro, amino, alkoxyl, mercapto, alkylmercapto, nitro, nitroso, sulfoxy, etc.) in minor amounts (*e.g.*, where the heteroatom(s) do not substantially alter the hydrocarbon properties of the hydrocarbon compound).

[0046] The term "**hydrocarbyl**" means a radical that contains hydrogen and carbon atoms. Preferably, the group consists essentially of, more preferably consists only of, hydrogen and carbon atoms, unless specified otherwise. Preferably, the hydrocarbyl group comprises an aliphatic hydrocarbyl group. The term "hydrocarbyl" includes "alkyl", "alkenyl", "alkynyl", and "aryl" as defined herein. Hydrocarbyl groups may contain one or more atoms/groups other than carbon and hydrogen provided they do not affect the essentially hydrocarbyl nature of the hydrocarbyl group. Those skilled in the art will be aware of such atoms/groups (*e.g.*, halo, especially chloro and fluoro, amino, alkoxyl, mercapto, alkylmercapto, nitro, nitroso, sulfoxy, etc.).

[0047] The term "**alkyl**" means a radical of carbon and hydrogen (such as a C_1 to C_{30}, such as a C_1 to C_{12} group). Alkyl groups in a compound are typically bonded to the compound directly via a carbon atom. Unless otherwise specified, alkyl groups may be linear (*i.e.,* unbranched) or branched, be cyclic, acyclic, or part cyclic/acyclic. Preferably, the alkyl group comprises a linear or branched acyclic alkyl group. Representative examples of alkyl groups include, but are not limited to, methyl, ethyl, n-propyl, iso-propyl, n-butyl, sec-butyl, iso-butyl, tert-butyl, n-pentyl, iso-pentyl, neo-pentyl, hexyl, heptyl, octyl, dimethyl hexyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, icosyl and triacontyl.

[0048] The term "**alkenyl**" means a radical of carbon and hydrogen (such as a C_2 to C_{30} radical, such as a C_2 to C_{12} radical) having at least one double bond. Alkenyl groups in a compound are typically bonded to the compound directly via a carbon atom. Unless otherwise specified, alkenyl groups may be linear (*i.e.*, unbranched) or branched, be cyclic, acyclic or part cyclic/acyclic.

[0049] The term "**alkylene**" means a C_1 to C_{20}, preferably a C_1 to C_{10}, bivalent saturated aliphatic radical, which may be linear or branched. Representative examples of alkylene include methylene, ethylene, propylene, butylene, pentylene, hexylene, heptylene, octylene, nonylene, decylene, 1-methyl ethylene, 1-ethyl ethylene, 1-ethyl-2-methyl ethylene, 1,1-dimethyl ethylene and 1-ethyl propylene.

[0050] An "**olefin**", alternatively referred to as "**alkene**", is a linear, branched, or cyclic compound of carbon and hydrogen having at least one double bond. For purposes of this specification and the claims appended thereto, when a polymer or copolymer is referred to as comprising an olefin, the olefin present in such polymer or copolymer is the polymerized form of the olefin. For example, when a copolymer is said to have an "isoprene" content of 55 mass% to 95 mass%, it is understood that the mer unit in the copolymer is derived from isoprene in the polymerization reaction and said derived units are present at 55 mass% to 95 mass%, based upon the weight of the copolymer. A "**polymer**" has two or more of the same or different mer units. A "**homopolymer**" is a polymer having mer units that are the same. A "**copolymer**" is a polymer having two or more mer units that are different from each other. "Different" as used to refer to mer units indicates that the mer units differ from each other by at least one atom or are different isomerically. An "isoprene polymer" or "isoprene copolymer" is a polymer or copolymer comprising at least 50 mol % isoprene derived units, a "butadiene polymer" or "butadiene copolymer" is a polymer or copolymer comprising at least 50 mol % butadiene derived units, and so on. Likewise, when a polymer is referred to as a "partially or fully saturated polymer comprising C_{4-5} olefins", the C_{4-5} olefin(s) present in such polymer or copolymer are the polymerized form of the olefin(s), and the polymer has been partially or fully saturated (such as by hydrogenation) after polymerization of the monomers.

[0051] The term "**alkynyl**" means a C_2 to C_{30} (such as a C_2 to C_{12}) radical, which includes at least one carbon-to-carbon triple bond.

[0052] The term "**aryl**" means a group containing at least one aromatic ring, such a cyclopentadiene, phenyl, naphthyl, anthracenyl, and the like. Aryl groups are typically C_5 to C_{40} (such as C_5 to C_{18}, such as C_6 to C_{14}) aryl groups, optionally substituted by one or more hydrocarbyl groups, heteroatoms, or heteroatom-containing groups (such as halo, hydroxyl, alkoxy and amino groups). Preferred aryl groups include phenyl and naphthyl groups and substituted derivatives thereof, especially phenyl, and alkyl substituted derivatives of phenyl.

[0053] The term "**substituted**" means that a hydrogen atom has been replaced with hydrocarbon group, a heteroatom, or a heteroatom-containing group. An alkyl substituted derivative means a hydrogen atom has been replaced with an alkyl group. An "alkyl substituted phenyl" is a phenyl group where a hydrogen atom has been replaced by an alkyl group, such as a C_1 to C_{20} alkyl group, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, sec-butyl, iso-butyl, tert-butyl, n-pentyl, iso-pentyl, neo-pentyl, hexyl, heptyl, octyl, dimethyl hexyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, icosyl and/or triacontyl. A "**substituted phenyl**" is a phenyl group where a hydrogen atom has been replaced by hydrocarbon group, a heteroatom, or a heteroatom-containing group (such an alkyl group, such as a C_1 to C_{20} alkyl group, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, sec-butyl, iso-butyl, tert-butyl, n-pentyl, iso-pentyl, neo-pentyl, hexyl, heptyl, octyl, dimethyl hexyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, icosyl and/or triacontyl).

[0054] The term "**antioxidant**" or equivalent term (e.g., "oxidation stabilizer" or "oxidation inhibitor") refers to a composition with the capability of controlling (reducing) oxidation, and consequently preventing components in a lubricating oil composition from breakdown and causing thickening (increasing viscosity) of the LOC. Based on the mechanism of action, antioxidants are categorized as **primary antioxidants** (radical scavengers), **secondary antioxidants** (peroxide decomposers), and metal deactivators (complex-forming or chelating agents).

[0055] A "**hindered phenol**" is a phenol with one or more bulky functional groups (i.e. functional groups having at least 4 non-hydrogen atoms, such as substituted or unsubstituted C_4 to C_{40} alkyl groups.) Common hindered phenols include butylated hydroxy toluene and substituted butylated hydroxy toluenes.

[0056] The term "**halogen**" or "**halo**" means a group 17 atom or a radical of group 17 atom, such as fluoro, chloro, bromo, and iodo.

[0057] The term "**ashless**" in relation to an additive means the composition does not include a metal.

[0058] The term "**ash-containing**" in relation to an additive means the composition includes a metal.

[0059] The term "**effective amount**" in respect of an additive means an amount of such an additive in a lubricating oil composition so that the additive provides the desired technical effect.

[0060] The term "**effective minor amount**" in respect of an additive means an amount of such an additive of less than 50 mass% of the lubricating oil composition so that the additive provides the desired technical effect.

[0061] The term "**effective major amount**" in respect of an additive means an amount of such an additive of 50 mass% or more of the lubricating oil composition so that the additive provides the desired technical effect.

[0062] The term "**ppm**" means parts per million by mass, based on the total mass of the lubricating oil composition, unless otherwise indicated.

[0063] The term "**metal content**" of a lubricating oil composition or of an additive component, for example, magnesium content, molybdenum content or total metal content (*i.e.,* the sum of all individual metal contents), is measured by ASTM D5185.

[0064] The term "**aliphatic hydrocarbyl fatty acid**" means a monocarboxylic acid having an aliphatic C_7 to C_{29}, preferably a C_9 to C_{27}, most preferably a C_{11} to C_{23} hydrocarbyl chain. Such compounds may be referred to herein as aliphatic (C_7 to C_{29}), more preferably (C_9 to C_{27}), most preferably (C_{11} to C_{23}), hydrocarbyl monocarboxylic acid(s) or hydrocarbyl fatty acid(s) (wherein C_x to C_y designates the total number of carbon atoms in the aliphatic hydrocarbyl chain of the fatty acid, the fatty acid itself due to the presence of the carboxyl carbon atom includes a total of C_{x+1} to C_{y+1} carbon atoms). Preferably, the aliphatic hydrocarbyl fatty acid, inclusive of the carboxyl carbon atom, has an even number of carbon atoms. The aliphatic hydrocarbyl chain of the fatty acid may be saturated or unsaturated (*i.e.*, includes at least one carbon-to-carbon double bond); preferably, the aliphatic hydrocarbyl chain is unsaturated and includes at least one carbon-to-carbon double bond - such fatty acids may be obtained from natural sources (*e.g.*, derived from animal or vegetable oils) and/or by reduction of the corresponding saturated fatty acid. It will be appreciated that a proportion of the aliphatic hydrocarbyl chain(s) of the corresponding aliphatic hydrocarbyl fatty acid ester(s) is unsaturated (*i.e.*, includes at least one carbon-to-carbon double bond) to permit reaction with other agents, such as sulfur, to form the corresponding functionalized, such as sulfurized, aliphatic hydrocarbyl fatty acid ester(s).

[0065] The term "**aliphatic hydrocarbyl fatty acid ester**" means an ester obtainable by converting the monocarboxylic acid functional group of the corresponding aliphatic hydrocarbyl fatty acid into an ester group. Suitably, the monocarboxylic acid functional group of the aliphatic hydrocarbyl fatty acid is converted to a hydrocarbyl ester, preferably a C_1 to C_{30} aliphatic hydrocarbyl ester, such as an alkyl ester, preferably a C_1 to C_6 alkyl ester, especially a methyl ester. Alternatively, or additionally, the monocarboxylic acid functional group of the aliphatic hydrocarbyl fatty acid may be in the form of the natural glycerol ester. Accordingly, the term "aliphatic hydrocarbyl fatty acid ester" embraces aliphatic hydrocarbyl fatty acid glycerol ester(s) and aliphatic hydrocarbyl fatty acid C_1 to C_{30} aliphatic hydrocarbyl ester(s), [*e.g.*, aliphatic hydrocarbyl fatty acid alkyl ester(s), more preferably aliphatic hydrocarbyl fatty acid C_1 to C_6 alkyl ester(s), especially aliphatic hydrocarbyl fatty acid methyl ester(s)]. Suitably, the term "aliphatic hydrocarbyl fatty acid ester" embraces aliphatic (C_7 to C_{29}) hydrocarbyl, more preferably aliphatic (C_9 to C_{27}) hydrocarbyl, most preferably aliphatic (C_{11} to C_{23}) hydrocarbyl fatty acid glycerol ester(s) and aliphatic (C_7 to C_{29}) hydrocarbyl, more preferably aliphatic (C_9 to C_{27}) hydrocarbyl, most preferably aliphatic (C_{11} to C_{23}) hydrocarbyl fatty acid C_1 to C_{30} aliphatic hydrocarbyl ester(s). Suitably, to permit functionalization, such as sulfurization, of the aliphatic hydrocarbyl fatty acid ester(s) a proportion of the aliphatic hydrocarbyl chain(s) of the fatty acid ester(s) is unsaturated and includes at least one carbon-to-carbon double bond.

[0066] The term "**sulfurized aliphatic hydrocarbyl fatty acid ester**" means a compound obtained by sulfurizing an aliphatic hydrocarbyl fatty acid ester as defined herein.

[0067] The term "**absent**" as it relates to components included within the lubricating oil compositions described herein and the claims thereto means that the particular component is present at 0 mass%, based upon the weight of the lubricating oil composition, or if present in the lubricating oil composition the component is present at levels that do not impact the lubricating oil composition properties, such as less than 10 ppm, or less than 1 ppm or less than 0.001 ppm. When the term "absent" is used in relation to monomer reactants and/or to repeat units in (co)polymers described herein, it means present at 0 mass%, based upon the weight of all (co)monomers in the (co)polymer, or, if present at all, at levels so low that they do not substantially impact the physical properties of the (co)polymer, such as at 0.2 mass% or less, or at 0.1 mass% or less.

[0068] The term "**absent or present at less than 0.3 mass%**" as it relates to components included within the lubricating oil compositions described herein and the claims thereto means that the particular component is absent as defined above, or is present at any of the following amounts: less than 0.3 mass%, 0.29 mass% or less, 0.28 mass% or less, 0.27 mass% or less, 0.26 mass% or less, 0.25 mass% or less, 0.24 mass% or less, 0.23 mass% or less, 0.22 mass% or less, 0.21 mass% or less, 0.20 mass% or less, 0.19 mass% or less, 0.18 mass% or less, 0.17 mass% or less, 0.16 mass% or less, 0.15 mass% or less, 0.14 mass% or less, 0.13 mass% or less, 0.12 mass% or less, 0.11 mass% or less, 0.10 mass% or less, 0.09 mass% or less, 0.08 mass% or less, 0.07 mass% or less, 0.06 mass% or less, 0.05 mass% , or less 0.04 mass% or less, 0.03 mass% or less, 0.02 mass% or less, 0.01 mass% or less. If any of the lesser amounts are referred to (for example a component is "present at 0.19 mass% or less"), each of the lesser amounts above are included therein.

[0069] The term "**absent or present at less than 0.2 mass%**" as it relates to components included within the lubricating oil compositions described herein and the claims thereto means that the particular component is absent as defined above, or is present at any of the following amounts: 0.19 mass% or less, 0.18 mass% or less, 0.17 mass% or less, 0.16 mass% or less, 0.15 mass% or less, 0.14 mass% or less, 0.13 mass% or less, 0.12 mass% or less, 0.11 mass% or less, 0.10 mass% or less, 0.09 mass% or less, 0.08 mass% or less, 0.07 mass% or less, 0.06 mass% or less, 0.05 mass% or less, 0.04 mass% or less, 0.03 mass% or less, 0.02 mass% or less, 0.01 mass% or less. If any of the lesser amounts are referred to (for example a component is "present at 0.19 mass% or less"), each of the lesser amounts above are included therein.

[0070] As used herein, **Mn** is number average molecular weight, **Mw** is weight average molecular weight, and **Mz** is z average molecular weight. **Molecular weight distribution** (MWD), also referred to as **polydispersity index** (PDI), is defined to be Mw divided by Mn. Unless otherwise noted, all molecular weight units (*e.g.*, Mw, Mn, Mz) are reported in g/mol.

[0071] **Total Base Number** also referred to as "TBN", in relation to an additive component or of a lubricating oil composition (*i.e.*, unused lubricating oil composition) means total base number as measured by ASTM D2896 and reported in units of mgKOH/g.

[0072] **Total Acid Number** ("TAN") is determined by ASTM D664.

[0073] **Phosphorus, Boron, Calcium, Zinc, Molybdenum, Sodium, Silicon,** and **Magnesium** content are measured by ASTM D5185.

[0074] **Sulfur content in oil** formulations is measured by ASTM D5185.

[0075] **Sulfated ash** ("SASH") content is measured by ASTM D874.

[0076] **Kinematic viscosity** (KV100, KV40, etc.) is determined pursuant to ASTM D445-19a and reported in units of cSt, unless otherwise specified.

[0077] **Viscosity index** is determined according to ASTM D2270.

[0078] **Saponification number** is determined by ASTM D94, and reported in units of mgKOH/g.

[0079] Unless otherwise indicated, all percentages reported are mass% on an active ingredient basis, *i.e.*, without regard to carrier or diluent oil, unless otherwise indicated.

[0080] Also, it will be understood that various components used, essential as well as optimal and customary, may react under conditions of formulation, storage or use and that the disclosure also provides the product obtainable or obtained as a result of any such reaction.

[0081] Further, it is understood that any upper and lower quantity, range and ratio limits set forth herein may be independently combined.

[0082] Also, it will be understood that the preferred features of each aspect of the present disclosure are regarded as preferred features of every other aspect of the present disclosure. Accordingly, preferred and more preferred features of one aspect of the present disclosure may be independently combined with other preferred and/or more preferred features of the same aspect or different aspects of the present disclosure.

DETAILED DESCRIPTION OF THE INVENTION

[0083] The features of the disclosure relating, where appropriate, to each and all aspects of the disclosure, will now be described in more detail as follows.

[0084] The lubricating oil compositions, concentrates and booster packs of the disclosure comprise components that may or may not remain the same chemically before and after mixing with an oleaginous carrier (such as a base oil) and/or other additives. This disclosure encompasses compositions which comprise the components before mixing, or after mixing, or both before and after mixing.

[0085] C_9 alkylated diphenylamines (such as Naugalube™ 438L, Songnox™ L670, Irganox™ L67, Vanlube™ DND) are antioxidants that are commonly used in the lubricant, rubber and plastics industries. The C_9 alkylated diphenylamines are typically prepared from the reaction of diphenylamine with tripropylene or other C_9 alkene. These reactions give a complex mixture of products made of a mixture of C_9 alkyl isomers, ortho-, meta-, and paradiphenylamine substitution, and mono/di-/tri-C_9 alkyl diphenylamine substitution.

[0086] In this invention we disclose that an antioxidant prepared by removing the mono-C_9 alkyldiphylamine (such as by distillation) from the C_9 alkyl diphenylamine component has greater control of oxidation driven viscosity increase in engine oils than the C_9 alkyl diphenylamine that still contains the mono-C_9 alkyl diphenylamine. In general, the diphenylamine isomers can be separated by well-known techniques such as distillation (such as thin film evaporation and or flash distillation), dialysis, chromatography, and the like. The isomer content may be determined by mass spectrometry as described in the Experimental Section.

[0087] In this invention we also note, that at higher treat rates, the mono- C_9 alkylated diphenylamine is a less effective antioxidant at controlling oxidation driven viscosity growth. Without wishing to be bound by theory, it is believed that this is due to unwanted side reactions involving the unsubstituted aromatic ring that form compounds that promote viscosity growth.

[0088] This is surprising as, mono-C_9 alkylated diphenylamine can show antioxidant performance when the mono- C_9 alkylated diphenylamine is present at greater than ten percent of the C_9 alkyl diphenylamine component. From a performance perspective it has been considered as a benefit to have mono- C_9 alkylated diphenylamine in the component because it has a higher percent nitrogen content weight for weight compared to the di-C_9 alkylated diphenylamine. Typically nitrogen levels in aminic antioxidants are indicative of the components antioxidant performance. However, for very high temperature applications the greater volatility of the mono-substituted diphenylamine compared to the di-substituted diphenylamine has been considered potentially detrimental to antioxidant performance.

[0089] For purposes of this invention and the claims thereto "**mono-C_9-alkyl substituted diphenyl amine**", also referred to as "(C_9-alkyl substituted phenyl)(phenyl)amine" or "(nonylphenyl)(phenyl)amine", means a nitrogen atom bound to: 1) hydrogen, 2) an unsubstituted phenyl group, and 3) a phenyl group substituted with one C_9 alkyl group.

[0090] For purposes of this invention and the claims thereto "**di-C_9-alkyl substituted diphenyl amine**", also referred to as "di(C_9-alkyl substituted phenyl) amine" or "di(nonylphenyl)amine" or "bis(nonylphenyl)amine", means a nitrogen atom bound to: 1) hydrogen, and 2) two phenyl groups each independently substituted with one C_9 alkyl group, each of which is independently linear or branched.

[0091] For purposes of this invention and the claims thereto "**tri-C_9-alkyl substituted diphenyl amine**", also referred to as "(diC_9-alkyl substituted phenyl) (C_9-alkyl substituted phenyl)amine", means a nitrogen atom bound to 1) hydrogen, 2) a phenyl group independently substituted with two C_9 alkyl groups, each of which is independently linear or branched, and 3) a phenyl group substituted with one C_9 alkyl group.

[0092] For purposes of this invention and the claims thereto "**diphenyl amine antioxidant**" also referred to as "**aminic antioxidant**" means antioxidant comprising a nitrogen atom bound to 1) hydrogen, 2) two phenyl groups each of which may independently be substituted with one or more C_9 alkyl group.

[0093] For purposes of this invention and the claims thereto "**unsubstituted diphenyl amine**", means a nitrogen atom bound to 1) hydrogen, and 2) two unsubstituted phenyl groups.

[0094] For purposes of this invention and the claims thereto "**enhanced aminic antioxidant**" or "**enhanced diphenyl amine antioxidant**" is:

A) diphenyl amine antioxidant comprising: 1) 90 (or 91, or 92, or 93, or 94, or 95, or 96, or 97, or 98, or 99, or 99.3, or 99.5, or 99.8) mass% or more (such as 100 mass%) of di-C_9-alkyl substituted diphenyl amine, and 2) 0 mass% or 10 (or 9, or 8, or 7, or 6, or 5, or 4, or 3 or 2, or 1) mass% or less of mono-C_9-alkyl substituted diphenyl amine, based on the total mass% of the di-C_9-alkyl substituted diphenyl amine and mono-C_9-alkyl substituted diphenyl amine; or
B) diphenyl amine antioxidant comprising: 1) 85 (or 90, or 91, or 92, or 93, or 94, or 95, or 96, or 97, or 98, or 99, or 99.3, or 99.5, or 99.8) mass% or more (such as 100 mass%) of di-C_9-alkyl substituted diphenyl amine, and 2) zero mass% or 10 (or 9, or 8, or 7, or 6, or 5, or 4, or 3 or 2, or 1) mass % or less of mono-C_9-alkyl substituted diphenyl amine, and 3) 0 mass % or 20 (or 15, or 10, or 9, or 8, or 7, or 6, or 5, or 4, or 3 or 2, or 1) mass% or less of tri-C_9-alkyl substituted diphenyl amine, based on the total mass% of the tri-C_9-alkyl substituted diphenyl amine, di-C_9-alkyl substituted diphenyl amine and mono-C_9-alkyl substituted diphenyl amine; or
C) diphenyl amine antioxidant comprising: 1) 85 (or 90, or 91, or 92, or 93, or 94, or 95, or 96, or 97, or 98, or 99, or 99.3, or 99.5, or 99.8) mass% or more (such as 100 mass%) of di-C_9-alkyl substituted diphenyl amine, and 2) zero mass% or 10 (or 9, or 8, or 7, or 6, or 5, or 4, or 3 or 2, or 1) mass % or less of mono-C_9-alkyl substituted diphenyl amine, 3) 0 mass % or 20 (or 15, or 10, or 9, or 8, or 7, or 6, or 5, or 4, or 3 or 2, or 1) mass% or less of tri-C_9-alkyl substituted diphenyl amine, and 4) 0 mass% or 5 (or 4, or 3 or 2, or 1, or 0.5, or 0.1) mass% or less of unsubstituted diphenyl amine, based on the total mass% of the tri-C_9-alkyl substituted diphenyl amine, di-C_9-alkyl substituted diphenyl amine, mono-C_9-alkyl substituted diphenyl amine, and unsubstituted diphenyl amine.

[0095] In this invention we also note unique and or improved effects, and even synergistic defects, from combinations of:

A) enhanced aminic antioxidants (such as diphenyl amine antioxidant comprising 90 mass% or more of bis(nonylphenyl) amine and 10 mass% or less of (nonylphenyl)(phenyl)amine based on the weight of the bis(nonylphenyl)amine and (nonylphenyl)(phenyl)amine) as compared to the same composition where the aminic antioxidant(s) are replaced with Component 2 from the Experimental section; with **B**) one, two, three, four, five, six or more additives selected from the group consisting of:

1) glycerol-based friction modifiers,
2) sulfonate-based detergents,
3) organomolybdenum-based friction modifiers,
4) magnesium-based detergents providing 400 ppm or more (such as 600 ppm or more) of Mg to the composition,
5) salicylate based detergents (such as salicylate based detergents),
6) zinc-based antiwear agents (such as derived ZDDP from primary alcohol), and
7) base oils combinations comprising Group III oil, Group II oil, and or renewable base oils, and combinations thereof (such as combinations of Group III and Group II oil and/or Group III oil and renewable base oil (such as Group II or Group III renewable base oil),

and combinations thereof, and variants thereof.

[0096] This invention further relates to compositions (and lubricating oil compositions comprising these compositions), wherein the compositions comprise:

A) an enhanced aminic antioxidant (such as antioxidant comprising 90 mass% or more of bis(nonylphenyl)amine and 10 mass% or less of (nonylphenyl)(phenyl)amine based on the weight of the bis(nonylphenyl)amine and (nonylphenyl)(phenyl)amine) in combination with, or resulting from the admixing with
B) one, two, three, four, five, six or more additives selected from the group consisting of:

1) glycerol-based friction modifiers, such as glycerol mono-oleate;
2) sulfonate-based detergents, such as magnesium and or calcium sulfonate detergents;
3) organomolybdenum-based friction modifiers, such as molybdenum dithiocarbamate dimers and or trimers;
4) magnesium-based detergents providing 400 ppm or more of Mg to the composition, such as magnesium salicylate and or sulfonate detergents;
5) carboxylate based detergents, such as such as magnesium and or calcium salicylate detergents;
6) zinc-based antiwear agents, such as zinc dialkyldithiophosphaetes where the alkyl group is derived from primary alcohols; and

C) optionally, one, two, three or more base oils selected from Group IV base oil(s), refined and or renewable Group II base oil(s), refined and or renewable Group III base oil(s), or combinations thereof, (such as combinations of: Group III base oil(s) and Group II and/or III renewable base oil(s); combinations of Group III base oil(s) and Group II base oil(s); combinations of Group III base oil(s); combinations of Group IV base oil(s), Group III base oil(s) and Group II and/or III renewable base oil(s); and combinations of Group IV base oils, Group III base oil(s) and Group II base oil(s).

[0097] In a further aspect, this invention relates to a composition (such as a concentrate or booster pack), comprising,

a) from 1 to 99.99 mass% (such as 5 to 99 mass%, 10 to 90 mass%, such as 20 to 80 mass%, such as 30 to 70 mass%, such as 40 to 50 mass%), based upon the weight of the composition, of aminic antioxidant comprising:

i) 90 to 100 mass% of bis(nonylphenyl)amine (such as 91 to 99.9 mass%, such as 92 to 99.5 mass%, such as 93 to 99 mass%, such as 94 to 100 mass%, such as 95 to 100 mass%, such as 96 to 99.99 mass%, such as 97 to 99.5 mass%, such as 98 to 100 mass%, such as 99 to 100 mass%), the bis(nonylphenyl)amine and (nonylphenyl)(phenyl)amine, and,
ii) 10 to 0 mass% (such as 9 to 0.1 mass%, such as 8 to 0.5 mass%, such as 7 to 1 mass%, such as 6 to 1 mass%, such as 5 to 0.1 mass%, such as 4 to 0.01 mass%, such as 4 to 0.5 mass%, such as 2 to 0 mass%, such as 1 to 0 mass%) of (nonylphenyl)(phenyl)amine, based on the weight of the bis(nonylphenyl)amine and (nonylphenyl)(phenyl)amine; and

b) one, two, three, four, five, six or more of:

1) from 0.01 to 99 mass%, based upon the weight of the composition, such as 0.01 to 20 mass%, such as 0.1 to 10 mass%, such as 0.1 to 5 mass%, such as 0.1 to 1 mass%, such as 0.1 to 0.8 mass%, such as 0.15 to 0.7 mass%,

such as 0.15 to 0.65 mass%, such as 0.10 to 0.60 mass%, such as 0.10 to 0.50 mass% of glycerol-based friction modifiers, such as glycerol mono-oleate;

2) from 0.01 to 99 mass%, based upon the weight of the composition, such as 0.01 to 20 mass%, such as 0.1 to 10 mass%, such as 0.1 to 5 mass%, sulfonate-based detergents, such as magnesium and or calcium sulfonate detergents;

3) from 0.01 to 99 mass%, based upon the weight of the composition, such as 0.01 to 20 mass%, such as 0.05 to 10 mass%, such as 0.1 to 5 mass%, organomolybdenum-based friction modifier, such as molybdenum dithiocarbamate dimers and or trimers;

4) from 0.01 to 99 mass%, based upon the weight of the composition, such as 0.01 to 20 mass%, such as 0.1 to 10 mass%, such as 0.1 to 5 mass%, magnesium-based detergent such as magnesium salicylate and or sulfonate detergents) providing high amounts of Mg to the composition (such as 400 ppm to 20,000 ppm, such as 450 to 10,000 ppm, such as 500 ppm to 8000ppm, such as 600 ppm or more, such as 700 ppm or more, such as 800 ppm or more, such as 1000 ppm or more, such as 1200 ppm or more, such as 2000 ppm or more, such as 3000 ppm or more, such as 4000 ppm or or more, such as 5000 ppm or more);

5) from 0.01 to 99 mass%, based upon the weight of the composition, such as 0.01 to 20 mass%, such as 0.1 to 10 mass%, such as 0.1 to 5 mass%, zinc-based antiwear agents, such as zinc dialkyldithiophosphaetes where the alkyl group is derived from primary alcohols (such as C_4 to C_{30} primary alcohols); and

6) from 0.01 to 99 mass%, based upon the weight of the composition, such as 0.01 to 80 mass%, such as 0.01 to 50 mass%, such as 0.1 to 40 mass%, such as 0.1 to 20 mass%, salicylate-based detergent, such as calcium and or magnesium salicylate-based detergent (optionally providing high amounts of Ca and or Mg to the composition (such as 40 ppm to 20,000 ppm, such as 200 to 15,000 ppm, such as 500 ppm to 8000 ppm, such as 600 ppm or more, such as 700 ppm or more, such as 800 ppm or more, such as 1000 ppm or more, such as 1200 ppm or more, such as 2000 ppm or more, such as 3000 ppm or more, such as 4000 ppm or or more, such as 5000 ppm or more) Ca and or Mg optionally in ratios of Ca:Mg of 1:2 to 2:1; and

7) optionally from 0.01 to 99 mass%, based upon the weight of the composition, such as 0.01 to 50 mass%, such as 1 to 40, such as 1 to 30 mass%, such as 1 to 20 mass%, such as 0.1 to 10 mass%, such as 0.1 to 5 mass%, dispersants (such as PIBSA-PAM) derived from a polymer (such as polyisobutylene) having an Mn of 1600 g/mol or less (such as 600 to less than 1600 g/mol, such as 650 to 1500 g/mol, such as 700 to 1400 g/mol, such as 800 to 1300 g/mol, such as 850 to 1200 g/mol, such as 900 to 1150 g/mol, such as 900 to 1000 g/mol).

[0098] In a further aspect, this invention relates to a composition, comprising,

A) 0.1 to 99 mass% (such as 10 to 99 mass%, such as 10 to 90 mass%, such as 50 to 99 mass%, such as 60 to 95 mass%, such as 70 mass% or more), based on total weight of the composition, of one, two, three or more refined and or renewable Group II base oil(s), refined and or renewable Group III base oil(s), and Group IV base oil(s), or combinations thereof (such as combinations of Group III base oil(s) and renewable base oil(s), combinations of Group III base oil(s) and Group II base oil(s), combinations of Group IV base oil(s) with refined and renewable Group III base oils(s), and or combinations of Group III base oil(s), Group IV base oil and Group II base oil(s)), and

B) from 0.1 to 99.99 mass% (such as 0.5 to 30 mass%, such as 1 to 20 mass%, such as 1 to 5 mass%), based upon the weight of the composition, of aminic antioxidant comprising:

i) 90 to 100 mass% of bis(nonylphenyl)amine (such as 91 to 99.9 mass%, such as 92 to 99.5 mass%, such as 93 to 99 mass%, such as 94 to 100 mass%, such as 95 to 100 mass%, such as 96 to 99.99 mass%, such as 97 to 99.5 mass%, such as 98 to 100 mass%, such as 99 to 100 mass%), based upon the weight of the bis(nonylphenyl) amine and (nonylphenyl)(phenyl)amine and

ii) 10 to 0 mass% (such as 9 to 0.1 mass%, such as 8 to 0.5 mass%, such as 7 to 1 mass%, such as 6 to 0.5 mass%, such as 5 to 0.5 mass%, such as 4 to 0.01 mass%, such as 4 to 0.5 mass%, such as 2 to 0 mass%, such as 1 to 0 mass%) of (nonylphenyl)(phenyl)amine, based on the weight of the bis(nonylphenyl)amine and (nonylphenyl) (phenyl)amine; and,

Q) optionally, one, two, three, four, five, six or more of:

1) from 0.01 to 99 mass%, based upon the weight of the composition, such as 0.01 to 20 mass%, such as 0.1 to 10 mass%, such as 0.1 to 5 mass%, such as 0.1 to 1 mass%, such as 0.1 to 0.8 mass%, such as 0.15 to 0.7 mass%, such as 0.15 to 0.65 mass%, such as 0.10 to 0.60 mass%, such as 0.10 to 0.50 mass% **glycerol-based friction modifiers,** such as glycerol mono-oleate;

2) from 0.01 to 99 mass%, based upon the weight of the composition, such as 0.01 to 20 mass%, such as 0.1 to 10 mass%, such as 0.1 to 5 mass%, **sulfonate-based detergents,** such as magnesium and or calcium sulfonate

detergents;

3) from 0.01 to 99 mass%, based upon the weight of the composition, such as 0.01 to 20 mass%, such as 0.05 to 10 mass%, such as 0.05 to 5 mass%, **organomolybdenum-based friction modifier,** such as molybdenum dithiocarbamate dimers and or trimers;

4) from 0.01 to 99 mass%, based upon the weight of the composition, such as 0.01 to 20 mass%, such as 0.1 to 10 mass%, such as 0.1 to 5 mass%, **magnesium-based detergent,** such as magnesium salicylate and or sulfonate detergents, preferably providing high amounts of Mg to the composition(such as 400 ppm to 10,000 ppm, such as 500 ppm to 8000ppm, such as 600 ppm or more, such as 700 ppm or more, such as 800 ppm or more, such as 1000 ppm or more, such as 1200 ppm or more, such as 2000 ppm or more, such as 3000ppm or more, such as 4000 ppm or or more, such as 5000 ppm or more);

5) from 0.01 to 99 mass%, such as 0.05 to 10 mass%, such as 0.1 to 5 mass%, such as 0.01 to 20 mass%, such as 0.1 to 2 mass%, **zinc-based antiwear agents,** such as zinc dialkyldithiophosphaetes where the alkyl group is derived from one or more primary alcohol(s);

6) from 0.01 to 99 mass%, based upon the weight of the composition, such as 0.01 to 25 mass%, such as 0.1 to 20 mass%, such as 0.1 to 10 mass%, such as 0.1 to 5 mass% **salicylate-based detergent,** optionally providing high amounts of Ca and or Mg to the composition (such as 40 ppm to 1,000 ppm, such as 50 ppm to 800ppm, such as 60 ppm or more, such as 70 ppm or more, such as 80 ppm or more, such as 1000 ppm or more, such as 1200 ppm or more, such as 2000 ppm or more, such as 3000 ppm or more, such as 4000 ppm or or more, such as 5000 ppm or more); and

7) optionally from 0.01 to 99 mass%, such as 0.01 to 20 mass%, such as 0.1 to 10 mass%, such as 0.1 to 5 mass%, such as 0.1 to 3 mass%, dispersants (such as PIBSA-PAM) derived from a polymer (such as polyisobutylene) having an Mn of 1600 g/mol or less (such as 600 to less than 1600 g/mol, such as 650 to 1500 g/mol, such as 700 to 1400 g/mol, such as 800 to 1300 g/mol, such as 850 to 1200 g/mol, such as 900 to 1150 g/mol, such as 900 to 1000 g/mol); and

C) from 0.10 to 20 mass% (in particular, 0.15 to 10 mass%, alternately 0.20 mass% to 5 mass%, alternately 0.25 to 2 mass%), based upon the weight of the lubricating oil composition, of one or more **detergents,** other than the sulfonate and salicylate detergents listed in Q above, (such as blends of detergents);

D) optionally, from 0.01 to 5 mass% (in particular 0.1 to 4 mass%, alternately 0.25 to 3 mass%, alternately 0.045-0.15 mass%), based on total weight of the lubricating oil composition, of one or more **friction modifiers,** other than molybdenum compounds and glycerol-based friction modifiers listed in Q above, (such as blends of friction modifiers);

F) optionally, from 0.01 to 5 mass% (in particular, 0.01 to 3 mass%, alternately 0.1 to 1.5 mass%), based on total weight of the lubricating oil composition, of one or more **pour point depressants** (such as blends of pour point depressants);

G) optionally, from 0.001 to 3 mass% (in particular, 0.01 to 2 mass%, alternately 0.1 to 1.5 mass%), based on total weight of the lubricating oil composition, of one or more **anti-foam agents** (such as blends of anti-foam agents);

H) optionally, from 0.001 to 10 mass% (in particular, 0.01 to 6 mass%, alternately 0.01 to 5 mass%, alternately 0.1 to 4 mass%, alternately 0.1 to 2 mass%, alternately 0.1 to 1 mass%), based on total weight of the lubricating oil composition, of one or more **viscosity modifiers** (such as blends of viscosity modifiers);

I) optionally, from 0.01 to 20 mass% (in particular, 0.1 to 12 mass%, alternately 0.1 to 8 mass%), based on total weight of the lubricating oil composition, of one or more **dispersants,** other than the low Mn dispersants listed in Q above (such as blends of dispersants);

J) optionally, from 0.01 to 5 mass% (in particular, 0.1 to 3 mass%, alternately 0.1 to 1.5 mass%), based on total weight of the lubricating oil composition, of one or more **inhibitors and/or anti-rust agents** (such as blends of inhibitors and /or anti-rust agents (such as triazole based agents, such as benzotriazole based agents);

K) from 0.001 to 10 mass% (in particular, 0.01 to 5 mass%, alternately 0.1 to 3 mass%, alternately 0. to 1.5 mass%), based on total weight of the lubricating oil composition, of one or more **antiwear agents,** other than the zinc-based antiwear agents listed in Q above (such as blends of antiwear agents);

M) optionally, from 0.01 to 5 mass% (in particular, 0.05 to 2 mass%, alternately 0.1 to 1 mass%), based on total weight of the lubricating oil composition, of one or more **seal compatibility agents,** such as seal swell agents, and/or

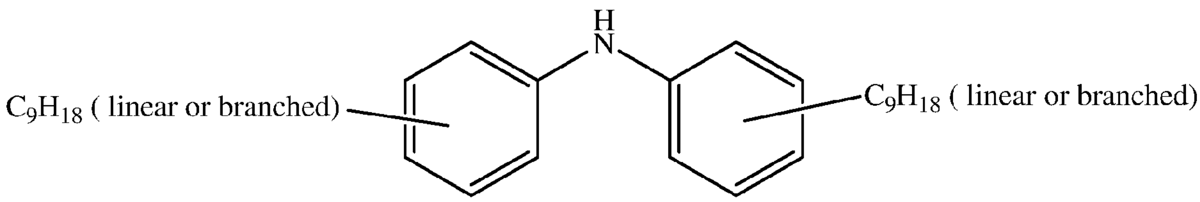
O) optionally, from 0.01 to 5 mass% (in particular, 0.1 to 3 mass%, alternately 0.1 to 1.5 mass%), based on total weight of the lubricating oil composition, of one or more **unsaturated C_{12}-C_{60} hydrocarbons** (such as C_{12}-C_{24} linear alpha-olefins (LAOs), oligomers/polymers of polyisobutylenes, and/or blends thereof).

[0099] For purposes of this disclosure, component B) antioxidants are not added in the elements C, D, F, G, H, I, J, K, M, and/or O above for determining weight percentages, even though they may show similar properties, e.g., element B) antioxidants may impact wear positively, but is not added into element K) for determining weight percent of anti-wear agents.

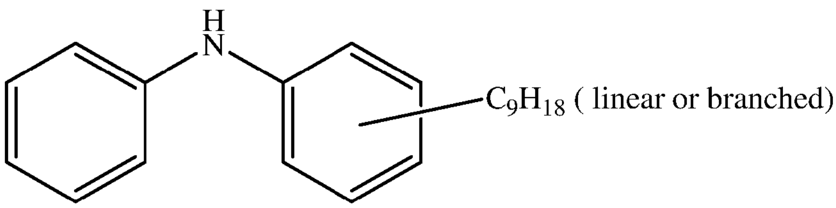
Lubricating Oil Compositions

[0100] This disclosure relates to lubricating oil compositions (also referred to as "LOC", "lubricant compositions", "lubricating compositions", or "lubricant oil compositions") comprising or resulting from the admixing of:

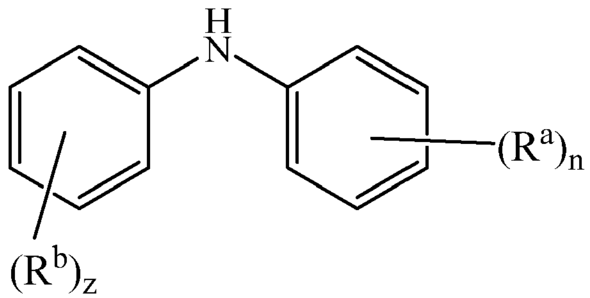
(a) from 1 to 99 mass% (alternately 30 to 95 mass%, alternately 50 to 90 mass%, alternately 60 to 95 mass%, alternately 70 to 85 mass%) of one or more **base oils,** based upon the weight of the lubricating composition;
(b) from 0.01 to 20 mass% (in particular 0.1 to 12 mass%, alternately 0.1 to 8 mass%), based on total weight of the lubricating composition, of one or more **dispersants** (such as blends of dispersants);
(c) from 0.10 to 20 mass% (in particular 0.15 to 10 mass%, alternately 0.20 mass% to 5 mass%, alternately 0.25 to 2 mass%), based upon the weight of the composition, of one or more **detergents**; and
(d) from 0.01 to 20 mass% (in particular 0.10 to 15 mass%, alternately 0.15 to 10 mass%, alternately 0.20 mass% to 5 mass%, alternately 0.25 to 2 mass%, alternately 0.5 to 1 mass%), based upon the weight of the lubricating oil composition, of antioxidant comprising one or more **diphenyl amine antioxidants** represented by Formula (A) (such as Formula (I), where n is 1 and z is 1), and from 0 to 2 mass% of diphenyl amine antioxidants represented by Formula (B) (such as Formula (I), where n is 1 and z is 0, such as 0 to 1 mass% (such as 0.001 to less than 0.3 mass% such as 0.005 to less than 0.1 mass%, such as 0.01 to 0.05 mass%), based upon the weight of the lubricating oil composition:



Formula (A), and



Formula (B), and



Formula (I),

where the branched C_9H_{18} may be singly, doubly or triply branched at one, two, three, four or more carbons, and may be symmetrically branched or asymmetrically branched; and
where each R^a and R^b is independently linear C_9 alkyl or branched C_9 alkyl group and n is 1 and z is 0 or 1;
where the lubricating oil composition may preferably exhibit:

a) an oxidation (FTIR, CEC-L-109-14 Oxidation Test) of the lubricating oil composition that is less than or within 20%, such as within 10 %, of the oxidation of **Comparative Formulation A [**where **Comparative Formulation A** is the same lubricating oil composition except that the diphenyl amine antioxidant has been replaced with the same amount of diphenyl amine antioxidant having:

1) about 68 mass% di-C_9-alkyl diphenyl amine,
2) about 29 mass% of mono-C_9-alkyl diphenyl amine, and
3) about 3 mass% of tri-C_9-alkyl diphenyl amine, based on the weight of 1), 2) and 3), as determined by UPLC in the Experimental section**]**, and

b) wherein the lubricating oil composition has a percent viscosity increase between the initial KV100 and the KV100 at 216 hours of the CEC-L-109-14 Oxidation Test that is at least 2% less (such as at least 5% less, such as at least 7% less, such as at least 8% less, such as at least 20% less, such as at least 30% less) than the percent viscosity increase of **Comparative Formulation A.**

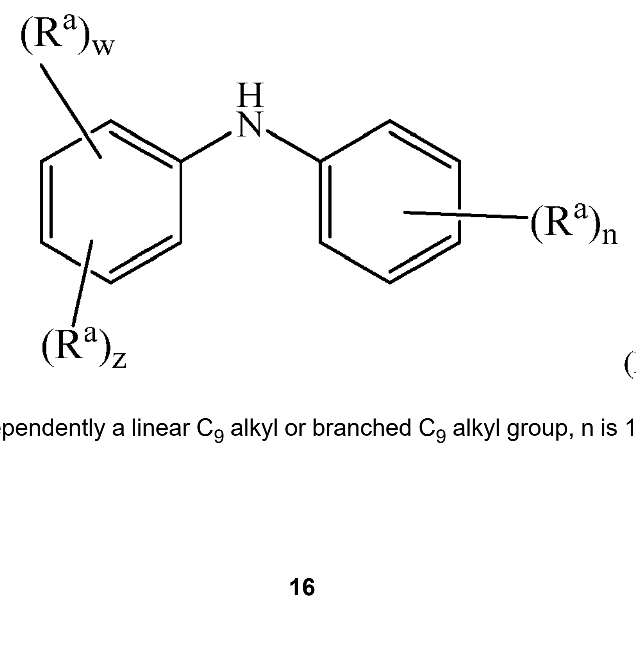
[0101] In embodiments, the lubricating oil composition may comprise less than 0.30 mass% (such as 0.29 mass% or less, such as 0.28 mass% or less, such as 0.27 mass% or less, such as 0.26 mass% or less, such as 0.25 mass% or less, such as 0.24 mass% or less, such as 0.23 mass% or less, such as 0.22 mass% or less, such as 0.21 mass% or less, such as 0.20 mass% or less such as 0.19 mass% or less, such as 0.18 mass% or less, such as 0.17 mass% or less, such as 0.16 mass% or less, such as 0.15 mass% or less such as 0.14 mass% or less, such as 0.13 mass% or less, such as 0.12 mass% or less, such as 0.11 mass% or less, such as less than 0.10 mass%, such as 0.09 mass% or less, such as 0.08 mass% or less, such as 0.07 mass% or less, such as 0.06 mass% or less, such as 0.05 mass% or less such as 0.04 mass% or less, such as 0.03 mass% or less, such as 0.02 mass% or less, such as 0.01 mass% or less, such as 0 mass%) of mono-C_9-alkyl substituted diphenyl amines represented by Formula (B) (preferably phenyl amines represented by Formula (I), where n is 1 and z is 0), based upon the weight of the lubricating oil composition.

[0102] In embodiments, the lubricating oil composition may comprise 0.1 mass% or more (or 0.2 mass% or more, or 0.3 mass% or more, or 0.4 mass% or more, or 0.5 mass% or more, or 0.6 mass% or more, or 0.7 mass% or more, or 0.8 mass% or more, or 0.9 mass% or more, or 1.0 mass% or more, or 1.5 mass% or more, or 2.0 mass% or more, or 3.0 mass% or more, 4.0 mass% or more) of di-C_9-alkyl substituted diphenyl amines represented by Formula (A), preferably di-C_9-alkyl substituted diphenyl amines represented by Formula (I), where n is 1 and z is 1, based upon the weight of the phenyl amine antioxidant composition.

[0103] This disclosure also relates to lubricating oil compositions comprising or resulting from the admixing of:

A) from 1 to 99 mass% (alternately 30 to 95 mass%, alternately 50 to 90 mass%, alternately 60 to 95 mass%, alternately 70 to 85 mass%) based upon the weight of the lubricating oil composition, of one or more **base oils**;
B) from 0.01 to 20 mass% (in particular 0.10 to 15 mass%, alternately, 0.15 to 10 mass%, alternately 0.20 mass% to 5 mass%, alternately 0.25 to 2.5 mass%, alternately 0.5 to 1 mass%), based upon the weight of the lubricating oil composition, of **diphenyl amine antioxidant** comprising (or consisting essentially of, or consisting of):

i) one or more di-C_9-alkyl substituted diphenyl amine represented by Formula (III) below, where n is 1, w is 0, and z is 1, and
ii) from 0 to less than 0.3 mass% (such as less than 0.1 mass%, such as less than 0.01 mass%, such as less than 0.001 mass%, such as less than 0.0005 mass%) based upon the weight of the lubricating oil composition, of mono- C_9-alkyl substituted diphenyl amines represented by the Formula (III), where n is 1, w is 0, and z is 0, and
iii) from 0 to less than 0.3 mass% (such as less than 0.1 mass%, such as less than 0.01 mass%, such as less than 0.001 mass%, such as less than 0.0005 mass%) of tri-C_9-alkyl substituted diphenyl amines represented by the Formula (III), where n is 1, w is 1, and z is 1, based upon the weight of the lubricating oil composition, where Formula (III) is:



(III)

where each R^a is independently a linear C_9 alkyl or branched C_9 alkyl group, n is 1, z is 0 or 1, and w is 0 or 1;

C) from 0.10 to 20 mass% (in particular, 0.15 to 10 mass%, alternately 0.20 mass% to 5 mass%, alternately 0.25 to 2 mass%), based upon the weight of the lubricating oil composition, of one or more **detergents,** preferably carboxylate detergents (such as blends of detergents);
D) optionally, from 0.01 to 5 mass% (in particular 0.1 to 4 mass%, alternately 0.25 to 3 mass%, alternately 0.045-0.15 mass%), based on total weight of the lubricating oil composition, of one or more **friction modifiers** (such as blends of friction modifiers);
F) optionally, from 0.01 to 5 mass% (in particular, 0.01 to 3 mass%, alternately 0.1 to 1.5 mass%), based on total weight of the lubricating oil composition, of one or more **pour point depressants** (such as blends of pour point depressants);
G) optionally, from 0.001 to 3 mass% (in particular, 0.01 to 2 mass%, alternately 0.1 to 1.5 mass%), based on total weight of the lubricating oil composition, of one or more **anti-foam agents** (such as blends of anti-foam agents);
H) optionally, from 0.001 to 10 mass% (in particular, 0.01 to 6 mass%, alternately 0.01 to 5 mass%, alternately 0.1 to 4 mass%, alternately 0.1 to 2 mass%, alternately 0.1 to 1 mass%), based on total weight of the lubricating oil composition, of one or more **viscosity modifiers** (such as blends of viscosity modifiers);
I) optionally, from 0.01 to 20 mass% (in particular, 0.1 to 12 mass%, alternately 0.1 to 8 mass%), based on total weight of the lubricating oil composition, of one or more **dispersants** (such as blends of dispersants);
J) optionally, from 0.01 to 5 mass% (in particular, 0.1 to 3 mass%, alternately 0.1 to 1.5 mass%), based on total weight of the lubricating oil composition, of one or more **inhibitors and/or anti-rust agents** (such as blends of inhibitors and /or anti-rust agents);
K) from 0.001 to 10 mass% (in particular, 0.01 to 5 mass%, alternately 0.1 to 3 mass%, alternately 0. to 1.5 mass%), based on total weight of the lubricating oil composition, of one or more **antiwear agents** (such as blends of antiwear agents, such as ZDDP);
M) optionally, from 0.01 to 5 mass% (in particular, 0.05 to 2 mass%, alternately 0.1 to 1 mass%), based on total weight of the lubricating oil composition, of one or more **seal compatibility agents,** such as seal swell agents, and/or
O) optionally, from 0.01 to 5 mass% (in particular, 0.1 to 3 mass%, alternately 0.1 to 1.5 mass%), based on total weight of the lubricating oil composition, of one or more **unsaturated C_{12}-C_{60} hydrocarbons** (such as C_{12}-C_{24} linear alpha-olefins (LAOs), oligomers/polymers of polyisobutylenes, and/or blends thereof).

[0104] All elements A through O are as described more fully herein.
For purposes of this disclosure, component B) antioxidants are not added in the elements C, D, F, G, H, I, J, K, M, and/or O above for determining weight percentages, even though they may show similar properties, *e.g.*, element B) antioxidants may impact wear positively, but is not added into element K) for determining weight percent of anti-wear agents.

[0105] In embodiments, all of elements D, F, G, H, I, J, K, M, and O are present in addition to the base oil, detergent, and the optional one or more functionalized polymers described herein (such as the amide, imide, and/or ester functionalized partially or fully saturated polymer comprising C_{4-5} olefins described below).

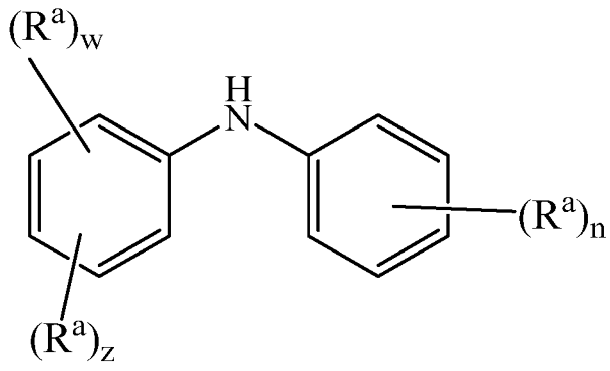
[0106] In embodiments, elements D, F, G, H, I, and J are present in addition to the base oil, detergent, and the optional one or more functionalized polymers described herein (such as the amide, imide, and/or ester functionalized partially or fully saturated polymer comprising C_{4-5} olefins described below).

[0107] In embodiments, elements I, F, and G are present in addition to the base oil, detergent, and the optional one or more functionalized polymers described herein (such as the amide, imide, and/or ester functionalized partially or fully saturated polymer comprising C_{4-5} olefins described below).

[0108] In embodiments, element K is present in addition to the base oil, detergent, and the one or more functionalized polymers described herein (such as the amide, imide, and/or ester functionalized partially or fully saturated polymer comprising C_{4-5} olefins described below).

[0109] In embodiments, element D **(friction modifier(s),** such as one or more friction modifiers, such as one or more glycerol-based friction modifiers, such as glycerol mono-oleate) is present, in addition to the base oil and **diphenyl amine antioxidant(s),** at from 0.01 to 5 mass% (in particular 0.1 to 4 mass%, alternately 0.25 to 3 mass%, alternately 0.045-0.15 mass%), based on total weight of the lubricating oil composition.

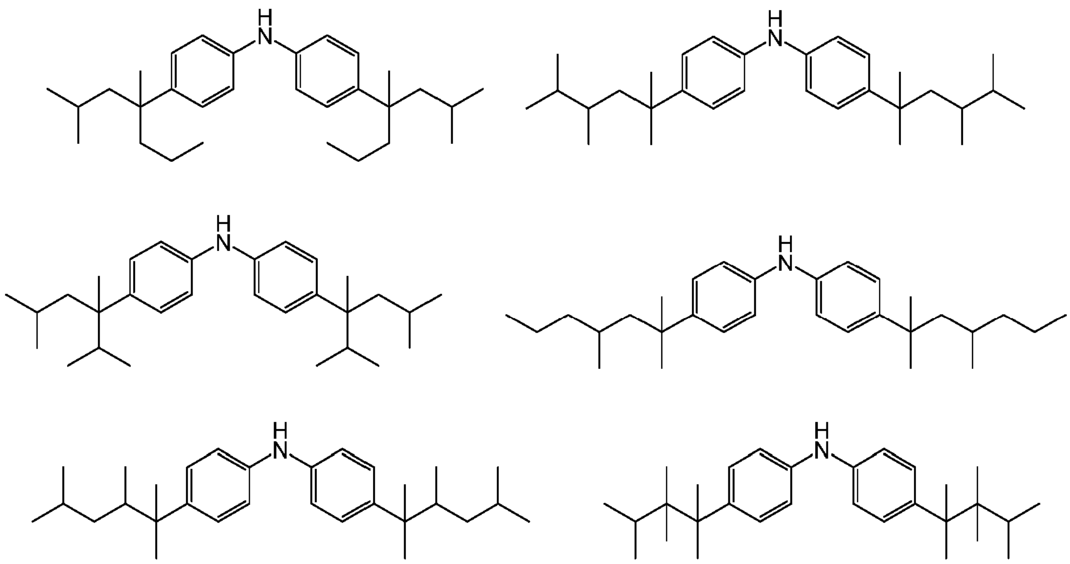
[0110] This invention further relates to a lubricating oil composition comprising antioxidants, where mono- C_9-alkyl substituted diphenyl amines represented by the Formula (III), where n is 1, w is 0 and z is 0, are absent or present a less than 0.30 mass% (such as 0.29 mass% or less, such as 0.28 mass% or less, such as 0.27 mass% or less, such as 0.26 mass% or less, such as 0.25 mass% or less, such as 0.24 mass% or less, such as 0.23 mass% or less, such as 0.22 mass% or less, such as 0.21 mass% or less, such as 0.20 mass% or less such as 0.19 mass% or less, such as 0.18 mass% or less, such as 0.17 mass% or less, such as 0.16 mass% or less, such as 0.15 mass% or less such as 0.14 mass% or less, such as 0.13 mass% or less, such as 0.12 mass% or less, such as 0.11 mass% or less, such as less than 0.10 mass%, such as 0.09 mass% or less, such as 0.08 mass% or less, such as 0.07 mass% or less, such as 0.06 mass% or less, such as 0.05 mass% or less such as 0.04 mass% or less, such as 0.03 mass% or less, such as 0.02 mass% or less, such as 0.01 mass% or less, such as 0 mass%), based upon the weight of the lubricating oil composition, where Formula (III) is:



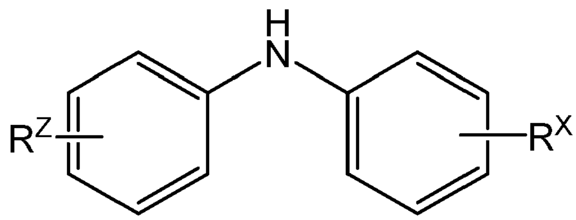
(III)

where each R^a is independently a linear C_9 alkyl or branched C_9 alkyl group, n is 1, z is 0 or 1, and w is 0 or 1.

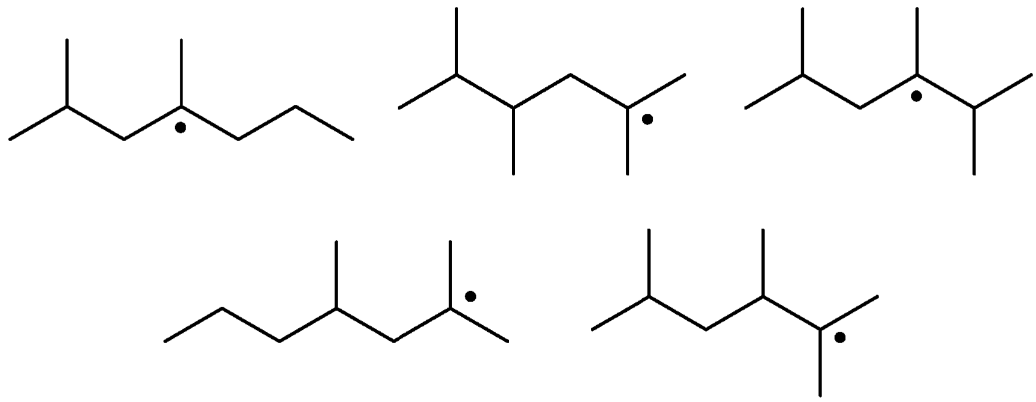
[0111] This invention further relates to a lubricating oil composition comprising antioxidants, where combinations comprising one, two, three, or four of the following substituted phenyl amines depicted below are absent or present at 0.1 mass% or more, (or 0.2 mass% or more, or 0.3 mass% or more, or 0.4 mass% or more, or 0.5 mass% or more, or 0.6 mass% or more, or 0.7 mass% or more, or 0.8 mass% or more, or 0.9 mass% or more, or 1.0 mass% or more, or 2.0 mass% or more, or 3.0 mass% or more, or 4.0 mass% or more) based upon the weight of the lubricating oil composition:



[0112] This invention further relates to a lubricating oil composition comprising antioxidants, where combinations comprising one, two, three, or four of the following substituted phenyl amines depicted below are absent or present at 0.1 mass% or more, (or 0.2 mass% or more, or 0.3 mass% or more, or 0.4 mass% or more, or 0.5 mass% or more, or 0.6 mass% or more, or 0.7 mass% or more, or 0.8 mass% or more, or 0.9 mass% or more, or 1.0 mass% or more, or 2.0 mass% or more, or 3.0 mass% or more, or 4.0 mass% or more) based upon the weight of the lubricating oil composition:



where R^X and R^Z are independently selected from:



[0113] This invention further relates to a lubricating oil composition comprising an antioxidant composition comprising or made by admixing:

1) phenylamine antioxidant comprising one or more di-C_9-alkyl substituted diphenyl amine as represented by Formula (A), preferably Formula (III) where n is 1, z is 1 and w is 0, above, and
2) optionally, one or more additional antioxidants (such as diphenyl amines other than 1) above, hindered phenol, sulfurized fatty acid esters, molybdenum containing compounds, ashless dithiocarbamates, and the like),

where alkyl substituted diphenylamine(s) represented by the Formula (B) (such as Formula (III), where n is 0, w is 0 and z is 1) are absent or present at less than 0.30 mass%, such as less than 0.1 mass%, based upon the weight of the lubricating oil composition.

[0114] This invention further relates to a lubricating oil composition wherein di-C_9-alkyl substituted diphenyl amine represented by Formula (III), where w is 0, n is 1, and z is 1, is present in the lubricating oil composition at 0.5 mass% or more, 1.0 mass% or more, or 2.0 mass% or more, or 3.0 mass% or more, based upon the mass of the lubricating composition and mono-C_9-alkyl substituted diphenyl amine represented by Formula (III), where w is 0, n is 1, and z is 0, is present in the lubricating oil composition at 0.3 mass% or less, or at 0.1 mass% or less, based upon the mass of the lubricating composition.

[0115] This invention further relates to lubricating oil compositions as described above comprising **element B** (aminic antioxidant, such as antioxidant comprising 90 mass% or more of bis(nonylphenyl)amine and 10 mass% or less of (nonylphenyl)(phenyl)amine based on the weight of the bis(nonylphenyl)amine and (nonylphenyl)(phenyl)amine) in combination with, or resulting from the admixing with, one or more additives selected from the group consisting of: **element D** (such as glycerol-based friction modifiers and or organomolybdenum-based friction modifiers);

element C (such as calcium and or magnesium sulfonate-based detergents and or calcium and or magnesium salicylate based detergents, such as detergents providing high levels of Mg to the lubricating oil composition);
element K (such as zinc-based antiwear agents, such as ZDDPs derived from primary alcohols);
element I (such as dispersants, such as PIBSA-PAM, derived from a polymer, such as PIB, having an Mn of 1600 g/mol or less); and
element A (such as refined and or renewable Group II base oil(s), refined and or renewable Group III base oil(s), Group IV base oil(s)), and combinations thereof, and variants thereof).

[0116] The invention also includes lubricating oil composition comprising **element B** aminic antioxidant (such as antioxidant comprising 90 mass% or more of bis(nonylphenyl)amine and 10 mass% or less of (nonylphenyl)(phenyl)amine based on the weight of the bis(nonylphenyl)amine and (nonylphenyl)(phenyl)amine) and **element A** base oil, selected from Group I, II III, IV and or V base oils, such as base oils selected from the group of Group I base oils, Group II base oils, Group III vase oils, renewable oils (plant and/or microbe-based oils, such as group II and or Group III renewable oils), and combinations thereof, and variants thereof.

[0117] Common commercially available di(nonylphenyl) aminic antioxidants typically comprise a large (typically greater than 10 mass%, based on the weight of total mass% of the mono-, di- and tri-nonyl substituted diphenyl aminic components in the di(nonylphenyl) aminic antioxidant) amount of (nonylphenyl)(phenyl)amine. As used herein, these are referred to as "baseline aminic antioxidants" and are typically compositions of about 68 mass% bis(nonylphenyl)amine, about 29 mass% of mono(nonylphenyl) amine, and about 3 mass% of tri(nonylphenyl) amine based on the total mass% of the mono-, di- and tri- substituted (nonylphenyl) aminic components. It has been found that aminic antioxidants that comprise larger amounts of bis(nonylphenyl)amine are preferred and in fact may act synergistically with other lubricant oil additives.

As used herein, these may be referred to as "enhanced aminic antioxidants (defined above)" and are typically a composition of several components, most preferably 90 (or 91, or 92, or 93, or 94, or 95, or 96, or 97, or 98, or 99, or 99.3) mass% or more of bis(nonylphenyl)amine and 10 (or 9, or 8, or 7, or 6, or 5, or 4, or 3 or 2, or 1) mass% or less of (nonylphenyl)(phenyl)amine, based on the total mass% of the mono- and di-substituted (nonylphenyl) aminic components. Enhanced aminic antioxidants can be obtained by any means such as by distilling or otherwise separating out the bis(nonylphenyl)amine component from the other baseline aminic antioxidant components, or through direct organic synthesis. The lubricating oil composition comprising baseline aminic antioxidant used for comparison purposes herein is **Comparative Formulation A [**where **Comparative Formulation A** is the same lubricating oil composition except that the diphenyl amine antioxidant has been replaced with the same amount of diphenyl amine antioxidant having:

1) about 68 mass% di-C_9-alkyl diphenyl amine,
2) about 29 mass% of mono-C_9-alkyl diphenyl amine, and
3) about 3 mass% of tri-C_9-alkyl diphenyl amine, based on the weight of 1), 2) and 3), as determined by UPLC, as described in the Experimental section below**].**

While the benefits and synergies available with the enhanced aminic antioxidants are illustrated by comparison with the Component 1"s in the Experimental section below, it is expected that the same advantages will be shown when compared to other C_9-alkyl diphenyl amine antioxidant compositions containing amounts, such as more than 10 (or 20, or 25, or 30, or 40, or 50) mass% of mono-C_9-alkyl diphenyl amine, as determined by UPLC in the Experimental section.

[0118] In any embodiment, inventive aspects of the lubricating oil compositions are demonstrated in their enhanced viscometric growth properties. In any embodiment the viscometric growth (CEC-L-109-14, 216 hr., 150°C) of a lubricating oil composition that includes one or more of di-C_9-alkyl diphenyl amine antioxidants described herein is at least 5 % (preferably at least 10%, at least 15%, at least 20%, at least 25%, at least 30 %) lower relative to a lubricating oil composition of the same formulation except that the enhanced aminic antioxidant is replaced at the same mass percentage by nonylphenyl amine antioxidant comprising about 68 mass% of bis(nonylphenyl)amine, about 29 mass% of (nonylphenyl)(phenyl)amine and about 3 mass% of tri(nonylphenyl)amine based upon the weight of the mono-(nonylphenyl)amine, bis(nonylphenyl)amine, and tri(nonylphenyl)amine, as determined by UPLC (as described in the Experimental section below).

[0119] Due to the improved viscosity control when using the enhanced aminic antioxidant relative to the baseline aminic antioxidant in otherwise equivalent lubricating oil compositions, the inventors were able to compare treat rates (mass% in the lubricating oil compositions) of the additives named above, for instance, the glycerol-based friction modifiers, when formulating lubricating oil compositions with enhanced aminic antioxidant. In the embodiments comprising glycerol-based friction modifier, the linear equation with baseline aminic antioxidant is $Y = 53.667X + 56.8$, wherein X is the mass% of the glycerol-based friction modifier and Y is the L109 % viscosity increase. The linear equation with the enhanced aminic antioxidant is $Z = 71.167X + 41.4$, where Z is the L109 % viscosity increase and X is the mass% of the glycerol-based friction modifier. To calculate the additional amount of glycerol-based friction modifier that can be added with the enhanced aminic antioxidant, the relationship $X = (56.8 - 41.4)/71.17$ was found, where X is the mass% of glycerol-based friction modifier. These relationships are demonstrated graphically in Fig. 2 when the additive is a glycerol-based friction modifier, glycerol mono-oleate. In any embodiment, a similar relationship also exists with the organomolybdenum-based friction modifiers and the magnesium-based detergents (see Fig. 3), among others.

[0120] In embodiments, benefit of the lubricating oil compositions is demonstrated in their enhanced coefficient of friction in a crankcase. Thus in any embodiment is a method of reducing friction in a crankcase of an internal combustion engine comprising providing to the crankcase a lubricating oil composition comprising the compositions described herein such that the coefficient of friction, Q, (as measured by HFRR, 140°C) is at least 5 % less, such as at least 10 % less, such as at least 20% less when in the presence of the enhanced aminic antioxidant than the coefficient of friction (as measured by HFRR, 140°C), at the same temperature ramp conditions in the presence of the baseline aminic antioxidant, wherein Q is within a range from, for instance, 0.140 to 0.145 in the presence of the enhanced aminic antioxidant and glycerol-based friction modifiers. The value of Q will vary with the added agent, such as with the with the sulfonate-based detergents, organomolybdenum-based friction modifiers and the calcium/magnesium-based detergents.

[0121] Glycerol-based friction modifiers useful herein in combination with the enhanced aminic antioxidant(s) are described further herein, and in any embodiment include compounds such as glycerol monooleates, saturated mono-, di-, and tri-glyceride esters, glycerol monostearates, and polyols. In a preferred embodiment the glycerol-based friction modifier comprises glycerol mono-oleate.

[0122] Organomolybdenum-based friction modifiers useful herein in combination with the enhanced aminic antioxidant(s) are described further herein, and in any embodiment include compounds such as organomolybdenum compounds of dithiocarbamates, dithiophosphates, dithiophosphinates, xanthates, thioxanthates, sulfides, and the like, and mixtures thereof. Desirable organomolybdenum-based friction modifiers include molybdenum dithiocarbamates, dialkyldithiophosphates, alkyl xanthates and alkylthioxanthates. In a more preferred embodiment, the organomolybdenum-based friction modifiers are selected from dimeric molybdenum dialkyldithiocarbamates and trimeric molybdenum dialkyldithiocarbamates, and most preferably dimeric dialkyldithiocarbamate (where the alkyls are selected from C_6 to C_{14} alkyl groups, and may be combinations of C_{10} to C_{14} and C_6 to C_{12} alkyls, such as hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, or isomers thereof).

[0123] Sulfonate-based detergents useful herein in combination with the enhanced aminic antioxidant(s) are described further herein, and in any embodiment include overbased calcium and/or magnesium sulfonate salts. Useful sulfonate based detergents include those having TBN's of greater than 100 such as 200 to 600, such as 300 to 500 mgKOH/g (as determined by ASTM D2896).

[0124] Magnesium based detergents, useful for providing high Mg content (such as 400 to 10,000 ppm) to the lubricating oil(s) comprising enhanced aminic antioxidant(s) include magnesium sulfonates, phenates, carboxylates (such as salicylates) as described below. Preferred magnesium based detergents useful herein in combination with the enhanced aminic antioxidant(s) include those having TBN's of greater than 100, such as 200 to 600, such as 300 to 500 mgKOH/g (as determined by ASTM D2896).

[0125] Calcium based detergents, useful for providing high Ca content (such as 400 to 20,000 ppm) to the lubricating oil(s) comprising enhanced aminic antioxidant(s) include calcium carboxylates (such as salicylates) and calcium sulfonates as described below. Preferred calcium based detergents include those having TBN's of greater than 50, such as 50 to 650, such as 100 to 600, such as 200 to 500 mgKOH/g (as determined by ASTM D2896).

[0126] Zinc-based antiwear agents useful in combination with enhanced aminic antioxidant(s) are described further herein, and in any embodiment include compounds such as zinc dialkyldithiophosphate, where the alkyl groups are derived from one or more primary alcohols, one or more secondary alcohols or combinations of primary and secondary alcohols. Typically, the alcohols are mono-alcohols represented by the formula R-alkyl, where the alkyls are selected from C_4 to C_{30} alkyl groups, and may be combinations of alkyl groups selected from butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, and icosyl or isomers thereof). In embodiments useful primary alcohols for use in preparing zinc-based antiwear agents, such as zinc dialkyldithiophosphaetes, include C_4 to C_{30} primary alcohols, such as linear or branched alcohols having a CH_2OH group, such butanol, pentanol, hexanol, heptanol, octanol, nonanol, decanol, undecanol, dodecanol, tridecanol, tetradecanol, pentadecanol, hexadecanol, heptadecanol, octadecanol, nonadecanol, and icosanol or isomers and mixtures thereof.

[0127] Low Mn dispersants (such as less than 1600 g/mol) useful herein in combination with the enhanced aminic antioxidant(s) are described below. Preferred Low Mn dispersants include dispersants PIBSA-PAMs derived from polyisobutylene (PIB) having an Mn of from 400 to less than 1600g/mol. PIBSA-PAM's are PIB's that are treated with an acid or anhydride (such as succinic acid or succinic anhydride) to form a PIB-succinate, then combined with a polyamine to form a PIBSA-PAM as further described below.

[0128] In embodiments, the lubricating oil composition may further comprising zinc dialkyldithiophosphate.

[0129] In embodiments, the lubricating oil composition may further comprise hindered phenolic antioxidant.

[0130] In embodiments, the lubricating oil composition may further comprises a molybdenum containing compound such as a dimeric and or trimeric molybdenum containing compound providing 50 to 1000 ppm Mo to the lubricating oil composition.

[0131] In embodiments, the lubricating oil composition may further comprises additional antioxidant comprising oil-soluble or oil-dispersible sulfur-containing antioxidant(s), sulfurized aliphatic (C_7 to C_{29}) hydrocarbyl fatty acid ester(s), sulfur-containing organomolybdenum compound(s), and combinations thereof.

[0132] In embodiments, the lubricating oil composition may further comprise ethoxylated alcohol.

[0133] In embodiments, the lubricating oil composition the detergent in the lubricating oil composition comprises carboxylate detergent, such as salicylate detergent, such as alkaline earth metal salicylate detergent, such as calcium or magnesium salicylate detergent, optionally having a TBN of 100 or less and or optionally providing from 1 to 30 mmol soap, such as 5 to 25 mmol/kg soap to the lubricating oil composition.

[0134] This invention further relates to a lubricating oil composition where the lubricating oil composition exhibits: an oxidation (FTIR, CEC-L-109-14 Oxidation Test) of the lubricating oil composition that is less than or within 20%, such as within 10 %, of the oxidation of **Comparative Formulation A [Comparative Formulation A** is defined to be the same lubricating oil composition except that the diphenyl amine antioxidant has been replaced with the same amount of diphenyl amine antioxidant having:

1) about 68 mass% di-C_9-alkyl diphenyl amine,
2) about 29 mass% of mono-C_9-alkyl diphenyl amine, and
3) about 3 mass% of tri-C_9-alkyl diphenyl amine, based on the weight of 1), 2) and 3), as determined by UPLC in the Experimental section],

[0135] This invention further relates to a lubricating oil composition where the lubricating oil composition exhibits a percent viscosity increase between the initial KV100 and the KV100 at 216 hours of the CEC-L-109-14 Oxidation Test that is at least 2% less (such as at least 5% less, such as at least 7% less, such as at least 8% less, such as at least 20% less, such as at least 30% less) than the percent viscosity increase of **Comparative Formulation A.**

[0136] Note that the improvements in viscosity control, such as shown in the CEC-L-109-14 Oxidation Test, allows the addition of components that can negatively impact viscosity control but also can improve other desirable properties, such as fuel economy performance. For example, the addition of friction modifiers (such as glycerol mono-oleate and/or molybdenum compounds, such as Mo DTC dimers and or trimers), and / or one or more ZDDP's (such as ZDDP's derived from desirable alcohols or combination of alcohols, such as primary and or secondary alcohols, such as iso-octanol and/or 4-methyl-pentan-2-ol and/or 2-butanol) to the compositions herein can improve fuel economy in to improve fuel economy, while maintaining good viscosity control.

[0137] This invention further relates to a lubricating oil composition where the lubricating oil composition exhibits having higher Sequence IIIH (ASTM D8111) weighted piston deposits merits (such as 0.5 WPD higher, such as 0.8 WPD or higher, such as 0.85 WPD or higher) as compared to **Comparative Formulation A,** while also preferably maintaining good viscosity control (e.g., showing a percent viscosity increase between the KV40 at the end of the Sequence IIIH test relative to the KV40 at the start of the Sequence IIIH test that is at least 2% less (such as at least 3% less, such as at least 4% less, such as at least 4.5% less, such as at least 4.8% less) as compared to **Comparative Formulation A.**

[0138] Generally, the total base number of the lubricating composition may range from 1 to 30, such as 4 to 15 mgKOH/g, such as 5 to 15 mgKOH/g, such as 5 to 12 mgKOH/g, such as 7 to 12 mgKOH/g, such as 8 to 11 mgKOH/g, as measured by ASTM D2896.

[0139] The lubricating compositions of the present disclosure may contain low levels of phosphorus, namely not greater than 1600, preferably not greater than 1200, more preferably not greater than 800, such as 1 to 1600, such as 50 to 1200, such as 100 to 800 parts per million (ppm) by mass of phosphorus, expressed as atoms of phosphorus, based on the total mass of the lubricating compositions, as measured by ASTM D5185.

[0140] Suitably, the lubricant composition may have a phosphorus level of 1200 ppm or less, alternately 1000 ppm or less, alternately 800ppm or less, as measured by ASTM D5185.

[0141] The lubricating compositions of the present disclosure may contain a ratio of atoms of Magnesium to atoms of Calcium based on the total mass of the lubricating compositions, as measured by ASTM D5185, of at least to 0.5, preferably at least 0.6, more preferably at least 0.65.

[0142] Typically, the lubricating compositions may contain low levels of sulfur. Preferably, the lubricating composition contains up to 0.4, more preferably up to 0.3, most preferably up to 0.2, such as 0.1 to 0.4 mass% sulfur, based on the total mass of the lubricating oil composition, as measured by ASTM D5185.

[0143] Typically, the lubricating compositions may contain low levels of sulfated ash, such as 1.2 % or less, such as 1.0 mass% or less, preferably 0.9 mass or less %, preferably 0.8 mass% or less, alternately 0.0001 to 0.5 mass% or less sulfated ash, based on the total mass of the lubricating composition, as measured by ASTM D874-13a (2018).

[0144] Generally, the kinematic viscosity at 100° C ("KV100") of the lubricating composition may range from 2 to 30 cSt, such as 2 to 20 cSt, such as 5 to 15 cSt as determined according to ASTM D 445-19a).

[0145] In embodiments, the kinematic viscosity at 100° C ("KV100") of the lubricating composition may range from 1 to 30 cSt, alternately 3 to 20, alternately 3 to 17 cSt, alternately 3.5 to 16.3 cSt alternately 9.3 to less than 12.5 cSt, alternately 12.5 to less than 16.3 cSt, as determined according to ASTM D 445-19a).

[0146] Preferably, the lubricating composition of the present disclosure may be a multigrade oil identified by the viscometric descriptor SAE 40W-X, SAE 30W-X, SAE 25W-X, SAE 20W-X, SAE 15W-X, SAE 10W-X, SAE 5W-X or SAE 0W-X, where X represents any one of 8, 12, 16, 20, 30, 40, and 50; the characteristics of the different viscometric grades can be found in the SAE J300 classification. Alternately, the lubricating composition may be the form of viscosity grade SAE 15W-X, SAE 10W-X, SAE 5W-X or SAE 0W-X, such as in the form of SAE 15W-X or SAE 10W-X, wherein X represents any one of 8, 12, 16, 20, 30, 40, and 50. Alternately, the lubricating composition of the present disclosure may be a multigrade oil identified by the viscometric descriptor SAE 10W-30, 15W-40, 5W-30, 5W-40, 10W-40, 5W-50. (See standard SAE J300 published January 2015 by SAE International, formerly known as Society of Automotive Engineers).

[0147] Optionally, the lubricating oil composition containing diphenyl amine antioxidants described herein may be absent phenolic antioxidant.

[0148] In embodiments, the lubricating oil composition may comprise 1 to 500 ppm of boron, such as 25 to 400 ppm of boron, such as 50 to 300 ppm boron, such as 50 to 200 ppm boron.

[0149] In embodiments, the lubricating oil composition may comprise less than 75 ppm boron, alternately less than 60 ppm boron, alternately from 1 to 70 ppm boron. Alternately, the lubricating oil composition may be absent boron.

[0150] In embodiments, the lubricating oil composition may comprise acylated polymers, such as polyisobutylene succinic acid (PIBSA), optionally having an Mn of 500 to 50,000 g/mol, such as 600 to 5,000 g/mol, such as 700 to 3000 g/mol, such as 700 to 2000 g/mol, such as 700 to 1500 g/mol such as 800 to 1400 g/mol, such as 800 to less than 1000 g/mol. In embodiments, the lubricating oil composition may comprise acylated polymers, such as polyisobutylene succinic acid, having an Mn of 500 to 1600 g/mol, such as 700 to 1200 g/mol. In embodiments, the lubricating oil composition comprises more than 0.1 mass% (such as 0.1 to 10 mass%, such as 0.5 to 8 mass%), functionalized (such as aminated) polybutene (such as polyisobutylene), such as PIBSA-PAM.

[0151] In embodiments, the lubricating oil composition may comprise 20 mass% or less (such as 15 mass% or less, such as 10 mass% or less, such as 5 mass% or less, such as 3 mass% or less, such as 1 mass% or less) of block copolymer, such as block, radial (aka "star"), random, and/or tapered block copolymer. In embodiments, the lubricating oil composition may be substantially free of or may be absent block copolymer, such as block, radial, random, and/or tapered block copolymer.

[0152] In embodiments, the lubricating oil composition may comprise 20 mass% or less (such as 15 mass% or less, such as 10 mass% or less, such as 5 mass% or less, such as 3 mass% or less, such as 1 mass% or less) styrenic copolymer, such as block, radial, random, and/or tapered styrenic block copolymer. In embodiments, the lubricating oil composition may be substantially free or absent styrenic copolymer, such as block, star, random, and/or tapered styrenic block copolymer.

[0153] In another advantageous form, the lubricating oil composition of the instant disclosure further optionally includes one or more functionalized polymers at from 0.2 to 2.0 mass%, or 0.4 to 1.8 mass%, or 0.6 to 1.6 mass%, or 0.8 to 1.4 mass%, or 1.0 to 1.2 mass% of the composition comprising an amide, imide, and/or ester functionalized partially or fully saturated polymer comprising C_{4-5} olefins having:

i) an Mw/Mn of less than 2, or less than 1.8, or less than 1.6,
ii) a Functionality Distribution (Fd) value of 3.5 or less, or 3.2 or less, or 3.0 or less, or 2.5 or less, and
iii) an Mn of 10,000 g/mol or more, or 15,000 g/mol or more, or 20,000 g/mol or more, or 25,000 g/mol or more (GPC-PS) of the polymer prior to functionalization,

provided that, if the polymer prior to functionalization is a copolymer of isoprene and butadiene, then the Mn of the copolymer is greater than 25,000 g/mol, or 30,000 g/mol or more, or 35,000 g/mol or more, or 40,000 g/mol or more (GPC-PS). (GPC-PS is determined as set out in United States Patent Application USSN 18/480,571, filed October 4, 2023.)

[0154] The functionalized polymer of the lubricating oil composition of the instant disclosure may include at least 50 %, or at least 60%, or at least 70% of 1,4-insertions of monomer. Furthermore, the functionalized polymer of the lubricating oil composition of the instant disclosure may include a partially or fully saturated homopolyisoprene containing one or more pendant amine groups and having an Mn of 25,000 to 100,000 g/mol, or 35,000 to 90,000 g/mol, or 45,000 to 80,000 g/mol, or 55,000 to 75,000 g/mol (GPC-PS) and at least 50%, or at least 60%, or at least 70% of 1,4-insertions prior to functionalization.

[0155] The functionalized polymer of the lubricating oil composition of the instant disclosure may be absent of styrene repeat units, or absent of butadiene repeat units, or is not a homo-polyisobutylene, or is not a copolymer of isoprene and butadiene.

[0156] In embodiments, the lubricating oil composition may have a total saponification number (SAP) of 25 (such as 28, such as 30, such as 32) mgKOH/g or more, as determined by ASTM 94.

[0157] In embodiments, the lubricating compositions of the present disclosure may be a heavy-duty diesel oil (*e.g.,* for use in an engine for a heavy-duty diesel vehicle, *i.e.,* a heavy-duty diesel vehicle having a gross vehicle weight rating of 10,000 pounds or more.)

[0158] In embodiments, the lubricating compositions of the present disclosure may be a passenger car motor oil.

[0159] In embodiments, the lubricating compositions of the present disclosure may be a passenger car diesel oil.

[0160] In embodiments, the lubricating composition of the present disclosure may be a lubricating composition comprising: an oil of lubricating viscosity having greater than 50 mass% of Group I, II, III, IV, and/or V oil (such as a Group III base oil, a Group IV base oil, a Group V base oil, or mixtures thereof); a first PIB succinimide dispersant derived from an 1800 to 2500 Mn PIB; a second PIB succinimide dispersant derived from a PIB with an Mn less than 1600, where at least one of the first PIB succinimide dispersant(s) and the second PIB succinimide dispersant is boron-free (optionally, at least one of the first PIB succinimide dispersant(s) and the second PIB succinimide dispersant is borated); optionally an amide, imide, and/or ester functionalized partially or fully saturated polymer comprising C_{4-5} olefins as described in United States serial number USSN 18/480,571, filed October 4, 2023 (sometimes referred to as a dispersant viscosity modifier); an alkaline earth metal salicylate detergent; an alkaline earth metal sulfonate detergent present in an amount to deliver 0.1 mass% to 1.2 mass% of alkaline earth metal soap to the lubricating composition; and a phosphorus anti wear agent present in an amount to deliver 300 to 900 ppm phosphorous to the lubricating composition, the lubricating composition having a total sulfated ash of between 0.3 to 1.1 mass%.

[0161] In embodiments, the lubricating oil compositions of the present disclosure comprise: an oil of lubricating viscosity having greater than 50 mass% of Group I, II, III, IV, and/or V oil (such as refined and or renewable Group II base oil, refined and or renewable Group III base oil, Group IV base oil, Group V base oil, or mixtures thereof) and a lower Mn dispersant (such as PIB succinimide dispersant derived from a PIB having an Mn of less than 1600 g/mol, such as 600 to less than 1600 g/mol, such as 650 to 1500 g/mol, such as 700 to 1400 g/mol, such as 800 to 1300 g/mol, such as 850 to 1200 g/mol, such as 900 to 1150 g/mol, such as 900 to 1000 g/mol). The lower molecular weight dispersant (such as lower molecular weight PIBSA-PAM dispersant) may be present in the lubricating composition in an amount of from 0.5 to 10 mass%, or from 0.8 to 6 mass%, or from 1.0 to 5 mass%, or from 1.5 to 5 mass% or from 1.5 to 4.0 mass% or from 1.5 to 4.8 mass%, or at 2 mass% or more, such as 2 to 5 mass%, based upon the weight of the lubricating oil composition.

[0162] The lubricating compositions disclosed herein may have a kinematic viscosity as measured by ASTM D-445 at 100° C of 3 cSt (mm^2/s), or more, such as from 3 to 26.1 cSt, such as from 4.0 to less than 6.1 cSt, such as from 5.0 to less than 7.1 cSt, such as from 6.9 to less than 9.3 cSt, such as 9.3 to less than 12.5 cSt, such as 12.5 to less than 16.3 cSt, such as 16.3 to less than 21.9 cSt, such as 21.9 to 26.1 cSt.

[0163] The lubricating composition disclosed herein, may have a high temperature high shear viscosity (HTHS) as measured by ASTM D4683 at 150° C of 4.0 mPa•s or more, or 3.7 mPa•s or more, or 3.5 mPa•s, or more, or 2.9 mPa•s or more, or 2.6 mPa•s or more, or 2.3 mPa•s or more, or 2.0 mPa•s or more, or 1.7 mPa•s or more.

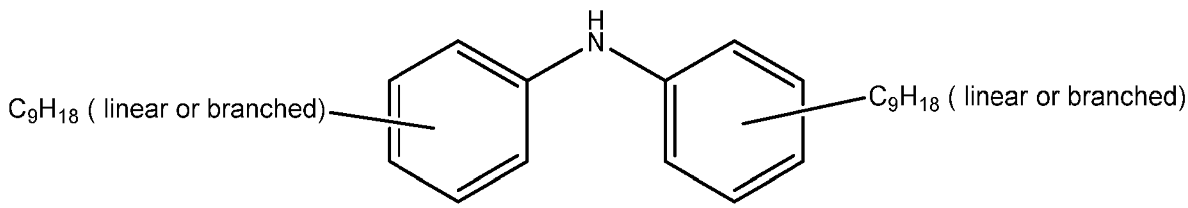
[0164] The lubricating composition disclosed herein may have a SAE viscosity grade of 0W-Y, wherein Y may be 12, 16, or 20. In one embodiment, the lubricating composition has an SAE viscosity grade of 0W-12.

Concentrates

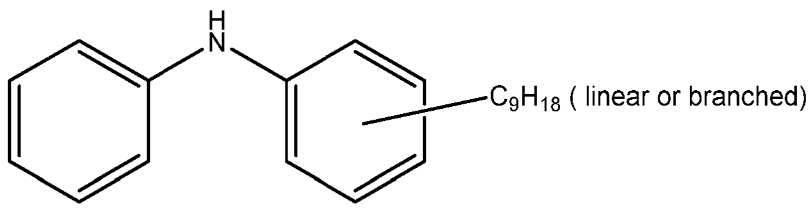
[0165] A concentrate, also referred to as an additive package, adpak, or addpack, is a composition having less than 50 mass% (such as less than 40 mass%, such as less than 30 mass%, such as less than 25 mass%, such as less than 20 mass%) base oil and lubricant composition additives (such as described herein) which is typically then further blended with additional base oil to form a lubricating oil product.

[0166] This disclosure relates to concentrate compositions comprising or resulting from the admixing of:

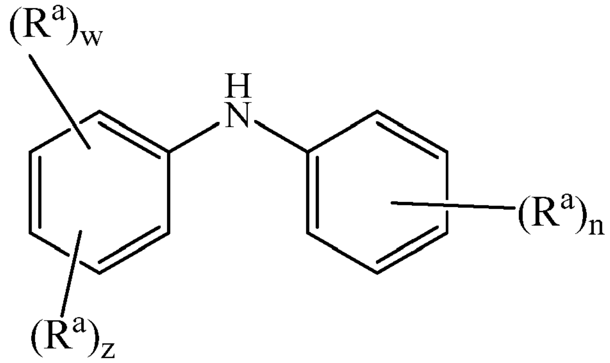
(i) from 1 to less than 50 mass% (alternately 5 to 45 mass%, alternately 7 to 40 mass%, alternately 10 to 35 mass%, alternately 10 to 25 mass%), based upon the weight of the composition, of one or more **base oil(s)**;
(ii) from 0.10 to 20 mass% (in particular 0.15 to 10 mass%, alternately 0.20 mass% to 5 mass%, alternately 0.25 to 2 mass%), based upon the weight of the composition, of one or more **detergent(s),** such as carboxylate detergents, such as calcium salicylate;
(iii) from 0.10 to 20 mass% (in particular 0.15 to 10 mass%, alternately 0.20 mass% to 5 mass%, alternately 0.25 to 2 mass%), based upon the weight of the composition, of one or more **dispersant(s)** (such as PIBSA-PAM); and
(iv) from 0.010 to 20 mass% (in particular 0.10 to 15 mass%, alternately 0.15 to 10 mass%, alternately 0.20 mass% to 5 mass%, alternately 0.25 to 2 mass%), based upon the weight of the concentrate, of diphenyl amine antioxidant comprising: 1) one or more **di-C_9-alkyl substituted diphenyl amine** represented by Formula (A) (such as Formula (III), where n is 1, z is 1 and w is 0), and 2) from 0 to 1.5 mass% (such as 0 to 1 mass%, such as 0.001 to 0.5 mass%, such as 0.005 to less than 0.3 mass%, such as 0.001 to 0.1 mass%) of **mono-C_9-alkyl substituted diphenyl amine** represented by Formula (B) (such as Formula (III), where n is 1, z is 0 and w is 0), based upon the weight of the concentrate:



Formula (A), and



Formula (B), and



Formula (III) is:

where: the branched C_9H_{18} may be singly, doubly or triply branched at one, two, three, four or more carbons, and may be symmetrically branched or asymmetrically branched; each R^a is independently a linear C_9 alkyl or branched C_9 alkyl group, n is 1, z is 0 or 1, and w is 0 or 1;

(v) optional additional components, antioxidants (other than (iv) above), pour point depressants, anti-foam agents, viscosity modifiers, corrosion inhibitors, antiwear agents, extreme pressure additives, demulsifiers, seal compatibility agents, additive diluent base oils, friction modifier(s) (such as, organic FM, such as organic ester, such as fatty acid ester), etc.

[0167] In embodiments, the concentrate composition may optionally be absent solvent (such as aliphatic or aromatic solvent) and/or absent functionalized base oil.

[0168] This disclosure also relates to concentrate compositions comprising or resulting from the admixing of:

A) from 1 to less than 50 mass% (alternately 5 to 45 mass%, alternately 7 to 40 mass%, alternately 10 to 35 mass%, alternately 10 to 25 mass%), based upon the weight of the concentrate composition, of one or more **base oil(s)**;

B) from 0.10 to 35 mass% (in particular, 0.15 to 20 mass%, alternately 0.20 mass% to 5 mass%, alternately 0.25 to 3 mass%), based upon the weight of the concentrate composition, of one or more **di-C_9-alkyl substituted diphenyl amine** represented by Formula (A), such as Formula (III), where n is 1, w is 0, and z is 1, and optionally hindered phenol antioxidants, where **mono-C_9-alkyl substituted diphenyl amine** represented by Formula (B), such as those represented by Formula (III) where z is 0, w is 0 and n is 1, are absent or present at less than 0.30 mass% (such as less than 0.1 mass%), based upon the weight of the concentrate;

C) from 0.1 to 20 mass% (in particular 0.5 to 10 mass%, alternately 2 to 6 mass%), based on total weight of the concentrate composition, of one or more **detergent(s)** (such as blends of detergents);

D) optionally, from 0.01 to 5 mass% (in particular, 0.1 to 4 mass%, alternately 0.25 to 3 mass%, alternately 0.25 to .075 mass%), based on total weight of the concentrate composition, of one or more **friction modifier(s)** (such as organic friction modifiers, such as glycerol monoeoleate);

E) optionally, from 0.01 to 20 mass% (in particular, 0.01 to 15 mass%, alternately 0.1 to 10 mass%), based on total weight of the concentrate composition, of one or more **antioxidant(s)** (such as blends of antioxidants), other than B) above;

F) optionally, from 0.01 to 5 mass% (in particular, 0.01 to 3 mass%, alternately 0.1 to 1.5 mass%), based on total weight of the concentrate composition, of one or more **pour point depressants** (such as blends of pour point depressants);

G) optionally, from 0.001 to 3 mass% (in particular, 0.01 to 2 mass%, alternately 0.02 to 1 mass%), based on total weight of the concentrate composition, of one or more **anti-foam agents** (such as blends of anti-foam agents);

I) optionally, from 0.01 to 40 mass% (in particular, 0.1 to 30 mass%, alternately 1 to 20 mass%), based on total weight of the concentrate composition, of one or more **dispersants** (such as blends of dispersants);

K) optionally, from 0.001 to 10 mass% (in particular, 0.1 to 8 mass%, alternately 1 to 5 mass% alternately 0.25 to .075 mass%), based on total weight of the lubricating composition, of one or more **antiwear agents** (such as blends of antiwear agents, such as ZDDP).

[0169] Concentrates may be present in the lubricating oil composition at from of 0.5 mass% to 35 mass%, such as 5 mass% to 30 mass%, such as 7.5 mass% to 25 mass%, such as 10 to 22.5 mass%, such as 15 to 20 mass%, based upon the mass of the lubricating oil composition.

[0170] Optionally, the concentrate may be absent functionalized oil.

[0171] In embodiments, the concentrate composition may optionally be absent solvent (such as aliphatic or aromatic solvent) and/or absent functionalized base oil.

[0172] Optionally, the concentrate may be absent phenolic antioxidant.

[0173] In embodiments, the concentrate may comprise less than 20 mass%(such as less than 15 mass%, such as less than 10 mass%, such as less than 5 mass%, such as less than 3 mass%, such as less than 1 mass%), functionalized (such as aminated) polybutene (such as polyisobutylene), such as PIBSA-PAM. In embodiments, the concentrate comprises is substantially free or absent, functionalized (such as aminated) polybutene (such as polyisobutylene), such as PIBSA-PAM.

[0174] In embodiments, the concentrate may comprise acylated polymers, such as polyisobutylene succinic acid, optionally, having an Mn of 500 to 50,000 g/mol, such as 600 to 5,000 g/mol, such as 700 to 3000 g/mol. In embodiments, the concentrate may comprise acylated polymers, such as polyisobutylene succinic acid, having an Mn of 500 1600 g/mol, such as 700 to 1200 g/mol.

[0175] In embodiments, the concentrate may comprise 20 mass% or less (such as 15 mass%, such as 10 mass%, such as 5 mass%, such as 3 mass%, such as 1 mass% or less) block copolymer, such as block, star, random, and/or tapered block copolymer.

[0176] In embodiments, the concentrate may be substantially free of or absent block copolymer, such as block, star, random, and/or tapered block copolymer.

[0177] In embodiments, the concentrate may comprise 20 mass% or less (such as 15 mass% or less, such as 10 mass% or less, such as 5 mass% or less, such as 3 mass% or less, such as 1 mass% or less) styrenic copolymer, such as block, star, random, and/or tapered styrenic block copolymer).

[0178] In embodiments, the concentrate may be substantially free of or absent styrenic copolymer, such as block, star, random, and/or tapered sytrenic block copolymer).

[0179] In embodiments, the concentrate may comprise less than 20 mass% (such as less than 15 mass%, such as 10 mass%, such as less than 5 mass%, such as less than 3 mass%, such as less than 1 mass%) of functionalized diluent, such as functionalized oil.

[0180] In embodiments, the concentrate may substantially free of or absent functionalized diluent, such as functionalized oil.

[0181] In embodiments, the concentrate may comprise less than 0.5 mass% (such as less than 0.4 mass%, such as less than 0.3 mass%, such as less than 0.2 mass%, such as less than 0.1 mass%, such as 0 mass%, based upon the weight of the concentrate, of secondary hydrocarbyl amine compounds and tertiary hydrocarbyl amine compounds.

[0182] In embodiments, the concentrate may have a kinematic viscosity at 100° C of less than 1000 cSt, such as less than 500 cSt, such as less than 200 cSt.

[0183] Concentrates are typically combined with base oils to form lubricating oil compositions, where the concentrate typically is present at rates of 1 to 50 mass% (such as 2.5 to 40 mass%, such as 5 to 30 mass%, such as 8 to 25 mass%, such as 10 to 20 mass%), based upon the weight of the lubricating oil composition.

[0184] The invention also includes concentrates comprising: 1) enhanced aminic antioxidant (such as antioxidant comprising 90 mass% or more of bis(nonylphenyl)amine and 10 mass% or less of (nonylphenyl)(phenyl)amine based on the weight of the bis(nonylphenyl)amine and (nonylphenyl)(phenyl)amine), and 2) base oil selected from one or more refined and or renewable Group I base oils, refined and or renewable Group II base oils, refined and or renewable Group III base oils or combinations thereof (such as combinations of Group III base oil(s) and renewable base oil(s); and or combinations of Group III base oil(s) and Group II base oils, and or combinations of Group I base oil(s) and Group II base oils). A useful petroleum derived base oil/renewable base oil combination herein is available commercially as Nexbase4PLUS™ (which can be described as being a combination of a renewable Group III oil combined with a refined Group III oil).

[0185] This invention also relates to booster packages comprising the enhanced aminic antioxidants described herein and or other additives useful in combination with a concentrate or lubricating oil composition containing the enhanced aminic antioxidants described herein. Booster packages are typically compositions containing a few (such as 1, 2, 3, or 4) components (such as detergents, dispersants, ZDDP's molybdenum components, such as MoDTC, dimers and or trimers, etc. antioxidants, such as he enhanced diphenylamine antioxidants described herein) that are added to a concentrate by a manufacturer or distributor immediately before providing the concentrate to a customer who will then use the concentrate to form a lubricating composition. Booster packages can also be proved separately for a customer to add to a concentrate or lubricating oil composition. The invention also includes booster packages comprising: 1) enhanced aminic antioxidant (such as antioxidant comprising 90 mass% or more of bis(nonylphenyl)amine and 10 mass% or less of (nonylphenyl)(phenyl)amine based on the weight of the bis(nonylphenyl)amine and (nonylphenyl)(phenyl)amine), and one or more of the components listed in Q above, such as one, two, three, four, five, six or more of:

1) glycerol-based friction modifiers, such as glycerol mono-oleate;
2) sulfonate-based detergents, such as magnesium and or calcium sulfonate detergents;
3) organomolybdenum-based friction modifiers, such as molybdenum dithiocarbamate dimers and or trimers;
4) magnesium-based detergents providing 400 ppm or more of Mg to the composition, such as magnesium salicylate and or sulfonate detergents;

5) carboxylate based detergents, such as such as magnesium and or calcium salicylate detergents; and
6) zinc-based antiwear agents, such as zinc dialkyldithiophosphaetes where the alkyl group is derived from primary alcohols; and
7) dispersants (such as PIBSA-PAM) derived from a polymer (such as polyisobutylene) having an Mn of 1600 g/mol or less.

A. Base Oil

[0186] The base oil (also referred to as "base stock", "lubricating oil basestock", or "oil of lubricating viscosity") useful herein may be a single oil or a blend of oils, and is typically a large liquid constituent of a lubricating composition, also referred to as a lubricant, into which additives and optional additional oils are blended, for example, to produce a lubricating composition, such as a final lubricant composition, a concentrate, or other lubricating composition.

[0187] A base oil may be selected from vegetable, animal, mineral, and synthetic lubricating oils, and mixtures thereof. It may range in viscosity from light distillate mineral oils to heavy lubricating oils, such as those for gas engine oil, mineral lubricating oil, motor vehicle oil, and heavy-duty diesel oil. Generally, the kinematic viscosity at 100° C ("KV100") of the base oil ranges from 1 to 30, such as 2 to 25 cSt, such as 5 to 20 cSt, as determined according to ASTM D445-19a, in particular, from 1.0 cSt to 10 cSt, from 1.5 cSt to 3.3 cSt, from 2.7 cSt to 8.1 cSt, from 3.0 cSt to 7.2 cSt, or from 2.5 cSt to 6.5 cSt. Generally, the high temperature high shear (HTHS) viscosity at 150° C of the base oil ranges from 0.5 to 20 cP such as 1 to 10 cP, such as 2 to 5 cP as determined according to ASTM D4683-20.

[0188] Typically, when lubricating oil basestock(s) is used to make a concentrate, it may advantageously be present in a concentrate-forming amount to give a concentrate containing, from 5 mass% to 80 mass%, from 10 mass% to 70 mass%, or from 5 mass% to 50 mass% of active ingredient, based upon the weight of the concentrate.

[0189] Common oils useful as base oils include animal and vegetable oils (e.g., castor and lard oil), liquid petroleum oils, and hydrorefined and/or solvent-treated mineral lubricating oils of the paraffinic, naphthenic, and mixed paraffinic-naphthenic types. Oils derived from coal or shale are also useful base oils. Base stocks may be manufactured using a variety of different processes including, but not limited to, distillation, solvent refining, hydrogen processing, oligomerization, esterification, and re-refining.

[0190] Synthetic lubricating oils useful herein as base oils include hydrocarbon oils such as homopolymerized and copolymerized olefins, referred to as polyalphaolefins or PAO's or group IV base oils [according to the API EOLCS 1509 definition (American Petroleum Institute Publication 1509, see section E.1.3, 22th edition, October 2023, www.API.org)]. Examples of PAO's useful as base oils include: poly(ethylenes), copolymers of ethylene and propylene, polybutylenes, polypropylenes, propylene-isobutylene copolymers, chlorinated polybutylenes, poly(1-hexenes), poly(1-octenes), poly(1-decenes), homo- or co-polymers of C_8 to C_{20} alkenes, homo- or co-polymers of Ca, and/or C_{10}, and/or C_{12} alkenes, C_8/C_{10} copolymers, $C_8/C_{10}/C_{12}$ copolymers, and C_{10}/C_{12} copolymers, and the derivatives, analogues and homologues thereof.

[0191] In another embodiment, the base oil may comprise polyalphaolefins comprising oligomers of linear olefins having 6 to 14 carbon atoms, more preferably 8 to 12 carbon atoms, more preferably 10 carbon atoms having a Kinematic viscosity at 100° C of 10 cSt or more (as measured by ASTM D445); and preferably having a viscosity index ("VI"), as determined by ASTM D2270, of 100 or more, preferably 110 or more, more preferably 120 or more, more preferably 130 or more, more preferably 140 or more; and/or having a pour point of -5° C or less (as determined by ASTM D97), more preferably -10° C or less, more preferably -20° C or less.

[0192] In another embodiment polyalphaolefin oligomers useful in the present disclosure may comprise C_{20} to C_{1500} paraffins, preferably C_{40} to C_{1000} paraffins, preferably C_{50} to C_{750} paraffins, preferably C_{50} to C_{500} paraffins. The PAO oligomers are dimers, trimers, tetramers, pentamers, *etc.,* of C_5 to C_{14} alpha-olefins in one embodiment, and C_6 to C_{12} alpha-olefins in another embodiment, and Ca to C_{12} alpha-olefins in another embodiment. Suitable olefins include 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, and 1-dodecene. In one embodiment, the olefin is a combination of 1-octene, 1-decene, and 1-dodecene, or alternately may be substantially 1-decene, and the PAO is a mixture of dimers, trimers, tetramers, and pentamers (and higher) thereof. Useful PAO's are described more particularly in, for example, US Patent Nos. 5,171,908 and 5,783,531, and in Synthetic Lubricants and High-Performance Functional Fluids 1-52 (Leslie R. Rudnick & Ronald L. Shubkin, ed. Marcel Dekker, Inc. 1999).

[0193] PAO's useful in the present disclosure typically possess a number average molecular weight of from 100 to 21,000 g/mol in one embodiment, and from 200 to 10,000 g/mol in another embodiment, and from 200 to 7,000 g/mol in yet another embodiment, and from 200 to 2,000 g/mol in yet another embodiment, and from 200 to 500 g/mol in yet another embodiment. Desirable PAO's are commercially available as SpectraSyn™ Hi-Vis, SpectraSyn™ Low-Vis, SpectraSyn™ plus, SpectraSyn™ Elite PAO's (ExxonMobil Chemical Company, Houston Texas) and Durasyn PAO's from Ineos Oligomers USA LLC.

[0194] Synthetic lubricating oils useful as base oils also include hydrocarbon oils such as homopolymerized and copolymerized: alkylbenzenes (*e.g.,* dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di(2-ethylhexyl)benzenes); polyphenols (*e.g.,* biphenyls, terphenyls, alkylated polyphenols); and alkylated diphenyl ethers, and alkylated diphenyl sulfides; and the derivatives, analogues, and homologues thereof.

[0195] Another suitable class of synthetic lubricating oils useful as base oils comprises the esters of dicarboxylic acids (*e.g.,* phthalic acid, succinic acid, alkyl succinic acids and alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebasic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkylmalonic acids, alkenyl malonic acids) reacted with a variety of alcohols (*e.g.,* butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol). Specific examples of 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.

[0196] Esters useful as synthetic oils herein also include those made from C_5 to C_{12} monocarboxylic acids and polyols, and polyol ethers such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol, and tripentaerythritol.

[0197] Desirable ester base oils are commercially available as Esterex™ Esters (ExxonMobil Chemical Company, Houston, Texas).

[0198] Silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy- or polyaryloxysilicone oils and silicate oils comprise another useful class of synthetic lubricants useful herein; such oils include tetraethyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl) silicate, tetra-(4-methyl-2-ethylhexyl)silicate, tetra-(p-tert-butyl-phenyl) silicate, hexa-(4-methyl-2-ethylhexyl)disiloxane, poly(methyl)siloxanes, and poly(methylphenyl)-siloxanes.

[0199] Other synthetic lubricating oils useful herein include liquid esters of phosphorous-containing acids (*e.g.,* tricresyl phosphate, trioctyl phosphate, diethyl ester of decylphosphonic acid) and polymeric tetrahydrofurans.

[0200] Unrefined, refined, and re-refined oils can be used in the lubricating compositions of the present disclosure. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. For example, a shale oil obtained directly from retorting operations, a petroleum oil obtained directly from distillation, or an ester oil obtained directly from an esterification process and used without further treatment is considered an unrefined oil. 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. Many such purification techniques, such as distillation, solvent extraction, acid or base extraction, filtration, and percolation are used by those in the art. Re-refined oils are oils obtained by processes similar to those used to obtain refined oils where the refining processes are applied to previously refined oils which have been previously used in service. Such re-refined oils are also referred to as reclaimed or reprocessed oils and often are additionally processed for removal of spent additive and oil breakdown products. A re-refined base oil is preferably substantially free from materials introduced through manufacturing, contamination, or previous use.

[0201] Other examples of useful base oils are gas-to-liquid ("GTL") base oils, *i.e.,* the base oil is an oil derived from hydrocarbons made from synthesis gas ("syn gas") containing H2 and CO using a Fischer-Tropsch catalyst. These hydrocarbons typically require further processing in order to be useful as a base oil. For example, they may, by methods known in the art, be hydroisomerized; hydrocracked and hydroisomerized; dewaxed; or hydroisomerized and dewaxed. For further information on useful GTL base oils and blends thereof, please see US Patent No. 10,913,916 (col 4, ln 62 to col 5, ln 60) and US Patent No. 10,781,397 (col 14, ln 54 to col 15, ln 5, and col 16, ln 44 to col 17, ln 55).

[0202] In particular, oils from renewable sources, *i.e.,* based in part on carbon and energy captured from the environment, such as biological sources (biomass), are useful herein. The renewable source may be (or is derived from) vegetable oil (such as palm oil, coconut oil, rapeseed oil, soybean oil, jatropha oil, corn oil), microbial oil (such as algae oil), animal fats (such as cooking oil, animal fat, and/or fish fat). Renewable oils may be combined with **refined oils** (e.g., oils derived from petroleum, coal or other non-renewable, i.e., not replaceable within 100 years, resources) for use herein. A useful base oil combination may comprise a refined Group III oil blended with one or more oils derived from renewable materials, such as a mixture of SynNova™ 4 and Nexbase™3043. A useful base oil containing renewable material is Nexbase™ 4Plus (KV100 ~ 4 cSt).

[0203] Renewable oil, also referred to as renewable base oil, refers to oil produced from renewable sources, *i.e.,* based in part on carbon and/or energy captured from the environment, such as from biological resources (e.g., biomass) Renewable oils may have greater than 90 % saturates, sulfur content of less than 0.3 mass%, and viscosity index properties falling in API Groups II and or III, and thus for purposes of this invention and claims renewable oils can be Group II or Group III base oils (API EOLCS 1509 definition (American Petroleum Institute Publication 1509, see section E.1.3, 22th edition, October 2023, www.API.org).

[0204] The various base oils are often categorized as Group I, II, III, IV, or V according to the API EOLCS 1509 definition (American Petroleum Institute Publication 1509, see section E.1.3, 19th edition, January 2021, www.API.org). Generally speaking, Group I base stocks have a viscosity index of between about 80 to 120 and contain greater than about 0.03 % sulfur and/or less than about 90 % saturates. Group II base stocks have a viscosity index of between about 80 to 120 and contain less than or equal to about 0.03 % sulfur and greater than or equal to about 90 % saturates. Group III base stocks have a viscosity index greater than about 120 and contain less than or equal to about 0.03 % sulfur and greater than about 90 % saturates. Group IV base stocks includes polyalphaolefins (PAO). Group V base stocks include base stocks not included in Groups I-IV. (Viscosity index measured by ASTM D 2270, saturates is measured by ASTM D2007, and sulfur is measured by ASTM D5185, D2622, ASTM D4294, ASTM D4927, and ASTM D3120).

[0205] Base oils for use in the formulated lubricating compositions useful in the present disclosure are any one, two, three, or more of the variety of oils described herein. In desirable embodiments, base oils for use in the formulated lubricating compositions useful in the present disclosure are those described as API Group I(including Group I+), Group II (including Group II+), Group III (including Group III+), Group IV, and Group V oils and mixtures thereof, preferably API Group II, Group III, Group IV, and Group V oils and mixtures thereof. The base oil may be a Group III, Group III+, IV, and Group V base oils due to their exceptional volatility, stability, viscometric, and cleanliness features. Minor quantities of Group I basestock, such as the amount used to dilute additives for blending into formulated lube oil products, can be tolerated but are typically kept to a minimum, *e.g.,* amounts only associated with their use as diluent/carrier oil for additives used on an "as-received" basis. In regard to the Group II stocks, it is often more useful that the Group II base stock be in the higher quality range associated with that stock, *i.e.,* a Group II stock having a viscosity index in the range from 100 to 120.

[0206] The base oil useful herein may be selected from any of the synthetic, natural, or re-refined oils (such as those typically used as crankcase lubricating oils for spark-ignited and compression-ignited engines). Mixtures of synthetic and/or natural and/or re-refined base oils may be used if desired. Multi-modal mixtures (such as bi- or tri-modal mixtures) of Group I, II, III, IV, and/or V base stocks may be used if desired.

[0207] The base oil or base oil blend used herein conveniently has a kinematic viscosity at 100° C (KV100, as measured according to ASTM D445-19a, and reported in units of centistoke (cSt) or it its equivalent, mm2/s), of about 2 to about 40 cSt, alternately of 3 to 30 cSt, alternately 4 to 20 cSt at 100° C, alternately 5 to 10 cSt, alternately the base oil or base oil blend may have a kinematic viscosity at 100° C of 2 to 20 cSt, of 2.5 to 2 cSt, and preferably of about 2.5 cSt to about 9 cSt.

[0208] The base oil or base oil blend preferably has a saturate content of at least 65 mass%, more preferably at least 75 mass%, such as at least 85 mass%, such as at least than 90 mass% as determined by ASTM D2007.

[0209] Preferably, the base oil or base oil blend will have a sulfur content of less than 1 mass%, preferably less than 0.6 mass%, most preferably less than 0.4 mass%, such as less than 0.3 mass%, based on the total mass of the lubricating composition, as measured by ASTM D5185.

[0210] In embodiments, the volatility of the base oil or base oil blend, as measured by the Noack test (ASTM D5800, procedure B), is less than or equal to 30 mass%, such as less than or equal to 25 mass%, such as less than or equal to 20 mass%, such as less than or equal to 16 mass%, such as less than or equal to 12 mass%, such as less than or equal to 10 mass%, based on the total mass of the lubricating composition.

[0211] In embodiments, the viscosity index (VI) of the base oil is at least 95, preferably at least 110, more preferably at least 120, even more preferably at least 125, most preferably from about 130 to 240, in particular from about 105 to 140 (as determined by ASTM D2270).

[0212] The base oil may be provided in a major amount, in combination with a minor amount of one or more additive components as described hereinafter, constituting a lubricant. This preparation may be accomplished by adding the additives directly to the oil or by adding the one or more additives in the form of a concentrate thereof to disperse or dissolve the additive(s). Additives may be added to the oil by any method known to those skilled in the art, either before, at the same time as, or after addition of other additives.

[0213] The base oil may be provided in a minor amount, in combination with minor amounts of one or more additive components as described hereinafter, constituting an additive concentrate. This preparation may be accomplished by adding the additives directly to the oil or by adding the one or more additives in the form of a solution, slurry or suspension thereof to disperse or dissolve the additive(s) in the oil. Additives may be added to the oil by any method known to those skilled in the art, either before, at the same time as, or after addition of other additives.

[0214] The base oil typically constitutes the major component of an engine oil lubricant composition of the present disclosure and typically is present in an amount ranging from about 50 to about 99 mass%, preferably from about 70 to about 95 mass%, and more preferably from about 80 to about 95 mass%, based on the total weight of the composition.

[0215] Typically, one or more base oils are present in the lubricating composition in an amount of 32 mass% or more, alternately 55 mass% or more, alternately 60 mass% or more, alternately 65 mass% or more, based on the total weight of the lubricating composition. Typically, one or more base oils are present in the lubricating composition at an amount of 98 mass% or less, more preferably 95 mass% or less, even more preferably 90 mass% or less. Alternately, one or more base oils are present in the lubricating composition at from 1 to 99 mass%, alternately 50 to 97 mass%, alternately to 60 to 95 mass%, alternately 70 to 95 mass%, based upon the weight of the lubricating composition.

[0216] The base oils and blends thereof described above are also useful for making concentrates as well as for making lubricants therefrom.

[0217] Concentrates constitute a convenient means of handling additives before their use, as well as facilitating solution or dispersion of additives in lubricants. When preparing a lubricant that contains more than one type of additive (sometime referred to as "additive components"), each additive may be incorporated separately, each in the form of a concentrate. In many instances, however, it is convenient to provide a so-called additive "package" (also referred to as an "addpack") comprising one or more additives/co-additives, such as described hereinafter, in a single concentrate.

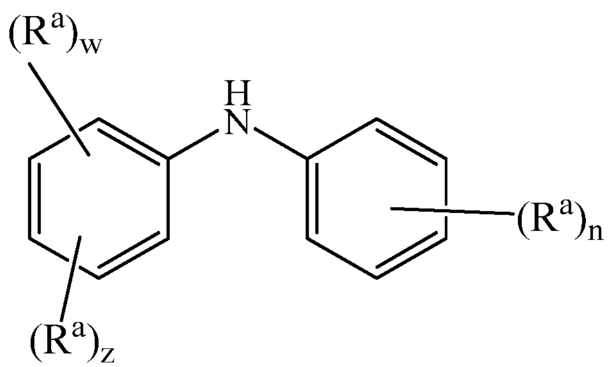
[0218] Typically, one or more base oils are present in the concentrate composition in an amount of 50 mass% or less, alternately 40 mass% or less, alternately 30 mass% or less, alternately 20 mass% or less, based on the total weight of the concentrate composition. Typically, one or more base oils are present in the concentrate composition at an amount of 0.1 to 49 mass%, alternately 5 to 40 mass%, alternately to 10 to 30 mass%, alternately 15 to 25 mass%, based upon the weight of the concentrate composition.

B. Antioxidants

[0219] The present invention relates to antioxidants that disrupt oxidation and increase the useful life of lubricating oils. More particularly, the present invention may describe antioxidant compositions comprising a plurality of antioxidative lubricant additives. In embodiments, the antioxidant comprises **diphenyl amine antioxidant** and optionally one or more additional antioxidants and/or optionally one or more carboxylate detergents, where **mono-C_9-alkyl substituted diphenyl amines** are absent or present at less than 15 mass% (such as less than 10 mass%), based upon the weight of the **diphenyl amine antioxidant**, to provide enhanced oxidative performance. The enhanced performance is related to previously unknown synergies arising from the lubricant additive components of the present invention in lubricating oil compositions. Primary antioxidants, optional additional antioxidants and detergents compatible with the present invention are described herein.

[0220] The antioxidant composition useful herein typically comprises a primary antioxidant and one or more optional additional antioxidants. Preferred primary antioxidants of the present invention typically comprise **diphenyl amine antioxidants** comprising at least 85 mass% (such as 90 mass% or more, such as 95 mass% or more, such as 99 mass% or more, such as 100 mass%) of **di-C_9-alkyl substituted diphenyl amine** and 15 mass% or less, (such as 10 mass% or less, such as 5 mass% or less, such as 1 mass% or less, such as 0 mass%) of **mono-C_9-alkyl substituted diphenyl amine** are present, based upon the weight of the mono- and di-**C_9-alkyl substituted diphenyl amines.**

[0221] The primary antioxidants employed in the lubricating oil of the present invention are typically represented by Formula (III):



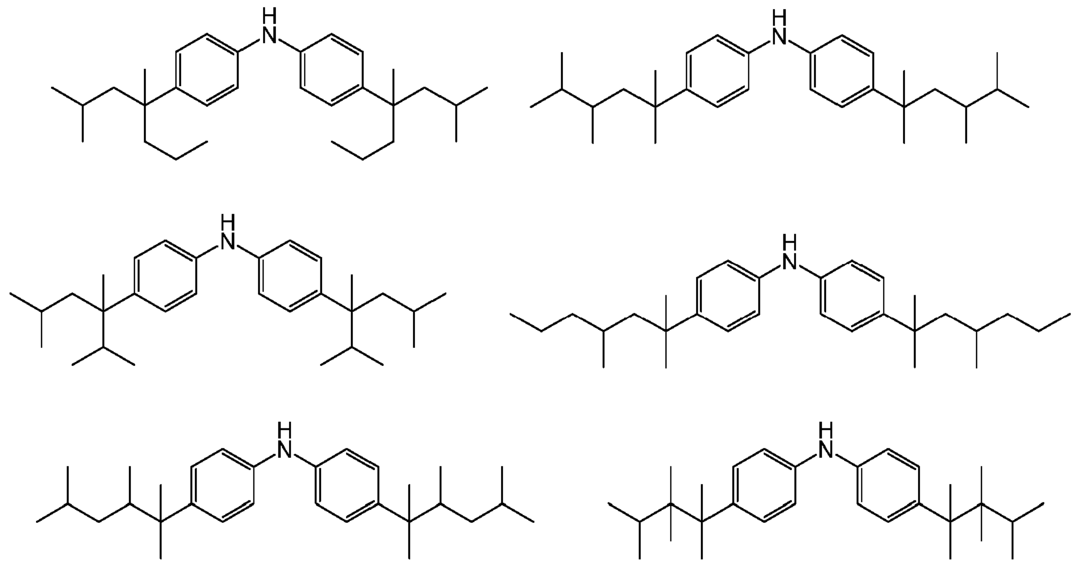
where each R^a is independently a linear C_9 alkyl or branched C_9 alkyl group, n is 0 or 1, z is 0 or 1 and w is 0 or 1, where the at least 85% of the primary antioxidant is n is 1, z is 1 and w is 0, based upon the weight of compounds represented by Formula (III). Examples of branched C_9 alkyl groups (C_9H_{18} alkyl groups) useful herein include, isononyl, methyloctyl, ethylheptyl, dimethylheptyl, propylhexyl, trimethylhexyl, methylethylhexyl, tetramethylpentyl, dimethylethylpentyl, diethylpentyl, butylpentyl, and the like.

[0222] In embodiments, the diphenyl amine antioxidant composition may comprise less than 15 mass%, or 14 mass% or less, or 13 mass% or less, or 12 mass% or less, or 11 mass% or less, or 10 mass% or less, 9 mass% or less, or 8 mass% or less, or 7 mass% or less, or 6 mass% or less, or 5 mass% or less, or 4 mass% or less, 3 mass% or less, or 2 mass% or less, or 1 mass% or less, or 0.5 mass% or less, or 0.1 mass% or less, or 0 mass%) of mono-C_9-alkyl substituted diphenyl amines represented by Formula (III), where w is 0, n is 1 and z is 0), based upon the weight of the diphenyl amine antioxidant composition.

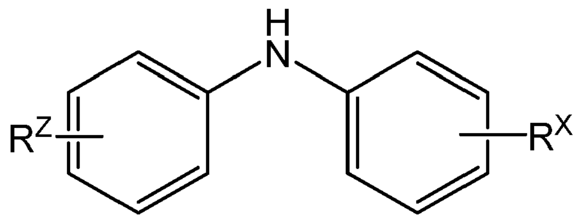
[0223] In embodiments, the diphenyl amine antioxidant composition may comprise more than 85 mass%, or 86 mass% or more, or 87 mass% or more, or 88 mass% or more, or 89 mass% or more, or 90 mass% or more, or 91 mass% or more, or 92 mass% or more, or 93 mass% or more, or 94 mass% or more, or 95 mass% or more, or 96 mass% or more, or 97 mass% or more, or 98 mass% or more, or 99 mass% or more, or 99.5 mass% or more, or 99.9 mass% or more, or 100 mass% of di-C_9-alkyl substituted diphenyl amines represented by Formula (III), where n is 1, w is 0, and z is 1, based upon the weight of the diphenyl amine antioxidant composition.

[0224] This invention further relates to diphenylamine antioxidant, where combinations comprising one, two, three, or four of the following substituted phenyl amines depicted below are present at 85 mass% or more, (or 90 mass% or more, or

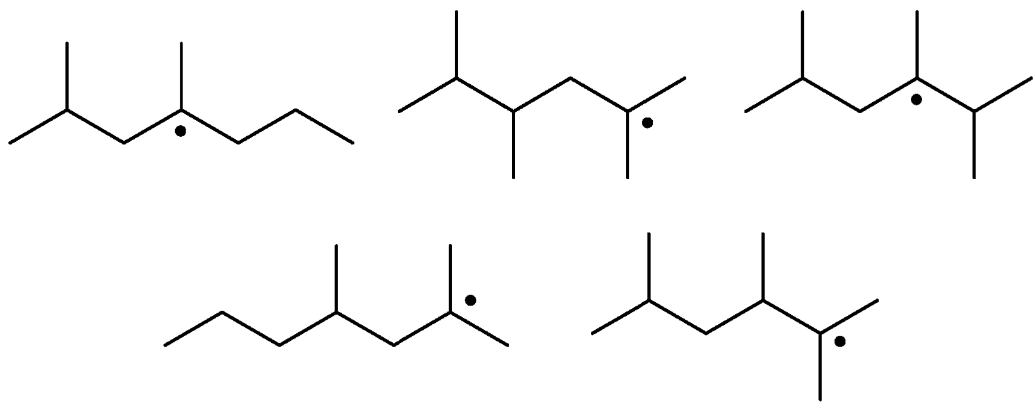
91 mass% or more, or 92 mass% or more, or 93 mass% or more, or 94 mass% or more, or 95 mass% or more, or 96 mass% or more, or 97 mass% or more, or 98 mass% or more, or 99 mass% or more, or 0.99.5 mass% or more, or 99.9 mass% or more, or 100 mass%) based upon the weight of the **diphenyl amine antioxidant** composition:



[0225] This invention further relates to diphenylamine antioxidant, where combinations comprising one, two, three, or four of the following substituted phenyl amines depicted below are present at 85 mass% or more, (or 90 mass% or more, or 91 mass% or more, or 92 mass% or more, or 93 mass% or more, or 94 mass% or more, or 95 mass% or more, or 96 mass% or more, or 97 mass% or more, or 98 mass% or more, or 99 mass% or more, or 0.99.5 mass% or more, or 99.9 mass% or more, or 100 mass%) based upon the weight of the **diphenyl amine antioxidant** composition:



where R^X and R^Z are independently selected from:



[0226] This invention further relates to an antioxidant composition comprising an antioxidant composition comprising or made by admixing:

1) phenylamine antioxidant comprising one or more di-C_9-alkyl substituted diphenyl amine as represented by Formula (III) where n is 1, z is 1 and w is 0, and

2) optionally, one or more additional antioxidants (such as diphenyl amines other than 1) above, hindered phenol, sulfurized fatty acid esters, molybdenum containing compounds, ashless dithiocarbamates, and the like),

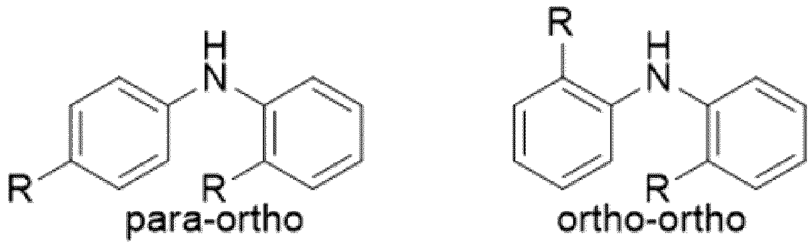
where, alkyl substituted diphenylamine(s) represented by Formula (III) where n is 0, w is 0 and z is 1, are absent or present at less than 15 mass%, such as less than 0.1 mass%, based upon the weight of **diphenyl amine antioxidant** composition.

[0227] In embodiments, the di-C_9-alkyl substituted diphenyl amine (such as represented by Formula (III) where n is 1 and z is 1 and w is 0), has:

i) more than 40% (such as 45 % or more, such as 50% or more such as 55% or more, such as 60% or more such as 65% or more, such as 70% or more, such as 80% or more such as 90% or more, such as 95% or more, such as 99% or more, such a 100%) of the alkyl groups in the para position (i.e., para to the bond to the phenylamine);
(ii) optionally less than 40%, such 30% or less, such as 20% or less, such as 10 % or less, such as 0%, of the alkyl groups in an ortho position (i.e., ortho to the bond to the phenylamine); and iii) optionally less than 10%, such 5% or less, such as 0%, of the alkyl groups in a meta position (i.e., meta to the bond to the phenylamine),

based upon the weight of the di-C_9-alkyl substituted diphenyl amine.

[0228] In embodiments, the di-C_9-alkyl substituted diphenyl amine such as represented by Formula (III) where n is 1, z is 1 and w is 0), comprises less than 5 mass% (or less than 4 mass%, or less than 3 mass%, or less than 2 mass%, or less than 1 mass%, or 0 mass%) of the isomers shown below, where each R is independently a linear C_9 alkyl or branched C_9 alkyl group:



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based upon the weight of di-C_9-alkyl substituted diphenyl amine represented by Formula (III) where n is 1, z is 1 and w is 0.

[0229] This invention further relates to diphenyl amine antioxidant comprising:

1) di(C_9-alkyl substituted phenyl) amine, and
2) from 0 to less than 10 mass% mono-C_9-alkyl substituted diphenyl amine, based upon the weight of the mono- and di-phenyl amines present.

[0230] This invention further relates to diphenyl amine antioxidant comprising:

1) 90 mass% or more of di(C_9-alkyl substituted phenyl) amines,
2) from 0 to less than 10 mass% of mono-C_9-alkyl substituted diphenyl amine, and
3) from 0 to less than 10 mass% of tri-C_9-alkyl substituted diphenyl amine, based upon the weight of 1), 2) and 3).

[0231] This invention further relates to diphenyl amine antioxidant composition comprising:

a) from 0 to less than 10 mass% mono-C_9-alkyl substituted diphenyl amine represented by the Formula (III) where n is 1, w is 0, and z is 0,
b) 90 mass% or more of di(C_9-alkyl substituted diphenyl) amines represented by Formula (III), where n is 1, w is 0, and z is 1,
c) from 0 to less than 10 mass% tri-C_9-alkyl substituted diphenyl amines represented by Formula (III), where w + n + z = 3,
d) from 0 to 1 mass% of unsubstituted diphenyl amine represented by Formula (III) where n is 0 and z is 0,

based upon the total weight of a), b), c) and d).

[0232] This invention further relates to diphenyl amine antioxidant composition comprising:

a) from 0 to less than 5 mass% mono-C_9-alkyl substituted diphenyl amines represented by the Formula (III) where n is

1, w is 0, and z is 0,
b) 90 mass% or more of di-C_9-alkyl substituted diphenyl amines represented by Formula (III), where w is 0, n is 1 and z is 1
c) 5 mass% or less of tri-C_9-alkyl substituted diphenyl amines represented by Formula (III), where w + n + z = 3,
d) 1 mass% or less of unsubstituted diphenyl amines represented by Formula (I) where n is 0 and z is 0,

based upon the total weight of the diphenyl amines of a), b), c) and d) present in the lubricating oil composition.

[0233] This invention further relates to diphenyl amine antioxidant composition comprising:

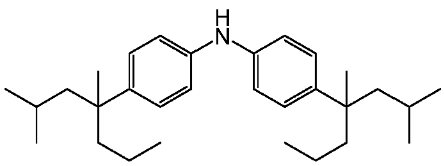
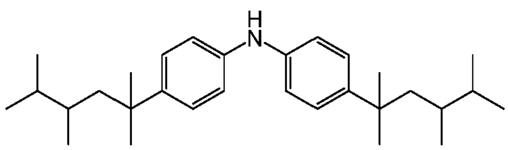
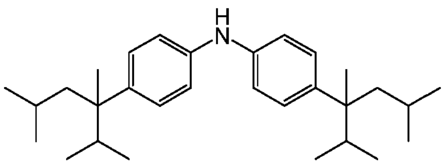
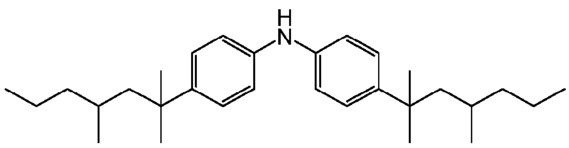
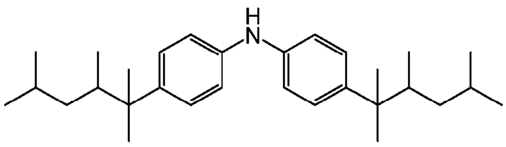
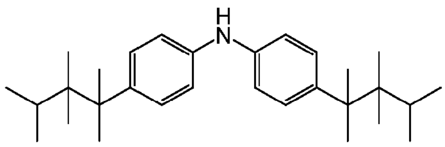
a) from 0 to less than 3 mass% mono-C_9-alkyl substituted diphenyl amines represented by the Formula (III) where w is 0, n is 1 and z is 0,
b) 95 mass% or more of di-C_9-alkyl substituted diphenyl amines represented by Formula (III), where w is 0, n is 1 and z is 1,
c) 5 mass% or less of tri-C_9-alkyl substituted diphenyl amines represented by Formula (III), where w + n + z = 3,
d) from 0 to 0.5 mass% or less of unsubstituted diphenyl amines represented by Formula (III) where z is 0, w is 0, and n is 0,

based upon the total weight of the diphenyl amines of a), b), c) and d).

[0234] This invention further relates to diphenyl amine antioxidant composition comprising:

a) 0 to less than 1 mass% of mono-C_9-alkyl substituted diphenyl amines (represented by Formula (III), where n is 1, z is 0, and w is 0); and
b) more than 99 mass% of di-C_9-alkyl substituted diphenyl amines represented by Formula (III), where w is 0, n is 1 and z is 1, based upon the total weight of the diphenyl amine antioxidants of a) and b) present in the lubricating oil composition.

[0235] In embodiments, each R^a in Formula (III) is independently a branched C_9 alkyl group, such as one or more of: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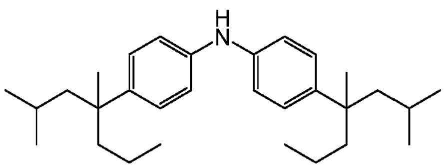
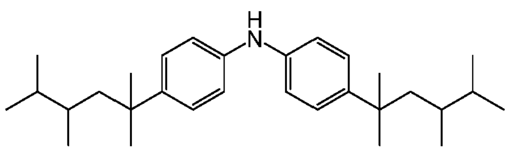
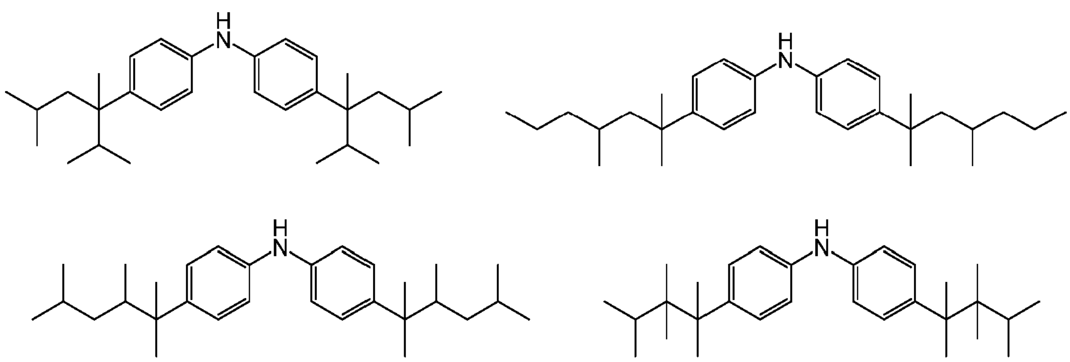
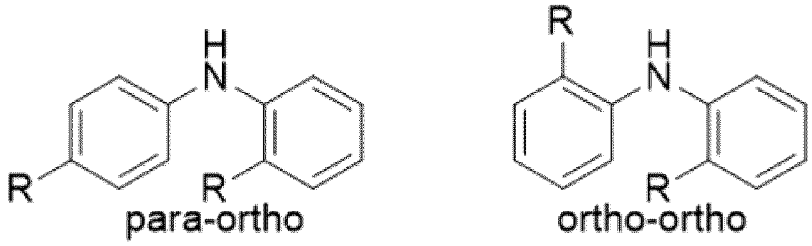
[0236] In embodiments, the di-C_9-alkyl substituted diphenyl amines represented by Formula (A) comprise di(p-nonylphenyl)amine.

[0237] In embodiments, the di-C_9-alkyl substituted diphenyl amines represented by Formula (A) comprises one or more isomers selected from the group consisting of:



[0238] In embodiments, the di-C_9-alkyl substituted diphenyl amine represented by Formula (III), where w is 0, n is 1, and z is 1, comprises less than 5 mass% of the isomers shown below, where each R is independently a linear C_9 alkyl or branched C_9 alkyl group:



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based upon the weight of di-C_9-alkyl substituted diphenyl amine represented by Formula (III), where w is 0, n is 1, and z is 1.

[0239] In general, the diphenylamine isomers can be separated by well-known techniques such as distillation (such as thin film evaporation and or flash distillation), dialysis, chromatography, and the like. The isomer content may be determined by mass spectrometry as described in the Experimental Section.

[0240] The di-C_9-alkyl substituted diphenyl amines described herein are typically synthesized by reaction of nonene with diphenylamine in the presence of Lewis acid catalyst. Further, di-C_9-alkyl substituted diphenyl amines may also be synthesized by a reaction of nonyl phenol with ammonia in the presence of hydrogen transfer catalyst and hydrogen (see for example, see US 5,449,829 which exemplifies such synthesis using a Pd/C catalyst).

[0241] The primary antioxidant may be present at about 0.01 mass% to about 20 mass% of the lubricating oil composition, such as from about 0.05 mass% to about 15 mass%, 0.1 mass% to about 10 mass%, 0.5 mass% to about 8 mass%, or 1 mass% to about 5 mass%.

[0242] When present in a concentrate, the primary antioxidant may be present at about 0.01 mass% to about 40 mass% of the concentrate, such as from about 0.020 mass% to about 30 mass%, such as from about 0.025 mass% to about 20 mass%, such as from about 0.05 mass% to about 15 mass%, 0.1 mass% to about 10 mass%, 0.5 mass% to about 8 mass%, or 1 mass% to about 5 mass%.

Additional Antioxidants

[0243] The present invention employs one or more additional antioxidants in combination with the primary antioxidants. The additional antioxidants may be present at about 0.01 mass% to about 20 mass% of the lubricating oil composition, such as from about 0.05 mass% to about 15 mass%, 0.1 mass% to about 10 mass%, 0.5 mass% to about 8 mass%, or 1 mass% to about 5 mass%.

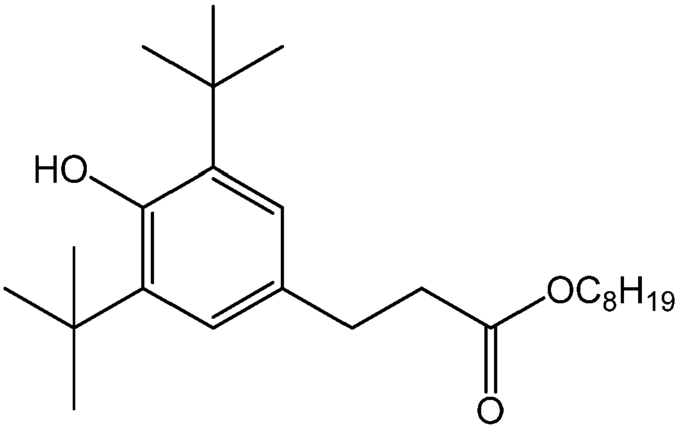
[0244] When present in a concentrate, the additional antioxidant may be present at about 0.01 mass% to about 30 mass% of the concentrate, such as from about 0.025 mass% to about 20 mass%, such as from about 0.05 mass% to about 15 mass%, 0.1 mass% to about 10 mass%, 0.5 mass% to about 8 mass%, or 1 mass% to about 5 mass%.

[0245] A number of additional antioxidants are compatible with the present invention. Examples of additional antioxidants include hindered phenols, molybdenum succinimides, and dithiocarbamates (such Zn or Mo-dialkyldithiocarbamates). These oil-soluble components are generally known.

[0246] A preferred additional antioxidant employed in the lubricating oil of the present invention may be a hindered phenol, such as a sterically hindered phenol. The phenolic antioxidants may be ashless (metal-free) phenolic compounds or neutral or basic metal salts of certain phenolic compounds. Typical phenolic antioxidant compounds are the hindered phenolics, which contain a sterically hindered hydroxyl group, and these include those derivatives of dihydroxy aryl compounds in which the hydroxyl groups are in the o- or p-position to each other. Typical phenolic antioxidants include the hindered phenols substituted with C_{6+} alkyl groups and the alkylene coupled derivatives of these hindered phenols. Examples of phenolic materials of this type include 2-t-butyl-4-heptyl phenol; 2-t-butyl-4-octyl phenol; 2-t-butyl-4-dodecyl phenol; 2,6-di-t-butyl-4-heptyl phenol; 2,6-di-t-butyl-4-dodecyl phenol; 2-methyl-6-t-butyl-4-heptyl phenol; and 2-methyl-6-t-butyl-4-dodecyl phenol. Other useful hindered mono-phenolic antioxidants may include, for example, hindered 2,6-di-alkyl-phenolic proprionic ester derivatives, such as C_7-C_9-(branched)-alkyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propanoate) available as IRGANOX™ L135. Bis-phenolic antioxidants may also be advantageously used herein. Examples of ortho-coupled phenols include: 2,2'-bis(4-heptyl-6-t-butyl-phenol); 2,2'-bis(4-octyl-6-t-butyl-phenol); and 2,2'-bis(4-dodecyl-6-t-butylphenol). Para-coupled bisphenols include, for example, 4,4'-bis(2,6-di-t-butyl-phenol) and 4,4'-methylene-bis(2,6-di-t-butyl-phenol).

[0247] Particularly useful hindered phenol antioxidants often contains a secondary butyl and/or a tertiary butyl group as a sterically hindering group. The phenol group is often further substituted with a hydrocarbyl group and/or a bridging group linking to a second aromatic group. Suitable hindered phenols include, but are not limited to, 2,6-di-tert-butylphenol, 4-methyl-2,6-di-tert-butylphenol, 4- ethyl-2,6-di-tert-butylphenol, 4-propyl-2,6-di-tert-butylphenol or 4-butyl-2,6-di-tert- butylphenol, 4-dodecyl-2,6-di-tert-butylphenol, 4-alkylester-2,6-di-tert-butylphenol, such as C_7-C_9-(branched)-alkyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propanoate).

[0248] A preferred hindered phenol may be represented by the formula:



[0249] Effective amounts of one or more catalytic antioxidants may also be used. The catalytic antioxidants comprise an effective amount of a) one or more oil soluble polymetal organic compounds; and, effective amounts of b) one or more substituted N,N'-diaryl-o-phenylenediamine compounds or c) one or more hindered phenol compounds; or a combination of both b) and c). Catalytic antioxidants useful herein are more fully described in US Patent No. 8,048,833.

[0250] Non-phenolic oxidation inhibitors, which may be used include aromatic amine antioxidants (other than those represented by Formula (A) or Formula (I) above) and these may be used either as such or in combination with phenolics. Typical examples of non-phenolic antioxidants include: alkylated and non-alkylated aromatic amines such as aromatic monoamines of the formula $R_8R_9R_{10}N$, where R_8 is an aliphatic, aromatic or substituted aromatic group, R_9 is an aromatic or a substituted aromatic group, and R_{10} is H, alkyl, aryl or $R_{11}S(O)XR_{12}$ where R_{11} is an alkylene, alkenylene, or aralkylene group, R_{12} is an alkyl group, or an alkenyl, aryl, or alkaryl group, and x is 0, 1, or 2. The aliphatic group R_8 may contain from 1 to about 20 carbon atoms, and preferably contains from about 6 to 12 carbon atoms. The aliphatic group is typically a saturated aliphatic group. Preferably, both R_8 and R_9 are aromatic or substituted aromatic groups, and the aromatic group may be a fused ring aromatic group such as naphthyl. Aromatic groups R_8 and R_9 may be joined together with other groups such as S.

[0251] Typical aromatic amines antioxidants have alkyl substituent groups of at least about 6 carbon atoms. Examples of aliphatic groups include hexyl, heptyl, octyl, nonyl, and decyl. Generally, the aliphatic groups will not contain more than about 14 carbon atoms. The general types of amine antioxidants useful in the present compositions include phenyl naphthylamines, phenothiazines, imidodibenzyls and diphenyl phenylene diamines. Mixtures of two or more aromatic amines are also useful. Polymeric amine antioxidants can also be used.

[0252] Sulfur-containing antioxidants are also useful herein. In particular, one or more oil-soluble or oil-dispersible sulfur-containing antioxidant(s) can be used as an antioxidant additive. For example, sulfurized alkyl phenols and alkali or alkaline earth metal salts thereof also are useful antioxidants herein. Suitably, the lubricating oil composition(s) of the present disclosure may include the one or more sulfur-containing antioxidant(s) in an amount to provide the lubricating oil composition with from 0.02 to 0.2, preferably from 0.02 to 0.15, even more preferably 0.02 to 0.1, even more preferably 0.04 to 0.1, mass% sulfur based on the total mass of the lubricating oil composition. Optionally the oil-soluble or oil-dispersible sulfur-containing antioxidant(s) are selected from sulfurized C_4 to C_{25} olefin(s), sulfurized aliphatic (C_7 to C_{29}) hydrocarbyl fatty acid ester(s), ashless sulfurized phenolic antioxidant(s), sulfur-containing organo-molybdenum compound(s), and combinations thereof. For further information, on sulfurized materials useful as antioxidants herein, please see US Patent No. 10,731,101 (col 15, ln 55 to col 22, ln 12).

[0253] An additional antioxidant employed in the lubricating oil of the present invention may be a molybdenum succinimide. The mono and polysuccinimides that can be used to prepare the molybdenum succinimide complexes described herein are disclosed in numerous references and are well known in the art. Certain fundamental types of succinimides and the related materials encompassed by the term of art "succinimide" are taught in U.S. Pat. No's. 3,219,666; 3,172,892; and 3,272,746, the disclosures of which are hereby incorporated by reference. The term "succinimide" is understood in the art to include many of the amide, imide, and amidine species which may also be formed. The predominant product however is a succinimide and this term has been generally accepted as meaning the product of a reaction of an alkenyl substituted succinic acid or anhydride with a nitrogen-containing compound.

[0254] Suitable dithiocarbamates include, but are not limited to, dithiocarbamates wherein the metal is zinc, copper or molybdenum, ashless thiocarbamates or dithiocarbamates (i.e., essentially metal free) such as methylenebis(dialkyldithiocarbamate), ethylenebis(dialkyldithiocarbamate), and isobutyl disulfide-2, 2'-bis(dialkyldithiocarbamate) where the alkyl groups of the dialkyldithiocarbamate can preferably have from 1 to 6 carbon atoms. Examples of preferred ashless dithiocarbamates are methylenebis(dibutyldithiocarbamate), ethylenebis(dibutylthiocarbamate) and isobutyl disulfide-2, 2'- bis(dibutyldithiocarbamate).

[0255] The additional antioxidant employed in the lubricating oil of the present invention may be a sterically hindered phenol described in US 9,512,380, such as those shown at columns 82 to 100.

[0256] Antioxidant additives may be used in an amount of about 0.01 to 10 (alternately 0.01 to 5, alternately 0.01 to 3) mass%, alternately about 0.03 to 5 mass%, alternately 0.05 to less than 3 mass%, based upon the weight of the lubricating composition.

[0257] Compositions according to the present disclosure may contain an additive having a different enumerated function that also has secondary effects as an antioxidant (for example, phosphorus-containing antiwear agents (such as ZDDP) may also have antioxidant effects). These additives are not included as antioxidants for purposes of determining the amount of antioxidant in a lubricating oil composition or concentrate herein.

[0258] The lubricating composition according to the present disclosure may further comprise one or more additives such as detergents, friction modifiers, pour point depressants, anti-foam agents, viscosity modifiers, dispersants, corrosion inhibitors, antiwear agents, extreme pressure additives, demulsifiers, seal compatibility agents, additive diluent base oils, etc. Specific examples of such additives are described in, for example, Kirk-Othmer Encyclopedia of Chemical Technology, third edition, volume 14, pp. 477-526, and several are discussed in further detail below.

C. Detergents

[0259] The lubricating composition may comprise one or more metal detergents (such as blends of metal detergents) also referred to as a "detergent additive." Metal detergents typically function both as detergents to reduce or remove deposits and as acid neutralizers or rust inhibitors, thereby reducing wear and corrosion and extending engine life. Detergents generally comprise a polar head with a long hydrophobic tail, with the polar head comprising a metal salt of an acidic organic compound. The salts may contain a substantially stoichiometric amount of the metal in which case they are usually described as normal or neutral salts, and would typically have a total base number ("TBN" as measured by ASTM D2896) of up to 150 mgKOH/g, such as from 0 to 80 (or 5-30) mgKOH/g. A large amount of a metal base may be incorporated by reacting excess metal compound (e.g., an oxide or hydroxide) with an acidic gas (e.g., carbon dioxide). Such detergents, sometimes referred to as overbased, may have a TBN of 100 mgKOH/g or more (such as more than 150 mgKOH/g, such as 200 mgKOH/g or more), and typically will have a TBN of 250 mgKOH/g or more, such as 300 mgKOH/g or more, such as from 200 to 800 mgKOH/g, 225 to 700 mgKOH/g, 250 to 650 mgKOH/g, or 300 to 600 mgKOH/g, such as 150 to 650 mgKOH/g.

[0260] Suitable detergents include, oil-soluble neutral and overbased sulfonates, phenates, sulfurized phenates, thiophosphonates, salicylates, naphthenates and other oil-soluble carboxylates of a metal, particularly the alkali metals (Group 1 metals, *e.g.,* Li, Na, K, Rb) or alkaline earth metals (Group 2 metals, *e.g.,* Be, Mg, Ca, Sr, Ba), particularly, sodium, potassium, lithium, calcium, and magnesium, such as calcium and/or magnesium. Furthermore, the detergent may comprise a hybrid detergent comprising any combination of sodium, potassium, lithium, calcium, or magnesium salts of sulfonates, phenates, sulfurized phenates, thiophosphonates, salicylates, and naphthenates or other oil-soluble carboxylates of a Group 1 and/or 2 metal.

[0261] Sulfonate detergents are particularly useful in the blends described herein. In particular overbased calcium sulfonate, magnesium sulfonate, combinations of magnesium and calcium sulfonate detergents, and hybrid detergents comprising at least one sulfonate based detergent are useful in the blends described herein.

[0262] Preferably, the detergent additive(s) useful in the present disclosure comprises calcium and/or magnesium metal salts. The detergent may be one or more calcium and/or magnesium carboxylate (*e.g.,* salicylate), sulfonate, or phenate detergents. More preferably, the detergent additives are selected from magnesium salicylate, calcium salicylate, magnesium sulfonate, calcium sulfonate, magnesium phenate, calcium phenate, and hybrid detergents comprising two, three, four, or more of more of these detergents and/or combinations thereof.

[0263] Magnesium based detergents are useful in the blends described herein. In particular magnesium carboxylate (*e.g.,* salicylate), sulfonate, or phenate detergents are useful in the blends described herein, such as magnesium salicylate, magnesium sulfonate, magnesium phenate, combinations of magnesium salicylate and magnesium sulfonate, and hybrid detergents comprising at least one magnesium based detergent as described below.

[0264] The metal-containing detergent may also include "hybrid" 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 US Patent Nos. 6,429,178; 6,429,179; 6,153,565; and 6,281,179. Where, for example, a hybrid sulfonate/phenate detergent is employed, the hybrid detergent would be considered equivalent to amounts of distinct phenate and sulfonate detergents introducing like amounts of phenate and sulfonate soaps, respectively.

[0265] The overbased metal-containing detergent may be sodium salts, calcium salts, magnesium salts, or mixtures thereof of the phenates, sulfur-containing phenates, sulfonates, salixarates, and salicylates. Overbased phenates and salicylates typically have a total base number of 180 to 650 mgKOH/g, such as 200 to 450 TBN mgKOH/g. Overbased sulfonates typically have a total base number of 250 to 600 mgKOH/g, or 300 to 500 mgKOH/g. In embodiments, the sulfonate detergent may be predominantly a linear alkylbenzene sulfonate detergent having a metal ratio of at least 8 as is described in paragraphs [0026] to [0037] of US Patent Application Publication No. 2005/065045 (and granted as US Patent No. 7,407,919). The overbased detergent may be present at 0 mass% to 15 mass%, or 0.1 mass% to 10 mass%, or 0.2 mass% to 8 mass%, or 0.2 mass% to 3 mass%, based upon of the lubricating composition. For example, in a heavy-duty diesel engine, the detergent may be present at 2 mass% to 3 mass% of the lubricating composition. For a passenger car engine, the detergent may be present at 0.2 mass% to 1 mass% of the lubricating composition.

[0266] The detergent additive(s) may comprise one or more magnesium sulfonate detergents. The magnesium detergent may be a neutral salt or an overbased salt. Suitably the magnesium detergent is an overbased magnesium sulfonate having a TBN of from 80 to 650 mgKOH/g (ASTM D2896), such as 200 to 500 mgKOH/g, such as 240 to 450 mgKOH/g.

[0267] Alternately, the detergent additive(s) is a magnesium salicylate. Suitably the magnesium detergent is a magnesium salicylate having TBN of from 30 to 650 mgKOH/g (ASTM D2896), such as 50 to 500 mgKOH/g, such as 200 to 500 mgKOH/g, such as 240 to 450 mgKOH/g or alternately of 150 mgKOH/g or less, such as 100 mgKOH/g or less.

[0268] Alternately, the detergent additive(s) is a combination of magnesium salicylate and magnesium sulfonate.

[0269] The magnesium detergent typically provides the lubricating composition thereof with from 200 ppm or more of magnesium atoms, suitably 200-4000 ppm, from 200-2000 ppm, from 300 to 1500 or from 450-1200 ppm of magnesium atoms (ASTM D5185). In embodiments, the magnesium-based detergent providing high amounts of Mg to compositions described herein, provides at least 400 ppm (such as 400 ppm to 20,000 ppm, such as 450 to 10,000 ppm, such as 500 ppm to 8000ppm, such as 600 ppm or more, such as 700 ppm or more, such as 800 ppm or more, such as 1000 ppm or more, such as 1200 ppm or more, such as 2000 ppm or more, such as 3000 ppm or more, such as 4000 ppm or or more, such as 5000 ppm or more) of magnesium atoms (ASTM D5185) to the composition (booster pack, concentrate, lubricating oil composition, etc. described herein). The detergent may comprise one or more magnesium detergents such as magnesium carboxylate (*e.g.,* salicylate), sulfonate, or phenate detergent. The detergent may comprise one or more magnesium sulfonates.

[0270] Suitably the magnesium detergent has a TBN of from 30 to 700 mgKOH/g (ASTM D2896), such as 50 to 650 mgKOH/g, such as 200 to 500 mgKOH/g, such as 240 to 450 mgKOH/g or alternately of 150 mgKOH/g or less, such as 100 mgKOH/g or less, or 200 mgKOH/g or more, or 300 mgKOH/g or more, or 350 mgKOH/g or more.

[0271] Suitably, the magnesium detergent is a magnesium salicylate, sulfonate, or phenate having a TBN of from 30 to 700 mgKOH/g, 30 to 650 mgKOH/g (ASTM D2896), such as 50 to 650 mgKOH/g, such as 200 to 500 mgKOH/g, such as 240 to 450 mgKOH/g or alternately of 150 mgKOH/g or less, such as 100 mgKOH/g or less, or 200 mgKOH/g or more, or 300 mgKOH/g or more, or 350 mgKOH/g or more.

[0272] The detergent composition may comprise (or consist of) a combination of one or more magnesium sulfonate detergents and one or more calcium salicylate detergents.

[0273] The combination of one or more magnesium sulfonate detergents and one or more calcium salicylate detergents preferably provides the lubricating composition thereof with: 1) from 200-4000 ppm of magnesium atoms, suitably from 200-2000 ppm, from 300 to 1500 ppm or from 450-1200 ppm of magnesium atoms (ASTM D5185), and 2) at least 500 ppm, preferably at least 750 ppm, more preferably at least 900 ppm of atomic calcium, such as from 500-4000 ppm, preferably from 750-3000 ppm, more preferably from 900-2000 ppm atomic calcium atoms (ASTM D5185).

[0274] The detergent may comprise one or more calcium detergents such as calcium carboxylate (*e.g.,* salicylate), sulfonate, or phenate detergent. The detergent may comprise one or more calcium salicylates.

[0275] Suitably the calcium detergent has a TBN of from 30 to 700 mgKOH/g (ASTM D2896), such as 50 to 650 mgKOH/g, such as 200 to 500 mgKOH/g, such as 240 to 450 mgKOH/g or alternately of 150 mgKOH/g or less, such as 100 mgKOH/g or less, or 200 mgKOH/g or more, or 300 mgKOH/g or more, or 350 mgKOH/g or more.

[0276] Suitably, the calcium detergent is a calcium salicylate, sulfonate, or phenate having a TBN of from 30 to 700 mgKOH/g, 30 to 650 mgKOH/g (ASTM D2896), such as 50 to 650 mgKOH/g, such as 200 to 500 mgKOH/g, such as 240 to 450 mgKOH/g or alternately of 150 mgKOH/g or less, such as 100 mgKOH/g or less, or 200 mgKOH/g or more, or 300 mgKOH/g or more, or 350 mgKOH/g or more.

[0277] Suitably, the calcium detergent is a calcium carboxylate (salicylate) detergent having a TBN of from 30 to 700 mgKOH/g, 30 to 650 mgKOH/g (ASTM D2896), such as 50 to 650 mgKOH/g, such as 200 to 500 mgKOH/g, such as 240 to 450 mgKOH/g or alternately of 150 mgKOH/g or less, such as 100 mgKOH/g or less, or 200 mgKOH/g or more, or 300 mgKOH/g or more, or 350 mgKOH/g or more.

[0278] Calcium detergent is typically present in amount sufficient to provide at least 500 ppm, preferably at least 750 more preferably at least 900 ppm atomic calcium to the lubricating oil composition (ASTM D5185). If present, any calcium detergent is suitably present in amount sufficient to provide no more than 4000 ppm, preferably no more than 3000 ppm, more preferably no more than 2000 ppm atomic calcium to the lubricating oil composition (ASTM D5185). If present, any calcium detergent is suitably present in amount sufficient to provide at from 500-4000 ppm, preferably from 750-3000 ppm more preferably from 900-2000 ppm atomic calcium to the lubricating oil composition (ASTM D5185).

[0279] In embodiments, the calcium salicylate-based detergent provides high amounts of Ca to compositions described here, and provides at least 400 ppm (such as 400 ppm to 20,000 ppm, such as 450 to 10,000 ppm, such as 500 ppm to 8000ppm, such as 600 ppm or more, such as 700 ppm or more, such as 800 ppm or more, such as 1000 ppm or more, such as 1200 ppm or more, such as 2000 ppm or more, such as 2100 ppm or more, such as 3000 ppm or more, such as 4000 ppm or or more, such as 5000 ppm or more) of calcium atoms (ASTM D5185) to the composition (booster pack, concentrate, lubricating oil composition, etc.).

[0280] Suitably the total atomic amount of metal from detergent in the lubrication composition according to all aspects of the disclosure is less than 5000 ppm, preferably less than 4000 pm and more preferably less than 2000 ppm (ASTM D5185). The total amount of atomic metal from detergent in the lubrication oil composition according to all aspects of the disclosure is suitably at least 500 ppm, preferably at least 800 ppm and more preferably at least 1000 ppm (ASTM D5185). The total amount of atomic metal from detergent in the lubrication oil composition according to all aspects of the disclosure is suitably from 500 to 5000 ppm, preferably from 500 to 3000 ppm and more preferably from 500 to 2000 ppm (ASTM D5185).

[0281] Sulfonate detergents may be prepared from sulfonic acids which are typically obtained by the sulfonation of alkyl substituted aromatic hydrocarbons, such as those obtained from the fractionation of petroleum or by the alkylation of aromatic hydrocarbons. Examples include those obtained by alkylating benzene, toluene, xylene, naphthalene, diphenyl, or their halogen derivatives such as chlorobenzene, chlorotoluene, and chloronaphthalene. The alkylation may be carried out in the presence of a catalyst with alkylating agents having from about 3 to more than 70 carbon atoms. The alkaryl sulfonates usually contain from about 9 to about 80 or more carbon atoms, preferably from about 16 to about 60 carbon atoms per alkyl substituted aromatic moiety. The oil soluble sulfonates or alkaryl sulfonic acids may be neutralized with oxides, hydroxides, alkoxides, carbonates, carboxylate, sulfides, hydrosulfides, nitrates, borates and ethers of the metal. The amount of metal compound is chosen having regard to the desired TBN of the final product, but typically ranges from about 100 to 220 mass% (preferably at least 125 mass%) of that stoichiometrically required.

[0282] Metal salts of phenols and sulfurized phenols are prepared by reaction with an appropriate metal compound such as an oxide or hydroxide and neutral or overbased products may be obtained by methods well known in the art. Sulfurized phenols may be prepared by reacting a phenol with sulfur or a sulfur-containing compound such as hydrogen sulfide, sulfur monohalide, or sulfur dihalide, to form products which are generally mixtures of compounds in which 2 or more phenols are bridged by sulfur-containing bridges.

[0283] Carboxylate detergents, e.g., salicylates, can be prepared by reacting an aromatic carboxylic acid (such as a C_{5}-$_{100}$, C_{9}-$_{30}$, C_{14}-$_{24}$ alkyl-substituted hydroxy-benzoic acid) with an appropriate metal compound such as an oxide or hydroxide and neutral or overbased products may be obtained by methods well known in the art. The aromatic moiety of the aromatic carboxylic acid can contain heteroatoms, such as nitrogen and oxygen. Preferably, the moiety contains only carbon atoms; more preferably the moiety contains six or more carbon atoms; for example, benzene is a preferred moiety. The aromatic carboxylic acid may contain one or more aromatic moieties, such as one or more benzene rings, either fused or connected via alkylene bridges.

[0284] Preferred substituents in oil-soluble salicylic acids are alkyl substituents. In alkyl - substituted salicylic acids, the alkyl groups advantageously contain 5 to 100, preferably 9 to 30, especially 14 to 20, carbon atoms. Where there is more than one alkyl group, the average number of carbon atoms in all of the alkyl groups is preferably at least 9 to ensure adequate oil solubility.

[0285] In preferred embodiments, the composition of the present invention may include one or more alkali or alkaline earth metals carboxylate (such as barium, sodium potassium, lithium, calcium, and/or magnesium salicylate) detergents.

Such carboxylate detergents (such as salicylate detergents) may be present at about 0.01 mass% to about 10 mass% of the lubricating oil composition, such as from about 0.05 mass% to about 8 mass%, 0.1 mass% to about 5 mass%, 0.5 mass% to about 4 mass%, or 1 mass% to about 3 mass%. Carboxylate detergents include aromatic carboxylates (e.g., salicylates, naphthenates), aliphatic carboxylates (e.g., stearates), and the like. The carboxylate detergents may be overbased (as measured by ASTM D2896), for example, low overbased (TBN from 15 to 30), medium overbased (TBN from 31 to 170), high overbased (TBN from 171 to 400) and high high overbased (TBN > 400) carboxylate detergents. One or more overbased carboxylate detergents (e.g., low overbased and medium overbased) may be used.

[0286] In embodiments, the ratio of atomic detergent metal to atomic molybdenum in the lubricating oil composition may be less than 3:1, such as less than 2:1.

[0287] Further, as metal organic and inorganic base salts, which are used as detergents can contribute to the sulfated ash content of a lubricating oil composition, in embodiments of the present disclosure, the amounts of such additives are minimized. In order to maintain a low sulfur level, salicylate detergents can be used and the lubricating composition herein may comprise one or more salicylate detergents (said detergents are preferably used in amounts in the range of 0.05 to 20.0 mass%, more preferably from 1.0 to 10.0 mass% and most preferably in the range of from 2.0 to 5.0 mass%, based on the total weight of the lubricating composition).

[0288] The total sulfated ash content of the lubricating composition herein is typically not greater than 2.0 mass%, alternately at a level of not greater than 1.0 mass% and alternately at a level of not greater than 0.8 mass%, based on the total weight of the lubricating composition as determined by ASTM D874.

[0289] Furthermore, it is useful that each of the detergents, independently, have a TBN (total base number) value in the range of from 10 to 700 mgKOH/g, 10 to 500 mgKOH/g, alternately in the range of from 100 to 650, alternately in the range of from 10 to 500 mgKOH/g, alternately in the range of from 30 to 350 mgKOH/g, and alternately in the range of from 50 to 300 mgKOH/g, as measured by ASTM D2896.

[0290] The sulfonate detergents (such as Ca and/or Mg sulfonate detergents) may be present in an amount to deliver 0.1 mass% to 1.5 mass%, or 0.15 to 1.2 mass%, or 0.2 mass% to 0.9 mass% sulfonate soap to the lubricant composition.

[0291] The salicylate detergents (such as Ca and/or Mg salicylate detergents) are present in an amount to deliver 0.3 mass% to 1.4 mass%, or 0.35 mass% to 1.2 mass%, or 0.4 mass% to 1.0 mass% salicylate soap to the lubricant composition.

[0292] The sulfonate soap may be present in an amount 0.2 mass% to 0.8 mass% of the lubricant composition, and the salicylate soap may be present in an amount 0.3 mass% to 1.0 mass% of the lubricant composition.

[0293] The total of all alkaline earth metal detergent soap may be present in an amount 0.6 mass% to 2.1 mass%, or 0.7 mass% to 1.4 mass% of the lubricant composition.

[0294] Typically, lubricating compositions formulated for use in heavy-duty diesel engines comprise detergents at from about 0.1 to about 10 mass%, alternately from about 0.5 to about 7.5 mass%, alternately from about 1 to about 6.5 mass%, based on the lubricating composition.

[0295] Typically, lubricating compositions formulated for use in a passenger-car engines comprise detergents at from about 0.1 to about 10 mass%, alternately from about 0.5 to about 7.5 mass%, alternately from about 1 to about 6.5 mass%, based on the lubricating composition.

[0296] Typically, lubricating compositions formulated for use in a drive train (*e.g.,* transmissions) comprise detergents at from about 0.1 to about 10 mass%, alternately from about 0.5 to about 7.5 mass%, alternately from about 2 to about 6.5 mass%, based on the lubricating composition.

D. Friction Modifiers

[0297] A friction modifier is any material or materials that can alter the coefficient of friction of a surface lubricated by any lubricant or fluid-containing such material(s). Friction modifiers, also known as friction reducers, or lubricity agents or oiliness agents, and other such agents that change the ability of base oils, formulated lubricating compositions, or functional fluids, to modify the coefficient of friction of a lubricated surface may be effectively used in combination with the base oils or lubricating compositions of the present disclosure if desired. Friction modifiers that lower the coefficient of friction are particularly advantageous in combination with the base oils and lubricating compositions of this disclosure.

[0298] Illustrative friction modifiers may include, for example, organometallic compounds or materials, or mixtures thereof. Illustrative organometallic friction modifiers useful in the lubricating oil formulations of this disclosure include, for example, tungsten and/or molybdenum compounds, such as molybdenum amine, molybdenum diamine, an organotungstenate, a molybdenum dithiocarbamate, molybdenum dithiophosphates, molybdenum amine complexes, molybdenum carboxylates, and the like, and mixtures thereof. Examples of useful molybdenum-containing compounds may conveniently include molybdenum dithiocarbamates, trinuclear molybdenum compounds, for example, as described in PCT Publication No. WO 98/26030, sulfides of molybdenum and molybdenum dithiophosphate.

[0299] Other known friction modifiers comprise oil-soluble organo-molybdenum compounds. Such organo-molybdenum friction modifiers may also provide antioxidant and antiwear credits to a lubricating oil composition. Examples of such oil-soluble organo-molybdenum compounds include dithiocarbamates, dithiophosphates, dithiophosphinates, xanthates, thioxanthates, sulfides, and the like, and mixtures thereof. Particularly preferred are molybdenum dithiocarbamates, dialkyldithiophosphates, alkyl xanthates and alkylthioxanthates.

[0300] Additionally, the molybdenum compound may be an acidic molybdenum compound. These compounds will react with a basic nitrogen compound as measured by ASTM test D664 or D2896 titration procedure and are typically hexavalent. Included are molybdic acid, ammonium molybdate, sodium molybdate, potassium molybdate, and other alkali metal molybdates and other molybdenum salts, *e.g.,* hydrogen sodium molybdate, $MoOC_{14}$, MoO_2Br_2, $Mo_2O_3C_{16}$, molybdenum trioxide or similar acidic molybdenum compounds.

[0301] Among the molybdenum compounds useful in the compositions of this disclosure are organo-molybdenum compounds of the formula $Mo(R''OCS_2)_4$ and $Mo(R''SCS_2)_4$, wherein R" is an organo group selected from the group consisting of alkyl, aryl, aralkyl and alkoxyalkyl, generally of from 1 to 30 carbon atoms, and preferably 2 to 12 carbon atoms and most preferably alkyl of 2 to 12 carbon atoms. Especially preferred are the dialkyldithiocarbamates of molybdenum.

[0302] Another group of organo-molybdenum compounds useful in the lubricating compositions of this disclosure are trinuclear molybdenum compounds, especially those of the formula $Mo_3S_kL_nQ_z$ and mixtures thereof wherein the L are independently selected ligands having organo groups with a sufficient number of carbon atoms to render the compound soluble or dispersible in the oil, n is from 1 to 4, k varies from 4 to 7, Q is selected from the group of neutral electron-donating compounds such as water, amines, alcohols, phosphines, and ethers, and z ranges from 0 to 5 and includes non-stoichiometric values. at least 21 carbon atoms should be present among all the ligand/organo groups, such as at least 25, at least 30, or at least 35, carbon atoms.

[0303] Lubricating oil compositions useful in all aspects of the present disclosure preferably contain at least 10 ppm, at least 30 ppm, at least 40 ppm and more preferably at least 50 ppm molybdenum. Suitably, lubricating oil compositions useful in all aspects of the present disclosure contain no more than 1000 ppm, no more than 750 ppm, or no more than 500 ppm of molybdenum. Lubricating oil compositions useful in all aspects of the present disclosure preferably contain from 10 to 1000, such as 30 to 750 or 40 to 500, ppm of molybdenum (measured as atoms of molybdenum).

[0304] Organomolybdenum-based friction modifiers useful herein, such as in compositions and lubricating oils, include those described in this Section D and may in any embodiment include compounds such as organomolybdenum compounds of dithiocarbamates, dithiophosphates, dithiophosphinates, xanthates, thioxanthates, sulfides, and the like, and mixtures thereof. Desirable organomolybdenum-based friction modifiers include molybdenum dithiocarbamates, dialkyldithiophosphates, alkyl xanthates and alkylthioxanthates. In a more preferred embodiment, the organomolybdenum-based friction modifiers are selected from dimeric molybdenum dialkyldithiocarbamates and trimeric molybdenum dialkyldithiocarbamates, and most preferably dimeric dialkyldithiocarbamate (where the alkyl groups are independently selected from C_6 to C_{14} alkyl groups, and may be selected from C_{10}-C_{14} and C_6-C_{12} alkyl groups, such as hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, or isomers thereof).

[0305] For more information on useful friction modifiers containing molybdenum, please see US Patent No. 10,829,712 (col 8, ln 58 to col 11, ln 31).

[0306] Ashless friction modifiers may be present in the lubricating oil compositions of the present disclosure and are known generally and include esters formed by reacting carboxylic acids and anhydrides with alkanols and amine-based friction modifiers. Other useful friction modifiers generally include a polar terminal group (*e.g.,* carboxyl or hydroxyl) covalently bonded to an oleophilic hydrocarbon chain. Esters of carboxylic acids and anhydrides with alkanols are described in US Patent No. 4,702,850. Examples of other conventional organic friction modifiers are described by M. Belzer in the "Journal of Tribology" (1992), Vol. 114, pp. 675-682 and M. Belzer and S. Jahanmir in "Lubrication Science" (1988), Vol. 1, pp. 3-26. Typically, the total amount of organic ashless friction modifier in a lubricant according to the present disclosure does not exceed 5 mass%, based on the total mass of the lubricating oil composition and preferably does not exceed 2 mass% and more preferably does not exceed 0.5 mass%.

[0307] Illustrative friction modifiers useful in the lubricating compositions described herein include, for example, alkoxylated fatty acid esters, alkanolamides, polyol fatty acid esters, borated glycerol fatty acid esters, fatty alcohol ethers, and mixtures thereof.

[0308] Illustrative alkoxylated fatty acid esters include, for example, polyoxyethylene stearate, fatty acid polyglycol ester, and the like. These can include polyoxypropylene stearate, polyoxybutylene stearate, polyoxyethylene isosterate, polyoxypropylene isostearate, polyoxyethylene palmitate, and the like.

[0309] Illustrative alkanolamides include, for example, lauric acid diethylalkanolamide, palmic acid diethylalkanolamide, and the like. These can include oleic acid diethyalkanolamide, stearic acid diethylalkanolamide, oleic acid diethylalkanolamide, polyethoxylated hydrocarbylamides, polypropoxylated hydrocarbylamides, and the like.

[0310] Illustrative polyol fatty acid esters include, for example, glycerol monooleate, saturated mono-, di-, and triglyceride esters, glycerol monostearate, and the like. These can include polyol esters, hydroxyl-containing polyol esters, and the like.

[0311] Illustrative borated glycerol fatty acid esters include, for example, borated glycerol monooleate, borated saturated mono-, di-, and tri-glyceride esters, borated glycerol monosterate, and the like. In addition to glycerol polyols, these can include trimethylolpropane, pentaerythritol, sorbitan, and the like. These esters can be polyol monocarboxylate esters, polyol dicarboxylate esters, and on occasion polyoltricarboxylate esters. Preferred can be the glycerol mono-oleates, glycerol di-oleates, glycerol tri-oleates, glycerol mono-oleates, glycerol di-stearates, and glycerol tri-stearates and the corresponding glycerol mono-palmitates, glycerol di-palmitates, and glycerol tri-palmitates, and the respective isostearates, linoleates, and the like. Ethoxylated, propoxylated, and/or butoxylated fatty acid esters of polyols, especially using glycerol as underlying polyol are useful herein. Ashless friction modifiers, such as glycerol-based friction modifiers useful herein, such as in compositions and lubricating oils, include those described in this Section D and may in any embodiment include glycerol-based friction modifiers such as glycerol monooleates, saturated mono-, di-, and tri-glyceride esters, glycerol monostearates, and polyols. In a preferred embodiment the glycerol-based friction modifier is glycerol mono-oleate.

[0312] Illustrative fatty alcohol ethers include, for example, stearyl ether, myristyl ether, and the like. Alcohols, including those that have carbon numbers from C_3 to C_{50}, can be ethoxylated, propoxylated, or butoxylated to form the corresponding fatty alkyl ethers. The underlying alcohol portion can preferably be stearyl, myristyl, C_{11}-C_{13} hydrocarbon, oleyl, isosteryl, and the like.

[0313] Useful concentrations of friction modifiers may range from 0.01 mass% to 5 mass%, or about 001 mass% to about 2.5 mass%, or about 0.05 mass% to about 1.5 mass%, or about 0.051 mass% to about 1 mass%. Concentrations of molybdenum-containing materials are often described in terms of Mo metal concentration. Advantageous concentrations of Mo may range from 25 ppm to 700 ppm or more, and often with a preferred range of 50-200 ppm. Friction modifiers of all types may be used alone or in mixtures with the materials of this disclosure. Often mixtures of two or more friction modifiers, or mixtures of friction modifier(s) with alternate surface-active material(s), are also desirable. For example, combinations of Mo-containing compounds with polyol fatty acid esters, such as glycerol mono-oleate are useful herein.

F. Pour Point Depressants

[0314] Conventional pour point depressants (also known as lube oil flow improvers) may be added to the compositions of the present disclosure if desired. These pour point depressants may be added to lubricating compositions of the present disclosure to lower the minimum temperature at which the fluid will flow or can be poured. Examples of suitable pour point depressants include polymethacrylates, polyacrylates, polyarylamides, condensation products of haloparaffin waxes and aromatic compounds, vinyl carboxylate polymers, and terpolymers of dialkylfumarates, vinyl esters of fatty acids and allyl vinyl ethers. US Patent Nos. 1,815,022; 2,015,748; 2,191,498; 2,387,501; 2,655,479; 2,666,746; 2,721,877; 2,721,878; and 3,250,715 describe useful pour point depressants and/or the preparation thereof. Such additives may be used in an amount of about 0.01 to 5 mass%, preferably about 0.01 to 1.5 mass%, based upon the weight of the lubricating composition.

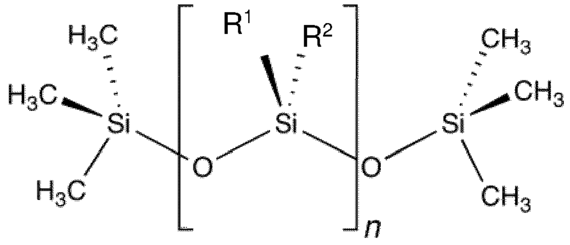
G. Anti-Foam Agents

[0315] Anti-foam agents may advantageously be added to lubricant compositions described herein. These agents prevent or retard the formation of stable foams. Silicones, fluoro-silicones, and/organic polymers are typical anti-foam agents. For example, polysiloxanes, such as silicon oil or polydimethyl siloxane, provide anti-foam properties.

[0316] Anti-foam agents are commercially available and may be used in minor amounts such as 5 mass% or less, 3 mass% or less, 1 mass% or less, 0.1 mass% or less, such as from 5 to mass% to 0.1 ppm such as from 3 mass% to 0.5 ppm, such as from 1 mass% to 10 ppm.

[0317] For example, it may be that the lubricating oil composition comprises an anti-foam agent comprising polyalkyl siloxane, such as a polydialkyl siloxane, for example, wherein the alkyl is a C_1-C_{10} alkyl group, *e.g.,* a polydimethylsiloxane (PDMS), also known as a silicone oil. Alternately, the siloxane is a poly(R^3)siloxane, wherein R^3 is one or more same or different linear branched or cyclic hydrocarbyls, such as alkyls or aryls, typically having 1 to 20 carbon atoms. It may be that, for example, the lubricating oil composition comprises a polymeric siloxane compound according to Formula 1 below wherein R^1 and R^2 are independently methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl or decyl, phenyl, naphthyl, alkyl substituted phenyl, or isomers thereof (such as methyl, phenyl) and n is from 2 to 1000, such as 50 to 450, alternately such as 40 to 100.

[0318] Additionally, or alternatively, it may be that the lubricating oil composition comprises an organo-modified siloxane (OMS), such as a siloxane modified with an organo group such as a polyether (*e.g.,* ethylene-propyleneoxide copolymer), long chain hydrocarbyl (*e.g.,* C_{11}-C_{100} alkyl), or aryl (*e.g.,* C_6-C_{14} aryl). It may be that, for example, the lubricating oil composition comprises an organo-modified siloxane compound according to Formula 1, wherein n is from 2 to 2000, such as 50 to 450 (alternately such as 40 to 100), and wherein R^1 and R^2 are the same or different, optionally wherein each of R^1 and R^2 is, independently an organo group, such as an organo group selected from polyether (e.g., ethylene-propylene-oxide copolymer), long chain hydrocarbyl *(e.g.,* C_{11}-C_{100} alkyl), or aryl (*e.g.,* C_6-C_{14} aryl). Preferably, one of R^1 and R^2 is CH_3.



Formula 1

[0319] Based on the total weight of the lubricant composition, the siloxane according to Formula 1 is incorporated so as to provide about 0.1 to less than about 30 ppm Si, or about 0.1 to about 25 ppm Si, or about 0.1 to about 20 ppm Si, or about 0.1 to about 15 ppm Si, or about 0.1 to about 10 ppm Si. More preferably, it is in the range of about 3-10 ppm Si.

[0320] In embodiments, silicone anti-foam agents useful herein are available from Dow Corning Corporation and Union Carbide Corporation, such as Dow Corning FS-1265 (1000 centistokes), Dow Corning DC-200, and Union Carbide UC-L45. Silicone anti-foamants useful herein include polydimethylsiloxane, phenyl-methyl polysiloxane, linear, cyclic or branched siloxanes, silicone polymers and copolymers, and/organo-silicone copolymers. Also, a siloxane polyether copolymer Anti-foamant available from OSI Specialties, Inc. of Farmington Hills, Michigan and may be substituted or included. One such material is sold as SILWET-L-7220.

[0321] Acrylate polymer anti-foam agent can also be used herein. Typical acrylate anti-foamants include polyacrylate anti-foamant available from Monsanto Polymer Products Co. known as PC-1244. A preferred acrylate polymer anti-foam agent useful herein is PX™3841 (*i.e.,* an alkyl acrylate polymer), commercially available from Dorf Ketl, also referred to as Mobilad™C402.

[0322] In embodiments, a combination of silicone anti-foamant and acrylate anti-foamant can be used, such as at a weight ratio of the silicone anti-foamant to the acrylate anti-foamant of from about 5:1 to about 1:5, see, for example, US Patent Application Publication No. 2021/0189283.

H. Viscosity Modifiers

[0323] Viscosity modifiers (also referred to as viscosity index improvers or viscosity improvers) can be included in the lubricating compositions described herein. Viscosity modifiers provide lubricants with high and low temperature operability. These additives impart shear stability at elevated temperatures and acceptable viscosity at low temperatures. Suitable viscosity modifiers include high molecular weight hydrocarbons, polyesters, and viscosity modifier dispersants (also referred to as a dispersant viscosity modifiers or DVMs) that can function as both a viscosity modifier and a dispersant. Typical molecular weights of the viscosity modifier polymers are between about 10,000 to 1,500,000 g/mol, more typically about 20,000 to 1,200,000 g/mol, and even more typically between about 50,000 and 1,000,000 g/mol.

[0324] Examples of suitable viscosity modifiers are linear or radial (star-shaped) polymers and copolymers of methacrylate, butadiene, olefins, or alkylated styrenes. Polyisobutylene is a commonly used viscosity modifier. Another suitable viscosity modifier is polymethacrylate (copolymers of various chain length alkyl methacrylates, for example), some formulations of which also serve as pour point depressants. Other suitable viscosity modifiers include copolymers of ethylene and propylene, hydrogenated block copolymers of styrene and isoprene, and polyacrylates (copolymers of various chain length acrylates, for example). Specific examples include styrene-isoprene or styrene-butadiene based polymers of 50,000 to 200,000 g/mol molecular weight.

[0325] Copolymers useful as viscosity modifiers include those commercially available from Chevron Oronite Company LLC under the trade designation "PARATONE™" (such as "PARATONE™ 8921", "PARATONE™ 68231", and "PARATONE™ 8941"); from Afton Chemical Corporation under the trade designation "HiTEC™" (such as HiTEC™ 5850B, and HiTEC™5777); and from The Lubrizol Corporation under the trade designation "Lubrizol™ 7067C". Hydrogenated polyisoprene radial (star) polymers useful as viscosity modifiers herein include those commercially available from Infineum International Limited, *e.g.,* under the trade designation "SV200™" and "SV600™". Hydrogenated diene-styrene block copolymers useful as viscosity modifiers herein are commercially available from Infineum International Limited, *e.g.,* under the trade designation "SV 50™".

[0326] Polymers useful as viscosity modifiers herein include polymethacrylate or polyacrylate polymers, such as linear polymethacrylate or polyacrylate polymers, such as those available from Evnoik Industries under the trade designation "Viscoplex™" (*e.g.,* Viscoplex™ 6-954) or star polymers which are available from Lubrizol Corporation under the trade designation Asteric™ (*e.g.,* Lubrizol™ 87708 and Lubrizol™ 87725).

[0327] Vinyl aromatic-containing polymers useful as viscosity modifiers herein may be derived from vinyl aromatic hydrocarbon monomers, such as styrenic monomers, such as styrene. Illustrative vinyl aromatic-containing copolymers useful herein may be represented by the following general formula: A-B wherein A is a polymeric block derived predominantly from vinyl aromatic hydrocarbon monomer (such as styrene), and B is a polymeric block derived predominantly from conjugated diene monomer (such as isoprene).

[0328] Vinyl aromatic-containing polymers useful as viscosity modifiers may have a Kinematic viscosity at 100° C of 20 cSt or less, such as 15 cSt or less, such as 12 cSt or less, but may be diluted (such as in Group I, II, and/or III basestock) to higher Kinematic viscosities at 100° C, such as to 40 cSt or more, such as 100 cSt or more, such as 1000 cSt or more, such as 1000 to 2000 cSt.).

[0329] Dispersant viscosity modifiers useful herein include the amide, imide, and/or ester functionalized partially or fully saturated polymer comprising C_{4-5} olefins as described in United States Serial number USSN 18/480,571, filed October 4, 2023 These DVM's (also referred to as "**functionalized polymer(s)**") are a functionalized hydrogenated polyisoprene family of polymers for use in lubricating oil compositions, which are disclosed in commonly owned United States Application 18/480,571, filed October 4, 2023 which claims priority to and the benefit of U.S. Provisional Application No. 63/379,006, filed October 11, 2022, which is herein incorporated by reference in its entirety. For the **functionalized polymer** family of polymers, Average Functionality [also referred to as Average Functionality Value (Fv)] and Functionality Distribution (Fd) value are determined by Gel Permeation Chromatography using polystyrene standards as described in the Experimental section of US Patent Application USSN 18/480,571, filed October 4, 2023 which claims priority to USSN 63/379,006.

[0330] Other useful DVM's include functionalized olefin copolymers (such as amine functionalized ethylene propylene copolymers).

[0331] Typically, the viscosity modifiers may be used in an amount of about 0.01 to about 10 mass%, such as about 0.1 to about 7 mass%, such as 0.1 to about 4 mass%, such as about 0.2 to about 2 mass%, such as about 0.2 to about 1 mass%, and such as about 0.2 to about 0.5 mass%, based on the total weight of the formulated lubricant composition.

[0332] Viscosity modifiers are typically added as concentrates, in large amounts of diluent oil. The "as delivered" viscosity modifier typically contains from 20 mass% to 75 mass% of an active polymer for polymethacrylate or polyacrylate polymers, or from 8 mass% to 20 mass% of an active polymer for olefin copolymers, hydrogenated polyisoprene star polymers, or hydrogenated diene-styrene block copolymers, in the "as delivered" polymer concentrate.

I. Dispersants

[0333] During engine operation, oil-insoluble oxidation byproducts are produced. Dispersants help keep these byproducts in solution, thus diminishing their deposition on metal surfaces. Dispersants used in the formulation of the lubricating compositions herein may be ashless or ash-forming in nature. Preferably, the dispersant is ashless. So called ashless dispersants are organic materials that form substantially no ash upon combustion. For example, non-metal-containing or borated metal-free dispersants are considered ashless. In contrast, metal-containing detergents tend to form ash upon combustion.

[0334] Dispersants useful herein typically contain a polar group attached to a relatively high molecular weight hydrocarbon chain. The polar group typically contains at least one element of nitrogen, oxygen, or phosphorus. Typical hydrocarbon chains contain 40 to 500, such as 50 to 400 carbon atoms. When used in context of functionalized polymers operating as dispersants, the molecular weights are typically reported in terms of the base polymer prior to modification. For example PIBSA-PAM dispersant molecular weights are typically reported for the base polymer prior to functionalization with the acylating agent (maleic acid or anhydride) and functional group (such as polyamine).

Dispersants of (Poly)alkenylsuccinic derivatives

[0335] A particularly useful class of dispersants includes the (poly)alkenylsuccinic derivatives, typically produced by the reaction of a long chain hydrocarbyl-substituted succinic compound, usually a hydrocarbyl-substituted succinic anhydride, with a polyhydroxy or polyamino compound. The long chain hydrocarbyl group constituting the oleophilic portion of the molecule which confers solubility in the oil, is often a polyisobutylene group (typically the long chain hydrocarbyl group, such as a polyisobutylene group, has an Mn of 400 to 3000 g/mol, such as 450 to 2500 g/mol). Many examples of this type of dispersant are well known commercially and in the literature. Exemplary US Patents describing such dispersants include US PatentNos. 3,172,892; 3,2145,707; 3,219,666; 3,316,177; 3,341,542; 3,444,170; 3,454,607; 3,541,012; 3,630,904; 3,632,511; 3,787,374 and 4,234,435. Other types of dispersants are described in US Patent Nos. 3,036,003; 3,200,107; 3,254,025; 3,275,554; 3,438,757; 3,454,555; 3,565,804; 3,413,347; 3,697,574; 3,725,277; 3,725,480; 3,726,882; 4,454,059; 3,329,658; 3,449,250; 3,519,565; 3,666,730; 3,687,849; 3,702,300; 4,100,082; 5,705,458. A further description of dispersants useful herein may be found, for example, in European Patent Applications Nos. 0 471 071 and 0 451 380, to which reference is made for this purpose.

[0336] Hydrocarbyl-substituted succinic acid and hydrocarbyl-substituted succinic anhydride derivatives are useful dispersants. In particular, succinimide, succinate esters, or succinate ester amides prepared by the reaction of a hydrocarbon-substituted succinic acid or anhydride compound (typically having at least 25 carbon atoms, such as 28 to 400 carbon atoms, in the hydrocarbon substituent), with at least one equivalent of a polyhydroxy or polyamino compound (such as an alkylene amine) are particularly useful herein. Hydrocarbyl-substituted succinic acid and hydrocarbyl-substituted succinic anhydride derivatives may have a number average molecular weight of at least 400 g/mol, such as at least 900 g/mol, such as at least 1500 g/mol, such as from 400 to 4000 g/mol, such as from 800 to 3000, such as from 2000 to 2800 g/mol, such from about 2100 to 2500 g/mol, and such as from about 2200 to about 2400 g/mol.

[0337] Succinimides, which are particularly useful herein, are formed by the condensation reaction between: 1) hydrocarbyl-substituted succinic anhydrides, such as polyisobutylene succinic anhydride (PIBSA); and 2) polyamine (PAM). Examples of suitable polyamines include: polyhydrocarbyl polyamines, polyalkylene polyamines, hydroxy-substituted polyamines, polyoxyalkylene polyamines, and combinations thereof. Examples of polyamines include tetraethylene pentamine, pentaethylene hexamine, tetraethylenepentamine (TEPA), pentaethylenehaxamine (PEHA), N-phenyl-p-phenylenediamine (ADPA), and other polyamines having an average of 5, 6, 7, 8, or 9 nitrogen atoms per molecule. Mixtures where the average number of nitrogen atoms per polyamine molecule is greater than 7 are commonly called heavy polyamines or H-PAMs and may be commercially available under trade names such as HPA™ and HPA-X™ from DowChemical, E-100™ from Huntsman Chemical, et al. Examples of hydroxy-substituted polyamines include N-hydroxyalkyl-alkylene polyamines such as N-(2-hydroxyethyl)ethylene diamine, N-(2-hydroxyethyl)piperazine, and/or N-hydroxyalkylated alkylene diamines of the type described, for example, in US Patent No. 4,873,009. Examples of polyoxyalkylene polyamines include polyoxyethylene and/or polyoxypropylene diamines and triamines (as well as co-oligomers thereof) having an average Mn from about 200 to about 5000 g/mol. Products of this type are commercially available under the tradename Jeffamine™. Representative examples of useful succinimides are shown in US Patent Nos. 3,087,936; 3,172,892; 3,219,666; 3,272,746; 3,322,670; 3,652,616; 3,948,800; and 6,821,307; and CA Patent No. 1,094,044.

[0338] The dispersants may comprise one or more, optionally borated, higher molecular weight (Mn 1600 g/mol or more, such as 1800 to 3000 g/mol) succinimides and one or more, optionally borated, lower molecular weight (Mn less than 1600 g/mol) succinimides, where the higher molecular weight may be 1600 to 3000 g/mol, such as 1700 to 2800 g/mol, such as 1800 to 2500 g/mol, such as 1850 to 2300 g/mol; and the lower molecular weight may be 600 to less than 1600 g/mol, such as 650 to 1500 g/mol, such as 700 to 1400 g/mol, such as 800 to 1300 g/mol, such as 850 to 1200 g/mol such as 900 to 1150 g/mol, such as 900 to 1000 g/mol. The higher molecular weight succinimide dispersant may be present in the lubricating composition in an amount of from 0.5 to 10 mass%, or from 0.8 to 6 mass%, or from 1.0 to 5 mass%, or from 1.5 to 5 mass%, or from 1.5 to 4.0 mass%; and the lower molecular weight succinimides dispersant may be present in the lubricating composition in an amount of from 1 to 5 mass%, or from 1.5 to 4.8 mass%, or from 1.8 to 4.6 mass%, or from 1.9 to 4.6 mass%, or at 2 mass% or more, such as 2 to 5 mass%. The lower molecular weight succinimides may differ from the higher molecular weight succinimides, by 500 g/mol or more, such as by 750 g/mol or more, such as by 1000 g/mol or more, such as by 1200 g/mol or more, such as by 500 to 3000 g/mol, such as by 750 to 2000 g/mol, such as by 1000 to 1500 g/mol.

[0339] Succinate esters useful as dispersants include those formed by the condensation reaction between hydrocarbyl-substituted succinic anhydrides and alcohols or polyols. For example, the condensation product of a hydrocarbyl-substituted succinic anhydride and pentaerythritol is a useful dispersant.

[0340] Succinate ester amides useful herein are formed by a condensation reaction between hydrocarbyl-substituted succinic anhydrides and alkanol amines. Suitable alkanol amines include ethoxylated polyalkylpolyamines, propoxylated polyalkylpolyamines, and polyalkenylpolyamines such as polyethylene polyamines and/or propoxylated hexamethylenediamine. Representative examples are shown in US Patent No. 4,426,305.

[0341] Hydrocarbyl-substituted succinic anhydrides (such as PIBSA) esters of hydrocarbyl bridged aryloxy alcohols are also useful as dispersants herein. For information on such dispersants, please see US Patent No. 7,485,603, particularly, col 2, ln 65 to col 6, ln 22 and col 23, ln 40 to col 26, ln 46. In particular, PIBSA esters of methylene-bridged naphthyloxy ethanol (*i.e.,* 2-hydroxyethyl-1-naphthol ether (or hydroxy-terminated ethylene oxide oligomer ether of naphthol) are useful herein.

[0342] The molecular weight of the hydrocarbyl-substituted succinic anhydrides used in the preceding paragraphs will typically range from 350 to 4000 g/mol, such as 400 to 3000 g/mol, such as 450 to 2800 g/mol, such as 800 to 2500 g/mol. The above (poly)alkenylsuccinic derivatives can be post-reacted with various reagents such as sulfur, oxygen, formaldehyde, carboxylic acids such as oleic acid.

[0343] The dispersants may be present in the lubricant in an amount 0.1 mass% to 20 mass% of the composition, such as 0.2 to 15 mass%, such as 0.25 to 10 mass%, such as 0.3 to 5 mass%, such as 1.0 mass% to 3.0 mass%, of the lubricating oil composition.

[0344] The above (poly)alkenylsuccinic derivatives, can also be post reacted with boron compounds such as boric acid, borate esters or highly borated dispersants, to form borated dispersants generally having from about 0.1 to about 5 moles of boron per mole of dispersant reaction product.

[0345] Dispersants useful herein include borated succinimides, including those derivatives from mono-succinimides, bis-succinimides, and/or mixtures of mono- and bis-succinimides, wherein the hydrocarbyl succinimide is derived from a hydrocarbylene group such as polyisobutylene having an Mn of from about 300 to about 5000 g/mol, or from about 500 to about 3000 g/mol, or about 1000 to about 2000 g/mol, or a mixture of such hydrocarbylene groups, often with high terminal vinylic groups.

[0346] The boron-containing dispersant may be present at 0.01 mass% to 20 mass%, or 0.1 mass% to 15 mass%, or 0.1 mass% to 10 mass%, or 0.5 mass% to 8 mass%, or 1.0 mass% to 6.5 mass%, or 0.5 mass% to 2.2 mass% of the lubricating composition.

[0347] The boron-containing dispersant may be present in an amount to deliver boron to the composition at 15 ppm to 2000 ppm, or 25 ppm to 1000 ppm, or 40 ppm to 600 ppm, or 80 ppm to 350 ppm.

[0348] The borated dispersant may be used in combination with non-borated dispersant and may be the same or different compound as the non-borated dispersant. In one embodiment, the lubricating composition may include one or more boron-containing dispersants and one or more non-borated dispersants, wherein the total amount of dispersant may be 0.01 mass% to 20 mass%, or 0.1 mass% to 15 mass%, or 0.1 mass% to 10 mass%, or 0.5 mass% to 8 mass%, or 1.0 mass% to 6.5 mass%, or 0.5 mass% to 2.2 mass% of the lubricating composition and wherein the ratio of borated dispersant to non-boroated dispersant may be 1:10 to 10:1 (weight:weight) or 1:5 to 3:1 or 1:3 to 2:1.

[0349] The borated dispersant may be used in combination with non-borated dispersant and may be a different compound as the non-borated dispersant. In one embodiment, the lubricating composition may include one or more boron-containing dispersants derived from polyisobutylene having an Mn lower (such as 1200 g/mol or less, such as 1100 g/mol or less, such as 1000 g/mol or less such as 900 g/mol or less) than the Mn of polyiosobutylene (such as 1300 g/mol or more, such as 1500 g/mol or more, such as 2000 g/mol or more, such as 2500 g/mol or more, such as 3000 g/mol or more) used to prepare one or more non-borated dispersants, wherein the total amount of dispersant may be 0.01 mass% to 20 mass%, or 0.1 mass% to 15 mass%, or 0.1 mass% to 10 mass%, or 0.5 mass% to 8 mass%, or 1.0 mass% to 6.5 mass%, or 0.5 mass% to 2.2 mass% of the lubricating composition and wherein the ratio of borated dispersant to non-borated dispersant may be 1:10 to 10:1 (weight:weight) or 1:5 to 3:1 or 1:3 to 2:1.

[0350] The dispersant may comprise one or more borated or unborated poly(alkenyl)succinimides, where the poly-alkyenyl is derived from polyisobutylene and the imide is derived from a polyamine ("PIBSA-PAM").

[0351] The dispersant may comprise one or more PIBSA-PAMs, where the PIB is derived from polyisobutylene having an Mn of from 600 to 5000, such as from 700 to 4000, such as from 800 to 3000, such as from 900 to 2500 g/mol, such as 600 to less than 1600 g/mol and the polyamine is derived from hydrocarbyl-substituted polyamines, such as tetraethylene pentamine, pentaethylene hexamine, tetraethylenepentamine (TEPA), pentaethylenehaxamine (PEHA), N-phenyl-p-phenylenediamine (ADPA), and other polyamines having an average of 5, 6, 7, 8, or 9 nitrogen atoms per molecule). The dispersant may be borated, typically at levels of up to 4 mass% such as from 1 to 3 mass%. For purposes of this invention ant the claims thereto, when a polyisobutylene polymer (PIB) derived dispersant (such as PIBSA-PAM) is referred to as having a specific Mn, that Mn refers to the Mn of the PIB that the PIB derived dispersant (such as PIBSA-PAM) was derived from. Unless otherwise indicated, the Mn of polyisobutylene is determined by Gel Permeation Chromatography-Size Exclusion Chromatography, equipped with a differential refractive index (DRI) detector and three Mixed D PL gel columns (300mm x7.5mm) containing 5 μm particle size gel, calibrated using polystyrene standards correlated to PIB samples of known molecular weight.

[0352] The dispersant may comprise one or more borated and one or more non-borated PIBSA-PAM's.

[0353] In embodiments, the dispersant may be one or more optionally borated lower Mn dispersant (such as PIBSA-PAM dispersant derived from a PIB having an Mn of less than 1600 g/mol, such as 600 to less than 1600 g/mol, such as 650 to 1500 g/mol, such as 700 to 1400 g/mol, such as 800 to 1300 g/mol, such as 850 to 1200 g/mol, such as 900 to 1150 g/mol, such as 900 to 1000 g/mol, where the PAM may optionally be TEPA, PEHA, and or ADPA). The optionally borated lower molecular weight dispersant(s) may be present in a lubricating oil composition in an amount of from 0.5 to 10 mass%, or from 0.8 to 6 mass%, or from 1.0 to 5 mass%, or from 1.5 to 5 mass% or from 1.5 to 4.0 mass% or from 1.5 to 4.8 mass%, or at 2 mass% or more, such as 2 to 5 mass%, based upon the weight of the lubricating oil composition.

[0354] The dispersant may comprise one or more borated PIBSA-PAM's derived from a PIB having an Mn of 700 to 1800 g/mol (such as 800 to 1500 g/mol) and one or more non-borated PIBSA-PAM's derived from a PIB having an Mn of more than 1800 to 5000 g/mol (such as 2000 to 3000 g/mol). The dispersant may comprise one or more non-borated PIBSA-PAM's derived from a PIB having an Mn of 700 to 1800 g/mol (such as 800 to 1500 g/mol) and one or more borated PIBSA-PAM's derived from a PIB having an Mn of more than 1800 to 5000 g/mol (such as 2000 to 3000 g/mol).

[0355] The dispersant may comprise PIBSA derived from a PIB having an Mn of 700 to 5000 g/mol (such as 800 to 3000 g/mol) and one or more borated or non-borated PIBSA-PAM's derived from a PIB having an Mn of 700 to 5000 g/mol.

[0356] The dispersant may comprise PIBSA derived from a PIB having an Mn of 700 to 5000 g/mol (such as 800 to 3000 g/mol) and one or more borated PIBSA-PAM's derived from a PIB having an Mn of 700 to 1800 g/mol (such as 800 to 1500 g/mol) and one or more non-borated PIBSA-PAM's derived from a PIB having an Mn of more than 1800 to 5000 g/mol (such as 2000 to 3000 g/mol). The dispersant may comprise PIBSA derived from a PIB having an Mn of 700 to 5000 g/mol (such as 800 to 3000 g/mol) one or more non-borated PIBSA-PAM's derived from a PIB having an Mn of 700 to 1800 g/mol (such as 800 to 1500 g/mol) and one or more borated PIBSA-PAM's derived from a PIB having an Mn of more than 1800 to 5000 g/mol (such as 2000 to 3000 g/mol).

[0357] The dispersant may comprise one or more borated or non-borated PIBSA-PAM's and one or more PIBSA-esters of hydrocarbyl bridged aryloxy alcohols.

[0358] The dispersant may comprise one or more borated and one or more non-borated PIBSA-PAM's.

[0359] The dispersant may comprise one or more, optionally borated, higher molecular weight (Mn 1600 g/mol or more, such as 1800 to 3000 g/mol) PIBSA-PAM's and one or more, optionally borated, lower molecular weight (Mn less than 1600 g/mol) PIBSA-PAM's, where the higher molecular weight may be 1600 to 3000 g/mol, such as 1700 to 2800 g/mol, such as 1800 to 2500 g/mol, such as 1850 to 2300 g/mol; and the lower molecular weight may be 600 to less than 1600 g/mol, such as 650 to 1500 g/mol, such as 700 to 1400 g/mol, such as 800 to 1300 g/mol, such as 850 to 1200 g/mol, such as 900 to 1150 g/mol, such as 900 to 100 g/mol. The higher molecular weight PIBSA-PAM dispersant may be present in the lubricating composition in an amount of from 0.5 to 10 mass%, or from 0.8 to 6 mass%, or from 1.0 to 5 mass%, or from 1.5 to 5 mass% or from 1.5 to 4.0 mass%; and the lower molecular weight PIBSA-PAM dispersant may be present in the lubricating composition in an amount of from 1 to 5 mass%, or from 1.5 to 4.8 mass%, or from 1.8 to 4.6 mass%, or from 1.9 to 4.6 mass%, or at 2 mass% or more, such as 2 to 5 mass%.

Dispersants of Mannich Bases

[0360] Mannich base dispersants useful herein are typically made from the reaction of an amine component, a hydroxy aromatic compound (substituted or unsubstituted, such as alkyl substituted), such as alkylphenols, and an aldehyde, such as formaldehyde. See US Patent Nos. 4,767,551 and 10,899,986. Process aids and catalysts, such as oleic acid and sulfonic acids, can also be part of the reaction mixture. Representative examples are shown in US Patent Nos. 3,697,574; 3,703,536; 3,704,308; 3,751,365; 3,756,953; 3,798,165; 3,803,039; 4,231,759; 9,938,479; 7,491,248; and 10,899,986, and PCT Publication No. WO 01/42399.

Dispersants of Polymethacrylate or Polyacrylate Derivatives

[0361] Polymethacrylate or polyacrylate derivatives are another class of dispersants useful herein. These dispersants are typically prepared by reacting a nitrogen-containing monomer and a methacrylic or acrylic acid esters containing 5-25 carbon atoms in the ester group. Representative examples are shown in US Patent Nos. 2,100,993, and 6,323,164. Polymethacrylate and polyacrylate dispersants are typically lower molecular weights.

[0362] The lubricating composition of the disclosure typically comprises dispersant at 0.1 mass% to 20 mass% of the composition, such as 0.2 to 15 mass%, such as 0.25 to 10 mass%, such as 0.3 to 5 mass%, such as 2.0 mass% to 4.0 mass% of the lubricating oil composition. Alternately the dispersant may be present at 0.1 mass% to 5 mass%, or 0.01 mass% to 4 mass% of the lubricating composition.

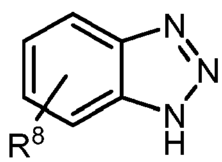
[0363] For further information on dispersants useful herein, please see US Patent No. 10,829,712, col 13, ln 36 to col 16, ln 67 and US Patent No. 7,485,603, col 2, ln 65 to col 6, ln 22, col 8, ln 25 to col 14, ln 53, and col 23, ln 40 to col 26, ln 46.

[0364] Compositions according to the present disclosure may contain an additive having a different enumerated function that also has secondary effects as a dispersant. These additives are not included as dispersants for purposes of determining the amount of dispersant in a lubricating oil composition or concentrate herein.

J. Corrosion Inhibitors/Anti-rust Agents

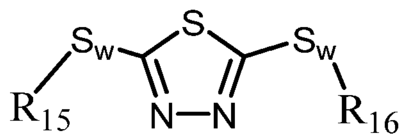
[0365] Corrosion inhibitors may be used to reduce the corrosion of metals and are often alternatively referred to as metal deactivators or metal passivators. Some corrosion inhibitors may alternatively be characterized as antioxidants.

[0366] Suitable corrosion inhibitors may include nitrogen and/or sulfur-containing heterocyclic compounds such as triazoles (*e.g.,* benzotriazoles), substituted thiadiazoles, imidazoles, thiazoles, tetrazoles, hydroxyquinolines, oxazolines, imidazolines, thiophenes, indoles, indazoles, quinolines, benzoxazines, dithiols, oxazoles, oxatriazoles, pyridines, piperazines, triazines and derivatives of any one or more thereof. A particular corrosion inhibitor is a benzotriazole represented by the structure:



wherein R_8 is absent (hydrogen) or is a C_1 to C_{20} hydrocarbyl or substituted hydrocarbyl group which may be linear or branched, saturated or unsaturated. It may contain ring structures that are alkyl or aromatic in nature and/or contain heteroatoms such as N, O, or S. Examples of suitable compounds may include benzotriazole, alkyl-substituted benzotriazoles (e.g., tolyltriazole, ethylbenzotriazole, hexylbenzotriazole, octylbenzotriazole, etc.), aryl substituted benzotriazole, alkylaryl- or arylalkyl-substituted benzotriazoles, and the like, as well as combinations thereof. For instance, the triazole may comprise or be a benzotriazole and/or an alkylbenzotriazole in which the alkyl group contains from 1 to about 20 carbon atoms or from 1 to about 8 carbon atoms. Non-limiting examples of such corrosion inhibitors may comprise or be benzotriazole, triazoles such as tolyltriazole, and/or optionally, substituted benzotriazoles, such as Irgamet™ 30 and Irgamet™ 39, which are commercially available from BASF of Ludwigshafen, Germany. A preferred corrosion inhibitor may comprise or be benzotriazole and/or tolyltriazole. A preferred corrosion inhibitor may comprise or be 1H-1,2,4-triazole-1-methanamine, N,N-bis(2-ethylhexyl) and or 1H-benzotriazole-1-methanamine, N,N-bis(2-ethylhexyl)-4-methyl).

[0367] Additionally, or alternatively, the corrosion inhibitor may include one or more substituted thiadiazoles represented by the structure:



wherein R_{15} and R_{16} are independently hydrogen or a hydrocarbon group, which group may be aliphatic or aromatic, including cyclic, alicyclic, aralkyl, aryl and alkaryl, and wherein each w is independently 1, 2, 3, 4, 5, or 6 (preferably 2, 3, or 4, such as 2). These substituted thiadiazoles are derived from the 2,5-dimercapto-1,3,4-thiadiazole (DMTD) molecule. Many derivatives of DMTD have been described in the art, and any such compounds may be included in the fluid used in the present disclosure. For example, US Patent Nos. 2,719,125; 2,719,126; and 3,087,937; describe the preparation of various 2, 5-bis-(hydrocarbon dithio)-1,3,4-thiadiazoles.

[0368] Further, additionally or alternatively, the corrosion inhibitor may include one or more other derivatives of DMTD, such as a carboxylic ester in which R_{15} and R_{16} may be joined to the sulfide sulfur atom through a carbonyl group. Preparation of these thioester-containing DMTD derivatives is described, for example, in US Patent No. 2,760,933. DMTD derivatives produced by condensation of DMTD with alpha-halogenated aliphatic carboxylic acids having at least 10 carbon atoms are described, for example, in US Patent No. 2,836,564. This process produces DMTD derivatives wherein R_{15} and R_{16} are HOOC-CH(R_{19})-(R_{19} being a hydrocarbyl group). DMTD derivatives further produced by amidation or esterification of these terminal carboxylic acid groups may also be useful.

[0369] The preparation of 2-hydrocarbyldithio-5-mercapto-1,3,4-thiadiazoles is described, for example, in US Patent No. 3,663,561.

[0370] A class of DMTD derivatives may include mixtures of a 2-hydrocarbyldithio-5-mercapto-1,3,4-thiadiazole and a 2,5-bis-hydrocarbyldithio-1,3,4-thiadiazole. Such mixtures may be sold under the tradename HiTEC™ 4313 and are commercially available from Afton Chemical Company.

[0371] The preparation of 2-hydrocarbyldithio-5-mercapto-1,3,4-thiadiazoles is described, for example, in US Patent No. 3,663,561.

[0372] Still further, additionally or alternatively, the corrosion inhibitor may include a trifunctional borate having the structure, $B(OR_{46})_3$, in which each R_{46} may be the same or different. As the borate may typically be desirably compatible with the non-aqueous medium of the composition, each R_{46} may, in particular, comprise or be a hydrocarbyl C_1-C_8 moiety. For compositions in which the non-aqueous medium comprises or is a lubricating oil basestock, for example, better compatibility can typically be achieved when the hydrocarbyl moieties are each at least C_4. Non-limiting examples of such corrosion inhibitors thus include, but are not limited to, triethylborate, tripropylborates such as triisopropylborate, tributylborates such as tri-tert-butylborate, tripentylborates, trihexylborates, trioctylborates such as tri-(2-ethylhexyl) borate, monohexyl dibutylborate, and the like, as well as combinations thereof.

[0373] When used, a corrosion inhibitor may comprise a substituted thiadiazole, a substituted benzotriazole, a substituted triazole, a trisubstituted borate, or a combination thereof.

[0374] When desired, corrosion inhibitors can be used in any effective amount, but, when used, may typically be used in amounts from about 0.001 mass% to 5.0 mass%, based on the weight of the composition, *e.g.,* from 0.005 mass% to 3.0 mass% or from 0.01 mass% to 1.0 mass%. Alternately, such additives may be used in an amount of about 0.01 to 5 mass%, preferably about 0.01 to 1.5 mass%, based upon the weight of the lubricating composition.

[0375] In some embodiments, 3,4-oxypyridinone-containing compositions may contain substantially no (*e.g.,* 0, or less than 0.001 mass%, 0.0005 mass% or less, not intentionally added, and/or absolutely no) triazoles, benzotriazoles, substituted thiadiazoles, imidazoles, thiazoles, tetrazoles, hydroxyquinolines, oxazolines, imidazolines, thiophenes, indoles, indazoles, quinolines, benzoxazines, dithiols, oxazoles, oxatriazoles, pyridines, piperazines, triazines, derivatives thereof, combinations thereof, or all corrosion inhibitors.

[0376] Compositions according to the present disclosure may contain an additive having a different enumerated function that also has secondary effects as a corrosion inhibitor (for example, Component B, may also have corrosion inhibitor effects). These additives are not included as corrosion inhibitor for purposes of determining the amount of corrosion inhibitor in a lubricating oil composition or concentrate herein.

K. Antiwear Agents

[0377] The lubricating oil composition of the present disclosure can contain one or more antiwear agents that can reduce friction and excessive wear. Any antiwear agent known by a person of ordinary skill in the art may be used in the lubricating oil composition. Non-limiting examples of suitable antiwear agents include zinc dithiophosphate, metal (*e.g.,* Pb, Sb, Mo, and the like) salts of dithiophosphates, metal (*e.g.,* Zn, Pb, Sb, Mo, and the like), salts of dithiocarbamates, metal (*e.g.,* Zn, Pb, Sb, and the like) salts of fatty acids, boron compounds, phosphate esters, phosphite esters, amine salts of phosphoric acid esters or thiophosphoric acid esters, reaction products of dicyclopentadiene and thiophosphoric acids and combinations thereof. The amount of the antiwear agent may vary from about 0.01 mass% to about 5 mass%, from about 0.05 mass% to about 3 mass%, or from about 0.1 mass% to about 1 mass%, based on the total weight of the lubricating oil composition.

[0378] In embodiments, the antiwear agent is or comprises a dihydrocarbyl dithiophosphate metal salt, such as zinc dialkyl dithiophosphate compounds. The metal of the dihydrocarbyl dithiophosphate metal salt may be an alkali or alkaline earth metal, or aluminum, lead, tin, molybdenum, manganese, nickel, or copper. In some embodiments, the metal is zinc. In other embodiments, the alkyl group of the dihydrocarbyl dithiophosphate metal salt has from about 3 to about 22 carbon atoms, from about 3 to about 18 carbon atoms, from about 3 to about 12 carbon atoms, or from about 3 to about 8 carbon atoms. In further embodiments, the alkyl group is linear or branched.

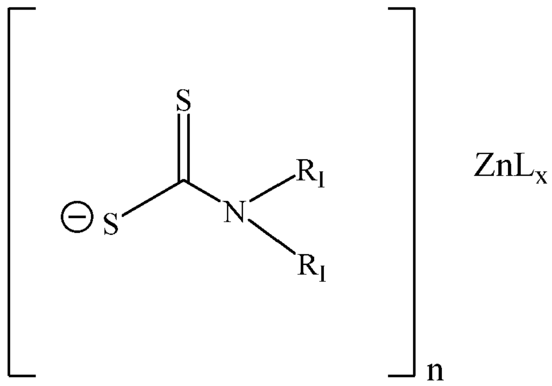
[0379] Useful antiwear agents also include substituted or unsubstituted thiophosphoric acids, and salts thereof include zinc-containing compounds such as zinc dithiophosphate compounds selected from zinc dialkyl-, diaryl- and/or alkylaryl-dithiophosphates.

[0380] A metal alkylthiophosphate and more particularly a metal dialkyl dithio phosphate in which the metal constituent is zinc, or zinc dialkyl dithio phosphate (ZDDP) can be a useful component of the lubricating compositions of this disclosure. ZDDP can be derived from primary alcohols, secondary alcohols or mixtures thereof. ZDDP compounds generally are of the formula $Zn[SP(S)(OR_1)(OR_2)]_2$ where R^1 and R^2 are C_1-C_{18} alkyl groups, preferably C_2-C_{12} alkyl groups. These alkyl groups may be straight chain or branched. Alcohols used in the ZDDP can be 2-propanol, butanol, secondary butanol, pentanols, hexanols such as 4-methyl-2-pentanol, n-hexanol, n-octanol, 2-ethyl hexanol, alkylated phenols, and the like. Mixtures of secondary alcohols or of primary and secondary alcohol can be used. Alkyl aryl groups may also be used.

[0381] Zinc-based antiwear agents useful in compositions described herein, and in any embodiment, include compounds such as zinc dialkyldithiophosphate, where the alkyl groups are derived from one or more primary alcohols, one or more secondary alcohols or combinations of primary and secondary alcohols. Typically, the alcohols are mono-alcohols represented by the formula R-alkyl, where the alkyls are selected from C_4 to C_{30} alkyl groups, and may be combinations of alkyl groups selected from butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, icosyl, triacontyl or isomers thereof). Useful ZDDP's include one or more ZDDP's (such as ZDDP's derived from desirable alcohols or combination of alcohols, such as primary and or secondary alcohols, such as iso-octanol and/or 4-methyl-pentan-2-ol and/or 2-butanol) to the compositions herein can improve fuel economy, while maintaining good viscosity control.

[0382] Useful zinc dithiophosphates include secondary zinc dithiophosphates such as those available from The Lubrizol Corporation under the trade designations "LZ™ 677A", "LZ™ 1095" and "L™Z 1371", from Chevron Oronite under the trade designation "OLOA™ 262" and from Afton Chemical under the trade designation "HiTEC™ 7169".

[0383] In embodiments, the zinc compound can be a zinc dithiocarbamate complex, such as the zinc dithiocarbamates represented by the formula:



where each R_I is independently a linear, cyclic, or branched, saturated or unsaturated, aliphatic hydrocarbon moiety having from 1 to about 10 carbon atoms, n is 0, 1, or 2, L is a ligand that saturates the coordination sphere of zinc, and x is 0, 1, 2, 3, or 4. In certain embodiments, the ligand, L, is selected from the group consisting of water, hydroxide, ammonia, amino, amido, alkylthiolate, halide, and combinations thereof.

[0384] The antiwear additives, such as ZDDP and/or the zinc carbamates, are typically used in amounts of from about 0.4 mass% to about 1.2 mass%, preferably from about 0.5 mass% to about 1.0 mass%, and more preferably from about 0.6 mass% to about 0.8 mass%, based on the total weight of the lubricating composition, although more or less can often be used advantageously. Preferably, the antiwear additive is ZDDP, preferably a secondary ZDDP, and is present in an amount of from about 0.6 to 1.0 mass% of the total weight of the lubricating composition.

[0385] Antiwear additives useful herein also include boron-containing compounds, such as borate esters, borated fatty amines, borated epoxides, alkali metal (or mixed alkali metal or alkaline earth metal) borates and borated overbased metal salts.

[0386] Compositions according to the present disclosure may contain an additive having a different enumerated function that also has secondary effects as an antiwear agent (for example, Component B described above, may also have antiwear effects). These additives are not included as antiwear agents for purposes of determining the amount of antiwear agents in a lubricating oil composition or concentrate herein.

L. Demulsifiers

[0387] Demulsifiers useful herein include those described in US Patent No. 10,829,712 (col 20, ln 34-40). Typically, a small amount of a demulsifying component may be used herein. A preferred demulsifying component is described in European Patent No. 330 522. It is obtained by reacting an alkylene oxide with an adduct obtained by reacting a bis-epoxide with a polyhydric alcohol. Such additives may be used in an amount of about 0.001 to 5 mass%, preferably about 0.01 to 2 mass%.

M. Seal Compatibility Agents

[0388] Other optional additives include seal compatibility agents such as organic phosphates, aromatic esters, aromatic hydrocarbons, esters (butylbenzyl phthalate, for example), and polybutenyl succinic anhydride. Such additives may be used in an amount of about 0.001 to 5 mass%, preferably about 0.01 to 2 mass%. In embodiments the seal compatibility agents are sea swell agents, such as PIBSA (polyisobutenyl succinic anhydride).

N. Extreme Pressure Agents

[0389] The lubricating oil composition of the present disclosure can contain one or more extreme pressure agents that can prevent sliding metal surfaces from seizing under conditions of extreme pressure. Any extreme pressure agent known by a person of ordinary skill in the art may be used in the lubricating oil composition. Generally, the extreme pressure agent is a compound that can combine chemically with a metal to form a surface film that prevents the welding of asperities in opposing metal surfaces under high loads. Non-limiting examples of suitable extreme pressure agents include sulfurized animal or vegetable fats or oils, sulfurized animal or vegetable fatty acid esters, fully or partially esterified esters of trivalent or pentavalent acids of phosphorus, sulfurized olefins, dihydrocarbyl polysulfides, sulfurized Diels-Alder adducts, sulfurized dicyclopentadiene, sulfurized or co-sulfurized mixtures of fatty acid esters and monounsaturated olefins, co-sulfurized blends of fatty acid, fatty acid ester and alpha-olefin, functionally substituted dihydrocarbyl polysulfides, thia-aldehydes, thia-ketones, epithio compounds, sulfur-containing acetal derivatives, co-sulfurized blends of terpene and acyclic olefins, and poly sulfide olefin products, amine salts of phosphoric acid esters or thiophosphoric acid esters, and combinations thereof. The amount of the extreme pressure agent may vary from about 0.01 mass% to about 5 mass%, from about 0.05 mass% to about 3 mass%, or from about 0.1 mass% to about 1 mass%, based on the total weight of the lubricating oil composition.

O. Non-basestock Unsaturated Hydrocarbons

[0390] The lubricating oil composition of the present disclosure can contain one or more unsaturated hydrocarbons. These unsaturated hydrocarbons are distinct from any baseoils (lubricating oil basestocks of Group I, II, III, IV and/or V) and/or viscosity modifiers that may be present in the compositions and always have at least one (and typically only one, in the case of linear alpha-olefins, or LAOs) unsaturation per molecule. Without being bound by theory, the unsaturation(s) may provide an antioxidation functionality and/or a sulfur-trapping functionality that may supplement and/or replace one or more antioxidant additives and/or one or more corrosion inhibitor additives, but unsaturated hydrocarbons (LAOs) will typically not provide the only antioxidant nor the only corrosion inhibition functionality in lubrication oil compositions. Non-limiting examples of unsaturated hydrocarbons can include one or more unsaturated C_{12}-C_{60} hydrocarbons (such as C_{12}-C_{48} hydrocarbons, C_{12}-C_{36} hydrocarbons, C_{12}-C_{30} hydrocarbons, or C_{12}-C_{24} hydrocarbons). When only one unsaturation is present, the unsaturated hydrocarbons may be termed linear alpha-olefins (LAOs). Other non-limiting examples of unsaturated hydrocarbons can include oligomers/polymers of polyisobutylenes that have retained (or been post-polymerization modified to exhibit) a (near-) terminal unsaturation, and/or blends thereof. When present, unsaturated hydrocarbons (LAOs) may be present from 0.01 to 5 mass% (in particular, 0.1 to 3 mass%, alternately 0.1 to 1.5 mass%), based on total weight of the lubricating oil composition.

[0391] When lubricating oil compositions contain one or more of the additives discussed above, the additive(s) are typically blended into the composition in an amount sufficient for it to perform its intended function. Typical amounts of such additives useful in the present disclosure, especially for use in crankcase lubricants, are shown in the Table below.

[0392] It is noted that many of the additives are shipped from the additive manufacturer as a concentrate, containing one or more additives together, with a certain amount of base oil or other diluents. Accordingly, the weight amounts in the table below, as well as other amounts mentioned herein, are directed to the amount of active ingredient (that is the non-diluent portion of the ingredient). The weight percent (mass%) indicated below is based on the total weight of the lubricating oil composition.

Typical Amounts of Lubricating Oil Components

[0393]

Additive Formulations	A (mass% a.i.)	B (mass% a.i.)	C (mass% a.i.)
Dispersant	0.1 - 20	0.1 - 20	1 - 8
Detergents (such as Salicylate)	0.1 - 20	0.1 - 20	0.2 - 9
Corrosion Inhibitor Anti-rust / extreme pressure agents	optional	0.05 - 7	0.1 - 1.5
di-C_9-alkyl substituted diphenyl amine	0.01 - 20	0.1 - 8	1 to 5
Additional Antioxidant that is not di-C_9-alkyl substituted diphenyl amine, such as hindered phenol	0.01 -10	0.1 - 5	0.1 - 4
Pour Point Depressant	optional	0 - 5	0.01 - 1.5
Anti-foaming Agent	optional	0 - 5	0.001 - 0.15
Functionalized Polymer	optional	0.01 - 10	0.1 - 5
Friction Modifier	optional	1.	0.5
Antiwear Agent	optional	0.01 - 5	0.1 - 3
Viscosity Modifier	optional	0.01 - 10	0.25 - 3
Seal Swell Agents	optional	0 - 5	0 - 2
Extreme Pressure Agents	optional	0 - 5	0 - 3
Unsaturated Hydrocarbons (LAOs)	optional	0 - 5	0 - 3

(continued)

Additive Formulations	A (mass% a.i.)	B (mass% a.i.)	C (mass% a.i.)
Basestock	Balance (such as 50 to 95 %)	Balance	Balance

Typical Amounts of Lubricating Oil Components in LOC (Continued)

[0394]

ADDITIVE FORMULATIONS	A (mass%)	B (mass%)	C (mass%)
Dispersant (borated and non-borated)	0.1 - 40	1 - 20	4 to 15
Detergents	0.1 - 20	0.2 - 15	2 to 10
di-C_9-alkyl substituted diphenyl amine	0.1 - 15	0.5 - 5	1 to 5
Amine (other than di-C_9-alkyl substituted diphenyl amine) and or phenol based Antioxidant	0.01 - 7	0.10 - 5	1 to 5
Sulfurized fatty acid ester	0 to 20, such as 0.01 - 20	0.1 to 10	0.5 - 5
Molybdenum containing compound	0.01 - 10	0.1 to 7	0.1 to 5
Antifoaming Agent	0.001 - 5	0.001 - 0.2	0.001 - 0.1
Friction Modifier	0 - 5	0 - 1.5	0.1 to 5
Viscosity Modifier	0.01 - 25	1 - 20	5 - 15
LAO (Linear Alpha Olefin)	0 to 10 such as 0.1 to 10	0.1 to 5	0.1 to 2.5
Optional additional additives	0 - 20	0.1 - 10	0.1 - 5
Basestock (50 to 99 mass%)	Balance	Balance	Balance

Typical Amounts of Lubricating Oil Components in LOC (Continued)

[0395]

ADDITIVE FORMULATIONS	D (mass%)	E (mass%)	F (mass%)
Dispersant borated	0.1 - 10	0.5 - 8	0.5 - 5
Dispersant non-borated	0.1 to 30	0.5 to 20	1 to 15
Detergent Ca high TBN	0.1 - 19.8	0.25 - 9	0.25 to 5
Detergent Mg, preferably high TBN	0.1 - 19.8	0.5 - 8	0.5 to 5
Detergent Ca low TBN	0.1 - 9.8	0.5 - 8	0.5 to 5
di-C_9-alkyl substituted diphenyl amine	0.1 - 15	0.5 - 5	0.5 to 3
Amine (other than di-C_9-alkyl substituted diphenyl amine) and or phenol (preferably amine) based antioxidant	0.01 - 7	0.10 - 5	1 to 5
Sulfurized fatty acid ester	0.01 - 20	0.1 to 10	0.5 - 5
Molybdenum containing compound	0.01 - 10	0.1 to 7	0.1 to 5
Antifoaming Agent	0.001 - 5	0.001 - 0.2	0.001 - 0.1
Friction Modifier	0 - 5	0 - 1.5	0.1 to 5
Viscosity Modifier	0.01 - 25	1 - 20	5 - 15
LAO (Linear Alpha Olefin)	0.1 to 10	0.1 to 5	0.1 to 2.5
Optional additional additives	0 - 20	0.1 - 10	0.1 - 10

(continued)

ADDITIVE FORMULATIONS	D (mass%)	E (mass%)	F (mass%)
Basestock (50 to 99 mass%)	Balance	Balance	Balance

[0396] The foregoing additives are typically commercially available materials. These additives may be added independently, but are usually pre-combined in packages, which can be obtained from suppliers of lubricant oil additives. Additive packages with a variety of ingredients, proportions and characteristics are available and selection of the appropriate package will take the use of the ultimate composition into account.

Fuels

[0397] This disclosure also relates to a method of lubricating an automotive internal combustion engine during operation of the engine comprising:

(i) providing to a crankcase of the automotive internal combustion engine an automotive crankcase the lubricating composition of described herein;
(ii) providing a hydrocarbon fuel in the automotive internal combustion engine; and
(iii) combusting the fuel in the automotive internal combustion engine, such as a spark-ignited or compression-ignited two- or four-stroke reciprocating engines such as a diesel engine or passenger car engine (such as a spark-ignited combustion engine).

[0398] This disclosure also relates to a fuel composition comprising the lubricating oil compositions described herein and a hydrocarbon fuel, wherein the fuel may be derived from petroleum and/or biological sources ("biofuel" or "renewable fuel"). In embodiments, the fuel comprises from 0.1 to 100 mass% renewable fuel, alternately from 1 to 75 mass% renewable fuel, alternately from 5 to 50 mass% renewable fuel, based upon the total mass of the from 1 to 50 mass% renewable fuel and the petroleum derived fuel.

[0399] The renewable fuel component is typically produced from vegetable oil (such as palm oil, coconut oil, rapeseed oil, soybean oil, jatropha oil), microbial oil (such as algae oil), animal fats (such as cooking oil, animal fat, and/or fish fat) and/or biogas. Renewable fuel refers to biofuel produced from biological resources formed through contemporary biological processes. In an embodiment, the renewable fuel component is produced by means of a hydrotreatment process. Hydrotreatment involves various reactions where molecular hydrogen reacts with other components, or the components undergo molecular conversions in the presence of molecular hydrogen and a solid catalyst. The reactions include, but are not limited to, hydrogenation, hydrodeoxygenation, hydrodesulfurization, hydrodenitrification, hydrodemetallization, hydrocracking, and isomerization. The renewable fuel component may have different distillation ranges, which provide the desired properties to the component, depending on the intended use.

Uses

[0400] The lubricating compositions of the disclosure may be used to lubricate mechanical engine components, particularly in internal combustion engines, *e.g.,* spark-ignited or compression-ignited, two- or four-stroke reciprocating engines, by adding the lubricant thereto. Typically, they are crankcase lubricants, such as passenger car motor oils or light and heavy-duty diesel engine lubricants.

[0401] In particular, the lubricating compositions of the present disclosure are suitably used in the lubrication of the crankcase of a compression-ignited, internal combustion engine, such as a heavy-duty diesel engine, marine engines, standing engines and the like.

[0402] In particular, the lubricating compositions of the present disclosure are suitably used in the lubrication of the crankcase of a spark-ignited turbo charged internal combustion engine.

[0403] In embodiments, the lubricating oils of this disclosure are used in spark-assisted high compression internal combustion engines and, when used in high compression spark ignition internal combustion engines the lubricating oil compositions of this disclosure are useful in lubricating high compression spark ignition engines.

[0404] In embodiments, the lubricating compositions of the present disclosure are suitably used in the lubrication of the crankcase of an engine for a heavy-duty diesel vehicle (*i.e.*, a heavy-duty diesel vehicle having a gross vehicle weight rating of 10,000 pounds or more.)

[0405] In embodiments, the lubricating compositions of the present disclosure are suitably used in the lubrication of the crankcase of a passenger car diesel engine.

[0406] In particular, lubricating oil formulations of this disclosure are particularly useful in compression-ignited internal combustion engines, *i.e.,* heavy-duty diesel engines, employing low viscosity oils, such as API FA-4 and future oil categories, in which wear protection of the valve train becomes challenging.

[0407] In particular, lubricating oil formulations of this disclosure are particularly useful in powertrain lubrication, such as in electric and or hybrid vehicles.

[0408] The lubricating oils described herein are also useful for lubricating an internal combustion engine (such as an automotive internal combustion engine) during operation of the engine comprising:

(i) providing to a crankcase of the internal combustion engine an automotive crankcase a lubricating composition described herein;
(ii) providing a hydrocarbon fuel in the internal combustion engine; and
(iii) combusting the fuel in the internal combustion engine.

[0409] In particular, the lubricating compositions of the present disclosure are suitably used in the lubrication of the oil sump of an internal combustion engine, such as a gasoline engine, a diesel engine (such as an automotive internal combustion engine, a spark-ignited internal combustion engine, a spark assisted, compression-ignited internal combustion engine, a compression-ignited internal combustion engine, such as a heavy-duty diesel engine), where the oil sump temperature is greater than 100 °C, such as 110 °C or more, such as 120 °C or more.

[0410] This disclosure further relates to:

1. A lubricating oil composition comprising diphenyl amine antioxidant comprising:

1) di(C_9-alkyl substituted phenyl) amine, and
2) from 0 to less than 10 mass% mono-C_9-alkyl substituted diphenyl amine, based upon the weight of the mono- and di-phenyl amines present in the lubricating oil composition.

2. The lubricating oil composition of paragraph 1, wherein the diphenyl amine antioxidant comprises:

1) 90 mass% or more of di(C_9-alkyl substituted phenyl) amines,
2) from 0 to 10 mass% of mono-C_9-alkyl substituted diphenyl amine, and
3) from 0 to 10 mass% of tri-C_9-alkyl substituted diphenyl amine, based upon the weight of 1), 2) and 3) present in the lubricating oil composition.

3. The lubricating oil composition of paragraph 1, comprising or resulting from the admixing of:

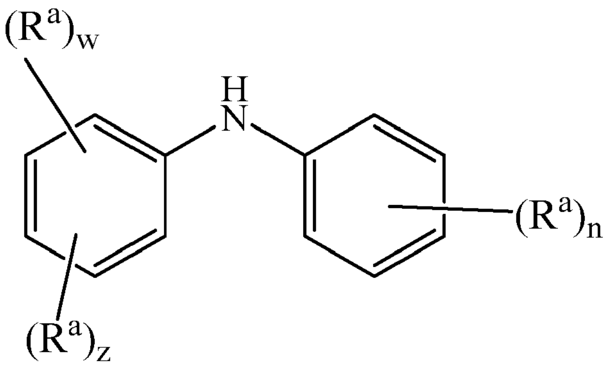
(i) at least 50 mass% of one or more base oils, based upon the weight of the lubricating oil composition;
(ii) one or more dispersants;
(iii) one or more detergents; and
(iv) phenyl amine antioxidant comprising: di(C_9-alkyl substituted diphenyl) amine and from 0 to less than 10 mass% of mono-C_9-alkyl substituted diphenyl amine, based upon the weight of the mono-C_9-alkyl substituted diphenyl amine and di(C_9-alkyl substituted diphenyl) amine present in the lubricating oil composition.

4. The lubricating oil composition of paragraph 1, comprising or resulting from the admixing of:

(i) at least 50 mass% of one or more base oils, based upon the weight of the lubricating oil composition;
(ii) one or more dispersants;
(iii) one or more detergents; and
(iv) diphenyl amine antioxidant composition comprising:

a) from 0 to less than 10 mass% mono-C_9-alkyl substituted diphenyl amine represented by the Formula (III) where n is 1, w is 0, and z is 0,
b) 90 mass% or more of di(C_9-alkyl substituted diphenyl) amines represented by Formula (III), where w is 0, n is 1, and z is 1,
c) from 0 to less than 10 mass% tri-C_9-alkyl substituted diphenyl amines represented by Formula (I), where w is 1, n is 1, and z is 1,
d) from 0 to 1 mass% of unsubstituted diphenyl amine represented by Formula (III) where w is 0, n is 0, and z is 0,

based upon the total weight of a), b), c) and d) present in the lubricating oil composition, where Formula (III) is:

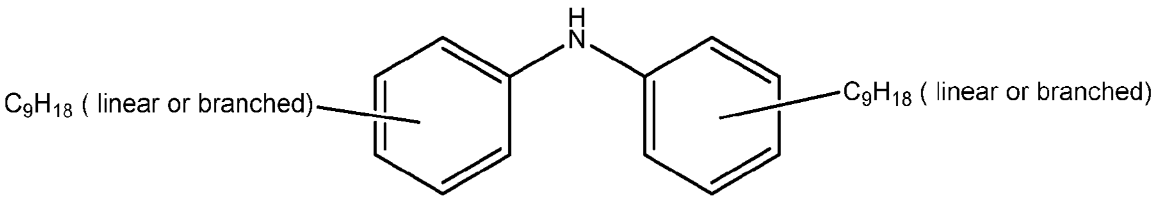


(III)

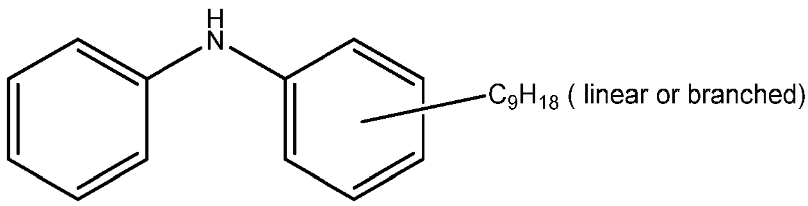
where each R^a is independently a linear C_9 alkyl or branched C_9 alkyl group, n is 1 or 0, z is 0 or 1, and w is 0 or 1.

5. The lubricating oil composition of paragraph 1, comprising or resulting from the admixing of:

(i) at least 50 mass% of one or more base oils, based upon the weight of the lubricating oil composition; and
(ii) one or more diphenyl amine antioxidants, where mono-C_9-alkyl substituted diphenyl amine represented by the Formula (B) are absent or present at less than 10 mass%, based upon the weight of the diphenyl amine antioxidants represented by Formulas A and B present in the lubricating oil composition:



Formula (A),



Formula (B),

where the branched C_9H_{18} may be singly, doubly or triply branched at one, two, three, four or more carbons, and may be symmetrically branched or asymmetrically branched.

6. The lubricating oil composition of paragraph 5, comprising or resulting from the admixing of:

(i) at least 50 mass% of one or more base oils, based upon the weight of the lubricating oil composition;
(ii) one or more dispersants;
(iii) one or more detergents; and
(iv) one or more diphenyl amine antioxidants, where mono-C_9-alkyl substituted diphenyl amines represented by the Formula (B) are absent or present at less than 5 mass%, and di-C_9-alkyl substituted diphenyl amines represented by Formula (A) are present at more than 90 mass%, based upon the weight of the diphenyl amine antioxidants represented by Formulas A and B present in the lubricating oil composition.

7. The lubricating oil composition of paragraph 4, comprising:

a) from 0 to less than 5 mass% mono-C_9-alkyl substituted diphenyl amines represented by the Formula (III) where w is 0, n is 1, and z is 0,
b) 90 mass% or more of di-C_9-alkyl substituted diphenyl amines represented by Formula (III), where w is 0, n is 1,

and z is 1,

c) 5 mass% or less of tri-C_9-alkyl substituted diphenyl amines represented by Formula (III), where w is 1, n is 1, and z is 1,

d) 1 mass% or less of unsubstituted diphenyl amines represented by Formula (III) where w is 0, n is 0, and z is 0,

based upon the total weight of the diphenyl amines of a), b), c) and d) present in the lubricating oil composition.

8. The lubricating oil composition of paragraph 4, comprising:

a) from 0 to less than 3 mass% mono-C_9-alkyl substituted diphenyl amines represented by the Formula (III) where w is 0, n is 1, and z is 0,

b) 95 mass% or more of di-C_9-alkyl substituted diphenyl amines represented by Formula (III), where w is 0, n is 1, and z is 1,

c) 5 mass% or less of tri-C_9-alkyl substituted diphenyl amines represented by Formula (III), where w is 1, n is 1, and z is 1,

d) from 0 to 0.5 mass% or less of unsubstituted diphenyl amines represented by Formula (III) where w is 0, n is 0, and z is 0,

based upon the total weight of the diphenyl amines of a), b), c) and d) present in the lubricating oil composition.

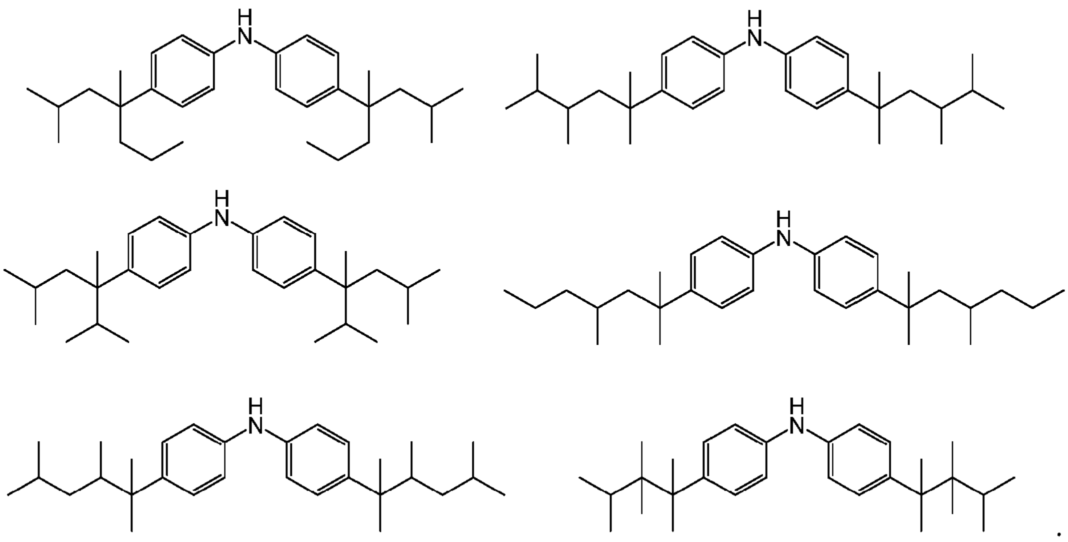
9. The lubricating oil composition of paragraph 5, wherein one or more mono-C_9-alkyl substituted diphenyl amines, represented by the Formula (B) are absent or present at less than 0.1 mass%, based upon the weight of the phenyl amine antioxidants represented by Formulas A and B present in the lubricating oil composition.

10. The lubricating oil composition of paragraph 4, wherein di-C_9-alkyl substituted diphenyl amines represented by Formula (III), where w is 0, n is 1 and z is 1, are present at 99 mass% or more, based upon the weight of the diphenyl amine antioxidants represented by Formula (III), when w is 0, z is 0 or 1 and n is 1, present in the lubricating oil composition.

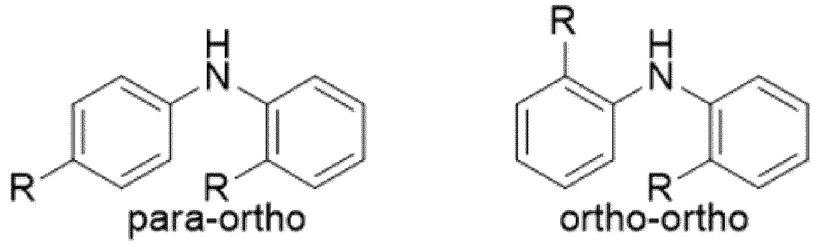
11. The lubricating oil composition of paragraph 4, wherein each R^a is independently a branched C_9 alkyl group.

12. The lubricating oil composition of paragraph 5, where the di-C_9-alkyl substituted diphenyl amines represented by Formula (A) comprise di(p-nonylphenyl)amine.

13. The lubricating oil composition of paragraph 5 where the di-C_9-alkyl substituted diphenyl amines represented by Formula (A) comprises one or more isomers selected from the group consisting of:



14. The lubricating oil composition of paragraph 4, wherein the di-C_9-alkyl substituted diphenyl amine represented by Formula (III), where w is 0, n is 1, and z is 1, comprises less than 5 mass% of the isomers shown below, where each R is independently a linear C_9 alkyl or branched C_9 alkyl group:



,

based upon the weight of di-C_9-alkyl substituted diphenyl amine represented by Formula (III), where w is 0, n is 1, and z is 1.

15. The lubricating oil composition of paragraph 1, wherein the lubricating oil composition has a percent viscosity increase between the initial KV100 and the KV100 at 216 hours of the CEC-L-109-14 Oxidation Test that is at least 2% less than the percent viscosity increase of the same lubricating oil composition except that the diphenyl amine antioxidant has been replaced with the same amount of diphenyl amine antioxidant having:

1) about 68 mass% di-C_9-alkyl substituted diphenyl amine,
2) about 29 mass% of mono-C_9-alkyl substituted diphenyl amine, and
3) about 3 mass% of tri-C_9-alkyl substituted diphenyl amine, based upon the weight of 1), 2) and 3), as determined by UPLC (described in the Experimental section).

16. The lubricating oil composition of paragraph 15, where the viscosity increase is at least 5% less.
17. The lubricating oil composition of paragraph 15, where the viscosity increase is at least 8% less.
18. The lubricating oil composition of paragraph 15, where the viscosity increase is at least 7% less.
19. The lubricating oil composition of paragraph 15, where the viscosity increase is at least 20% less.
20. The lubricating oil composition of paragraph 15, where the viscosity increase is at least 30% less.
21. The lubricating oil composition of paragraph 4, wherein di-C_9-alkyl substituted diphenyl amine represented by Formula (III), where w is 0, n is 1, and z is 1, is present in the lubricating oil composition at 1.0 mass% or more, or 2.0 mass% or more, or 3.0 mass% or more, based upon the mass of the lubricating composition.
22. The lubricating oil composition of paragraph 4, wherein mono-C_9-alkyl substituted diphenyl amine represented by Formula (III), where w is 0, n is 1, and z is 0, is present in the lubricating oil composition at 0.3 mass% or less, or at 0.1 mass% or less, based upon the mass of the lubricating composition.
23. The lubricating oil composition of paragraph 2, wherein di-C_9-alkyl substituted diphenyl amine represented by Formula (III), where w is 0, n is 1, and z is 1, is present in the lubricating oil composition at 2.0 mass% or more, based upon the mass of the lubricating composition, and the tri-C_9-alkyl substituted diphenyl amine represented by Formula (III), where w is 0, n is 1, and z is 2 is present in the lubricating oil composition at 0.9 mass% or less, based upon the mass of the lubricating composition.
24. The lubricating oil composition of paragraph 1, having improved Sequence IIIH piston deposits merit as compared to the same lubricating oil composition except that the diphenyl amine antioxidant has been replaced with the same amount of diphenyl amine antioxidant having:

1) about 68 mass% di-C_9-alkyl substituted diphenyl amine,
2) about 29 mass% of mono-C_9-alkyl substituted diphenyl amine, and
3) about 3 mass% of tri-C_9-alkyl substituted diphenyl amine, based upon the weight of 1), 2) and 3), as determined by UPLC in the Experimental section.

25. The lubricating oil composition of paragraph 15, wherein the oxidation (FTIR, CEC-L-109-14 Oxidation Test) of the lubricating oil composition is less than or within 10 % of the oxidation of the same lubricating oil composition except that the diphenyl amine antioxidant has been replaced with the same amount of diphenyl amine antioxidant having

1) about 68 mass% di-C_9-alkyl diphenyl amine,
2) about 29 mass% of mono-C_9-alkyl diphenyl amine, and
3) about 3 mass% of tri-C_9-alkyl diphenyl amine, based upon the weight of 1), 2) and 3), as determined by UPLC in the Experimental section.

26. The lubricating oil composition of paragraph 1, further comprising zinc dialkyldithiophosphate.
27. The lubricating oil composition of paragraph 1, wherein the lubricating oil composition further comprises hindered

phenolic antioxidant.

28. The lubricating oil composition of paragraph 1 wherein the lubricating oil composition further comprises a molybdenum containing compound.

29. The lubricating oil composition of paragraph 1 wherein the lubricating oil composition further comprises a dimeric and or trimeric molybdenum containing compound providing 50 to 1000 ppm Mo to the lubricating oil composition.

30. The lubricating oil composition of paragraph 1 wherein the lubricating oil composition further comprises additional antioxidant comprising oil-soluble or oil-dispersible sulfur-containing antioxidant(s), sulfurized aliphatic (C_7 to C_{29}) hydrocarbyl fatty acid ester(s), sulfur-containing organo-molybdenum compound(s), and combinations thereof.

31. The lubricating oil composition of paragraph 1, further comprising ethoxylated alcohol.

32. The lubricating oil composition of paragraph 3, where the detergent comprises carboxylate detergent, such as salicylate detergent, such as alkaline earth metal salicylate detergent, such as Ca salicylate detergent, optionally having a TBN of 100 or less and or optionally providing from 1 to 30 mmol/kg soap.

33. The lubricating oil composition of paragraph 3, where the detergent comprises alkaline earth metal salicylate detergent.

34. The lubricating oil composition of paragraph 3, where the detergent comprises calcium and or magnesium salicylate detergent, optionally providing 5 to 25 mmol/kg soap to the lubricating oil composition.

35. The lubricating composition of paragraph 4, further comprising one or more of the following components.

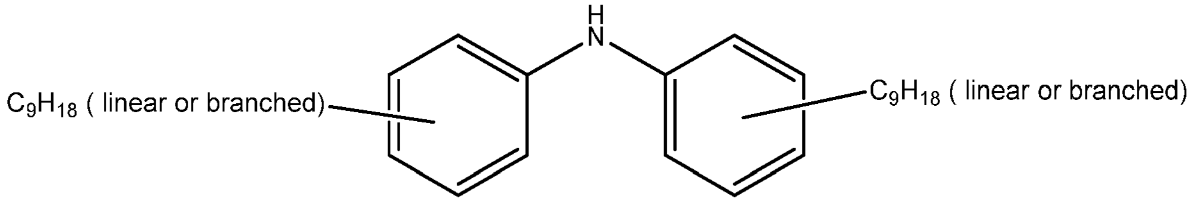
D) optionally, one or more friction modifiers;
E) optionally, one or more antioxidants, other than the antioxidants represented by Formula (III) (such as Formula I);
F) optionally, one or more pour point depressants;
G) optionally, one or more anti-foaming agents;
H) optionally, one or more viscosity modifiers;
J) optionally, one or more inhibitors and/or antirust agents; and/or
K) optionally, one or more anti-wear agents.

36. A concentrate composition comprising or resulting from the admixing of:

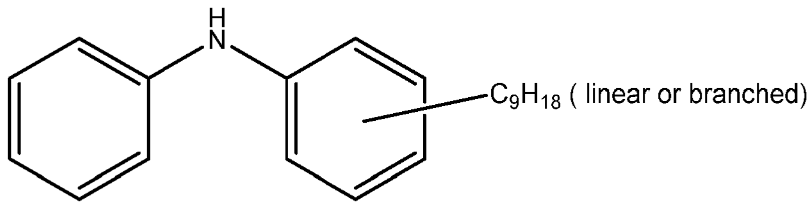
(i) less than 50 mass% of one or more base oils, based upon the weight of the concentrate composition;
(ii) one or more dispersants;
(iii) one or more detergents; and
(iv) diphenyl amine antioxidant comprising:

1) di-C_9-alkyl substituted diphenyl amine and
2) from 0 to less than 10 mass% of mono-C_9-alkyl substituted diphenyl amine, based upon the weight of the mono-C_9-alkyl substituted diphenyl amine and di-C_9-alkyl substituted diphenyl amine present in the lubricating oil composition.

37. The concentrate composition of paragraph 36 where the diphenyl amine antioxidant comprises from 0 to less than 10 mass% of one or more mono-C^9-alkyl substituted diphenyl amines represented by the Formula (B), and more than 90 mass% of di-C_9-alkyl substituted diphenyl amines represented by Formula (A), based upon the weight of the phenyl amine antioxidants represented by Formulas A and B present in the concentrate:



Formula (A), and



Formula (B),

where the branched C_9H_{18} may be singly, doubly or triply branched at one, two, three, four or more carbons, and may be symmetrically branched or asymmetrically branched.

38. The concentrate of paragraph 36, wherein the concentrate comprises:

1) diphenyl amine antioxidant comprising:
a) di-C_9-alkyl substituted diphenyl amine and b) from 0 to less than 10 mass% of mono-C_9-alkyl substituted diphenyl amine, based upon the weight of the mono- and di-phenyl amines present in the concentrate;
2) salicylate detergent.

39. The concentrate of paragraph 36 wherein the diphenyl amine antioxidant comprises:

1) 95 mass% or more of di-C_9-alkyl substituted diphenyl amine and
2) from 0 to less than 5 mass% of mono-C_9-alkyl substituted diphenyl amine, based upon the weight of the mono- and di-phenyl amines present in the lubricating oil composition.

40. The concentrate of paragraph 36 wherein the diphenyl amine antioxidant comprises:

1) 99 mass% or more of di-C_9-alkyl substituted diphenyl amine and
2) from 0 to less than 1 mass% of mono-C_9-alkyl substituted diphenyl amine, based upon the weight of 1) and 2) present in the concentrate.

41. A method of lubricating an internal combustion engine during operation of the engine comprising:

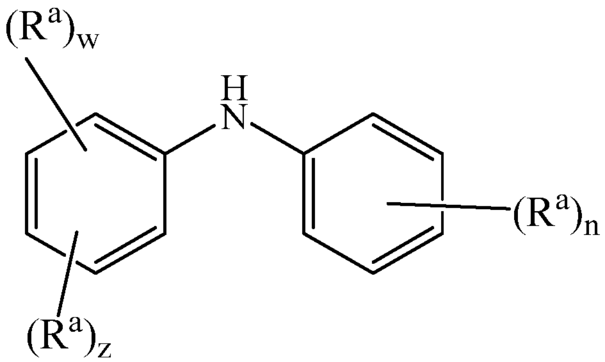
(i) providing to a crankcase of the internal combustion engine an automotive crankcase the lubricating composition of paragraph 1;
(ii) providing a hydrocarbon fuel in the internal combustion engine; and
(iii) combusting the fuel in the internal combustion engine.

42. The method of paragraph 33, wherein the internal combustion engine is an automotive internal combustion engine.

43. Diphenyl amine antioxidant, for use in a lubricating oil composition, comprising:

a) mono-C_9-alkyl substituted diphenyl amines represented by the Formula (III) where n is 1, z is 0 and w is 0, that are absent or present at less than 10 mass%,
b) di-C_9-alkyl substituted diphenyl amines represented by Formula (III), where n is 1 and z is 1, that are present at 90 mass% or more,
c) tri-C_9-alkyl substituted diphenyl amines represented by Formula (III), where n is 1, z is 1 and w is 1, are present at 0.01 to less than 10 mass%,

based upon the total weight of the phenyl amines of a) + b) + c),
where Formula (III) is:



where each R^a is independently a linear C_9 alkyl or branched C_9 alkyl group, n is 1, z is 0 or 1, and w is 0 or 1.

44. Diphenyl amine antioxidant comprising:

a) less than 5.0 mass% of mono-C_9-alkyl substituted diphenyl amines,
b) greater than 95.0 mass% di-C_9-alkyl substituted diphenyl amines,

based upon the total weight of mono-C_9-alkyl substituted diphenyl amines and the di-C_9-alkyl substituted diphenyl amines.
45. The diphenyl amine antioxidant of paragraph 44, where the diphenyl amine antioxidant comprises:

a) less than 4.0 mass% of mono-C_9-alkyl substituted diphenyl amines,
b) greater than 96.0 mass% di-C_9-alkyl substituted diphenyl amines,

based upon the total weight of mono-C_9-alkyl substituted diphenyl amines and the di-C_9-alkyl substituted diphenyl amines.
46. The diphenyl amine antioxidant of paragraph 44, where the diphenyl amine antioxidant comprises:

a) less than 3.0 mass% of mono-C_9-alkyl substituted diphenyl amines,
b) greater than 97.0 mass% di(C_9-alkyl substituted diphenyl) amines,

based upon the total weight of mono-C_9-alkyl substituted diphenyl amines and the di-C_9-alkyl substituted diphenyl amines.
47. The diphenyl amine antioxidant of paragraph 44, where the diphenyl amine antioxidant comprises:

a) less than 2.0 mass% of mono-C_9-alkyl substituted diphenyl amines,
b) greater than 98.0 mass% v.

based upon the total weight of mono-C_9-alkyl substituted diphenyl amines and the di-C_9-alkyl substituted diphenyl amines.
48. The diphenyl amine antioxidant of paragraph 44, where the diphenyl amine antioxidant comprises:

a) less than 1.0 mass% of mono-C_9-alkyl substituted diphenyl amines,
b) greater than 99.0 mass% di-C_9-alkyl substituted diphenyl amines,

based upon the total weight of mono-C_9-alkyl substituted diphenyl amines and the di-C_9-alkyl substituted diphenyl amines.
49. The diphenyl amine antioxidant of paragraph 44, where the diphenyl amine antioxidant comprises:

a) less than 0.5 mass% of mono-C_9-alkyl substituted diphenyl amines,
b) greater than 99.5 mass% di-C_9-alkyl substituted diphenyl amines,

based upon the total weight of mono-C_9-alkyl substituted diphenyl amines and the di-C_9-alkyl substituted diphenyl amines.
50. The diphenyl amine antioxidant of paragraph 44, where the diphenyl amine antioxidant comprises:

a) less than 0.5 mass% of mono-C_9-alkyl substituted diphenyl amines,
b) greater than 99.5 mass% di-C_9-alkyl substituted diphenyl amines,

based upon the total weight of mono-C_9-alkyl substituted diphenyl amines and the di-C_9-alkyl substituted diphenyl amines.

51. The diphenyl amine antioxidant of paragraph 44, where the diphenyl amine antioxidant comprises:

a) less than 0.3 mass% of mono-C_9-alkyl substituted diphenyl amines,
b) greater than 99.7 mass% di-C_9-alkyl substituted diphenyl amines,

based upon the total weight of mono-C_9-alkyl substituted diphenyl amines and the di-C_9-alkyl substituted diphenyl amines.

52. The diphenyl amine antioxidant of paragraph 44, where the diphenyl amine antioxidant comprises:

a) less than 0.1 mass% of mono-C_9-alkyl substituted diphenyl amines,
b) greater than 99.9 mass% di-C_9-alkyl substituted diphenyl amines,

based upon the total weight of mono-C_9-alkyl substituted diphenyl amines and the di-C_9-alkyl substituted diphenyl amines.

53. The diphenyl amine antioxidant of paragraph 44, where the diphenyl amine antioxidant comprises:

a) less than 0.05 mass% of mono-C_9-alkyl substituted diphenyl amines,
b) greater than 99.95 wt,

based upon the total weight of mono-C_9-alkyl substituted diphenyl amines and the di-C_9-alkyl substituted diphenyl amines.

54. A lubricating oil composition comprising antioxidants, where Irganox™ L57 and or Irganox™ L67 are absent or present at less than 0.30 mass%, such as less than 0.1 mass%, based upon the LOC.

55. A method to lubricate an internal combustion engine comprising introducing a lubricating oil composition comprising base oil and a composition comprising: 1) diphenyl amine antioxidant comprising 90 mass% or more of bis(nonylphenyl)amine and 10 mass% or less of (nonylphenyl)(phenyl)amine based on the weight of the bis(nonylphenyl)amine and (nonylphenyl)(phenyl)amine, and 2) one or more of dinuclear organomolybdenum-based friction modifier, magnesium-based detergents providing 400 ppm or more alternately 600 ppm or more) of Mg to the composition, and or sulfonate based detergents, to an internal combustion engine, wherein the **(CEC L-109-14**) viscosity growth of the lubricating oil composition is at least 5% less (such as at least 10% less, such as at least 20% less, such as at least 30% less, such as at least 40% less, such as at least 50% less, such as at least 60% less, such as at least 70% less, such as at least 75% less, such as at least 77% less) than the **(CEC L-109-14**) viscosity growth of a comparative lubricating oil composition having the same lubricating oil composition except that the diphenyl amine antioxidant has been replaced with the same amount of diphenyl amine antioxidant having: 1) about 68 mass% di-C_9-alkyl diphenyl amine, 2) about 29 mass% of mono-C_9-alkyl diphenyl amine, and 3) about 3 mass% of tri-C_9-alkyl diphenyl amine, based on the weight of 1), 2) and 3), as determined by UPLC).

56. The use of (or a method of using) diphenylamine amine antioxidant to reduce:
piston deposits (Sequence III), and or rod deposits (MHT4 TEOST), and or friction (such as HFRR friction coefficient at 140°C, and or MTM friction coefficient, 135°C, 0.02 m/s and or MTM-R: Traction Coefficient at 100°C), and or wear (such as HFRR: wear scar diameter and or MTM-R: wear scar volume), and or viscometric growth (CEC-L109-14), in a lubricating oil composition lubricating internal combustion engine, comprising providing the lubricating oil comprising 1) di(C_9-alkyl substituted diphenyl) amine and 2) from 0 to less than 10 mass% of mono-C_9-alkyl substituted diphenyl amine to the internal combustion engine (where the reduction is determined by comparison to the same lubricating oil composition except that the diphenyl amine antioxidant has been replaced with the same amount of diphenyl amine antioxidant having: 1) about 68 mass% di-C_9-alkyl diphenyl amine, 2) about 29 mass% of mono-C_9-alkyl diphenyl amine, and 3) about 3 mass% of tri-C_9-alkyl diphenyl amine, based on the weight of 1), 2) and 3), as determined by UPLC).

57. The use (or a method of using) of paragraph 56 where in the lubricating oil composition further comprises: one, two, three, four, five, six or more additives selected from the group consisting of: 1) glycerol-based friction modifiers, and or 2) sulfonate-based detergents, and or 3) organomolybdenum-based friction modifiers, and or 4) magnesium-based detergents providing 400 ppm or more of Mg to the composition, and or 5) salicylate based detergents, and or 6) zinc-based antiwear agents (such as derived ZDDP from primary alcohol), and/or 7) base oil comprising a combination of refined and renewable base oils and or a combination of Group III and Group II base oils.

58. The use of (or a method of using) diphenylamine amine antioxidant to reduce total rod deposits (MHT4 TEOST) of paragraph 57 wherein:

1) the lubricating oil composition further comprises **sulfonate based detergents** (such as solely sulfonate based detergents) and has at least 5% less (such as at least 10% less, such as at least 20% less, such as at least 25% less) MHT4 TEOST: Total rod deposits (mg); and or
2) the lubricating oil composition further comprises: 1) **salicylate based detergents** (such calcium salicylate based detergents), and 2) optionally dispersant (such as PIBSA-PAM) derived from polymer having an Mn of less than 1600 g/mol); and has at least 5% less (such as at least 10% less, such as at least 20% less, such as at least 30% less, such as at least 40% less) MHT4 TEOST: total rod deposits (mg); and or
3) the lubricating oil composition further comprises: 1) **magnesium based detergents** (such magnesium sulfonate and or magnesium salicylate based detergents providing at least 600 ppm Mg to the lubricating oil composition); and has at least 5% less (such as at least 10% less, such as at least 20% less, such as at least 30% less, such as at least 40% less, such as at least 50% less, such as at least 60% less, such as at least 70% less)) MHT4 TEOST: Total rod deposits (mg); and or
4) the lubricating oil composition further comprises: 1) **magnesium and calcium based detergents** (such magnesium sulfonate and/or salicylate detergents and calcium sulfonate and/or salicylate detergents present in the lubricating oil composition at a ratio of Mg:Ca of 1:2 to 2:1 (such as 1:1 to 2:1, such as 1.5:1 to 2:1); and has at least 5% less (such as at least 10% less, such as at least 20% less, such as at least 30% less, such as at least 40% less, such as at least 50% less, such as at least 60% less, such as at least 70% less) total rod deposits (mg).

59. The use of (or a method of using) diphenylamine amine antioxidant to reduce viscosity growth **(CEC L-109-14)** of paragraph 57 wherein:

1) the lubricating oil composition further comprises **glycerol-based friction modifier** (such as glycerol mono-oleate) and or magnesium based detergents (such magnesium sulfonate and or magnesium salicylate based detergents, optionally providing at least 600 ppm Mg to the lubricating oil composition) and has at least 5% less (such as at least 3% less) viscosity growth; and or
2) the lubricating oil composition further comprises **dinuclear organo-molybdenum compound** (such as one or more molybdenum dithiocarbamate dimers) and has at least 5% less (such as at least 10% less, such as at least 20% less, such as at least 30% less, such as at least 40% less, such as at least 50% less, such as at least 60% less, such as at least 70% less, such as such as at least 75% less, such as at least 77% less) viscosity growth; and or
3) the lubricating oil composition further comprises **trinuclear organo-molybdenum compound** (such as one or more molybdenum dithiocarbamate trimers) and has at has at least 5% less (such as at least 10% less, such as at least 13% less, such as at least 15% less, such as at least 17% less) viscosity growth; and or
4) the lubricating oil composition further comprises **renewable base oil** (such as refined Group II and or Group III base oil combined with Group III renewable base oil, and optionally Group IV base oil) and has at has at least 5% less (such as at least 10% less, such as at least 15% less) viscosity growth; and or
5) the lubricating oil composition further comprises **Group II and Group III base oil,** and optionally Group IV base oil and has at has at least 5% less (such as at least 10% less, such as at least 15% less, such as at least 20% less, such as at least 30% less, such as at least 33% less) viscosity growth; and or
6) the lubricating oil composition further comprises **magnesium based detergents** (such magnesium sulfonate and or magnesium salicylate based detergents providing at least 600 ppm Mg, such s at least 700 ppm, such as at least 800 ppm to the lubricating oil composition) and has at least 5% less (such as at least 10% less, such as at least 15% less, such as at least 20% less, such as at least 25% less, such as at least 30% less, such as at least 55% less, such as at least 40% less) viscosity growth; and or
7) the lubricating oil composition further comprises **salicylate based detergents** (such calcium and or magnesium salicylate based detergents) and has at least 5% less (such as at least 10% less, such as at least 14 % less) viscosity growth; and or
8) the lubricating oil composition further comprises **zero mass% glycerol based friction** modifier (such as glycerol mono-oleate) and has at least 5% less (such as at least 10% less, such as at least 15 % less) viscosity growth; and or
9) the lubricating oil composition further comprises **zinc based antiwear agents** derived from one or more primary alcohols (such as zinc dialkyldithiophosphates where the alkyl is derived from one or more primary alcohols) and has at least 5% less (such as at least 10% less, such as at least 15 % less, such as at least 20 % less) viscosity growth as compared to the same lubricating oil composition except that the Comparative LOC additionally contains the same amount of a ZDDP derived from a combination of isooctanol and 2-butanol.

60. The use of (or a method of using) diphenylamine amine antioxidant to reduce wear scar volume μm^3 (**MTM-R**) and or Avg Traction Coefficient at 100°C (**MTM-R**) and or wear scar area **(HFRR)** of paragraph 57 wherein:

1) 1the lubricating oil composition further comprises **dinuclear organo-molybdenum compound** (such as molybdenum dithiocarbamate dimer and has at has at least 5% less (such as at least 10% less, such as at least 20% less, such as at least 30% less, such as at least 40% less, such as at least 50% less, such as at least 60% less, such as at least 65% less) wear scar volume, and or; and or
2) the lubricating oil composition further comprises **magnesium and calcium based detergents** (such magnesium sulfonate and/or salicylate detergents and calcium sulfonate and/or salicylate detergents present in the lubricating oil composition at a ratio of Mg:Ca of 1:2 to 2:1 (such as 1:1 to 2:1, such as 1.5:1 to 2:1,), providing at least 600 ppm Mg to the lubricating oil composition); and has at least 5% less (such as at least 10% less, such as at least 15% less, such as at least 19% less) avg traction coefficient at 100°C ; and or
3) the lubricating oil composition further comprises **zinc based antiwear agents** derived from one or more primary alcohols (such as zinc dialkyldithiophosphates where the alkyl is derived from one or more primary alcohols) and has at has at least 5% less (such as at least 9% less) avg traction coefficient at 100°C, except that the Comparative LOC additionally contains the same amount of a ZDDP derived from a combination of isooctanol and 2-butanol, and or
4) the lubricating oil composition further comprises **trinuclear organo-molybdenum compound** and has at has at least 5% less (such as at least 10% less, such as at least 20% less, such as at least 30% less, such as at least 40% less, such as at least 50% less, such as at least 60% less, such as at least 65% less) wear scar volume; and or
5) the lubricating oil composition further comprises **trinuclear organo-molybdenum compound** and has at has at least 5% less (such as at least 10% less, such as at least 20% less, such as at least 30% less, such as at least 40% less, such as at least 50% less, such as at least 60% less, such as at least 65% less) avg traction coefficient at 100°C; and or
6) the lubricating oil composition further comprises **glycerol based friction** modifier (such as glycerol mono-oleate) and has at least 5% less (such as at least 10% less, such as at least 13 % less) avg traction coefficient at 100°C, and or
7) the lubricating oil composition further comprises **dinuclear organo-molybdenum compound** (such as molybdenum dithiocarbamate dimer and has at has at least 5% less (such as at least 10% less, such as at least 20% less, such as at least 30% less, such as at least 40% less, such as at least 50% less, such as at least 60% less, such as at least 65% less) wear scar area, and or
8) the lubricating oil composition further comprises **trinuclear organo-molybdenum compound** and has at has at least 5% less (such as at least 10% less, such as at least 20% less, such as at least 30% less, such as at least 40% less, such as at least 50% less, such as at least 60% less, such as at least 65% less) wear scar area.

61. The use of (or a method of using) diphenylamine amine antioxidant to reduce friction coefficient at 135°C (MTM) of paragraph 57 wherein: the lubricating oil composition further comprises **magnesium based detergents** (such magnesium sulfonate and or magnesium salicylate based detergents providing at least 600 ppm Mg, such s at least 700 ppm, such as at least 800 ppm to the lubricating oil composition) and has at least 5% less (such as at least 10% less, such as at least 15% less, such as at least 17% less) friction coefficient at 135°C.
62. A method of reducing friction in a crankcase of an internal combustion engine comprising providing to the crankcase a lubricating oil composition comprising,

a) 0.5 to 15 mass%, based on total weight of the lubricating oil composition, of an diphenylamine amine antioxidant comprising, based on the weight of the aminic antioxidant, wherein the enhanced aminic antioxidant comprises,

i) 90 mass% or more of bis(nonylphenyl) amine,
ii) from 0 to less than 10 mass% of mono(nonylphenyl) amine, based upon the mass of the (nonylphenyl)(phenyl)amine and bis(nonylphenyl)amine present in the lubricating oil composition, and

b) 0.01 to 30 mass%, based on total weight of the lubricating oil composition, of one or more additives selected from the group consisting of glycerol-based friction modifiers, sulfonate-based detergents, organomolybdenum-based friction modifier, calcium/magnesium-based detergents, zinc-based antiwear agents, and combinations thereof, and variants thereof,

wherein the amount of any one additive can be synergistically increased in the presence of the diphenylamine amine antioxidant to maintaining or decrease the friction (CEC-L-109-14, 216 hr., 150°C) relative to the friction in the presence of a diphenylamine amine antioxidant comprising a baseline antioxidant of nonylphenyl amine antioxidant comprising about 68 mass% of bis(nonylphenyl)amine, about 29 mass% of (nonylphenyl)(phenyl)amine and about 3 mass% of tri(nonylphenyl)amine, based upon the weight of the (nonylphenyl)(phenyl)amine, bis(nonylphenyl)amine, and tri(nonylphenyl)amine, as determined by UPLC.

63. A composition, comprising,

a) 0.1 to 99.9 mass%, based on total weight of the composition, of diphenylamine amine antioxidant comprising 90 mass% or more of bis(nonylphenyl)amine and 10 mass% or less of (nonylphenyl)(phenyl)amine based on the weight of the bis(nonylphenyl)amine and (nonylphenyl)(phenyl)amine, and
b) 99.9 to 0.1 mass%, based on total weight of the composition, of one, two, three, four, five, six or more additives selected from the group consisting of: 1) glycerol-based friction modifiers, and or 2) sulfonate-based detergents, and or 3) organomolybdenum-based friction modifiers, and or 4) magnesium-based detergents providing 400 ppm or more of Mg to the composition, and or 5) salicylate based detergents, and or and or 6) zinc-based antiwear agents (such as derived ZDDP from primary alcohol). and/or 7) base oil comprising a combination of refined and renewable base oils and or a combination of Group III and Group II base oils.

64. A composition comprising: 1) diphenyl amine antioxidant comprising 90 mass% or more of bis(nonylphenyl)amine and 10 mass% or less of (nonylphenyl)(phenyl)amine based on the weight of the bis(nonylphenyl)amine and (nonylphenyl)(phenyl)amine, and 2) one or more additives selected from the group consisting of: dinuclear organomolybdenum-based friction modifier, magnesium-based detergents providing 400 ppm or more alternately 600 ppm or more) of Mg to the composition, and sulfonate based detergents.

65. A lubricating oil composition comprising: 1) diphenyl amine antioxidant comprising 90 mass% or more of bis(nonylphenyl)amine and 10 mass% or less of (nonylphenyl)(phenyl)amine based on the weight of the bis(nonylphenyl)amine and (nonylphenyl)(phenyl)amine, and 2) one or more additives selected from the group consisting of: dinuclear organomolybdenum-based friction modifier, magnesium-based detergents providing 400 ppm or more alternately 600 ppm or more) of Mg to the composition, and or sulfonate based detergents, and 3) 50 mass % or more base oil, based upon the mass of the lubricating oil composition.

66. A lubricating oil composition comprising,

a) 0.1 to 99.9 mass%, based on total weight of the composition, of diphenylamine amine antioxidant comprising 90 mass% or more of bis(nonylphenyl)amine and 10 mass% or less of (nonylphenyl)(phenyl)amine based on the weight of the bis(nonylphenyl)amine and (nonylphenyl)(phenyl)amine, and
b) 99.9 to 0.1 mass%, based on total weight of the composition, of one, two, three, four, five, six or more additives selected from the group consisting of: 1) glycerol-based friction modifiers, and or 2) sulfonate-based detergents, and or 3) organomolybdenum-based friction modifiers, and or 4) magnesium-based detergents providing 400 ppm or more of Mg to the composition, and or 5) salicylate based detergents, and or 6) zinc-based antiwear agents (such as derived ZDDP from primary alcohol); and
c) from 50 mass% or more of base oil, optionally comprising a combination of refined and renewable base oils and or a combination of Group III and Group II base oils and or a combination of Group IV base oil, refined base oil and renewable base oil, and or a combination of Group IV base oil, Group III base oil and Group II base oil.

67. The composition of paragraph 63, 64, 65, or 66, wherein the viscometric growth (CEC-L-109-14, 216 hr., 150°C) of the lubricating oil composition is at least 5 % (preferably at least 10%, at least 15%, at least 20%, at least 25%, at least 30 %, at least 40%, at least 50%, at least 60 %, at least 70%, at least 75%, at least 80 %) lower relative to a lubricating oil composition of the same formulation except that the diphenylamine amine antioxidant is replaced at the same mass percentage by diphenyl amine antioxidant comprising about 68 mass% of bis(nonylphenyl)amine, about 29 mass% of (nonylphenyl)(phenyl)amine and about 3 mass% of tri(nonylphenyl)amine based upon the weight of the mono-(nonylphenyl)amine, bis(nonylphenyl)amine, and tri(nonylphenyl)amine, as determined by UPLC.

68. The composition of any of paragraphs 63, 64, 65, 66, or 67, wherein diphenylamine amine antioxidant comprises:

a) 85 mass% or more of bis(nonylphenyl)amine,
b) from 0 to 10 (such as 0.1 to 8 mass%, such as 1 to 6 mass%, such as 1 to 5 mass%, such as 2 to 4 mass%) of (nonylphenyl)(phenyl)amine, and
c) from 0 to 20 mass% of tri(nonylphenyl)amine,
d) based on the weight of the bis(nonylphenyl)amine, tri(nonylphenyl)amine, and (nonylphenyl)(phenyl)amine.

69. The composition of any of paragraphs 63 to 68, wherein the diphenylamine amine antioxidant comprises 95 mass% or more of bis(nonylphenyl)amine (such as 96 mass% or more, such as 97 mass% or more, such as 98 mass%

or more, such as 99 mass% or more, such as 99.5 mass% or more) and 5 mass% or less (or 4 mass% or less, or 3 mass% or less, or 2 mass% or less, or 1 mass% or less, or 0.5 mass% or less) of (nonylphenyl)(phenyl)amine, based on the weight of the bis(nonylphenyl)amine and (nonylphenyl)(phenyl)amine.

70. The composition of any of paragraphs 63 to 69, comprising:

a) from 10 to 99.99 mass% (such as 20 to 80 mass%, such as 30 to 70 mass%), of the diphenylamine amine antioxidant comprising:

iii) 90 to 100 mass% of bis(nonylphenyl)amine (such as 91 to 99.9 mass%, such as 92 to 99.5 mass%, such as 93 to 99 mass%, such as 94 to 100 mass%, such as 95 to 100 mass%, such as 96 to 99.99 mass%, such as 97 to 99.5 mass%, such as 98 to 100 mass%, such as 99 to 100 mass%), and 2)

iv) 10 to 0 mass% (such as 9 to 0.1 mass%, such as 8 to 0.5 mass%, such as 7 to 1 mass%, such as 6 to 0.5 mass%, such as 5 to 0.5 mass%, such as 4 to 0.01 mass%, such as 4 to 0.5 mass%, such as 2 to 0 mass%, such as 1 to 0 mass%)) of (nonylphenyl)(phenyl)amine, based on the weight of the bis(nonylphenyl)amine and (nonylphenyl)(phenyl)amine; and

b) from 0.01 to 90 mass% (such as 0.1 to 60 mass%, such as 0.1 to 50 mass%, such as 0.1 to 40 mass%, such as 0.1 to 20 mass%, such as 1 to 30 mass%) of on or more additive(s) selected from group consisting of:

1) glycerol-based friction modifiers,
2) sulfonate-based detergents,
3) organomolybdenum-based friction modifiers,
4) magnesium-based detergents providing 400 ppm or more of Mg to the composition,
5) salicylate based detergents, and
6) zinc-based antiwear agents (such as derived ZDDP from primary alcohol), based on total weight of the diphenylamine amine antioxidant and the additives.

71. The composition of any of paragraphs 63 to 70, wherein the additives comprise glycerol-based friction modifiers, such as glycerol mono-oleate.

72. The composition of any of paragraphs 63 to 71, wherein the additives comprise sulfonate-based detergents, such as magnesium and or calcium sulfonate detergents.

73. The composition of any of paragraphs 63 to 72, wherein the additives comprise organomolybdenum-based friction modifiers, such as dinuclear or trinuclear molybdenum dithiocarbamate.

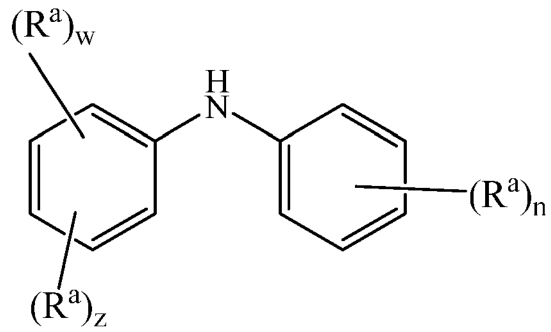
74. The composition of any of paragraphs 63 to 73, wherein the additives comprise magnesium-based detergents providing 400 ppm or more, such as 600 ppm or more or Mg to the composition, such as magnesium sulfonate detergents and or magnesium salicylate detergents.

75. The composition of any of paragraphs 63 to 74, wherein the additives comprise salicylate based detergents, such as calcium and or magnesium salicylate detergents.

76. The composition of any of paragraphs 63 to 75, wherein the additives comprise zinc-based antiwear agents, such as derived zinc dialkyldithiophosphate, where the alkyl groups are derived from one or more primary alcohol.

77. A lubricating oil composition comprising the composition of any of paragraphs 63 to 76, wherein the lubricating oil composition comprises or results from the admixing of at least 50 mass% of one or more base oils, based upon the weight of the lubricating oil composition, one or more additives, and diphenylamine amine antioxidant composition comprising:

a) from 0 to less than 10 mass% (nonylphenyl)(phenyl)amines represented by the Formula (III) where n is 1, w is 0, and z is 0;
b) 90 mass% or more of bis(nonylphenyl)amines represented by Formula (III), where w is 0, n is 1, and z is 1;
c) from 0 to less than 10 mass% tri(nonylphenyl)amines represented by Formula (III), where w is 1, n is 1, and z is 1;
d) from 0 to 1 mass% of unsubstituted diphenyl amine represented by Formula (III) where w is 0, n is 0, and z is 0;
based upon the total weight the enhanced diphenyl amine antioxidant present in the lubricating oil composition, where Formula (III) is,



where each R^a is independently a linear C_9 alkyl or branched C_9 alkyl group, n is 1 or 0, z is 0 or 1, and w is 0 or 1.

78. A concentrate comprising the composition of any one of paragraphs 63 to 76, comprising less than 50 mass% of base oil, based upon the weight of the concentrate.
79. A concentrate comprising:

a) one or more of:

i) from 0.01 to 5 mass% of glycerol-based friction modifiers,
ii) from 0.01 to 99 mass%, 0.01 to 80 mass%, such as 0.01 to 50 mass%, such as 0.01 to 20 mass%, such as 0.01 to 5 mass% of organomolybdenum-based friction modifiers,
iii) from 0.01 to 99 mass%, 0.01 to 40 mass%, such as 0.1 to 30 mass%, such as 0.1 to 20 mass%, such as 1 to 10 mass%, such as 1 to 5 mass% of sulfonate-based detergents (such as calcium sulfonate, magnesium sulfonate, or calcium and magnesium sulfonate detergents),
iv) from 0.01 to 15 mass%, such as 0.01 to 5 mass% of zinc-based antiwear agents,
v) from 0.01 to 99 mass%, such as 0.01 to 40 mass%, such as 0.1 to 30 mass%, such as 0.1 to 20 mass%, such as 1 to 10 mass%, such as 1 to 5 mass% magnesium-based detergents providing 400 ppm or more of Mg to the composition,
vi) from 0.01 to 99 mass%, such as from 0.01 to 40 mass%, such as 0.1 to 30 mass%, such as 0.1 to 20 mass%, such as 1 to 10 mass%, such as 1 to 5 mass% salicylate based detergents,

based upon the weight of the concentrate,
b) from 0.01 to 20 mass%, based upon the weight of the concentrate, of an diphenylamine amine antioxidant comprising: 1) 90 mass% or more of bis(nonylphenyl)amine, and 2) 10 mass% or less of (nonylphenyl)(phenyl) amine based on the weight of the bis(nonylphenyl)amine and (nonylphenyl)(phenyl)amine, and
c) from 1 to less than 50 mass%, based upon the weight of the concentrate, of one or more base oils.

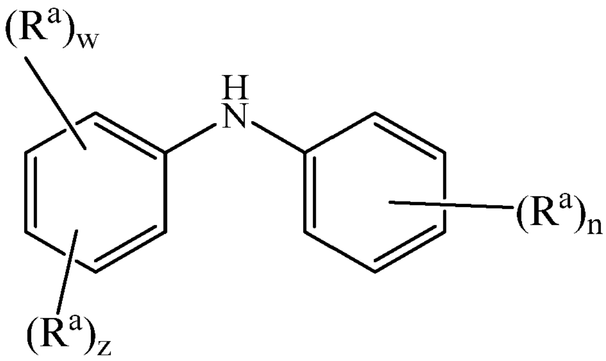
80. The concentrate of paragraph 78 or 79, further comprising,

d) one or more dispersant(s), which may optionally be borated,
e) one or more detergent(s) other than the detergents of paragraphs 77 and 78 (such as carboxylate detergent, phenate detergent, and or sulfonate detergent, such as (such as calcium sulfonate, magnesium sulfonate, or calcium and magnesium sulfonate detergents), optionally providing from 1 to 300 mmol/kg soap to the concentrate (such as 10 to 200 mmol/kg soap),
f) optionally, one or more friction modifier(s) other than glycerol-based friction modifiers),
g) optionally, one or more antioxidant(s), other than diphenylamine amine antioxidant comprising: 1) 90 mass% or more of bis(nonylphenyl)amine, and 2) 10 mass% or less of (nonylphenyl)(phenyl)amine based on the weight of the bis(nonylphenyl)amine and (nonylphenyl)(phenyl)amine, such as hindered phenolic antioxidant(s),
h) optionally one or more friction modifier compounds, other than the organomolybdenum-based compounds, and
i) optionally one or more fatty acid esters, such as sulfated fatty acid methyl esters.

81. The composition or concentrate of any one of paragraphs 63 to 80, further comprising one or more of the following components.

a) one or more friction modifiers other than organomolybdenum and glycerol-based friction modifiers,

b) one or more antioxidants other than the antioxidants represented by Formula (III),



(III)

where each R^a is independently a linear C_9 alkyl or branched C_9 alkyl group, n is 1 or 0, z is 0 or 1, and w is 0 or 1,
c) optionally, one or more pour point depressants,
d) optionally, one or more anti-foaming agents,
e) optionally, one or more viscosity modifiers,
f) optionally, one or more inhibitors and/or antirust agents (such as triazole based inhibitors),
g) dispersant other than dispersants derived from a dispersant derived from a polymer (such as PIB) having an Mn of less than 1600 g/mol, and/or
h) optionally, one or more anti-wear agents other than zinc based anti wear compounds derived solely from primary alcohols (such as one or more zinc dialkyldithiophospates derived from primary and or secondary alcohols).

82. The lubricating composition of any one of paragraphs 63 to 81, further comprising one or more functionalized polymers comprising an amide, imide, and/or ester functionalized partially or fully saturated polymer comprising C_{4-5} olefins having,

a) an Mw/Mn of less than 2,
b) a Functionality Distribution (Fd) value of 3.5 or less, and
c) an Mn of 10,000 g/mol or more (GPC-PS) of the polymer prior to functionalization, provided that, if the polymer prior to functionalization is a copolymer of isoprene and butadiene, then the Mn of the copolymer is greater than 25,000 g/mol.

83. A method of reducing friction in a crankcase of an internal combustion engine comprising providing to the crankcase the lubricating oil composition of any one of paragraphs 63 to 81, wherein the viscometric growth (CEC-L-109-14, 216 hr., 150°C) of the lubricating oil composition is at least 5 % (preferably at least 10%, at least 15%, at least 20%, at least 25%, at least 30 %) less than Y%, where Y% = 53.667x +56.8, where x is the mass% of glycerol-based friction modifier present in the lubricating oil composition.
84. The method of paragraph 83, wherein the viscometric growth (CEC-L-109-14, 216 hr., 150°C) of the lubricating oil composition is Z% or less, where Z = 71.167x + 41.4, where x is the mass% of glycerol-based friction modifier present in the lubricating oil composition.
85. A method of reducing friction in a crankcase of an internal combustion engine comprising providing to the crankcase the composition of any one of paragraphs 63 to 82, wherein the viscometric growth (CEC-L-109-14, 216 hr., 150°C) of the lubricating oil composition is at least 5 % (preferably at least 10%, at least 15%, at least 20%, at least 25%, at least 30 %) less than Y%, where Y% = 0.2411x -20.203, where x is the ppm magnesium from detergent present in the lubricating oil composition.
86. The method of paragraph 85, wherein the viscometric growth (CEC-L-109-14, 216 hr., 150°C) of the lubricating oil composition is Z% or less, where Z = 0.1273x +26.445, where x is the ppm magnesium from detergent present in the lubricating oil composition.
87. A method of reducing friction in a crankcase of an internal combustion engine comprising providing to the crankcase the lubricating oil composition of any one of paragraphs 63 to 81, such that the coefficient of friction, Q, (as measured by HFRR, 140°C) is at least 5 % less, such as at least 10 % less, such as at least 20% less when in the presence of the enhanced aminic antioxidant than the coefficient of friction (as measured by HFRR, 140°C), at the same temperature ramp conditions in the presence of the baseline aminic antioxidant, wherein Q is within a range from 0.140 to 0.145 in the presence of the enhanced aminic antioxidant.

88. The method of any one of paragraphs 63 to 87, wherein the viscometric growth (CEC-L-109-14, 216 hr., 150°C) of the lubricating oil composition is at least 5 % (preferably at least 10%, at least 15%, at least 20%, at least 25%, at least 30 %) lower relative to a lubricating oil composition of the same formulation when the diphenylamine antioxidant is replaced at the same mass percentage by diphenylamine antioxidant comprising about 68 mass% of bis(nonylphenyl) amine, about 29 mass% of (nonylphenyl)(phenyl)amine and about 3 mass% of tri(nonylphenyl)amine based upon the weight of the (nonylphenyl)(phenyl)amine, bis(nonylphenyl)amine, and tri(nonylphenyl)amine, as determined by UPLC.
89. The composition method or use of any of paragraphs 63 to 88, wherein the diphenylamine antioxidant comprises 90 mass% or more of bis(nonylphenyl)amine and 15 (or 10, 04 5, or 4, or 3, or 2, or 1, or 0.5) mass% or less of (nonylphenyl)(phenyl)amine, based on the weight of the enhanced aminic antioxidant.
90. The composition, method or use of any of paragraphs 63 to 89, wherein two or more lubricating oil compositions each comprising: a) diphenylamine amine antioxidant comprising 90 mass% or more of bis(nonylphenyl)amine and 10 mass% or less of (nonylphenyl)(phenyl)amine based on the weight of the bis(nonylphenyl)amine and (nonylphenyl)(phenyl)amine, and b) at least one different component selected from the group consisting of:

1) glycerol-based friction modifiers, (optionally 0.6 mass% or less glycerol-based friction modifier, based upon the weight of the composition)
2) sulfonate-based detergents (optionally calcium and/or magnesium sulfonate based detergents),
3) organomolybdenum-based friction modifiers (optionally di nuclear and or trinuclear molybdenum dithiocarbamates),
4) magnesium-based detergents, such as Mg salicylate and or Mg sulfonate detergents, optionally providing 400 ppm or more of Mg to the composition,
5) salicylate based detergents (optionally calcium salicylate based detergents, such as combinations of calcium and magnesium based detergents),
6) zinc dialkyldithiphosphates derived from one or more primary alcohol(s),
7) dispersants (such as PIBSA-PAM) derived from a polymer (such as polyisobutylene) having an Mn of less than 1600 g/mol,
8) calcium based detergents (optionally calcium salicylate and or calcium sulfonate based detergents, such as combinations of calcium and magnesium based salicylate and or sulfonate detergents),

where: **i)** the viscometric growth (CEC-L-109-14, 216 hr., 150°C) for each of two or more lubricating oil compositions is at least 5 % (optionally at least 10%, at least 15%, at least 20%, at least 25%, at least 30 % at least 35%, at least 40%, at least 55%, at least 60%, such as at least 70%, such as at least 75%, such as at least 77%) less than the viscometric growth of their respective reference formulations, and ii) where the reference lubricating oil composition for a formulation is the same as that formulation as the except that the diphenylamine antioxidant is replaced at the same mass percentage by diphenylamine antioxidant comprising about 68 mass% of bis(nonylphenyl)amine, about 29 mass% of (nonylphenyl)(phenyl)amine and about 3 mass% of tri(nonylphenyl)amine, based upon the weight of the (nonylphenyl)(phenyl)amine, bis(nonylphenyl)amine, and tri(nonylphenyl)amine, as determined by UPLC.
91. The use of (or a method of using) diphenylamine amine antioxidant to reduce wear scar volume μm^3 **(MTM-R)** of the composition, concentrate or lubricating oil composition of any of paragraphs 63 to 81, wherein organomolybdenum-based friction modifier comprises **trinuclear organo-molybdenum compound** (such as molybdenum dithiocarbamate trimer providing at least 100 ppm, such as at least 200 ppm Mo to the lubricating oil composition) and has at has at least 5% less (such as at least 10% less, such as at least 20% less, such as at least 30% less, such as at least 40% less, such as at least 50% less, such as at least 60% less, such as at least 65% less) wear scar volume μm^3, where the reduction is determined by comparison to the same lubricating oil composition except that the trinuclear organo-molybdenum compound has been replaced by dinuclear organo-molybdenum compound providing the same amount of molybdenum to the lubricating oil composition.

[0411] The following non-limiting examples are provided to illustrate the disclosure.

Experimental

[0412] All molecular weights are number average molecular weights (Mn) reported in g/mol, as determined by gel permeation chromatography using polystyrene standards, unless otherwise noted. "A.I.", "a.i.", and "ai" are mass% active ingredient, unless otherwise indicated.

Testing Procedures

[0413] **KV100** is Kinematic viscosity measured at 100° C according to ASTM D445-19a.

[0414] **L109 Oxidation** 216 hr (reported in units of absorbance per centimeter, A/cm) was determined using the CEC-L-109-14 Oxidation Test for Engine Oils Operating in the Presence of Biodiesel Fuel. The **CEC L-109-14** is a blown air bench oxidation test where the oil sample is aged for 216 hours at a temperature of 150°C with an air flow rate of 10 liters/hour in the presence of 7% B100 biodiesel (80% RME / 20% SME) and 100 ppm Fe^{III} catalyst. The oxidation of the aged oil at end of test is determined by infrared absorbance (IR) and reported in units of absorbance per centimeter, DIN 51453. Kinematic viscosity at 100°C is measured at the initiation of the test and at 216 hours and the percentage change in viscosity was calculated.

[0415] The **Daimler Truck Oxidation** (DTOXID or MBOXID) Test is a blown air oxidation test used to test diesel and petroleum engine lubricating oils for their resistance to oxidation and thermal/oxidation mediated viscosity growth. The test can be carried out on the engine oil directly, or the engine oil can be pretreated with 5 mass% B100 biodiesel. A 250 g sample of the test sample with iron (III) acetylacetonate (100 ppm Fe) is heated at 156°C for 168 hours with air bubbling through the heated sample at 10 L/h. Samples are taken at 72, 96, 120 and at 144 hours. The samples for the start of test, at the intermediary time points and at end of test were measured for kinematic viscosity at 100°C (KV100) using ASTM 445 method and oxidation by Fourier Transform infrared spectroscopy analysis using DIN 51453 method.

[0416] The relative amounts of mono-, di- and tri-C_9 alkylated diphenylamine are determined using either:

[0417] Analytical Method 1: gas chromatography with a flame ionisation detector (GC-FID) using the method described in Patent US 6,135,925 B1.

[0418] Ultra-Performance Liquid Chromatography (UPLC) with UV and mass spectrometer detectors using the conditions detailed in Table A. The mass spectrometer chromatograms were used to confirm identity of the mono-, di and tri-C_9 alkyl substituted diphenylamines. The UV chromatograms were used to establish the relative % of each C_9-substituted diphenylamine by comparing the area under the curve for each constituent.

Table A. UPLC method to analyse nonlated diphenylamines.

Ultra-performance liquid chromatograph	Agilent Infinite II 1260
Sample concentration	0.4 mg/mL in acetonitrile
Injection volume	1 mL
Flow rate	0.50 mL/min
Column description	InfinityLab Poroshell 120: Dimensions - 50 x 2.1 mm, EC C-8 5% carbon load, Particle size 2.7 mm
Mobile phase A	Water + 0.1% (volume/volume) formic acid
Mobile phase B	Acetonitrile + 0.1% (volume/volume) formic acid
Gradient elution method	Stage 1: 60% phase A, 40% phase B for 1 min Stage 2: 60-0% phase A, 40-100% phase B over 1.5 mins Stage 3: 0% phase A, 100% phase B for 7.5 mins Stage 4: 0-60% phase A, 100-40% phase B over 0.5 mins
UV detector	Agilent 1260 Infinity II Diode Array detector WR
Detection wave length	288 nm
Mass spectrometer	Agilent MSD iQ

[0419] In event of conflict between Method 1 GC-FID and Method 2: UPLC, Method 2 UPLC shall control.

[0420] **Sequence IIIH** test for control of viscosity and piston deposits was carried out in a 2012 Chrysler Pentastar naturally aspirated 4 stroke port injection gasoline engine according test procedure ASTM D8111. The Sequence IIIH test consists of 90 hours of engine operation at 3900 rpm which is broken up into 4x20-hour segments and 1 x10-hour segment. Oil samples are drawn from the engine at the end of each segment, as well as after a 10-minute operation check. Oil samples taken at 10 min, 20 hours, 40 hours, 60 hours, 80 hours, and 90 hours. Oil samples are measured for KV40 and KV100, ICP (Inductively Coupled Plasma Atomic Emission Spectrometry, ICP-AES, ASTM D5185), DIR oxidation and nitration (ASTM E168), total acid number (TAN, ASTM D664) and total base number (TBN, ASTM D2896). The performance of the oil is determined by the average weighted piston deposits (merits, ASTM D8111) and the percentage kinematic viscosity change at 40°C of the oil at the end of test relative to the start of test. The **Sequence IIIH** test is an industry standard test used to evaluate protection against oil thickening and piston deposits by internal combustion engine lubricating compositions.

MHT4-TEOST

[0421] Moderately high temperature deposits (MHT4-TEOST) was performed according to ASTM D 7097.

MTM-R Test

[0422] Each oil was tested using a Mini-Traction Machine with reciprocating function (MTM-R) available from PCS Instruments, London, UK. This machine employs an inch (19 mm) diameter ball as an upper specimen which is reciprocated under an applied load against a lower specimen in the form of a disc. The ball was made from AISI52100 grade steel and was uncoated, with surface roughness <0.02 μmRa and surface hardness = 800-920 Hv. The disc was made from AISI52100 grade steel and was uncoated, with surface roughness <0.02 μmRa and surface hardness = 720-780 Hv. The contact between the ball and the disc was thus between two ferrous (steel) surfaces. The test conditions were: Oil temperature 100°C, Disc frequency 10 Hz, Ball speed 350 mm/s, Stroke length 4mm, Applied load 50 N, Contact pressure 0.74 GPa, Test duration 45 minutes. The wear scars formed on the lower disc specimens were analyzed using a Zemetrics ZeScope 3D optical profilometer using non-contact interferometric focal scanning. This permitted a measurement of the amount of wear by determining the material lost from the disc during the test. This was reported as a wear scar volume (WSV) in units of μm^3. Additionally, the co-efficient of friction of the contact was recorded at the end of each test.

MTM TEST

[0423] Each oil was tested using a Mini-Traction Machine (MTM) available from PCS Instruments, London, UK. This machine employs an inch (19 mm) diameter ball as an upper specimen which is under an applied load against a lower specimen in the form of a disc. The ball was made from AISI52100 grade steel and was uncoated, with surface roughness <0.02 μmRa and surface hardness = 800-920 Hv. The disc was made from AISI52100 grade steel and was uncoated, with surface roughness <0.02 μmRa and surface hardness = 720-780 Hv. The contact between the ball and the disc was thus between two ferrous (steel) surfaces. The test conditions were: Oil temperatures of 60°C, 80°C, 100°C and 135°C, Ball speed ranges from 2 m/s to 0.2 m/s, Applied load 30 N, Mean contact pressure 0.62 GPa, Test duration 70 minutes. Additionally, the mean Stribeck co-efficient of friction of the contact at 135°C was recorded at the end of each test.

High-Frequency Reciprocating Rig (HFRR)

[0424] HFRR was measured according to (ISO 12156 (2nd Edition, 2018) as follows. An HFRR device commercially available from PCS Instruments, London, UK(AUTOHFR software, v2.0 PCS4 user manual) was used. This device employs a ~6mm diameter ball as an upper specimen which is reciprocated under an applied load against a lower specimen in the form of a ~10mm diameter x ~3mm thick disc. The ball and disc are made of AISI 52100 polished steel (and must have their antirust coating removed before testing). Test conditions are as follows: reciprocating frequency ~40Hz; stroke length ~1mm; applied load ~400g; and contact pressure ~1GPa. Samples are analyzed at temperatures ranging from ~40°C to ~140°C. Sample runs commence when a sample is held at ~40°C for ~1min, subject to test conditions for ~ 5mins, ramped at ~5-15°C/min up another ~20°C, held at that increased temperature for ~1min, and the cycle repeated every ~20°C up to ~140°C, after which the temperature is ramped down to room temperature (~20-25°C). Under those conditions, wear scars were typically formed. The wear scars on the upper ball specimens were measured with the ball located in the holder using an optical microscope with a calibrated micrometer. This was reported herein as a mean wear scar diameter (WSD, based on a simple average of Y-axis and X-axis measurements, Y being the longest length of the wear scar and X being the measurement at a 90° to the Y-axis) in units of μm. The HFRR device is (and the PCS device is) equipped with a piezoelectric transducer that can measure the average friction coefficient between the ball and the disc.

Materials

Component Chart

[0425]

Component	Description
Dispersant viscosity modifier (DVM)	Functionalized hydrogenated isoprene block copolymer produced according to methods disclosed in USSN 18/480,571 filed October 4, 2023.

(continued)

Component	Description
Borated-PIBSA-PAM	Borated PIBSA-PAM in oil derived from PIB having an Mn less than 1000 g/mol
PIBSA-PAM	PIBSA-PAM dispersant derived from PIB having an Mn 2000 g/mol or more
PIBSA-Ester Dispersant	PIBSA ester of hydrocarbyl-bridged naphthyloxy alcohol in oil, See US Patent No. 7,485,603.
LMW PIBSA-PAM	PIBSA-PAM in oil derived from PIB having an Mn less than 1000 g/mol
HMW PIBSA-PAM	PIBSA-PAM dispersant HR PIB 2300 Mn
Mg Salicylate	Magnesium Salicylate Detergent in oil
Ca Salicylate	Calcium Salicylate Detergent (200 to 400 TBN) in oil
Ca sulfonate	Calcium sulfonate detergent in oil
Mg sulfonate	Magnesium sulfonate detergent in oil
ZDDP	ZDDP (derived from primary and or secondary alcohols) in oil
1° ZDDP	ZDDP derived from primary alcohols in oil
Phenolic antioxidant	Hindered phenolic antioxidant
Mo-friction modifier	Trimeric MoDTC antioxidant/friction modifier
Mo-Dimer FM	Dimeric MoDTC antioxidant/friction modifier
Corrosion Inhibitor	Triazole corrosion inhibitor
Organic Friction Modifier	glycerol mono-oleate
Ester friction modifier	nitrogen containing fatty acid ester friction modifier
ODSA	Octadecenyl Succinic Anhydride
PIBSA	Polyisobutylene succinic anhydride
PIB	polyisobutylene
Anti-foamant	PDMS silicone anti-foamant
Olefin Copolymer VM	ethylene propylene olefin copolymer in oil
LOFI- lube oil flow improver	C8-18 dialkylfumarate/vinyl acetate copolymer in oil
Star H-SD block copol	Hydrogenated styrene-diene block star viscosity modifier in oil
PAO	based PAO VI 120-140, KV100 4-6 cSt
diluent	Group I base oil
Group II basestock	Group II basestock, ~5 cSt
NEXBASE4PLUS™	NEXBASE4PLUS™ -Group III Basestock, approx 2:1 mix of SynNova 4: Nexbase3043; KV100 ~ 4 cSt
Group III basestock	Group III Basestock ~4 cSt

Component 1 [distilled Di(C_9-alkyl phenyl)aminel

[0426] C_9-alkyl phenylamine, resulting from the reaction of tripropylene and diphenylamine (illustrated in Figure 1), was subjected to distillation to give pale yellow liquids containing mono-C_9-alkyl diphenylamine, tri-C_9- alkyl substituted diphenylamine and di-C_9-substituted diphenylamine isomers as shown in the table below. Isomer content determined by UPLC.

	Component 1				
	Batch 1 (mass%*)	Batch 2 (mass%*)	Batch 3 (mass%*)	Batch 4 (mass%*)	Batch 5 ("Bx 5") (mass%*)
Mono- Substituted	0.50%	0.10%	0.30%	0.04%	0.8%
Di- Substituted	95.2%	93.2%	95.6%	93.5%	95.3%
Tri- Substituted	4.30%	6.70%	4.10%	6.46%	3.9%
*based upon the weight of the mono-, di- and tri-C_9- alkyl substituted diphenylamines.					

Component 2 [Di(C_9-alkyl phenyl)amine]

[0427] Component 2 is a composition of C_9-alkyl phenyl amine having about 68 mass% of di(C_9-alkyl phenyl)amine, about 29 mass% of mono(C_9-alkyl phenyl)amine and about 3 mass% of tri(C_9-alkyl phenyl)amine, based upon the weight of the C_9-alkylated phenyl amines. Isomer content determined by UPLC.

Example 1

[0428] Component 1 (Batch 2) and Component 2 were each blended into the formulation described in Table 2 to form Oil A and Comparative Oil B, respectively.

Table 2.

Components* (Mass%)	**Oil A**	**Comparative Oil B**
Borated PIBSA-PAM	1.6	1.6
PIBSA-PAM	5.5	5.5
Magnesium salicylate	0.9	0.9
Calcium salicylate	1.3	1.3
ZDDP	0.9	0.9
Component 1 (Batch 2)	3.0	
Component 2		3.0
PAO	14.2	14.2
Group III Basestock	63.1	63.1
Elemental Analysis ICP		
Ash (mass%)	0.77	0.77
B ppm	208	208
Ca (mass%)	0.10	0.10
Mg (mass%)	0.07	0.07
Mo ppm	148	148
N (mass%)	0.21	0.21
P (mass%)	0.08	0.08
S (mass%)	0.20	0.20
Si ppm	18	18
*each oil had the same amount of organic friction modifier, Mo Friction modifier, corrosion inhibitor, PIBSA, anti-foamant, Group I diluent oil, LOFI, and Star H-SD block copol VM.		

[0429] Oil A and Comparative Oil B were tested for oxidation stability and viscosity control using the test conditions detailed in CEC-L-109-14, with a test run time of 216 hours. The data are reported in Table 3.

Table 3. Results

Component		**Oil A (mass%)**	**Comparative Oil B (mass%)**
Component 2			3.0
Component 1 (Batch 2)		3.0	
CEC-L-109-14 test results	Oxidation, FTIR (A/cm)	31.4	30.9
	% Change in K_v100	66.0	75.8

[0430] In Table 3, the data shows that at the end of the tests, Component 1 (Batch 2) maintained high levels of oxidation control, while obtaining excellent reduced viscosity increase (% Change in K_v100) at end of the test.

Example 2

[0431] Component 1 (Batch 2) and Component 2 were each blended into the formulation described in Table 4 to form Oils C, D and E and Comparative Oils F, G and H, respectively.

Table 4.

Components (Mass%)**	C	D	E	Comparative Oil F	Comparative Oil G	Comparative Oil H
Borated PIBSA-PAM	3.9	3.9	3.9	3.9	3.9	3.9
PIBSA-PAM	6.0	6.0	6.0	6.0	6.0	6.0
Calcium salicylate	1.9	1.9	1.9	1.9	1.9	1.9
ZDDP	0.8	0.8	0.8	0.8	0.8	0.8
Phenolic Antioxidant	0.4	0.4	0.4	0.4	0.4	0.4
Component 1 (Batch 2)	0.29	0.5	0.8			
Component 2				0.29	0.5	0.8
PAO	20.0	20.0	20.0	20.0	20.0	20.0
Group III Basestock	51.9	51.7	51.4	51.9	51.7	51.4
Elemental Analysis ICP						
Ash (mass%)	0.84	0.84	0.84	0.84	0.84	0.84
B ppm	500	500	500	500	500	500
Ca (mass%)	0.18	0.18	0.18	0.18	0.18	0.18
Mg (mass%)	0.001	0.001	0.001	0.001	0.001	0.001
Mo ppm	0	0	0	0	0	0
N (mass%)	0.13	0.14	0.15	0.13	0.14	0.15
P (mass%)	0.08	0.08	0.08	0.08	0.08	0.08
S (mass%)	0.19	0.19	0.19	0.19	0.19	0.19
Si ppm	7.0	7.0	7.0	7.0	7.0	7.0
**each oil had the same amount of PIBSA, anti-foamant, Group I diluent oil, LOFI, and Star H-SD block copol.						

[0432] Oils C, D and E and Comparative Oils F, G and H were tested for oxidation stability and viscosity control using the test conditions detailed in CEC -L-109-14, with a test run time of 216 hours. The data are reported in Table 5.

Table 5.

Component (Mass%)	Oil C	Oil D	Oil E	Comparative Oil F	Comparative Oil G	Comparative Oil H
Component 2				0.29	0.5	0.8

(continued)

Component (Mass%)		Oil C	Oil D	Oil E	Comparative Oil F	Comparative Oil G	Comparative Oil H
Component 1 (Batch 2)		0.29	0.5	0.8			
CEC-L-109-14 test results	Oxidation FTIR (A/cm)	47.7	43.0	38.5	47.7	41.9	39.0
	% Change in K_v100	87.4	74.6	61.1	85.7	79.5	69.7

[0433] Oils C, D and E show that oxidation performance can be maintained and at treat rates of 0.5 and 0.8 mass% of Component 1 (Batch 2) the viscosity control was better at end of test than Component 2.

Example 3

[0434] Component 1 (Batch 2) and Component 2 were each blended into the formulation described in Table 6 to form Oils I, J and K and Comparative Oils L, M and N, respectively.

Table 6.

Components*** (Mass%	Oil I	Oil J	Oil K	Compar ative Oil L	Compar ative Oil M	Compar ative Oil N
Borated PIBSA-PAM	0.6	0.6	0.6	0.6	0.6	0.6
PIBSA-PAM	6.0	6.0	6.0	6.0	6.0	6.0
Magnesium salicylate	0.6	0.6	0.6	0.6	0.6	0.6
Calcium salicylate	1.4	1.4	1.4	1.4	1.4	1.4
ZDDP	1.0	1.0	1.0	1.0	1.0	1.0
Phenolic antioxidant	0.2	0.2	0.2	0.2	0.2	0.2
Component 1 (Batch 2)	0.29	0.5	1.0			
Component 2				0.29	0.5	1.0
PAO	21.0	21.0	21.0	21.0	21.0	21.0
Group III Basestock	59.0	58.8	58.3	59.0	58.8	58.3
Elemental Analysis ICP						
Ash (mass%)	0.77	0.77	0.77	0.77	0.77	0.77
B ppm	72	72	72	72	72	72
Ca (mass%)	0.13	0.13	0.13	0.13	0.13	0.13
Mg (mass%)	0.05	0.05	0.05	0.05	0.05	0.05
Mo ppm	0	0	0	0	0	0
N (mass%)	0.09	0.10	0.11	0.09	0.10	0.11
P (mass%)	0.08	0.08	0.08	0.08	0.08	0.08
S (mass%)	0.18	0.18	0.18	0.18	0.18	0.18
Si ppm	6.2	6.2	6.2	6.2	6.2	6.2
***each oil had the same amount of organic friction modifier, PIBSA, anti-foamant, Group I diluent oil, PAO diluent, LOFI, and Star H-SD block copol.						

[0435] Oils I, J and K and Comparative Oils L, M and N were tested for oxidation stability and viscosity control using the test conditions detailed in CEC -L-109-14, with a test run time of 216 hours. The data are reported in Table 7.

Table 7.

Component Mass%		Oil I	Oil J	Oil K	Comparative Oil L	Comparative Oil M	Comparative Oil N
Component 2					0.29	0.5	1.0
Component 1 (Batch 2)		0.29	0.5	1.0			
CEC-L-109-14 test results	Oxidation FTIR (A/cm)	Too viscous	63.3	41.7	73.5	59.6	39.0
	% Change in K_V100	2168	432	59.9	843	333	92

[0436] At 0.29 mass% both components had poor control over viscosity; however, Component 1 (Batch 2) was too viscous for an oxidation measurement to be made. At 0.5 mass% of each Component 1(Batch 2) and Component 2, the oxidation measurements at end of the test were quite similar, but Oil J (Component 1, (Batch 2)) was more viscous at end of test than Oil M (Component 2).

[0437] At the highest treat rate (1.0 mass%), Component 1 (Batch 2) performed significantly better than Component 2 at controlling the oxidation mediated viscosity increase. The oxidation at end of test was about the same for Oil K and Oil N.

Example 4

[0438] Component 1 (Batch 1) and Component 2 were each blended into the formulations described in Table 6 to form Oils O, P, Q, R and Comparative Oils C-S, C-T, C-U, and C-V, respectively. Oils O, P, Q and R and Comparative Oils C-S, C-T, C-U and C-V were tested for oxidation stability and viscosity control according to CEC -L-109-14 test with a test run time of 216 hours. The data are reported in Table 9.

Table 8. Formulations.

Components ** Mass %**	O	P	Q	R	C-S	C-T	C-U	C-V
Borated PIBSA-PAM	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
PIBSA-PAM	5.8	5.8	5.8	5.8	5.8	5.8	5.8	5.8
PIBSA-Ester Dispersant	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Magnesium salicylate	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Calcium salicylate	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4
ZDDP	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Component 1(Batch 1)	0.5	0.75	1.0	1.25				
Component 2					0.5	0.75	1.0	1.25
Group III base oil	79.0	78.7	78.5	78.2	79.0	78.7	78.5	78.2
Elemental Analysis ICP								
Ash (mass%)	0.76	0.76	0.76	0.76	0.76	0.76	0.76	0.76
B ppm	101	101	101	101	101	101	101	101
Ca (mass%)	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11
Mg (mass%)	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06
Mo ppm	83	83	83	83	83	83	83	83
N (mass%)	0.10	0.11	0.12	0.13	0.10	0.11	0.12	0.13
P (mass%)	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08
S (mass%)	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19

(continued)

Elemental Analysis ICP								
Si ppm	13	13	13	13	13	13	13	13
**** each oil had the same amount of Mo Friction modifier, PIBSA, anti-foamant, Group I diluent oil, LOFI, and Star H-SD block copol VM-2.								

Table 9.

Component (Mass%)		**Oil O**	**Oil P**	**Oil Q**	**Oil R**	**C- S**	**C- T**	**C-U**	**C- Oil V**
Component 2						0.5	0.75	1.0	1.25
Component 1(Batch 1)		0.5	0.75	1.0	1.25				
CEC-L-109-14 test results	Oxidation FTIR (A/cm)	72.0	47.1	38.7	33.4	63.4	43.9	35.9	30.2
	% Change in K_V100	85.9	58.1	47.2	40.4	72.9	60.3	52.7	48.2

[0439] At all treat rates the oils containing Component 1 (Batch 1) maintained oxidation control. at 0.5 mass% Comparative Oil S performs better than Oil O at viscosity control. Oil P and Comparative Oil T have the same relative increase in viscosity at end of test. At the two highest treat rates, 1.0 mass% and 1.25 mass%, Component 1 (Batch 1) has a 5.5% and 7.8% lower relative viscosity increase in line with Examples 1, 2 and 3.

Example 5

[0440] Component 1 (Batch 3) and Component 2 were each blended into the formulation as described in Table 10 below to form Oils W and X, respectively.

Table 10.

Components (Mass%)***	**W**	**X**
Dispersant viscosity modifier	1.156	1.156
Borated PIBSA-PAM	0.5	0.5
PIBSA-PAM	6.0	6.0
Ca sulfonate	0.8	0.8
Mg sulfonate	0.8	0.8
ZDDP	1.0	1.0
Component 1 (Batch 3)	1.6	
Component 2		1.6
Group III base oil	82.0	82.0
Elemental Analysis ICP		
Ash (mass%)	0.76	0.76
B ppm	66	66
Ca (mass%)	0.09	0.09
Mg (mass%)	0.07	0.07
Mo ppm	66	66
N (mass%)	0.16	0.16
P (mass%)	0.08	0.08
S (mass%)	0.31	0.31

(continued)

Elemental Analysis ICP		
Si ppm	15	15
******each oil had the same amount of PIBSA, Mo Friction modifier, anti-foamant, PIB, Group I diluent oil, LOFI, and Olefin Copolymer VM.		

[0441] Oils W and Comparative Oil X were tested for oxidation stability and viscosity control using the Daimler Truck Oxidation Test doped with biodiesel as described above. The data are reported in Table 11.

Table 11.

Component		**Oil W (mass%)**	**Comparative Oil X (mass%)**
Component 2			1.6
Component 1 (Batch 3)		1.6	
Daimler Truck Oxidation Test results	Oxidation, FTIR (A/cm)	30.3	29.5
	% Change in K_V100	64.9	70.5

[0442] Oil W and Comparative Oil X at end of test have the same level of oxidation; however, Oil W has a lower relative increase in viscosity at end of test. This is consistent with the results for CEC -L-109-14 tests above.

Example 6

[0443] Component 1 (Batch 2) and Component 2 were each blended into the formulation described in Table 12 to form Oil Y and Comparative oil Z, respectively.

Table 12.

Constituent (Mass %)^	**Y**	**Z**
PIBSA-PAM	3.300	3.300
Ca sulfonate	0.850	0.850
Mg sulfonate	0.475	0.475
ZDDP	0.88	0.88
Component 1 (Batch 2)	1.0	
Component 2		1.0
Group III base oil	85.9	85.9
Elemental Analysis ICP		
Ash (mass%)	0.63	0.63
B ppm	0	0
Ca (mass%)	0.10	0.10
Mg (mass%)	0.04	0.04
Mo ppm	69	69
N (mass%)	0.09	0.09
P (mass%)	0.06	0.06
S (mass%)	0.20	0.20
Si ppm	9.2	9.2
^each oil had the same amount of ODSA, Mo Friction modifier, Ester friction modifier, anti-foamant, Group I diluent oil, LOFI, and Star H-SD block copol.		

[0444] Oils Y and Comparative Oils Z were tested for their ability to control viscosity increase (PVIS) and piston deposits (WPD) in the Seq IIIH test (ASTM D8111) as described above. The data are reported in Table 13.

Table 13.

Component		Oil Y (mass%)	Comparative Oil Z (mass%)
Component 2			1.0
Component 1 (Batch 2)		1.0	
Sequence IIIH	PVIS (%)	71.8	76.8
	WPD (merits)	5.21	4.36

[0445] Following similar trend to the blown air oxidation test, the viscosity growth is lower for Oil Y (Component 1, Batch 2) than Comparative Oil Z (Component 2). Unexpectedly, there was a greater difference in the level of piston deposits. Comparative Oil Z has weighted piston deposits (WPD) of 4.36 which is less than the anticipated API GF-7 level of 4.6; however, Oil Y has a WPD of 5.21 which represents a significant improvement in deposit control compared to Comparative Oil Z and the anticipated API GF-7 specification limit for WPD.

Example 7

[0446] It is shown in the preceding examples that the aminic antioxidant with low levels of mono-C_9-alkyl phenylamine performs better in a range of formulations in the CEC-L-109-14 test. In the examples below, it is demonstrated that this improved performance enables the use of higher treat rates of components that have been shown or are thought to be detrimental to performance in the CEC-L-109-14 test. The higher treat rates of such components give engine oils improved performance in areas such as friction lowering, metal wear, deposit control and low speed pre-ignition.

[0447] Component 1 Bx 5 and Component 2 were each blended into the formulations described in Tables 14 to 18 below.

[0448] In Table 14 lubricating oil formulations are formulated with and without glycerol mono-oleate (GMO) to compare the performance in the CEC-L-109-14 test. The impact of GMO on viscosity control can limit its use in oils, limiting the fuel economy benefits that a friction modifier like GMO can impart. For Example, Comparative Oil A1 showed 32% greater viscosity increase at the end of the test than the oil that did not contain GMO, Comparative Oil B1.

Table 14.

Constituent* (mass%)	Comparative Oil A1	Comparative Oil B1	Oil C1	Oil D1	Oil E1
Borated-PIBSA-PAM	0.6	0.6	0.6	0.6	0.6
Mg Salicylate	0.6	0.6	0.6	0.6	0.6
Ca Salicylate	1.4	1.4	1.4	1.4	1.4
Component 2	1.0	1.0			
Component 1 (Bx 5)			1.0	1.0	1.0
Organic Friction Modifier	0.6		0.6		0.2
Group III base oil	balance	balance	balance	balance	balance
Elemental Analysis ICP					
Ash (mass%)	0.77	0.77	0.77	0.77	0.77
B ppm	72	72	72	72	72
Ca (mass%)	0.13	0.13	0.13	0.13	0.13
Mg (mass%)	0.05	0.05	0.05	0.05	0.05
N (mass%)	0.11	0.11	0.11	0.11	0.11
P (mass%)	0.08	0.08	0.08	0.08	0.08
S (mass%)	0.18	0.18	0.18	0.18	0.18

(continued)

Performance Data					
CEC-L-109-14 test % Change in K_V100	89.0	56.8	84.1	41.4	
MTM: Friction Coefficient, 135°C, 0.02 m/s	0.104		0.093		
HFRR: Wear Scar Diameter (μm)	197		182.5		
HFRR: avg Friction Coefficient at 140°C		0.151			0.143
MTM-R: Avg Traction Coefficient at 100°C		0.103			0.090
*each oil had the same amount of HMW PIBSA-PAM, phenolic antioxidant, PIBSA, anti-foamant, ZDDP, Group I diluent oil, 20 mass% PAO basestock, LOFI, and Star H-SD block copol.					

[0449] Oil C1 and D1, containing Component 1, Batch 5 outperform their respective comparative oils with Component 2 (Comparative Oils A1 and B1), see Figure 2, consistent with the observations made in Examples 1, 2, 3 and 4.

[0450] Due to the improved L109 viscosity control performance when using Component 1 Bx5 versus Component 2, increased treat rates of GMO can be used when formulating with Component 1 Bx 5. To calculate the amount of GMO that would be used in the inventive examples to obtain the L109 viscosity performance equivalent to a comparative Component 2 blend, solve for X in the following equation (See Figure 2):

$$Y = 41.4 + 71.17X,$$

where Y equals the CEC-L-109 viscosity increase of the comparative Component 2 blend and X is equal to the GMO mass%. For example, to calculate the additional amount of GMO that can be added to inventive Oil D1 to give equivalent L109 viscosity control of the comparative Component 2 blend (Oil B1) the following equation is used:

$$X = (56.8 - 41.4)/71.17 = 0.22 \text{ mass\% GMO}.$$

[0451] Oil E1 was formulated with Component 1 Bx5 and 0.22 mass% GMO and was compared to Comparative Oil B1 formulated with Component 2 and zero mass% GMO. The data show good HFRR friction coefficient reduction (0.143 vs 0.151) and good MTM-R average traction coefficient reduction (0.090 vs 0.103). Lower friction will translate in an engine to greater fuel economy. For Comparative Oil B1 vs Oil E1, we predict that Oil E1 will have similar CEC-L-109-14 results to Comparative Oil B1.

[0452] Surprisingly, Oil C1 had lower friction coefficient in the MTM test than Comparative Oil A1 (0.093 vs 0.104), as well as showing less wear scar diameter in the HFRR test (182.5 vs 197 μm^2). Further note that for Comparative Oil A1 in comparison with Oil C1 (both containing 0.6 mass% GMO), Oil A1 obtains lower CEC-L-109-14 growth in viscosity (89.0% vs 84.1%) in addition to the lower MTM friction coefficient and reduced HFRR wear scar diameter. These data indicate that the inventive antioxidant Component 1 enables higher treat rates of friction modifier GMO for better viscosity control in the CEC-L-109-14 test. This confirms that use of enhanced antioxidant enables inclusion of higher concentrations of GMO friction modifier, which in turn enables lower friction and hence provides better fuel economy.

[0453] Also note, Component 1, Batch 5 also shows inherently lower friction and wear in the absence of GMO (Comparative Oil B1 vs Oil D1). In the absence of GMO (compare Comparative Oil B1 to Oil D1) show desirable reduced viscosity growth for component 1, Batch 5 in the CEC-L-109 test (56.8% vs 41.4%).

Example 8

[0454] **Table 15** shows inventive (Component 1 Bx 5) oils and comparative (Component 2) oils blended with either trimeric MoDTC friction modifier or dimeric MoDTC friction modifier.

Table 15.

Constituent* (mass %)	C-Oil F1	C-Oil G1	Oil H1	Oil J1	C-Oil K1	C-Oil L1
Borated-PIBSA-PAM	0.6	0.6	0.6	0.6	0.6	0.6
Mg Salicylate	0.6	0.6	0.6	0.6	0.6	0.6
Ca Salicylate	1.4	1.4	1.4	1.4	1.4	1.4
Mo-friction modifier		0.9		0.9		0.5

(continued)

Constituent* (mass %)	C-Oil F1	C-Oil G1	Oil H1	Oil J1	C-Oil K1	C-Oil L1
Mo-Dimer FM	0.5		0.5		0.08	
Component 2	1.0	1.0			1.0	1.0
Component 1 Bx 5			1.0	1.0		
Organic Friction Modifier	0.6	0.6	0.6	0.6	0.6	0.6
Group III base oil	balance	balance	balance	balance	balance	balance
Elemental Analysis						
Ash (mass %)	0.77	0.77	0.77	0.77	0.77	0.77
B ppm	72	72	72	72	72	72
Ca (mass %)	0.13	0.13	0.13	0.13	0.13	0.13
Mg (mass %)	0.05	0.05	0.05	0.05	0.05	0.05
Mo ppm	500	500	500	500	80	275
N (mass %)	0.11	0.11	0.11	0.11	0.11	0.11
P (mass %)	0.08	0.08	0.08	0.08	0.08	0.08
S (mass %)	0.18	0.18	0.18	0.18	0.18	0.18
Performance Testing						
CEC-L-109-14 % Change in Kv100	180.3	126.1	103.6	109.4		
HFRR: Wear Scar Diameter μm			197	170	255	233
HFRR Friction Coefficient at 140°C			0.075	0.076	0.134	0.072
MTM-R: Avg Traction Coefficient at 100°C			0.033	0.033	0.081	0.033
MTM-R: Wear Scar Volume/ μm^3			72,643	25,340	173,820	52,851
*each oil had the same amount of ZDDP, HMW PIBSA-PAM, phenolic antioxidant, PIBSA, anti-foamant, Group I diluent oil, 20 mass% PAO basestock, LOFI, and Star H-SD block copol.						

[0455] Comparative **Oil K1** was formulated with Component 2 and 0.08 mass % molybdenum dithiocarbamate dimer, providing 80 ppm Mo, and compared to compared to **Oil H1** formulated with Component 1 Bx5 and 0.5 mass % molybdenum dithiocarbamate dimer, providing 500 ppm Mo.

[0456] Inventive Oil H1, containing 420 ppm more Mo than Comparative **Oil K1** showed lower HFFR friction coefficient (0.075 vs. 0.134) and HFFR wear scar diameter (197 vs 255 μm) and lower MTM-R traction coefficient (0.033vs 0.081) and MTM-R wear scar volume (72,643 vs 173,820 μm^3). Lower friction is expected to translate in an engine into greater fuel economy. Likewise, the higher Mo content that we are capable of using in oil compositions because of the presence of Component 1 is expected to positively impact LSPI and reduce low speed pre-ignition events. **Oil H1** is expected to have a similar or better percent change in viscosity (CEC-L-109) as compared to Comparative **Oil K1.**

[0457] Comparative **Oil L1** was formulated with Component 2 and 0.50 mass % molybdenum dithiocarbamate trimer, providing 275 ppm Mo, and compared to compared to **Oil J1** formulated with Component 1 Bx5 and 0.9 mass % molybdenum dithiocarbamate trimer, providing 500 ppm Mo. Comparative **Oil L1** is expected to have a similar percent change in viscosity (CEC-L-109) as compared to **Oil J1.** Note that Oil J1 shows improved MTM-R wear scar volume (25,340 vs 52,851 μm^3) and improved HFRR wear scar diameter (170 vs 233 μm), while maintaining similar friction properties (MTM-R traction coefficient and HFFR friction coefficient).

[0458] Comparative **Oil F1** was formulated with Component 2 and 0.50 mass % molybdenum dithiocarbamate dimer, providing 500 ppm Mo, and compared to compared to **Oil H1** formulated with Component 1 Bx5 and 0.5 mass % molybdenum dithiocarbamate dimer, providing 500 ppm Mo. Note that **Oil H1** has a significantly reduced CEC-L-109-14 percent increase in viscosity as compared to Comparative **Oil F1** (103.6% vs 180.3%).

[0459] Comparative **Oil G1** was formulated with Component 2 and 0.50 mass % molybdenum dithiocarbamate dimer, providing 500 ppm Mo, and compared to compared to **Oil J1** formulated with Component 1 Bx5 and 0.5 mass % molybdenum dithiocarbamate dimer, providing 500 ppm Mo. Note that **Oil J1** has a reduced CEC-L-109-14 percent increase in viscosity as compared to Comparative **Oil G1** (109.4% vs 126.1%).

[0460] Due to the improved L109 viscosity control performance when using Component 1 Bx5 versus Component 2 in the presence of 500 ppm Mo, increased treat rates of molybdenum dithiocarbamate **dimer** can be used when formulating with Component 1 Bx 5. To calculate the amount of Mo (ppm) that would be used in the comparative examples to obtain the L109 viscosity performance equivalent to the inventive Component 1 Bx 5 blend, solve for X in the following equation:

$$Y = 89 + 0.183X,$$

where Y equals the L109 viscosity increase of the inventive Component 1 Bx 5 blend and X is equal to the Mo ppm from molybdenum dithiocarbamate dimer in comparative Component 2 blend.
For example, to calculate the Mo (ppm) that can be added to Comparative Oil A1 to give equivalent L109 viscosity control of the inventive Component 1 Bx 5 blend (Oil H1) solve for X in the equation above, where Y is 103.6. For our example, X= (103.6 - 89)/0.183 = 80 ppm Mo.

[0461] Due to the improved L109 viscosity control performance when using Component 1 Bx 5 vs Component 2 in the presence of 500 ppm Mo from molybdenum dithiocarbamate **trimer** (Mo-friction modifier, in Table 15), we are able to use increased treat rates of molybdenum dithiocarbamate trimer when formulating with Component 1 Bx 5. To calculate equivalent L109 viscosity increase performance the equation **Y = 0.0742X + 89** is used where Y equals L109 viscosity increase performance of Component 1 Bx 5 and X equals Mo ppm from molybdenum dithiocarbamate trimer.

[0462] For example, to calculate the amount of molybdenum from dithiocarbamate trimer that would be used in the inventive example (Oil H1) to give equivalent L109 viscosity control with to comparative example(Oil G1), solve for X in above equation where Y is 109.4. For our example, X =(109.4 - 89)/0.0742= 275 ppm Mo from molybdenum dithiocarbamate trimer.

Example 9

[0463] In **Table 16** Component 1, Batch 5 is shown to provide better deposit control than Component 2 in a standard industry bench test, MHT-4 TEOST. In a lubicating oil composition with an all sulfonate detergent system, Oil 01 (Component 1, Batch 5) had 40 % less deposits than Comparative Oil M1 (Component 2). In a lubricating oil composition that is boosted with low molecular weight dispersant (LMW PIBSA-PAM), Oil P1 (Component 1) had 53 % less deposits than Comparative Oil N1 (Component 2). The increase in deposit control observed with Component 1 is consistent with the results in **Example 6,** Sequence IIIH engine test.

Table 16.

Constituent* (mass%)	Comparative Oil M1	Comparative Oil N1	Oil O1	Oil P1	C-Oil Q1	Oil R1
LMW PIBSA-PAM		1.5		1.5		
Borated-PIBSA-PAM	0.6	0.6	0.6	0.6	0.6	0.6
Mg Salicylate		0.6		0.6		
Ca Salicylate		1.4		1.4		
Ca sulfonate	1.1		1.1		0.7	0.7
Mg sulfonate	0.5		0.5		0.9	0.9
Component 2	1.0	1.0			1.0	
Component 1 Bx 5			1.0	1.0		1.0
Organic Friction Modifier	0.6	0.6	0.6	0.6	0.6	0.6
Group III base oil	balance	balance	balance	balance	balance	balance
Elemental Analysis ICP						
Ash (mass%)	0.77	0.77	0.77	0.77	0.77	0.77
B ppm	72	72	72	72	72	72
Ca (mass%)	0.13	0.13	0.13	0.13	0.09	0.09
Mg (mass%)	0.05	0.05	0.05	0.05	0.08	0.08
N (mass%)	0.12	0.14	0.12	0.14	0.14	0.14

(continued)

Elemental Analysis ICP						
P (mass%)	0.08	0.08	0.08	0.08	0.08	0.08
S (mass%)	0.20	0.18	0.20	0.18	0.18	0.18
Performance Testing						
CEC-L-109-14 % Change in Kv100					170.3	94.5
MHT4 TEOST: Total rod deposits (mg)	38.2	22.8	28.8	13.4	28.8	8.5
MTM-R: Avg Traction Coefficient at 100°C					0.093	0.075
HFRR:Wear Scar Diameter μm					237	215
HFRR Friction Coefficient at 140°C					0.156	0.151
*each oil had the same amount of ZDDP, HMW PIBSA-PAM, phenolic antioxidant, PIBSA, anti-foamant, Group I diluent oil, 20 mass% PAO basestock, LOFI, and Star H-SD block copol.						

[0464] In **Table 16,** lubricating oil compositions with an all sulfonate detergent system (Ca:Mg, 2.6:1), a salicylate system with LMW detergent and a magnesium enriched sulfonate detergent systems (Ca: Mg, 1.1:1) and blended with Component 2 or Component 1, Bx 5 were tested for total rod deposits, friction and wear performance. Interestingly, Oil P1, having salicylate detergent content, and Oil O1 having lower sulfonate detergent content showed reduced MHT4 TEOST total rod deposits for compositions containing component 1, Bx 5 (28.8 vs 38.2 mg and 13.4 vs 22.8 mg, respectively), while Oil R1, having high magnesium sulfonate detergent content, showed significantly reduced MHT4 TEOST total rod deposits (8.5 vs 28.8 mg).

[0465] When comparing Oil R1 to Oil O1, which differs from Oil R1 in magnesium sulfonate detergent content, we note Oil O1 has desirable lower MHT4 TEOST total rod deposits of 28.8 mg and Oil R1 has even more desirable MHT4 TEOST total rod deposits of 8.5 mg. Thus, the magnesium content (500 ppm vs 800 ppm Mg) for Oils O1 and R1, suggests a particularly improved effect from the combination of higher magnesium content with Component 1, Bx 5.

[0466] Oil R1 (compared to Comparative Oil Q1) also showed lower MTM-R average traction coefficient (0.075 vs 0.093), lower HFRR wear scar diameter (215 to 237μm), lower HFRR friction coefficient (0.151 vs 0.156) substantially better CEC-L109-14 reduction in viscosity growth (94.5% vs 170.3%), see Figure 4.

[0467] When comparing Comparative Oil N1 to Oil P1 (salicylate detergent and low Mn dispersant), we note Oil P1 has desirable lower MHT4 TEOST total rod deposits (13.4 to 22.8 mg).

[0468] When comparing Comparative Oil M1 vs O1 standard sulfonate space, we note that Oil O1 also has desirable lower MHT4 TEOST total rod deposits (28.8 to 38.2 mg).

[0469] We also expect that the higher Mg content that we are capable of using in oil compositions because of the use of Component 1 will reduce LSPI events.

[0470] Overall, in Table 16, the Component 1 compatibility with sulfonate detergent systems has been demonstrated for friction, wear, viscosity growth, and deposit control.

<u>Example 10</u>

[0471] In **Table 17,** compatibility of Component 1, Batch 5 is demonstrated with Group II and renewable base stocks. These classes of base stocks can be less stable to oxidation than Group III basestocks. The performance of Component 1, Batch 5 was evaluated in these basestocks in the CEC-L109-14 test. Comparative Oil S1 and Oil U1 were formulated with a renewable basestock, Nexbase4plus™, and it was found that the enhanced viscosity control demonstrated in previous examples was maintained. Similarly, in a Group II/III blend, Component I, batch 5 (Oil V1) had a 33% lower viscosity increase in the L109 test than Component 2 (Comparative Oil T1). Component 1 can therefore successfully be used in formulations that are formulated to be lower cost or to be more sustainable.

Table 17.

Constituent* (mass%)	Comparative Oil S1	Comparative Oil T1	Oil U1	Oil V1
Borated-PIBSA-PAM	0.6	0.6	0.6	0.6
Mg Salicylate	1.4	1.4	1.4	1.4
Ca Salicylate	0.6	0.6	0.6	0.6
Component 2	1.0	1.0		
Component 1 Bx 5			1.0	1.0
Organic Friction Modifier	0.6	0.6	0.6	0.6
Group II		30.0		30.0
NEXBASE4PLUS™	59.3		59.3	
Group III base oil		29.3		29.3
Elemental Analysis ICP				
Ash (mass%)	0.77	0.77	0.77	0.77
B ppm	72	72	72	72
Ca (mass%)	0.13	0.13	0.13	0.13
Mg (mass%)	0.05	0.05	0.05	0.05
N (mass%)	0.11	0.11	0.11	0.11
P (mass%)	0.08	0.08	0.08	0.08
S (mass%)	0.18	0.18	0.18	0.18
Performance Testing				
CEC-L-109-14 test % Change in Kv100	79.3	81.1	64.2	47.8
*each oil had the same amount of ZDDP, HMW PIBSA-PAM, phenolic antioxidant, PIBSA, anti-foamant, Group I diluent oil, 20 mass% PAO basestock, LOFI, and Star H-SD block copol.				

Example 11

[0472] In **Table 18**, the CEC-L109-14, friction and wear performance of Component 1, Batch 5 was tested varying either the detergent system or ZDDP type. CEC-L109-14 viscosity increase is increased when a ZDDP system derived from primary and secondary alcohols is replaced with a ZDDP derived from primary alcohol in a system containing Component 2 (Comparative Oil A1 versus Comparative Oil C2, 89.0% versus 98.8%). Conversely, the same change with a system containing Component 1 Bx 5, showed an improvement in viscosity control, i.e., CEC-L109-14 viscosity increase was reduced, see oil Comparative Oil C2 and Oil F2 (98.8% versus 78.8 %).

[0473] Friction values remained similar across Component 1 Bx 5 and Component 2 oils with each of the ZDDP types. However, there was less wear scar diameter in the HFRR test for oils containing Component 1 Bx5 (see Comparative Oil C2 and Oil F2). Overall this demonstrates the suitability of Component 1 Bx5 to be formulated with a range of ZDDP types.

[0474] We also find that Component 1 Bx5 can have an impact on final oil properties when detergent systems are considered. For example when comparing Comparative Oil A2 to Oil D2 we see significant reductions in CEC-L-109-14 viscosity increase (50.3% vs 36.2%) in systems containing calcium salicylate detergent. Similarly, for when comparing Comparative Oil B2 to Oil E2 we see significant reductions in CEC-L-109-14 viscosity increase (169.5% vs 124.7%) in systems containing magnesium and calcium salicylate detergent. In addition, when comparing Comparative Oil G2 to Oil E2 we see significant reductions in MTM friction Coefficient (0.107 vs 0.089), HFRR wear scar diameter (270 vs 256 μm) while maintaining HFRR friction coefficient.

Table 18.

Constituent* (mass%)	C-Oil A1	C-Oil A2	C-Oil B2	C-Oil C2	Oil C1	Oil D2	Oil E2	Oil F2	C-Oil G2
Borated-PIB-SA-PAM	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Mg Salicylate	0.6		1.0	0.6	0.6		1.0	0.6	0.8
Ca Salicylate	1.4	2.0	1.0	1.4	1.4	2.0	1.0	1.4	1.0
ZDDP	1.0	1.0	1.0		1.0	1.0	1.0		1.0
1° ZDDP				1.1				1.1	
Component 2	1.0	1.0	1.0	1.0					1.0
Component 1 Bx 5					1.0	1.0	1.0	1.0	
Organic Friction Modifier	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Group III base oil	balance	balance	balance	balance	balance	balance	balance	balance	balance
Elemental Analysis ICP									
Ash (mass%)	0.77	0.86	0.74	0.77	0.77	0.86	0.74	0.77	0.67
B ppm	72	71	71	71	72	71	71	71	72
Ca (mass%)	0.13	0.21	0.08	0.13	0.13	0.21	0.08	0.13	0.08
Mg (mass%)	0.05	0	0.08	0.05	0.05	0	0.08	0.05	0.06
N (mass%)	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11
P (mass%)	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08
S (mass%)	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18
Performance Testing									
CEC-L-109-14 test % Change in Kv100	89.0	50.3	169.5	98.8	84.1	36.2	124.7	78.8	
MTM Test: Friction Coefficient, 135°C, 0.02 m/s	0.104				0.093		0.089		0.107
MTM-R: Traction Coefficient at 100°C	0.092			0.096	0.097			0.088	
HFRR: Wear Scar Diameter µm	197			172.5	182.5		256	160.5	270

(continued)

Performance Testing									
HFRR: Friction Coefficient at 140°C							0.13		0.14
*each oil had the same amount of HMW PIBSA-PAM, phenolic antioxidant, PIBSA, anti-foamant, Group I diluent oil, 20 mass% PAO basestock, LOFI, and Star H-SD block copol.									

[0475] Viscosity control typically becomes worse with increasing treat rates of magnesium salicylate detergent. In **Table 18,** with Component 2, increasing the Mg Salicylate amount results in an 81% increase in viscosity at the end of L109 test. Unexpectedly, oils containing Component 1, Batch 5 significantly attenuated the detrimental impact of the magnesium salicylate detergents on end of test viscosity compared to oils containing Component 2. This beneficially allows Mg Salicylate treat rates to be increased in oils for which treat rates are normally constrained by L109 performance.

[0476] Due to the improved L109 viscosity control performance when using Component 1 Bx 5 vs Component 2, increased treat rates of magnesium detergent can be used when formulating with Component 1 Bx 5. To calculate the Mg (ppm) content in a comparative Component 2 blend to give equivalent L109 viscosity control to the inventive Component 1 Bx 5 blend the following equation is used **Y = 0.2388X** - **18.469** where Y equals L109 viscosity increase of the inventive Component 1 Bx5 blend and X is equal to Mg ppm from the magnesium detergent in comparative Component 2 blend.

[0477] To calculate the amount of Mg (ppm) from magnesium detergent that can be used to give equivalent L109 viscosity control with the Component 1 Bx 5 formulation (Oil E2) versus comparative oil (C-B2), the below equation is used, Y = 0.2388X - 18.469, where Y equals L109 viscosity increase of the formulations containing Component 1 Bx5 and X is equal to Mg ppm. For Oil E2, we solve for X in equation Y = 0.2388X - 18.469, where Y 127.4, i.e. X = (124.7 + 18.469)/0.2388 = 600 ppm Mg.

[0478] As we can formulate with high magnesium to achieve equivalent predicted L109 performance we can also predict less low speed pre-ignition events as well. Comparison Oil G2 was formulated with Component 2 and 0.8 mass% magnesium detergent, which is calculated to give equivalent L109 viscosity increase performance to Oil E2.

[0479] The performance of the two oils were compared in friction (MTM) and wear (HFRR) tests. Oil E2 had lower friction and wear than Comparative Oil G2. As well improving fuel economy and engine wear, higher magnesium treat rates can help to combat low-speed pre-ignition in gasoline engines.

[0480] It is impressive to note that the positive impact of the inventive compositions here can be demonstrated across a wide variety of compositions. Figure 4 illustrates the positive impact across many compositions of interest to the lubricant industry obtained herein.

[0481] All documents described herein are incorporated by reference herein, including any priority documents and/or testing procedures, to the extent they are not inconsistent with this text. As is apparent from the foregoing general description and the specific embodiments, while forms of the invention have been illustrated and described, various modifications can be made without departing from the spirit and scope of the invention. Accordingly, it is not intended that the invention be limited thereby. The term "comprising" is considered synonymous with the term "including." Likewise, whenever a composition, an element, or a group of elements is preceded with the transitional phrase "comprising", it is understood that we also contemplate the same composition or group of elements with transitional phrases "consisting essentially of", "consisting of", "selected from the group of consisting of", or "is" preceding the recitation of the composition, element, or elements and vice versa.

Claims

1. A lubricating oil composition comprising diphenyl amine antioxidant comprising:

1) 90 mass% mass% or more of di(C_9-alkyl substituted phenyl) amine), and
2) from 0 to less than 10 mass% of mono-C_9-alkyl substituted diphenyl amine, based upon the mass of the mono-C_9-alkyl substituted diphenyl amine and di-C_9-alkyl substituted diphenyl amine present in the lubricating oil composition.

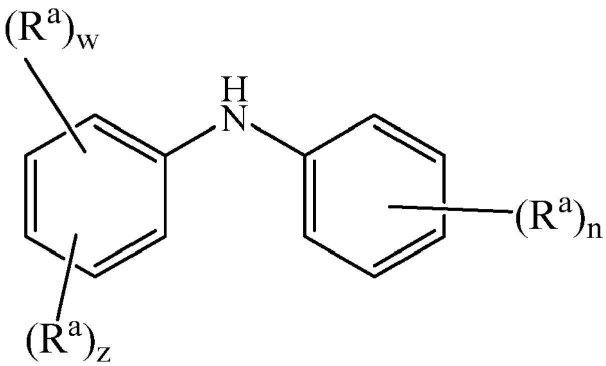
2. The lubricating oil composition of claim 1, comprising or resulting from the admixing of:

(i) at least 50 mass% of one or more base oils, based upon the weight of the lubricating oil composition;

(ii) one or more dispersants;
(iii) one or more detergents; and
(iv) diphenyl amine antioxidant composition comprising:

a) from 0 to less than 10 mass% mono-C_9-alkyl substituted diphenyl amine represented by the Formula (III) where n is 1, w is 0, and z is 0,
b) 90 mass% or more of di(C_9-alkyl substituted diphenyl) amines represented by Formula (III), where w is 0, n is 1, and z is 1,
c) from 0 to less than 10 mass% tri-C_9-alkyl substituted diphenyl amine represented by Formula (III), where w is 1, n is 1, and z is 1,
d) from 0 to 1 mass% of unsubstituted diphenyl amine represented by Formula (III) where w is 0, n is 0, and z is 0,

based upon the total mass of a), b), c) and d) present in the lubricating oil composition, where Formula (III) is:



(III)

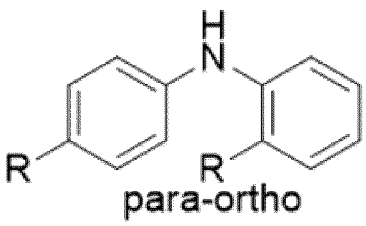
where each R^a is independently a linear C_9 alkyl or branched C_9 alkyl group, n is 1 or 0, z is 0 or 1, and w is 0 or 1.

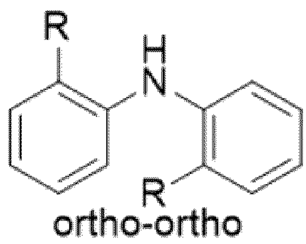
3. The lubricating oil composition of claim 2, comprising:

a) from 0 to less than 3 mass% mono-C_9-alkyl substituted diphenyl amines represented by the Formula (III) where w is 0, n is 1, and z is 0,
b) 90 mass% or more of di-C_9-alkyl substituted diphenyl amines represented by Formula (III), where w is 0, n is 1, and z is 1,
c) 10 mass% or less of tri-C_9-alkyl substituted diphenyl amines represented by Formula (III), where w is 1, n is 1, and z is 1,
d) from 0 to 0.5 mass% of unsubstituted diphenyl amines represented by Formula (III) where w is 0, n is 0, and z is 0,

based upon the total mass of the diphenyl amines of a), b), c) and d) present in the lubricating oil composition.

4. The lubricating oil composition of claim 2 or 3, wherein the di-C_9-alkyl substituted diphenyl amine represented by Formula (III), where w is 0, n is 1, and z is 1, comprises less than 5 mass% of the isomers shown below, where each R is independently a linear C_9 alkyl or branched C_9 alkyl group:





,

based upon the mass of di-C_9-alkyl substituted diphenyl amine represented by Formula (III), where w is 0, n is 1, and z is 1.

5. The lubricating oil composition of any of claims 2 to 4, wherein the ratio of the amount of di-C_9-alkyl substituted diphenyl amine represented by Formula (III), where w is 0, n is 1, and z is 1, to the amount of mono-C_9-alkyl substituted diphenyl amine represented by Formula (III), where w is 0, n is 1, and z is 0, present in the lubricating oil composition is 9:1 or more.

6. The lubricating oil composition of any of claims 1 to 5, further comprising zinc dialkyldithiophosphate, hindered phenolic antioxidant, molybdenum containing compound, ethoxylated alcohol and or oil-soluble or oil-dispersible sulfur-containing antioxidant(s), sulfurized aliphatic (C_7 to C_{29}) hydrocarbyl fatty acid ester(s), sulfur-containing organomolybdenum compound(s), and combinations thereof.

7. The lubricating oil composition of any of claims 2 to 6, where the detergent comprises salicylate detergent, optionally having a TBN of 100 or less and or optionally providing from 1 to 30 mmol/kg soap.

8. The lubricating oil composition of any of claims 2 to 7, further comprising one or more of the following components.

D) one or more friction modifiers;
E) one or more antioxidants, other than the antioxidants represented by Formula (III);
F) one or more pour point depressants;
G) one or more anti-foaming agents;
H) one or more viscosity modifiers;
J) one or more inhibitors and/or antirust agents; and/or
K) one or more anti-wear agents.

9. The lubricating oil composition of any of claims 1 to 8, wherein further comprising one or more functionalized polymers comprising an amide, imide, and/or ester functionalized partially or fully saturated polymer comprising C_{4-5} olefins having:

i) an Mw/Mn of less than 2,
ii) a Functionality Distribution (Fd) value of 3.5 or less, and
iii) an Mn of 10,000 g/mol or more (GPC-PS) of the polymer prior to functionalization, provided that, if the polymer prior to functionalization is a copolymer of isoprene and butadiene, then the Mn of the copolymer is greater than 25,000 g/mol.

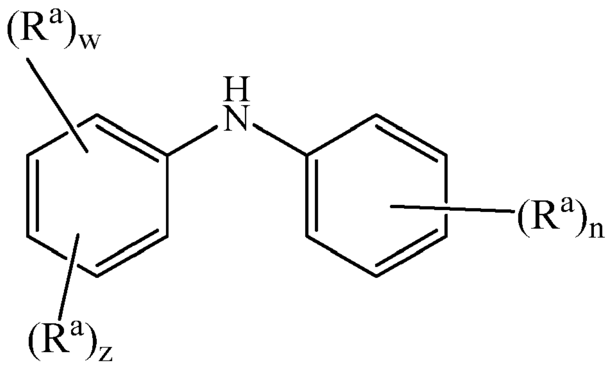
10. The lubricating oil composition of any of claims 2 to 9, wherein the amount of di-C_9-alkyl substituted diphenyl amine represented by Formula (III), where w is 0, n is 1, and z is 1, present in the lubricating oil composition is 0.5 mass% or more, or 0.75 mass% or more, or 0.9 mass% or more.

11. The lubricating oil composition of any of claims 1 to 10, comprising or resulting from the admixing of:

A) at least 50 mass% of one or more base oils, based upon the weight of the lubricating oil composition;
B) one or more dispersants;
C) one or more detergents; and
D) diphenyl amine antioxidant composition comprising:

a) from 0 to less than 10 mass% mono-C_9-alkyl substituted diphenyl amine represented by the Formula (III) where n is 1, w is 0, and z is 0,
b) 90 mass% or more of di(C_9-alkyl substituted diphenyl) amines represented by Formula (III), where w is 0, n is 1, and z is 1,

based upon the total weight of a) and b) present in the lubricating oil composition, where Formula (III) is:



(III)

where each R^a is independently a linear C_9 alkyl or branched C_9 alkyl group, n is 1 or 0, z is 0 or 1, and w is 0 or 1;
E) optionally, one or more antioxidants, other than the antioxidants represented by Formula (III);
F) optionally, one or more pour point depressants;
G) optionally, one or more anti-foaming agents;
H) optionally, one or more viscosity modifiers;
J) optionally, one or more inhibitors and/or antirust agents; and/or
K) optionally, one or more anti-wear agents; and / or
L) optionally, one or more friction modifiers.

12. The lubricating oil composition of claim 11, wherein: the dispersant comprises one or more PIBSA-PAMs, the detergent comprises one or more calcium and or magnesium sulfonate detergents, the friction modifier comprises one or more polyol fatty acid esters and or one or more molybdenum compounds.

13. A concentrate composition comprising or resulting from the admixing of:

(i) less than 50 mass% of one or more base oils, based upon the weight of the concentrate composition;
(ii) one or more dispersants;
(iii) one or more detergents; and
(iv) diphenyl amine antioxidant comprising:

1) more than 90 mass% di-C_9-alkyl substituted diphenyl amine and
2) from 0 to 10 mass% of mono-C_9-alkyl substituted diphenyl amine, based upon the mass of the mono-C_9-alkyl substituted diphenyl amine and di-C_9-alkyl substituted diphenyl amine present in the concentrate.

14. The concentrate of claim 13, wherein the concentrate comprises:

1) 95 mass% or more of diphenyl amine antioxidant comprising:
a) di-C_9-alkyl substituted diphenyl amine and b) from 0 to less than 5 mass% of mono-C_9-alkyl substituted diphenyl amine, based upon the weight of the mono- and di-phenyl amines present in the concentrate; and
2) one or more of magnesium detergent, optionally magnesium salicylate detergent and/or magnesium sulfonate detergent, one or more of calcium detergent, optionally calcium salicylate detergent and calcium sulfonate detergent, or calcium detergent and magnesium detergent; and
3) optional zinc dialkyldithiophosphate, a portion of which is derived from primary alcohol, secondary alcohol, or a combination of primary and secondary alcohol, and/or
4) optional organic friction modifier, such as glycerol monooleate and or organomolybdenum-based friction modifier.

15. The concentrate of claim 13 or 14 wherein the diphenyl amine antioxidant comprises:

1) 99 mass% or more of di-C_9-alkyl substituted diphenyl amine and
2) from 0 to less than 1 mass% of mono-C_9-alkyl substituted diphenyl amine, based upon the mass of 1) and 2).

16. The concentrate of claim 13, 14, or 15, further comprising one or more of the following:

D) one or more friction modifiers;

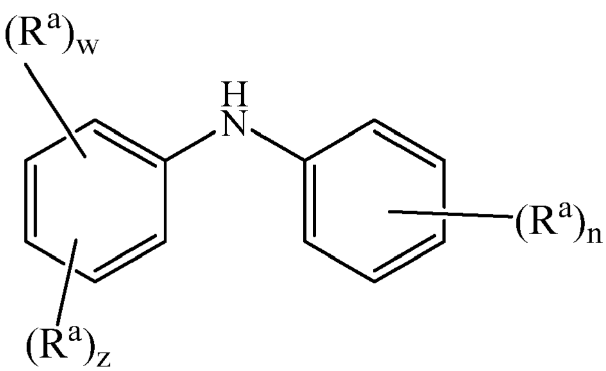
E) one or more antioxidants, other than the antioxidants of (iv);
F) one or more pour point depressants;
G) one or more anti-foaming agents;
H) one or more viscosity modifiers;
J) one or more inhibitors and/or antirust agents; and/or
K) one or more anti-wear agents.

17. The lubricating oil composition of claim 1, comprising diphenyl amine antioxidant comprising:

1) 85 mass% or more of di(C_9-alkyl substituted phenyl) amine,
2) from 0 to 5 mass% of mono-C_9-alkyl substituted diphenyl amine, and
3) from 0 to 15 mass% of tri-C_9-alkyl substituted diphenyl amine, based upon the weight of 1), 2) and 3) present in the lubricating oil composition, where if 2) an 3) do not combine to equal 5 mass% or more, then 90 mass% or more of di(C_9-alkyl substituted phenyl) amine are present.

18. Diphenyl amine antioxidant, for use in a lubricating oil composition or a concentrate, comprising:

a) mono-C_9-alkyl substituted diphenyl amines represented by the Formula (III) where n is 1, z is 0 and w is 0, that are absent or present at less than 10 mass%,
b) di-C_9-alkyl substituted diphenyl amines represented by Formula (III), where n is 1 and z is 1, that are present at 90 mass% or more,
c) tri-C_9-alkyl substituted diphenyl amines represented by Formula (III), where n is 1, z is 1 and w is 1, are present at 0.01 to less than 10 mass%,
based upon the total weight of the phenyl amines of a) + b) + c),
where Formula (III) is:



(III)

where each R^a is independently a linear C_9 alkyl or branched C_9 alkyl group, n is 1, z is 0 or 1, and w is 0 or 1.

19. Diphenyl amine antioxidant comprising:

a) less than 0.50 mass% of mono-C_9-alkyl substituted diphenyl amines,
b) greater than 99.50 mass% di-C_9-alkyl substituted diphenyl amines,

based upon the total weight of mono-C_9-alkyl substituted diphenyl amines and the di-C_9-alkyl substituted diphenyl amines.

20. A composition comprising: 1) diphenyl amine antioxidant comprising 90 mass% or more of bis(nonylphenyl)amine and 10 mass% or less of (nonylphenyl)(phenyl)amine based on the weight of the bis(nonylphenyl)amine and (nonylphenyl)(phenyl)amine, and 2) one or more of dinuclear organomolybdenum-based friction modifier, magnesium-based detergents optionally providing 400 ppm or more of Mg to the composition, and or sulfonate based detergents.

21. A composition (preferably an additive concentrate) comprising,

a) 0.1 to 99.9 mass%, based on total weight of the composition, of diphenylamine amine antioxidant comprising

90 mass% or more of bis(nonylphenyl)amine and 10 mass% or less of (nonylphenyl)(phenyl)amine based on the weight of the bis(nonylphenyl)amine and (nonylphenyl)(phenyl)amine, and
b) 99.9 to 0.1 mass%, based on total weight of the composition, of one, two, three, four, five, six or more additives selected from the group consisting of:

1) glycerol-based friction modifiers (optionally 0.6 mass% or less glycerol-based friction modifier, based upon the weight of the composition),
2) sulfonate-based detergents,
3) organomolybdenum-based friction modifiers,
4) magnesium-based detergents providing 400 ppm or more of Mg to the composition,
5) salicylate based detergents, and or
6) zinc-based antiwear agents (such as derived ZDDP from primary alcohol). and/or
7) base oil comprising a combination of refined and renewable base oils and or a combination of Group III and Group II base oils.

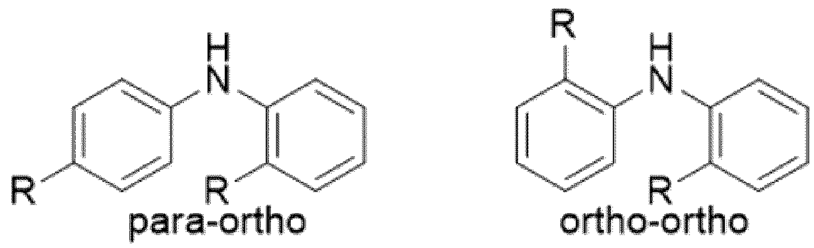
22. A lubricating oil composition comprising,

a) 0.1 to 99.9 mass%, based on total weight of the composition, of diphenylamine amine antioxidant comprising 90 mass% or more of bis(nonylphenyl)amine and 10 mass% or less of (nonylphenyl)(phenyl)amine based on the weight of the bis(nonylphenyl)amine and (nonylphenyl)(phenyl)amine, and
b) 99.9 to 0.1 mass%, based on total weight of the composition, of one, two, three, four, five, six or more additives selected from the group consisting of:

1) glycerol-based friction modifiers,
2) sulfonate-based detergents,
3) organomolybdenum-based friction modifiers,
4) magnesium-based detergents providing 400 ppm or more of Mg to the composition,
5) salicylate based detergents, and or
6) zinc-based antiwear agents (such as derived ZDDP from primary alcohol); and

c) from 50 mass% or more of base oil, optionally comprising a combination of refined and renewable base oils and or a combination of Group III and Group II base oils and or a combination of Group IV base oil, refined base oil and renewable base oil, and or a combination of Group IV base oil, Group III base oil and Group II base oil.

23. The composition of claim 21 or 22 wherein the di-C_9-alkyl substituted diphenyl amine comprises less than 5 mass% of the isomers shown below, where each R is independently a linear C_9 alkyl or branched C_9 alkyl group:



,

based upon the weight of di-C_9-alkyl substituted diphenyl amine.

24. A method of lubricating an internal combustion engine during operation of the engine comprising:

(i) providing to a crankcase of the internal combustion engine an automotive crankcase the lubricating oil composition or concentrate of any of claims 1 to 17 and 21 to 23;
(ii) providing a hydrocarbon fuel in the internal combustion engine; and
(iii) combusting the fuel in the internal combustion engine,

optionally, wherein the temperature of the oil sump of the internal combustion engine is greater than 100 °C.

25. A use, to reduce one or more of piston deposits (as determined by Sequence III), and or rod deposits (as determined by MHT4 TEOST), and or friction (such as determined by HFRR friction coefficient at 140°C, and or MTM friction coefficient, 135°C, 0.02 m/s and or MTM-R: Traction Coefficient at 100°C), and or wear (such as determined by HFRR: wear scar diameter and or MTM-R: wear scar volume), and or viscometric growth (such as determined by CEC-L109-14) in a lubricating oil composition lubricating an internal combustion engine, of diphenyl amine antioxidant comprising 1) di(C_9-alkyl substituted diphenyl) amine and 2) from 0 to less than 10 mass% of mono-C_9-alkyl substituted diphenyl amine, and preferably the diphenyl amine antioxidant defined in any preceding claim.

26. The use of claim 25 wherein the reduction is determined by comparison to the same lubricating oil composition except that the diphenyl amine antioxidant has been replaced with the same total amount of diphenyl amine antioxidant having: 1) 68 mass% di-C_9-alkyl diphenyl amine, 2) 29 mass% of mono-C_9-alkyl diphenyl amine, and 3) 3 mass% of tri-C_9-alkyl diphenyl amine, based on the weight of 1), 2) and 3), as determined by UPLC).

27. The method of claim 24, or use of clam 24 or 26, wherein the lubricating oil composition further comprises: one or more additives selected from the group consisting of:

1) glycerol-based friction modifiers,
2) sulfonate-based detergents,
3) organomolybdenum-based friction modifiers,
4) magnesium-based detergents providing 400 ppm or more of Mg to the composition,
5) salicylate based detergents (such as Ca salicylate based detergents, such as blends of Ca salicylate based detergents and Mg salicylate based detergents), and or
6) zinc-based antiwear agents (such as derived ZDDP from primary alcohol). and/or
7) base oil comprising a combination of refined and renewable base oils and or a combination of Group III and Group II base oils.

28. The method or use of any of claims 24 to 28 wherein:

1) the lubricating oil composition further comprises **sulfonate based detergents** and preferably solely sulfonate based detergents, and has preferably at least 5% less (such as at least 10% less, such as at least 20% less, such as at least 25% less) MHT4 TEOST: Total rod deposits (mg); and / or
2) the lubricating oil composition further comprises: 1) **salicylate based detergents** and preferably calcium salicylate based detergents, and 2) optionally dispersant preferably PIBSA-PAM derived from polymer having an Mn of less than 1600 g/mol; and preferably has at least 5% less (such as at least 10% less, such as at least 20% less, such as at least 30% less, such as at least 40% less) MHT4 TEOST: Total rod deposits (mg); and / or
3) the lubricating oil composition further comprises: 1) **magnesium based detergents,** preferably magnesium sulfonate and or magnesium salicylate based detergents providing at least 600 ppm Mg to the lubricating oil composition; and preferably has at least 5% less (such as at least 10% less, such as at least 20% less, such as at least 30% less, such as at least 40% less, such as at least 50% less, such as at least 60% less, such as at least 70% less)) MHT4 TEOST: Total rod deposits (mg); and / or
4) the lubricating oil composition further comprises: 1) **magnesium and calcium based detergents** preferably magnesium sulfonate and/or salicylate detergents and calcium sulfonate and/or salicylate detergents present in the lubricating oil composition at a ratio of Mg:Ca of 1:2 to 2:1; and has at least 5% less (such as at least 10% less, such as at least 20% less, such as at least 30% less, such as at least 40% less, such as at least 50% less, such as at least 60% less, such as at least 70% less) MHT4 TEOST: Total rod deposits (mg), and / or
5) the lubricating oil composition further comprises **glycerol-based friction modifier** preferably glycerol mono-oleate and or magnesium based detergents preferably magnesium sulfonate and or magnesium salicylate based detergents, optionally providing at least 600 ppm Mg to the lubricating oil composition and has at least 5% less(such as at least 3% less) viscosity growth; and / or
6) the lubricating oil composition further comprises **dinuclear organo-molybdenum compound** preferably one or more molybdenum dithiocarbamate dimers and preferably has at has at least 5% less (such as at least 10% less, such as at least 20% less, such as at least 30% less, such as at least 40% less, such as at least 50% less, such as at least 60% less, such as at least 70% less, such as such as at least 75% less, such as at least 77% less) viscosity growth; and / or
7) the lubricating oil composition further comprises **trinuclear organo-molybdenum compound** preferably one or more molybdenum dithiocarbamate trimers and preferably has at least 5% less (such as at least 10% less, such as at least 13% less, such as at least 15% less, such as at least 17% less) viscosity growth; and / or
8) the lubricating oil composition further comprises **renewable base oil** (such as refined Group II and or Group III

base oil combined with Group III renewable base oil, and optionally Group IV base oil) and preferably has at least 5% less (such as at least 10% less, such as at least 15% less) viscosity growth; and or

9) the lubricating oil composition further comprises **Group II and Group III base oil,** and optionally Group IV base oil and preferably has at least 5% less (such as at least 10% less, such as at least 15% less, such as at least 20% less, such as at least 30% less, such as at least 33% less) viscosity growth; and / or

10) the lubricating oil composition further comprises **magnesium based detergents** preferablymagnesium sulfonate and or magnesium salicylate based detergents providing at least 600 ppm Mg, preferably at least 700 ppm, such as at least 800 ppm to the lubricating oil composition and preferably has at least 5% less (such as at least 10% less, such as at least 15% less, such as at least 20% less, such as at least 25% less, such as at least 30% less, such as at least 55% less, such as at least 40% less) viscosity growth; and / or

11) the lubricating oil composition further comprises **salicylate based detergents** preferably calcium and or magnesium salicylate based detergents and has preferably at least 5% less (such as at least 10% less, such as at least 14 % less) viscosity growth; and / or

12) the lubricating oil composition further comprises **zero mass% glycerol based friction** modifier (such as glycerol mono-oleate) and preferably has at least 5% less (such as at least 10% less, such as at least 15 % less) viscosity growth; and / or

13) the lubricating oil composition further comprises **zinc based antiwear agents** derived from one or more primary alcohols preferably zinc dialkyldithiophosphates where the alkyl is derived from one or more primary alcohols and has at least 5% less preferably at least 10% less, such as at least 15 % less, such as at least 20 % less) viscosity growth as compared to the comparative lubricating oil composition that additionally contains the same amount of a ZDDP derived from a combination of isooctanol and 2-butanol, and / or

14) the lubricating oil composition further comprises **dinuclear organo-molybdenum compound** preferably molybdenum dithiocarbamate dimer and preferably has at has at least 5% less (such as at least 10% less, such as at least 20% less, such as at least 30% less, such as at least 40% less, such as at least 50% less, such as at least 60% less, such as at least 65% less) wear scar volume (**MTM-R**), and / or

15) the lubricating oil composition further comprises **magnesium and calcium based detergents** preferably magnesium sulfonate and/or salicylate detergents and calcium sulfonate and/or salicylate detergents present in the lubricating oil composition at a ratio of Mg:Ca of 1:2 to 2:1, providing at least 400 ppm Mg to the lubricating oil composition; and preferably has at least 5% less (such as at least 10% less, such as at least 15% less, such as at least 19% less) average traction coefficient at 100°C (**MTM-R**); and / or

16) the lubricating oil composition further comprises **zinc based antiwear agents** derived from one or more primary alcohols preferably zinc dialkyldithiophosphates where the alkyl is derived from one or more primary alcohols and preferably has at has at least 5% less (such as at least 9% less) average traction coefficient at 100°C (**MTM-R**), than a tcomparative composition that additionally contains the same amount of a ZDDP derived from a combination of isooctanol and 2-butanol, and / or

17) the lubricating oil composition further comprises **trinuclear organo-molybdenum compound** and preferably has at least 5% less (such as at least 10% less, such as at least 20% less, such as at least 30% less, such as at least 40% less, such as at least 50% less, such as at least 60% less, such as at least 65% less) wear scar volume (**MTM-R**); and / or

18) the lubricating oil composition further comprises **trinuclear organo-molybdenum compound** and preferably has at least 5% less (such as at least 10% less, such as at least 20% less, such as at least 30% less, such as at least 40% less, such as at least 50% less, such as at least 60% less, such as at least 65% less) average traction coefficient at 100°C(**MTM-R**); and / or

19) the lubricating oil composition further comprises **glycerol based friction** modifier (such as glycerol mono-oleate) and preferably has at least 5% less (such as at least 10% less, such as at least 13 % less) avg traction coefficient at 100°C(**MTM-R**), and or

20) the lubricating oil composition further comprises **dinuclear organo-molybdenum compound** (such as molybdenum dithiocarbamate dimer and has at has at least 5% less (such as at least 10% less, such as at least 20% less, such as at least 30% less, such as at least 40% less, such as at least 50% less, such as at least 60% less, such as at least 65% less) wear scar area (**HFRR**), and or

21) the lubricating oil composition further comprises **trinuclear organo-molybdenum compound** and has at has at least 5% less (such as at least 10% less, such as at least 20% less, such as at least 30% less, such as at least 40% less, such as at least 50% less, such as at least 60% less, such as at least 65% less) wear scar area (**HFRR**).

29. The method or use of any of claims 24 to 28 wherein the lubricating oil composition further comprises **magnesium based detergents,** preferably magnesium sulfonate and or magnesium salicylate based detergents, providing at least 600 ppm Mg, optionally at least 700 ppm, optionally at least 800 ppm Mg to the lubricating oil composition) and has at least 5% less (optionally at least 10% less, optionally at least 15% less, optionally at least 17% less) friction coefficient at 135°C (MTM).

30. A method of reducing friction in a crankcase of an internal combustion engine comprising providing to the crankcase a lubricating oil composition comprising,

a) 0.5 to 15 mass%, based on total weight of the lubricating oil composition, of a diphenylamine amine antioxidant comprising, based on the weight of the aminic antioxidant, wherein the diphenylamine amine antioxidant comprises,

i) 90 mass% or more of bis(nonylphenyl) amine,
ii) from 0 to less than 10 mass% of mono(nonylphenyl) amine, based upon the mass of the (nonylphenyl)(phenyl)amine and bis(nonylphenyl)amine present in the lubricating oil composition, and

b) 0.01 to 30 mass%, based on total weight of the lubricating oil composition, of one or more additives selected from the group consisting of glycerol-based friction modifiers, sulfonate-based detergents, organomolybdenum-based friction modifier, calcium/magnesium-based detergents, zinc-based antiwear agents, and combinations thereof, and variants thereof,

wherein the amount of any one additive can be synergistically increased in the presence of the diphenylamine amine antioxidant to maintaining or decrease the friction (as determined by CEC-L-109-14, 216 hr., 150°C) relative to the friction in the presence of a diphenylamine amine antioxidant comprising a baseline antioxidant of nonylphenyl amine antioxidant comprising 68 mass% of bis(nonylphenyl)amine, 29 mass% of (nonylphenyl)(phenyl)amine and 3 mass% of tri(nonylphenyl)amine, based upon the weight of the (nonylphenyl)(phenyl)amine, bis(nonylphenyl)amine, and tri(nonylphenyl)amine, as determined by UPLC.

31. A method to lubricate an internal combustion engine comprising introducing a lubricating oil composition comprising base oil and a composition comprising the composition of claim 22 or 23 into an internal combustion engine, wherein the (**CEC L-109-14**) viscosity growth of the lubricating oil composition is preferably at least 5% less (such as at least 10% less, such as at least 20% less, such as at least 30% less, such as at least 40% less, such as at least 50% less, such as at least 60% less, such as at least 70% less, such as such as at least 75% less, such as at least 77% less) than the (**CEC L-109-14**) viscosity growth of a comparative lubricating oil composition having the same lubricating oil composition except that the diphenyl amine antioxidant has been replaced with the same amount of diphenyl amine antioxidant having: 1) 68 mass% di-C_9-alkyl diphenyl amine, 2) 29 mass% of mono-C_9-alkyl diphenyl amine, and 3) 3 mass% of tri-C_9-alkyl diphenyl amine, based on the weight of 1), 2) and 3), as determined by UPLC).

32. The composition of claim 22 or 23 wherein two or more lubricating oil compositions each comprising: a) diphenylamine amine antioxidant comprising 90 mass% or more of bis(nonylphenyl)amine and 10 mass% or less of (nonylphenyl)(phenyl)amine based on the weight of the bis(nonylphenyl)amine and (nonylphenyl)(phenyl)amine, and b) at least one different component selected from the group consisting of:

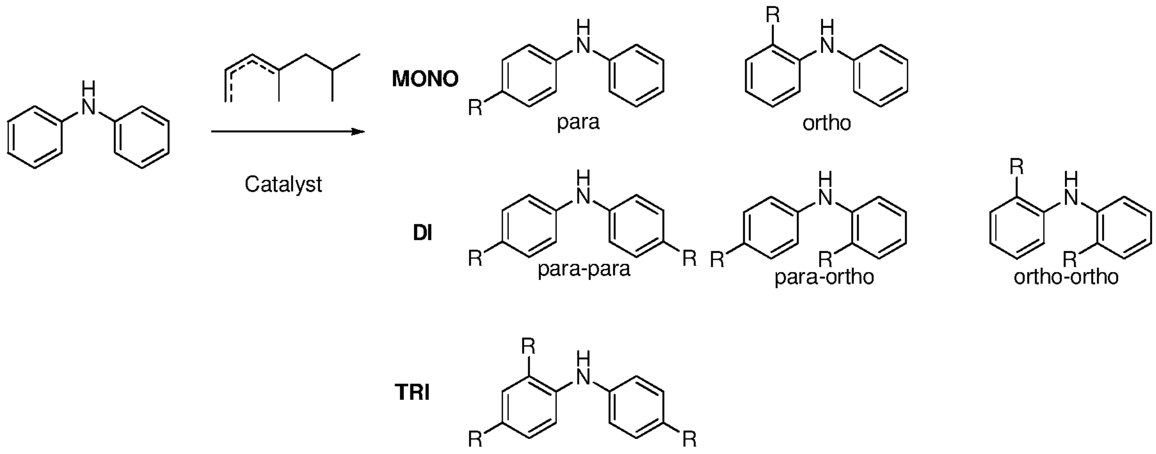
1) glycerol-based friction modifiers, (optionally 0.6 mass% or less glycerol-based friction modifier, based upon the weight of the composition)
2) sulfonate-based detergents,
3) organomolybdenum-based friction modifiers,
4) magnesium-based detergents, optionally providing 400 ppm or more of Mg to the composition,
5) salicylate based detergents (optionally calcium salicylate based detergents, such as combinations of calcium and magnesium based detergents),
6) zinc dialkyldithiphosphates derived from primary alcohol(s),
7) dispersants (such as PIBSA-PAM) derived from a polymer (such as polyisobutylene) having an Mn of less than 1600 g/mol,
8) calcium based detergents,

where: i) the viscometric growth (CEC-L-109-14, 216 hr., 150°C) for each of two or more lubricating oil compositions is at least 5 % (optionally at least 10%, at least 15%, at least 20%, at least 25%, at least 30 % at least 35%, at least 40%, at least 55%, at least 60%, such as at least 70%, such as at least 75%, such as at least 77%) less than the viscometric growth of their respective reference formulations, and ii) where the reference lubricating oil composition for a formulation is the same as that formulation as the except that the diphenylamine antioxidant is replaced at the same mass percentage by diphenylamine antioxidant comprising about 68 mass% of bis(nonylphenyl)amine, about 29 mass% of (nonylphenyl)(phenyl)amine and about 3 mass% of tri(nonylphenyl)amine, based upon the weight of the (nonylphenyl)(phenyl)amine, bis(nonylphenyl)amine, and tri(nonylphenyl)amine, as determined by UPLC.

33. The composition of claim 32, wherein the a) diphenylamine amine antioxidant comprises 95 mass% or more of bis(nonylphenyl)amine and 5 mass% or less of (nonylphenyl)(phenyl)amine based on the weight of the bis(nonylphenyl)amine and (nonylphenyl)(phenyl)amine.

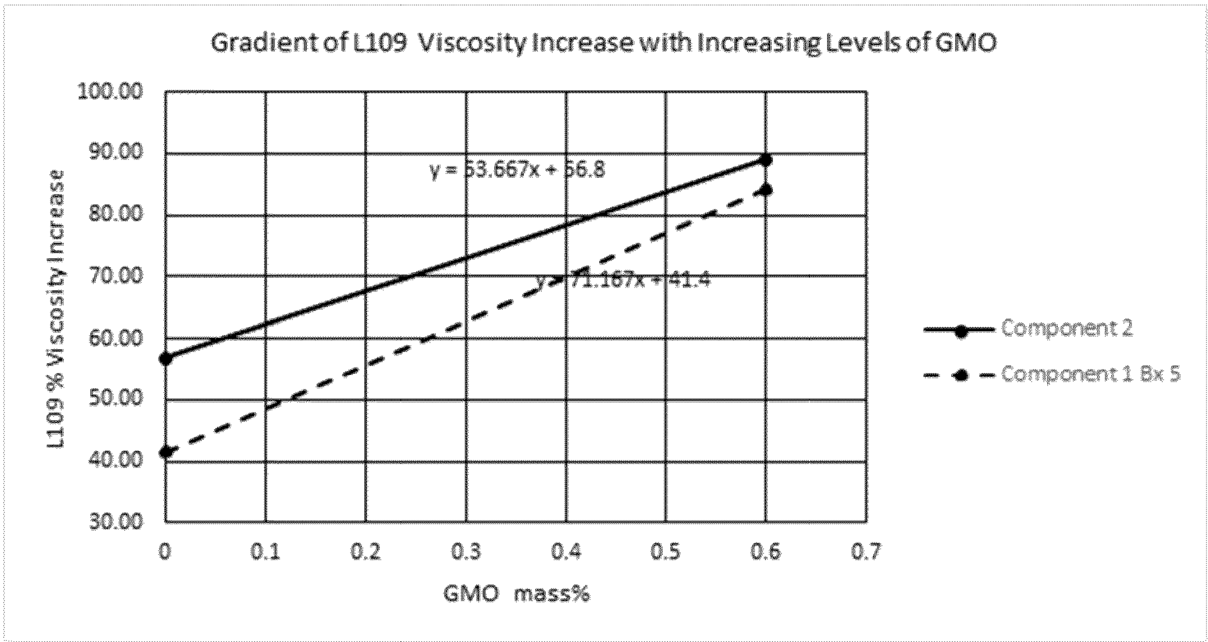
34. The use of (or a method of using) diphenylamine amine antioxidant to reduce wear scar volume μm^3 (**MTM-R**) and or wear scar area (**HFRR**) of the lubricating oil composition of any preceding claim, wherein organomolybdenum-based friction modifier comprises **trinuclear organo-molybdenum compound** preferably as molybdenum dithiocarbamate trimer providing at least 100 ppm, such as at least 200 ppm Mo to the lubricating oil composition and preferably has: 1) at least 5% less (such as at least 10% less, such as at least 15% less, such as at least 20% less) wear scar volume μm^3 and or 2) at least 5% less (such as at least 10% less, such as at least 20% less, such as at least 30% less, such as at least 40% less, such as at least 50% less, such as at least 60% less, such as at least 65% less) wear scar area μm^3, where the reduction is determined by comparison to the same lubricating oil composition except that the trinuclear organo-molybdenum compound has been replaced by dinuclear organo-molybdenum compound providing the same amount of molybdenum to the lubricating oil composition.

Fig. 1



Catalyst
MONO
para
ortho
DI
para-para
para-ortho
ortho-ortho
TRI

Fig.2



Gradient of L109 Viscosity Increase with Increasing Levels of GMO
L109 % Viscosity Increase
GMO mass%
y = 53.667x + 56.8
y = 71.167x + 41.4
Component 2
Component 1 Bx 5
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7

Fig. 3

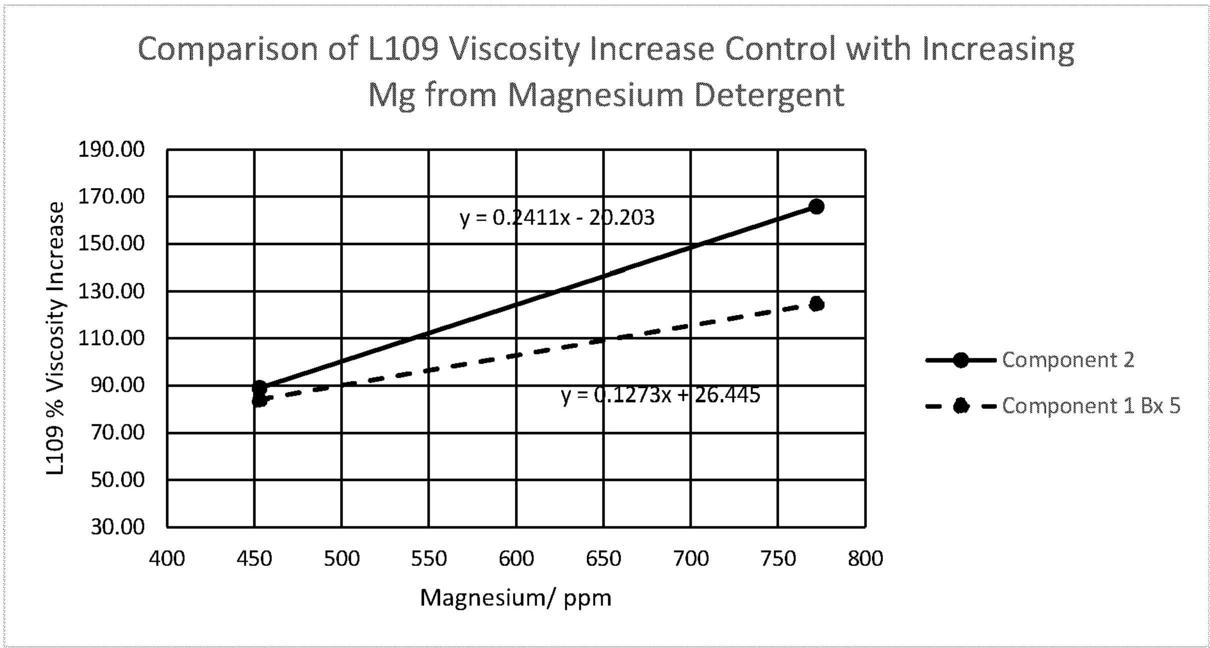
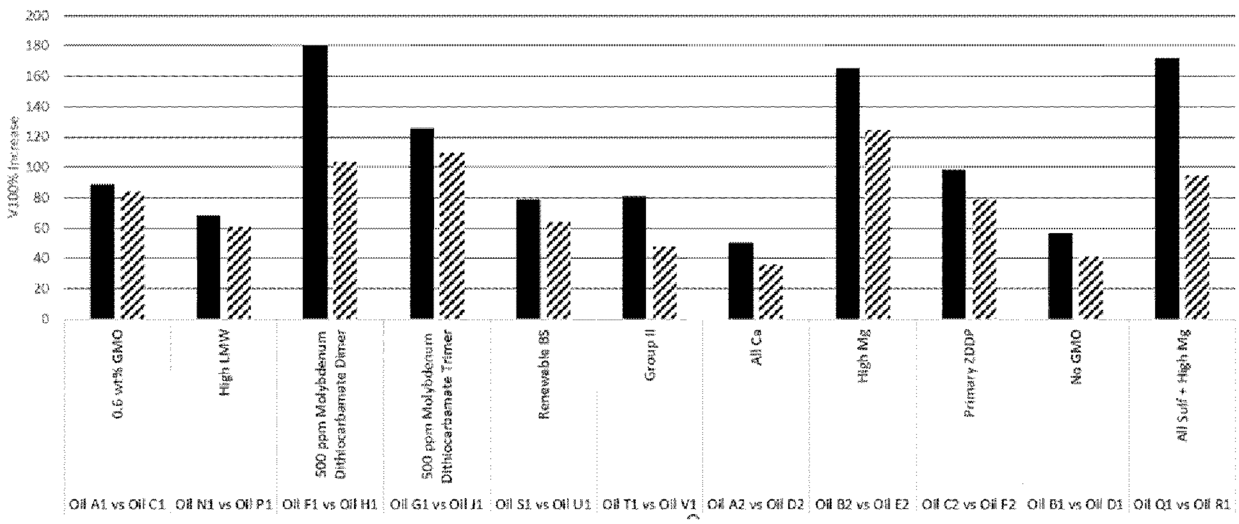

Comparison of L109 Viscosity Increase Control with Increasing Mg from Magnesium Detergent
190.00
170.00
150.00
130.00
110.00
90.00
70.00
50.00
30.00
L109 % Viscosity Increase
400
450
500
550
600
650
700
750
800
Magnesium/ ppm
y = 0.2411x - 20.203
y = 0.1273x + 26.445
Component 2
Component 1 Bx 5

Fig. 4 CEC-L109-14 Comparison (Component 2- black, Component 1, Bx 5 striped)



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