

Lubricant Compositions Containing C₈ Disubstituted Diphenylamine Antioxidant**PRIORITY**

This invention claims priority to and the benefit of European Patent Office Patent Application No. EP23218548, filed December 20, 2023.

FIELD OF THE INVENTION

[0001] This disclosure relates to the use of normally solid di(alkyl substituted phenyl)amine antioxidants as additives in lubricant oil compositions having good oxidation properties in internal combustion engine applications, especially in compression ignited engine and or spark ignited applications, where the lubricating oil composition comprises C₈ alkyl substituted diphenylamine antioxidants provided as a fluid, such as in molten form or as a solution or suspension of C₈ alkyl substituted diphenylamine antioxidant dissolved or suspended in polar materials or where the C₈ alkyl substituted diphenylamine antioxidant is blended into an additive package or lubricating oil composition in a specific order.

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 lubricating oil compositions for use in internal combustion engines, such as gasoline, diesel, natural gas, hydrogen, methanol, ammonia, and or ethanol internal combustion engines (including spark ignited, compression ignited, and spark assisted compression ignited), such compositions optionally 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 and or an engine. 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] Diphenylamine antioxidants, such as nonylated diphenylamines and octylated/butylated diphenylamines are commonly used in engine oil formulations. Other diphenylamine antioxidants are available for use, but have known issues in lubricating oil compositions (such as di(octylphenyl)amines)

and or do not blend into engine oils and/or are not stable in engine oils at treat rates commonly used in modern lubricating oils.

[0007] This can be a serious issue in the manufacturing and blending processes of lubricating fluids and concentrates (also referred to as additive packages) for lubricating fluids. For example, functional fluid additives manufacturers prefer to sell a homogeneous additive package of performance chemicals, which may then be added to a base oil to give a final lubricant, which in turn is sold in tanks, drums, cans and plastic containers for final delivery of the lubricant to the equipment to be lubricated. To maintain assurance of performance of the final lubricant, or any other functional fluid, in the equipment in which it is to be used, the concentrate and the formulated lubricant desirably remain homogeneous throughout these steps as shown by low or no levels of precipitation or cloudiness in the concentrate or formulated oil. This goal greatly limits the choices of and available treatment levels for many additives, including the octylated diphenylamine antioxidants. These antioxidants could provide improved performance to a functional fluid but are not widely used and/or are not used at the optimal level because the additive does not meet the solubility and/or compatibility requirements discussed above.

[0008] In the field, functional fluid compositions that drop out one or more components over time may not perform properly unless they are well-mixed before use or are filtered prior to use. The haziness and/or cloudiness of a functional fluid, which may be measured as the fluid's turbidity, is often seen as a sign the composition is not stable, or may be in an early stage of separation and/or component drop out. Such conditions are not desired in functional fluid compositions, for both performance and aesthetic related reasons. This deficit has created constraints on the use of various antioxidants, such as effective maximum treat rates.

[0009] C₈ alkylated diphenylamines are solids that are difficult to combine directly into lubricating oil compositions and even if they are combined into an oil formulations, the C₈ alkylated diphenylamines antioxidant materials can contribute to viscometric and or deposit problems. Thus there is a desire to improve the stability, deposit performance and or the viscosity impact of di(alkylphenyl)amines, such as octylphenylamines, in organic fluids such as engine oils, gear oils, hydraulic fluids, compressor oils, turbine oils, and grease. Specifically, octylated diphenylamine anti-oxidants are often polar solids (such as Naugalube™ 438) which can be difficult to combine into lubricating oil compositions that contain predominantly nonpolar hydrocarbon basestocks.

[0010] US 6,797,677 lists Naugalube™ 438 as a possible diarylamine to be used, however no extra information is presented.

[0011] EP 4 118 170 A1 discloses lubricating oil compositions with improved oxidative performance comprising carboxylate detergents and diphenylamine antioxidant, where the diphenylamine is alkylated with propylene tetramers.

[0012] US 10,487,043 discloses diphenylamine antioxidant, where the diphenylamine is alkylated with C₈ branched olefins. See for example at Ex. 7, an alkylated diphenylamine mixture containing, by GC analysis: 92% 4,4' bis(1-ethyl-1-methylpentyl)DPA; 4% 2,4,4-tris(1-ethyl-1-methylpentyl)DPA; 4% 2,4 bis(1-ethyl-1-methylpentyl)DPA, where 8% of the mixture is ortho-alkylated product.

[0013] EP 4 118 171 A1 discloses lubricating oil compositions with improved oxidative performance comprising alkylated diphenylamine antioxidant and sulfonate detergents.

[0014] US 9,650,587 (WO 2012/062020) discloses compositions containing limited solubility antioxidants combined with a compatibilizer for use in additive packages or lubricating oil compositions.

[0015] US 2023/0250353 discloses the use of diester materials to increase oxidation resistance of lubricating oil compositions.

[0016] US 9,315,760 discloses lubricant compositions containing a compatibilized additive composition containing a metal free sulfur-containing compound (such as ashless dithiocarbamates, such as methylenebis(dibutylthiocarbamate), 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.)

[0017] Other references of interest include: EP 2 155 657 B1; EP 0 630 881 A1; GB 1,112,784; US 5,236,610; US 4,036,767; US 5,449,829; US 5,236,610; US 7,960,322; US 7,145,038; US 8,999,903; US 9,512,380; US 11,499,117; US 11,518,732; WO98/11181A1; WO 2012/162020 A1; WO 2020/194125; WO 2023/133090 A1; WO 2023/209038A1; CA819715A; US2018/237722A1.

[0018] It has now surprisingly been found by the present inventors that compositions of di(octylphenyl)amine (such as di(para-octylphenyl)amine) can be used in an additive package and/or a lubricating oil composition, such as in internal combustion engines, to provide improved viscometric properties, such as reduced kinematic viscosity growth and/or enhanced oxidation performance and/or enhanced piston deposit performance.

SUMMARY OF THE INVENTION

[0019] This disclosure relates to lubricating oil additives that maintain or improve oxidation, wear, cleanliness, and/or friction performance and/or improve kinematic viscosity growth in lubricating oils.

[0020] This invention further relates to compositions (such as booster packs, concentrates, lubricating oil compositions and the like) comprising: fluid diphenyl amine antioxidant composition such as molten diphenyl amine antioxidant composition or liquid (such as a solution or suspension) diphenyl amine antioxidant composition comprising: 1) di(C₈-alkyl substituted diphenyl amine (such as 85 mass% or more of di(C₈-alkyl substituted diphenyl) amine) and 2) from 0 to 15 mass% of mono-C₈-alkyl substituted diphenyl amine, based upon the weight of the mono- and di-C₈-alkyl substituted phenyl amines present in the antioxidant composition.

[0021] In particular, this invention relates to a stable antioxidant composition comprising:

- a) molten diphenylamine antioxidant comprising: 1) di(C₈-alkyl substituted phenyl) amine and 2) less than 15 mass% of mono-C₈-alkyl substituted diphenylamine (based upon the weight of mono- C₈-alkyl substituted phenylamines, di- C₈-alkyl substituted phenylamines, and any tri-C₈-alkyl substituted phenylamines present in the antioxidant composition); and
- b) optionally, one or more of: polar diluent having an aniline point of 25°C or less, and at least 2 available hydrogen-bond acceptor groups (such as ester, ether or alcohol groups) that are 2, 3,

4, 5, or 6 atoms apart, octadecenylsuccinic anhydride-tetraethylenepentamine, one or more triazole corrosion inhibitors, and or one or more dialkyl fumarate/vinyl acetate copolymers, which may be added to the concentrate in the same or different blending stage as the molten diphenylamine antioxidant.

[0022] In particular, this invention relates to a stable antioxidant composition comprising:

- a) diphenylamine antioxidant comprising: 1) di(C₈-alkyl substituted phenyl) amine and 2) less than 15 mass% of mono-C₈-alkyl substituted diphenylamine (based upon the weight of mono- C₈-alkyl substituted phenylamines, di- C₈-alkyl substituted phenylamines, and any tri- C₈-alkyl substituted phenylamines present in the antioxidant composition); and
- b) polar diluent having an aniline point of 25°C or less, and at least 2 available hydrogen-bond acceptor groups (such as ester, ether or alcohol groups) that are 2, 3, 4, 5, or 6 atoms apart, where the polar diluent is optional when the di(C₈-alkyl substituted phenyl) amine is in molten or liquid crystal form,

wherein the composition comprising the polar diluent of b) combined with the diphenylamine antioxidant of a) is clear after 96 hours at 20 °C in a clear glass container without agitation.

[0023] This invention further relates to a stable antioxidant composition (that may optionally be homogeneous (such as a solution) or heterogeneous (such as a dispersion, a slurry, a colloid and the like), comprising:

- a) diphenylamine antioxidant comprising: 1) di(C₈-alkyl substituted phenyl) amine and 2) less than 15 mass% (such as 10 mass% or less) of mono-C₈-alkyl substituted diphenylamine (based upon the weight of mono- C₈-alkyl substituted phenylamines, di- C₈-alkyl substituted phenylamines, and tri- C₈-alkyl substituted phenylamines present in the antioxidant composition); and
- b) polar diluent having an aniline point of 25°C or less, and at least 2 available hydrogen-bond acceptor groups (such as ester, ether or alcohol groups) that are 2, 3, 4, 5, or 6 atoms apart,

wherein the combination of the polar diluent of b) combined with the diphenylamine antioxidant of a) is clear after 96 hours at 20 °C without agitation (such as a combination of 75 mass% of the polar diluent of b) combined with 25 mass% of the diphenylamine antioxidant of a) is clear after 96 hours at 20 °C).

[0024] This invention further relates to a stable concentrate comprising:

- i) an antioxidant composition (that may optionally be homogeneous or heterogeneous (such as a solution, a dispersion, a slurry, a colloid and the like), comprising:
 - a) diphenylamine antioxidant comprising: 1) di(C₈-alkyl substituted phenyl) amine and 2) less than 15 mass% (such as 10 mass% or less) of mono-C₈-alkyl substituted diphenylamine (based upon the weight of mono- C₈-alkyl substituted phenylamines, di- C₈-alkyl substituted phenylamines, and tri- C₈-alkyl substituted phenylamines present in the concentrate composition); and
 - b) polar diluent having an aniline point of 25°C or less, and at least 2 available hydrogen-bond acceptor groups (ester, ether or alcohol group) that are 2, 3, 4, 5, or 6 atoms apart,

wherein the combination of the polar diluent of b) combined with the diphenylamine antioxidant of a) is clear after 96 hours at 20 °C without agitation (such as a combination of 75 mass% of the polar diluent of b) combined with 25 mass% of the diphenylamine antioxidant of a) is clear after 96 hours at 20 °C);

- ii) detergent;
- iii) base oil;
- iv) optionally one or more dispersants, friction modifiers; antioxidants, other than the antioxidants of a), pour point depressants, anti-foaming agents, viscosity modifiers, corrosion inhibitors, antirust agents, and/or anti-wear agents.

[0025] This invention further relates to a stable concentrate comprising:

- i) an antioxidant composition (that may optionally be homogeneous or heterogeneous (such as a solution, a dispersion, a slurry, a colloid and the like), comprising:
 - a) diphenylamine antioxidant comprising: 1) di(C₈-alkyl substituted phenyl) amine and 2) less than 15 mass% (such as 10 mass% or less) of mono-C₈-alkyl substituted diphenylamine (based upon the weight of mono- C₈-alkyl substituted phenylamines, di- C₈-alkyl substituted phenylamines, and tri- C₈-alkyl substituted phenylamines present in the concentrate composition); and
 - b) polar diluent having an aniline point of 25°C or less, and at least 2 available hydrogen-bond acceptor groups (ester, ether or alcohol group) that are 2, 3, 4, 5, or 6 atoms apart,

wherein the combination of the polar diluent of b) combined with the diphenylamine antioxidant of a) is clear after 96 hours at 20 °C without agitation (such as a combination of 75 mass% of the polar diluent of b) combined with 25 mass% of the diphenylamine antioxidant of a) is clear after 96 hours at 20 °C);

- ii) detergent, preferably salicylate detergent;
- iii) base oil;
- iv) optionally one or more dispersants, friction modifiers; antioxidants, other than the antioxidants of a), pour point depressants, anti-foaming agents, viscosity modifiers, corrosion inhibitors, antirust agents, and/or anti-wear agents,

wherein the antioxidant composition is combined with the detergent at a temperature of about 45 °C or more, such as about 50°C or more, such as about 55°C or more, such as 60 °C or more.

[0026] This invention further relates to a stable concentrate comprising:

- i) an antioxidant composition (that may optionally be homogeneous or heterogeneous (such as a solution, a dispersion, a slurry, a colloid and the like), comprising:
 - a) diphenylamine antioxidant comprising: 1) di(C₈-alkyl substituted phenyl) amine and 2) less than 15 mass% (such as 10 mass% or less) of mono-C₈-alkyl substituted diphenylamine (based upon the weight of mono-C₈-alkyl substituted phenylamines, di-C₈-alkyl substituted phenylamines, and tri-C₈-alkyl substituted phenylamines present in the concentrate composition); and
 - b) optionally, polar diluent having an aniline point of 25°C or less, and at least 2 available hydrogen-bond acceptor groups (ester, ether or alcohol group) that are 2, 3, 4, 5, or 6 atoms

apart, wherein, if polar diluent is present, then the combination of polar diluent of b) combined with the diphenylamine antioxidant of a) is clear after 96 hours at 20 °C without agitation (such as a combination of 75 mass% of the polar diluent of b) combined with 25 mass% of the diphenylamine antioxidant of a) is clear after 96 hours at 20 °C, or such as a combination of 50 mass% of the polar diluent of b) combined with 50 mass% of the diphenylamine antioxidant of a) is clear after 96 hours at 20 °C);

- ii) detergent, preferably salicylate detergent;
 - iii) base oil;
 - iv) optionally one or more dispersants, friction modifiers; antioxidants, other than the antioxidants of a), pour point depressants, anti-foaming agents, viscosity modifiers, corrosion inhibitors, antirust agents, and/or anti-wear agents;
- wherein the antioxidant composition is combined with the detergent at a temperature of 70 °C or more, such as 75°C or more, such as 80°C or more.

[0027] This invention further relates to a stable concentrate comprising:

- i) an antioxidant composition (that may optionally be homogeneous or heterogeneous (such as a solution, a dispersion, a slurry, a colloid and the like), comprising:
 - a) diphenylamine antioxidant comprising: 1) di(C₈-alkyl substituted phenyl) amine and 2) less than 15 mass% (such as 10 mass% or less) of mono-C₈-alkyl substituted diphenylamine (based upon the weight of mono-C₈-alkyl substituted phenylamines, di- C₈-alkyl substituted phenylamines, and tri- C₈-alkyl substituted phenylamines present in the concentrate composition); and
 - b) optionally, polar diluent having an aniline point of 25°C or less, and at least 2 available hydrogen-bond acceptor groups (ester, ether or alcohol group) that are 2, 3, 4, 5, or 6 atoms apart, wherein, if polar diluent is present, then the combination of polar diluent of b) combined with the diphenylamine antioxidant of a) is clear after 96 hours at 20 °C without agitation (such as a combination of 75 mass% of the polar diluent of b) combined with 25 mass% of the diphenylamine antioxidant of a) is clear after 96 hours at 20 °C); and
- ii) detergent, preferably salicylate detergent;
- iii) base oil; and
- iv) optionally one or more dispersants, friction modifiers; antioxidants, other than the antioxidants of a), pour point depressants, anti-foaming agents, viscosity modifiers, corrosion inhibitors, antirust agents, and/or anti-wear agents;

wherein:

- 1) the antioxidant composition is heated to a fluid state (such as molten state or a liquid crystal state) (such as heating to 98 °C or more) and is combined with the concentrate at a temperature of 70 °C or more, such as 75°C or more, such as 80°C or more (preferably the antioxidant composition and detergent are combined at a temperature of 70 °C or more, such as 75°C or more, such as 80°C or more);

2) the temperature of combination of antioxidant composition and optional detergent is optionally reduced to 45 °C to less than 70 °C; and

3) the combination of antioxidant composition and optional detergent is optionally combined with one or more dispersants, friction modifiers; antioxidants, other than the antioxidants of a), pour point depressants, anti-foaming agents, viscosity modifiers, corrosion inhibitors, antirust agents, and/or anti-wear agents.

[0028] This invention further relates to a stable concentrate comprising:

i) an antioxidant composition (that may optionally be homogeneous or heterogeneous (such as a solution, a dispersion, a slurry, a colloid and the like), comprising:

a) diphenylamine antioxidant comprising: 1) di(C₈-alkyl substituted phenyl) amine and 2) less than 15 mass% (such as 10 mass% or less) of mono-C₈-alkyl substituted diphenylamine (based upon the weight of mono- C₈-alkyl substituted phenylamines, di- C₈-alkyl substituted phenylamines, and tri- C₈-alkyl substituted phenylamines present in the concentrate composition); and

b) optionally, polar diluent having an aniline point of 25°C or less, and at least 2 available hydrogen-bond acceptor groups (ester, ether or alcohol group) that are 2, 3, 4, 5, or 6 atoms apart, wherein, if polar diluent is present, then the combination of polar diluent of b) combined with the diphenylamine antioxidant of a) is clear after 96 hours at 20 °C without agitation (such as a combination of 75 mass% of the polar diluent of b) combined with 25 mass% of the diphenylamine antioxidant of a) is clear after 96 hours at 20 °C); and

ii) detergent, preferably salicylate detergent;

iii) base oil; and

iv) optionally one or more dispersants, friction modifiers; antioxidants, other than the antioxidants of a), pour point depressants, anti-foaming agents, viscosity modifiers, corrosion inhibitors, antirust agents, and/or anti-wear agents;

wherein:

1) the antioxidant composition is combined with the concentrate at a temperature of 70 °C or more, such as 75°C or more, such as 80°C or more, such as 90°C or more, such as 100°C or more (preferably the antioxidant composition and detergent are combined at a temperature of 70 °C or more, such as 75°C or more, such as 80°C or more, such as 90°C or more, such as 100°C or more);

2) the temperature of combination of antioxidant composition and optional detergent is optionally reduced to 45 °C to less than 70 °C; and

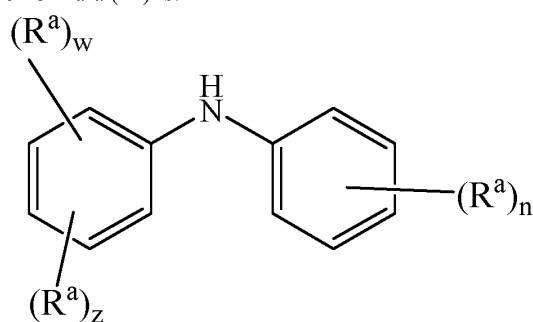
3) the combination of antioxidant composition and optional detergent is optionally combined with one or more dispersants, friction modifiers; antioxidants, other than the antioxidants of a), pour point depressants, anti-foaming agents, viscosity modifiers, corrosion inhibitors, antirust agents, and/or anti-wear agents.

[0029] This invention further relates to a stable 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) a stable antioxidant composition and or a stable concentrate as described herein, such as a liquid (molten and or solution) antioxidant composition and or a stable concentrate.

[0030] This invention further relates to stable antioxidant compositions, stable concentrates and or stable lubricating oil compositions wherein: the composition comprises:

- a) from 0 to less than 15 mass% (such as 10 mass% or less)% mono-C₈-alkyl substituted diphenylamine represented by the Formula (III) where n is 1, w is 0, and z is 0,
- b) 85 mass% or more (such as 90 mass% or more) of di-C₈-alkyl substituted diphenylamine represented by Formula (III), where n is 1, w is 0, and z is 1,
- c) from 0 to less than 10 mass% tri-C₈-alkyl substituted diphenylamine represented by Formula (III), where n is 1, w is 1 and z is 1,
- d) 1 mass% or less of unsubstituted diphenylamines represented by Formula (III) where n is 0, w is 0, and z is 0, based upon the total weight of the diphenylamines of a), b), c) and d) present in the composition where Formula (III) is:

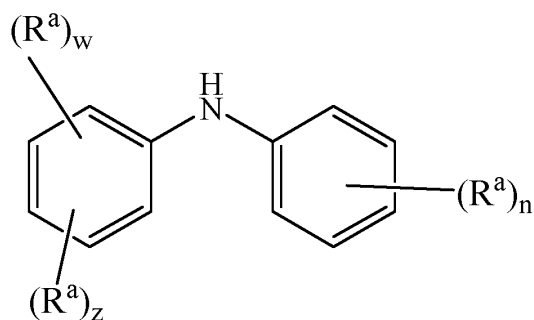


Formula (III)

where each R^a is independently a linear C₈ alkyl group or branched C₈ alkyl group, n is 1 or 0, z is 0 or 1, and w is 0 or 1, where the branched C₈ alkyl group may be singly, doubly or triply branched at one, two, three, four or more carbons, and may be symmetrically branched or asymmetrically branched.

[0031] Optionally the lubricating oil compositions described herein may be absent phenothiazine.

[0032] This invention further relates to stable antioxidant compositions, stable concentrates and or stable lubricating oil compositions wherein the C₈ alkyl substituted diphenylamines represented by the Formula (III) where n is 0, z is 0 and w is 1, 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 3 mass%, such as less than 1 mass%, such as less than 0.3 mass%, particularly less than 0.1 mass%), and di-alkyl substituted diphenylamines represented by Formula (III) where n is 1 z is 1 and w is 0, are present at more than 85 mass% (such as 90 mass% or more), based upon the weight of the phenylamine antioxidants represented by Formula (III) where w is 0, present in the lubricating oil composition:



Formula (III)

where each R^a is independently a linear C_8 alkyl or branched C_8 alkyl group, n is 1 or 0, z is 0 or 1, and w is 0 or 1, where the branched C_8 alkyl group may be singly, doubly or triply branched at one, two, three, four or more carbons, and may be symmetrically branched or asymmetrically branched.

[0033] This invention further relates to stable lubricating oil compositions 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 antioxidants not represented by Formula III, such as 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 (III) where each R^a is independently linear C_8 alkyl or branched C_8 alkyl group, w is 0, z is 0 and n is 1, are absent or present at less than 0.30 mass% (such as less than 0.10 mass%, such as less than 5 mass%, such as less than 3 mass%, such as less than 1 mass%, such as less than 0.01 mass%), based upon the weight of the lubricating oil composition.

[0034] 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 diphenylamine antioxidant comprising at least 85 mass% (such as 90 mass% or more, 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 (III), where w is 0, n is 1 and z is 1, and less than 15 mass% (such as 10 mass% or less, such as 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%) diphenylamine antioxidant represented by Formula (III), where w is 0, n is 1 and z is zero, based upon the weight of the diphenylamine antioxidant represented by Formula (III), as described herein.

[0035] This invention also relates to the use of diphenyl amine antioxidant 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 the diphenylamine antioxidant to the internal combustion engine, where the diphenyl amine antioxidant comprises: 1) di(C₈-alkyl substituted diphenyl) amine and 2) from 0 to 15 mass% (such as 5 to less than 10 mass%, such as 7 to 10 mass%) of mono-C₈-alkyl substituted diphenyl amine, based upon the weight of the di- and mono-C₈-alkyl substituted diphenyl amines.

[0036] This invention also relates to the use of diphenyl amine antioxidant to reduce piston deposits (Sequence IIIH), and or rod deposits (MHT4 TEOST, simulating piston deposits), 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 diphenylamine antioxidant to the internal combustion engine, such as to the crankcase or sump of the internal combustion engine, where in the C₈ diphenyl amine antioxidant comprises: 1) di(C₈-alkyl substituted diphenyl) amine (such as from 100 to 85 mass%, such as 95-85 mass%, such as 90-95 mass%, di(C₈-alkyl substituted diphenyl) amine), and 2) from 0 to 15 mass% (such as 5 to 15 mass%, such as 5 to 10 mass%) of mono-C₈-alkyl substituted diphenyl amine, based upon the weight of the di- and mono-C₈-alkyl substituted diphenyl amines, 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 (such as glycerol mono-oleate),
- 2) sulfonate-based detergents, salicylate based detergents, or a combination of sulfonate and salicylate based detergents,
- 3) borated compounds (such as borated dispersants),
- 4) dispersants derived from polymer having an Mn of 1600 g/mol or less (optionally having a TBN of 100 mgKOH/g or less),
- 5) organomolybdenum-based friction modifiers (such di- nuclear and or tri-nuclear molybdenum compounds, such as as MoDTC dimer and or MoDTC trimer),
- 6) magnesium-based detergents providing 400 ppm or more of Mg to the composition,
- 7) calcium based detergents,
- 8) combinations of calcium and magnesium based detergents,
- 9) zinc-based anti-wear agents (such as derived ZDDP from primary alcohol),
- 10) base oil comprising renewable base oil, such as a combination of refined and renewable base oils, optionally combined with a Group IV base oil,
- 11) Group II base oils 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, and combinations thereof, and variants thereof.

[0037] 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(octylphenyl)amine and 10 mass% or less (such as 10 mass% to 5 mass% such as 7 mass% to 10 mass%) of (octylphenyl)(phenyl)amine based on the weight of the bis(octylphenyl)amine and (octylphenyl)(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 selected from the group consisting of:
 - 1) glycerol-based friction modifiers (such as glycerol mono-oleate),
 - 2) sulfonate-based detergents, salicylate based detergents, or a combination of sulfonate and salicylate based detergents,
 - 3) borated compounds (such as borated dispersants),
 - 4) dispersants derived from polymer having an Mn of 1600 g/mol or less (optionally having a TBN of 100 mgKOH/g or less),
 - 5) organomolybdenum-based friction modifiers (such di- nuclear and or tri-nuclear molybdenum compounds, such as as MoDTC dimer and or MoDTC trimer),
 - 6) magnesium-based detergents providing 400 ppm or more of Mg to the composition,
 - 7) calcium based detergents,
 - 8) combinations of calcium and magnesium based detergents,
 - 9) zinc-based anti-wear agents (such as derived ZDDP from primary alcohol),
 - 10) base oil comprising renewable base oil, such as a combination of refined and renewable base oils, optionally combined with a Group IV base oil,
 - 11) Group II base oils 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,

and combinations thereof, and variants thereof.

[0038] 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 (such as 95 mass% or more, such as 90 to 97 mass%) of bis(octylphenyl)amine and 10 mass% or less (such as 5 mass% or less, such as 3 to 10 mass%, such as 5 to 10 mass%) of (octylphenyl)(phenyl)amine based on the weight of the bis(octylphenyl)amine and (octylphenyl)(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:

- 1) glycerol-based friction modifiers (such as glycerol mono-oleate),
- 2) sulfonate-based detergents, salicylate based detergents, or a combination of sulfonate and salicylate based detergents,
- 3) borated compounds (such as borated dispersants),
- 4) dispersants derived from polymer having an Mn of 1600 g/mol or less (optionally having a TBN of 100 mgKOH/g or less),
- 5) organomolybdenum-based friction modifiers (such di- nuclear and or tri-nuclear molybdenum compounds, such as as MoDTC dimer and or MoDTC trimer),
- 6) magnesium-based detergents providing 400 ppm or more of Mg to the composition,
- 7) calcium based detergents,
- 8) combinations of calcium and magnesium based detergents,
- 9) zinc-based anti-wear agents (such as derived ZDDP from primary alcohol), and combinations and variants thereof.

[0039] In a further aspect, this invention relates to a lubricating oil composition comprising the composition(s) described herein.

[0040] In a further aspect, this invention relates to a diphenyl amine antioxidant comprising: a) less than 10 mass% of mono-C₈-alkyl substituted diphenyl amines, such as 10 to 3 mass%, b) greater than 90 mass% di-C₈-alkyl substituted diphenyl amines, such as 90 to 97 mass%, based upon the total weight of mono-C₉-alkyl substituted diphenyl amines and the di-C₉-alkyl substituted diphenyl amines.

[0041] This invention further relates to lubricating oil compositions 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) a molten antioxidant composition as described herein. Molten antioxidant composition may be added at any point in the lubricating oil composition production process, such as directly to the base oil, directly to the concentrate, directly to the combination of base oil and concentrate, or directly to a lubricating oil composition.

[0042] According to another aspect of the present invention, there is provided the use of the lubricating oil composition described above for lubrication of an internal combustion engine.

BRIEF DESCRIPTION OF THE DRAWINGS

[0043] Figure 1 (Fig. 1) shows typical alkylated phenylamine isomers produced using C₈ alkyl, where the alkyl group is a branched C₈ alkyl radical.

[0044] Figure 2 (Fig. 2) is a graph of CEC L109-14 percent viscometric growth for compositions containing specific components and one of: 4,4'-di-octyldiphenylamine, Component 2, or a 50/50 blend of 4,4'-di-octyldiphenylamine and TMP ester.

[0045] Figure 3 (Fig. 3) is a graph of CEC L109-14 percent viscometric growth for compositions containing GMO and one of: 4,4'-di-octyldiphenylamine, C₉-diphenylamine, or a 50/50 blend of 4,4'-di-octyldiphenylamine and TMP ester.

[0046] Figure 4 (Fig. 4) is a graph of CEC L109-14 percent viscometric growth for compositions containing boron containing compound and one of: 4,4'-di-octyldiphenylamine, C9-diphenylamine, or a 50/50 blend of 4,4'-di-octyldiphenylamine and TMP ester.

DEFINITIONS

[0047] 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.

[0048] 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.).

[0049] 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 "**consists 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.

[0050] The term "**LOC**" means lubricating oil composition.

[0051] 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.

[0052] 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.

[0053] 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").

[0054] 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.

[0055] 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.

[0056] The terms "**group**" and "**radical**" are used interchangeably herein.

[0057] 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, alkoxy, 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).

[0058] 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, alkoxy, mercapto, alkylmercapto, nitro, nitroso, sulfoxy, etc.).

[0059] The term "**alkyl**" means a radical of carbon and hydrogen (such as a C₁ to C₃₀, such as a C₁ to C₁₂ 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.

[0060] The term "**alkenyl**" means a radical of carbon and hydrogen (such as a C₂ to C₃₀ radical, such as a C₂ to C₁₂ 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.

[0061] The term "**alkylene**" means a C₁ to C₂₀, preferably a C₁ to C₁₀, 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.

[0062] 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 C₄₋₅ olefins", the C₄₋₅ 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.

[0063] The term "**alkynyl**" means a C₂ to C₃₀ (such as a C₂ to C₁₂) radical, which includes at least one carbon-to-carbon triple bond.

[0064] The term "**aryl**" means a group containing at least one aromatic ring, such as cyclopentadiene, phenyl, naphthyl, anthracenyl, and the like. Aryl groups are typically C₅ to C₄₀ (such as C₅ to C₁₈, such as C₆ to C₁₄) 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.

[0065] 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 C₁ to C₂₀ 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 as an alkyl group, such as a C₁ to C₂₀ 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).

[0066] 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).

[0067] 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 C₄ to C₄₀ alkyl groups.) Common hindered phenols include butylated hydroxy toluene and substituted butylated hydroxy toluenes.

[0068] The term "**halogen**" or "**halo**" means a group 17 atom or a radical of group 17 atom, such as fluoro, chloro, bromo, and iodo.

[0069] The term "**ashless**" in relation to an additive means the composition does not include a metal.

[0070] The term "**ash-containing**" in relation to an additive means the composition includes a metal.

[0071] 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.

[0072] 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.

[0073] 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.

[0074] The term "**ppm**" means parts per million by mass, based on the total mass of the lubricating oil composition, unless otherwise indicated.

[0075] 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.

[0076] The term "**aliphatic hydrocarbyl fatty acid**" means a monocarboxylic acid having an aliphatic C₇ to C₂₉, preferably a C₉ to C₂₇, most preferably a C₁₁ to C₂₃ hydrocarbyl chain. Such compounds may be referred to herein as aliphatic (C₇ to C₂₉), more preferably (C₉ to C₂₇), most preferably (C₁₁ to C₂₃), 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).

[0077] 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 C₁ to C₃₀ aliphatic hydrocarbyl ester, such as an alkyl ester, preferably a C₁ to C₆ 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 C₁ to C₃₀ aliphatic hydrocarbyl ester(s), [*e.g.*, aliphatic hydrocarbyl fatty acid alkyl ester(s), more preferably aliphatic hydrocarbyl fatty acid C₁ to C₆ alkyl ester(s), especially aliphatic hydrocarbyl fatty acid methyl ester(s)]. Suitably, the term "aliphatic hydrocarbyl fatty

acid ester" embraces aliphatic (C₇ to C₂₉) hydrocarbyl, more preferably aliphatic (C₉ to C₂₇) hydrocarbyl, most preferably aliphatic (C₁₁ to C₂₃) hydrocarbyl fatty acid glycerol ester(s) and aliphatic (C₇ to C₂₉) hydrocarbyl, more preferably aliphatic (C₉ to C₂₇) hydrocarbyl, most preferably aliphatic (C₁₁ to C₂₃) hydrocarbyl fatty acid C₁ to C₃₀ 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.

[0078] The term "**sulfurized aliphatic hydrocarbyl fatty acid ester**" means a compound obtained by sulfurizing an aliphatic hydrocarbyl fatty acid ester as defined herein.

[0079] 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.

[0080] 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.

[0081] 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.

[0082] As used herein, **M_n** is number average molecular weight, **M_w** is weight average molecular weight, and **M_z** 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.

[0083] **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.

[0084] **Total Acid Number ("TAN")** is determined by ASTM D664.

[0085] **Phosphorus, Boron, Calcium, Zinc, Molybdenum, Sodium, Silicon, and Magnesium** content are measured by ASTM D5185.

[0086] **Sulfur content in oil** formulations is measured by ASTM D5185.

[0087] **Sulfated ash ("SASH")** content is measured by ASTM D874.

[0088] **Kinematic viscosity** (KV100, KV40, etc.) is determined pursuant to ASTM D445-19a and reported in units of cSt, unless otherwise specified.

[0089] **Viscosity index** is determined according to ASTM D2270.

[0090] **Saponification number** is determined by ASTM D94, and reported in units of mgKOH/g.

[0091] 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.

[0092] 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.

[0093] Further, it is understood that any upper and lower quantity, range and ratio limits set forth herein may be independently combined.

[0094] 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

[0095] 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.

[0096] The lubricating oil compositions, concentrates, antioxidant compositions, 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.

[0097] C₈ alkylated diphenylamines (such as Naugalube™ 438, and Irganox™ L01) are antioxidants that are commonly used in the lubricant, rubber and plastics industries. The C₈ alkylated diphenylamines are typically prepared from the reaction of diphenylamine with diisobutylene. This reaction gives predominantly the mono-substituted and di-substituted diphenylamines, N-phenyl-4-(2,4,4-trimethylpentan-2-yl)aniline and bis(4-(2,4,4-trimethylpentan-2-yl)phenyl)amine respectively.

[0098] Mono-C₈ alkylated diphenylamine can show antioxidant performance when the mono-C₈ alkylated diphenylamine is present at greater than ten percent of the C₈ alkyl diphenylamine component. From a performance perspective it has been considered as a benefit to have mono-C₈ alkylated diphenylamine in the component because it has a higher percent nitrogen content weight for weight compared to the di-C₈ alkylated diphenylamine. Typically nitrogen levels in aminic antioxidants are indicative of the components antioxidant performance. However, for 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.

[0099] For purposes of this invention and the claims thereto **"mono-C₈-alkyl substituted diphenylamine"**, also referred to as "(C₈-alkyl substituted phenyl)(phenyl)amine", means a nitrogen atom bound to: 1) hydrogen, 2) an unsubstituted phenyl group, and 3) a phenyl group substituted with one C₈ alkyl group.

[0100] For purposes of this invention and the claims thereto **"di-C₈-alkyl substituted diphenylamine"**, also referred to as "di(C₈-alkyl substituted phenyl) amine", means a nitrogen atom bound to: 1) hydrogen, and 2) two phenyl groups each independently substituted with one C₈ alkyl group, each of which is independently linear or branched.

[0101] For purposes of this invention and the claims thereto **"tri-C₈-alkyl substituted diphenylamine"**, also referred to as "di(C₈-alkyl substituted phenyl) (C₈-alkyl substituted phenyl) amine, means a nitrogen atom bound to 1) hydrogen, 2) a phenyl group independently substituted with two C₈ alkyl groups, each of which is independently linear or branched, and 3) a phenyl group substituted with one C₈ alkyl group.

[0102] For purposes of this invention and the claims thereto **"diphenylamine 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 C₈ alkyl groups.

[0103] For purposes of this invention and the claims thereto **"unsubstituted diphenylamine"**, means a nitrogen atom bound to 1) hydrogen, and 2) two unsubstituted phenyl groups.

[0104] For purposes of this invention and the claims thereto **"mono-C₉-alkyl substituted diphenylamine"**, also referred to as "(C₉-alkyl substituted phenyl)(phenyl)amine", means a nitrogen atom bound to: 1) hydrogen, 2) an unsubstituted phenyl group, and 3) a phenyl group substituted with one C₉ alkyl group.

[0105] For purposes of this invention and the claims thereto **"di-C₉-alkyl substituted diphenylamine"**, also referred to as "di(C₉-alkyl substituted phenyl) amine", or means a nitrogen atom bound to: 1) hydrogen, and 2) two phenyl groups each independently substituted with one C₉ alkyl group, each of which is independently linear or branched.

[0106] For purposes of this invention and the claims thereto **"tri-C₉-alkyl substituted diphenylamine"**, also referred to as "(diC₉-alkyl substituted phenyl) (phenyl)amine", means a nitrogen atom bound to 1) hydrogen, 2) a phenyl group independently substituted with two C₉ alkyl groups, each of which is independently linear or branched, and 3) a phenyl group substituted with one C₉ alkyl group.

[0107] For purposes of this invention and the claims thereto, when a composition (including, but not limited to antioxidant compositions, concentrate packages, lubricating oil compositions) comprising one or more polar diluents and one or more C₈-diphenylamine antioxidants is described as "**clear and/or stable at 20°C and 60 °C for 600 hours**", it means that the composition comprising the polar diluent(s) and the diphenylamine antioxidant(s) is observed to be clear (meaning having no crystallization, precipitation or cloudiness as described in the Experimental section below) after 600 hours of being held in a clear glass container at 20°C and the composition is observed to be clear after 600 hours of being held at 60 °C temperature in a clear glass container with no agitation.

[0108] For purposes of this invention and the claims thereto, when a composition (including, but not limited to antioxidant compositions, concentrate packages, lubricating oil compositions) comprising one or more polar diluents and one or more C₈-diphenylamine antioxidants is described as "**stable at X °C for Y hours**" or "**clear after Y hours at X °C**", it means that the composition comprising the polar diluent(s) and the diphenylamine antioxidant(s) is observed to be clear (meaning having no crystallization, precipitation or cloudiness as described in the Experimental section below) after X hours of being held at Y °C temperature in a clear glass container with no agitation.

[0109] For purposes of this invention and the claims thereto, when an antioxidant composition or concentrate composition comprising one or more polar diluents and one or more C₈-diphenylamine antioxidants is described as "**stable**" without indicating time and temperature, it means that the combination of the polar diluent(s) combined with the diphenylamine antioxidant(s) is observed to be clear (meaning having no crystallization, precipitation or cloudiness as described in the Experimental section below) after 96 hours of being held in a clear glass container at 20 °C with no agitation.

[0110] 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 alkyl groups, such as C₉ diphenyl amine antioxidant and or C₈ diphenyl amine antioxidant.

[0111] 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.

[0112] For purposes of this invention and the claims thereto "**enhanced aminic antioxidant**" or "**enhanced diphenyl amine antioxidant**" is:

- A) diphenyl amine antioxidant comprising: 1) 85, (or 86, or 87, or 88, or 89, 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-C₈-alkyl substituted diphenyl amine, and 2) 15 (or 14, or 13, or 12, or 11, or 10, or 9, or 8, or 7, or 6, or 5, or 4, or 3 or 2, or 1) mass% or less (such as 0 mass%) of mono-C₈-alkyl substituted diphenyl amine, based on the total mass% of the di-C₈-alkyl substituted diphenyl amine and mono-C₈-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-C₈-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-

C₈-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-C₈-alkyl substituted diphenyl amine, based on the total mass% of the tri-C₈-alkyl substituted diphenyl amine, di-C₈-alkyl substituted diphenyl amine and mono-C₈-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-C₈-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-C₈-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-C₈-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-C₈-alkyl substituted diphenyl amine, di-C₈-alkyl substituted diphenyl amine, mono-C₈-alkyl substituted diphenyl amine, and unsubstituted diphenyl amine.

[0113] In this invention we also note unique and or improved effects, and even synergistic effects, from combinations of: **A)** enhanced aminic antioxidants (such as diphenyl amine antioxidant comprising 85 mass% or more, such as 90 to 97 mass% of bis(octylphenyl)amine and less than 15 mas%, such as 3 to 10 mass% of (octylphenyl)(phenyl)amine based on the weight of the bis(octylphenyl)amine and (octylphenyl)(phenyl)amine) as compared to the same composition where the aminic antioxidant(s) are replaced with Component 2 (di(C₉-alkyl substituted phenyl) amine) from the Experimental section; and **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 consisting essentially of sulfonate based detergents), salicylate based detergents (such as consisting essentially of ssalicylate based detergents), or a combination of sulfonate and salicylate based detergents,
- 3) borated compounds (such as borated dispersants),
- 4) dispersants derived from polymer having an Mn of 1600 g/mol or less (optionally having a TBN of 100 mgKOH/g or less),
- 5) organomolybdenum-based friction modifiers (such di- nuclear and or tri-nuclear molybdenum compounds, such as as MoDTC dimer and or MoDTC trimer),
- 6) magnesium-based detergents providing 400 ppm or more of Mg to the composition (such as consisting essentially of Mg based detergents),
- 7) calcium based detergents (such as consisting essentially of Ca based detergents),
- 8) combinations of calcium and magnesium based detergents,
- 9) zinc-based anti-wear agents (such as derived ZDDP from primary alcohol),
- 10) base oil comprising renewable base oil, such as a combination of refined and renewable base oils, optionally combined with a Group IV base oil,
- 11) Group II base oils 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, and combinations thereof, and variants thereof.

[0114] 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 85 mass% or more of bis(octylphenyl)amine and 15 mass% or less of (octylphenyl)(phenyl)amine based on the weight of the bis(octylphenyl)amine and (octylphenyl)(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) calcium-based detergents, such as calcium salicylate and or calcium sulfonate detergents;
- 4) borated compounds (such as borated dispersants, such as borated PIBSA-PAM, such as borated PIBSA-PAM derived from PIB having an Mn of 1600 g/mol or less);
- 5) dispersants derived from polymer having an Mn of 1600 g/mol or less (optionally having a TBN of 100 mgKOH/g or less, such as PIBSA-PAM dispersants derived from polymer having an Mn of 1600 g/mol or less (optionally having a TBN of 100 mgKOH/g or less);
- 6) organomolybdenum-based friction modifiers, such as molybdenum dithiocarbamate dimers and or trimers;
- 7) magnesium-based detergents, preferably providing 400 ppm or more of Mg to the composition, such as magnesium salicylate and or sulfonate detergents;
- 8) carboxylate based detergents, such as such as magnesium and or calcium salicylate detergents;
- 9) zinc-based antiwear agents, such as zinc dialkyldithiophosphates 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).

[0115] 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(octylphenyl)amine (such as 90 to 92 mass%, such as 90 to 97 mass%, such as 90 to 95 mass%), based on the weight of the bis(octylphenyl)amine and (octylphenyl)(phenyl)amine, and,

- ii) 10 to 0 mass% (such as 10 to 8 mass%, such as 10 to 7 mass%, such as 10 to 5 mass%) of (octylphenyl)(phenyl)amine, based on the weight of the bis(octylphenyl)amine and (octylphenyl)(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 30 mass%, such as 0.01 to 20 mass%, such as 0.1 to 10 mass%, such as 0.1 to 5 mass%, of 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 30 mass%, such as 0.01 to 20 mass%, such as 0.1 to 10 mass%, such as 0.1 to 5 mass%, of calcium-based detergents, such as calcium sulfonate and or carboxylate (salicylate) detergents;
 - 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% of borated compounds (such as borated dispersants, such as borated PIBSA-PAM, such as borated PIBSA-PAM derived from PIB having an Mn of 1600 or less);
 - 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% of dispersants derived from polymer having an Mn of 1600 g/mol or less (optionally having a TBN of 100 mgKOH/g or less, such as PIBSA-PAM dispersants derived from polymer having an Mn of 1600 g/mol or less (optionally having a TBN of 100 mgKOH/g or less);
 - 6) 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;
 - 7) 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% of 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 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 more, such as 5000 ppm or more, such as 6000 ppm or more, such as 7000 ppm or more, such as 8000 ppm or more, such as 9000 ppm or more);

8) 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 dialkyldithiophosphates where the alkyl group is derived from primary alcohols (such as C₄ to C₃₀ primary alcohols); and

9) 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 more, such as 5000 ppm or more, such as 6000 ppm or more, such as 7000 ppm or more, such as 8000 ppm or more, such as 9000 ppm or more) Ca and or Mg optionally in mass% ratios of Ca:Mg of 1:2 to 2:1; and

10) 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).

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(octylphenyl)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(octylphenyl)amine and (octylphenyl)(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 (octylphenyl)(phenyl)amine, based on the weight of the bis(octylphenyl)amine and (octylphenyl)(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 30 mass%, 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 30 mass%, such as 0.01 to 20 mass%, such as 0.1 to 10 mass%, such as 0.1 to 5 mass%, of **calcium-based detergents**, such as calcium sulfonate and or carboxylate (salicylate) detergents;
- 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% of one or more **borated compounds** (such as borated dispersants, such as borated PIBSA-PAM, such as borated PIBSA-PAM derived from PIB having an Mn of 1600 or less);
- 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% of **dispersants derived from polymer having an Mn of 1600 g/mol or less** (optionally having a TBN of 100 mgKOH/g or less, such as PIBSA-PAM dispersants derived from polymer having an Mn of 1600 g/mol or less (optionally having a TBN of 100 mgKOH/g or less);
- 6) 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;
- 7) 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 more, such as 5000 ppm or more, such as 6000 ppm or more, such as 7000 ppm or more, such as 8000 ppm or more);

- 8) 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 dialkyldithiophosphates where the alkyl group is derived from one or more primary alcohol(s);
- 9) 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 800 ppm, 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 more, such as 5000 ppm or more, such as 6000 ppm or more, such as 7000 ppm or more, such as 8000 ppm or more); and
- 10) 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 40 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 20 mass% (in particular, 0.01 to 10 mass%, 0.01 to 5 mass%, alternately 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 **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 C₁₂-C₆₀ hydrocarbons** (such as C₁₂-C₂₄ linear alpha-olefins (LAOs), oligomers/polymers of polyisobutylenes, and/or blends thereof).

[0116] 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.

[0117] In preferred embodiments, the compositions described herein (concentrates, booster packages and or lubricating oils, comprise dinuclear molybdenum compound such as molybdenum dimer, such as molybdenum dithiocarbamate, and one, two, or three of:

a) one or more **borated compounds** (such as borated dispersants, such as borated PIBSA-PAM, such as borated PIBSA-PAM derived from PIB having an Mn of 1600 or less);

b) one or more **magnesium-based detergents**, 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 more, such as 5000 ppm or more, such as 6000 ppm or more, such as 7000 ppm or more, such as 8000 ppm or more);

c) one or more **zinc-based antiwear agents**, such as zinc dialkyldithiophosphates where the alkyl group is derived from one or more primary alcohol(s).

[0118] In preferred embodiments, the compositions described herein (such as concentrates, booster packages and or lubricating oils), comprise 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% of dinuclear molybdenum compound such as molybdenum dimer, such as molybdenum dithiocarbamate and 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% of one or more **borated compounds** (such as borated dispersants, such as borated PIBSA-PAM, such as borated PIBSA-PAM derived from PIB having an Mn of 1600 or less).

[0119] In preferred embodiments, the compositions described herein (such as concentrates, booster packages and or lubricating oils), comprise 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% of dinuclear molybdenum compound such as molybdenum dimer, such as molybdenum dithiocarbamate and 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% of one or more **magnesium-based detergents**, 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 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 3000ppm or more, such as 4000 ppm or more, such as 5000 ppm or more, such as 6000 ppm or more, such as 7000 ppm or more, such as 8000 ppm or more).

[0120] In preferred embodiments, the compositions described herein (such as concentrates, booster packages and or lubricating oils), comprise 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% of dinuclear molybdenum compound such as molybdenum dimer, such as molybdenum dithiocarbamate and 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% of **zinc-based antiwear agents**, such as zinc dialkyldithiophosphates where the alkyl group is derived from one or more primary alcohol(s).

[0121] In preferred embodiments, the compositions described herein (such as concentrates, booster packages and or lubricating oils), comprise: 1) 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% of dinuclear molybdenum compound such as molybdenum dimer, such as molybdenum dithiocarbamate and 2) 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% of **zinc-based antiwear agents**, such as zinc dialkyldithiophosphates where the alkyl group is derived from one or more primary alcohol(s), and 3) 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% of one or more **magnesium-based detergents**, 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 more, such as 5000 ppm or more, such as 6000 ppm or more, such as 7000 ppm or more, such as 8000 ppm or more).

[0122] In preferred embodiments, the compositions described herein (such as concentrates, booster packages and or lubricating oils), comprise 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% of dinuclear molybdenum compound such as molybdenum dimer, such as molybdenum dithiocarbamate, and one, two, or three of:

- a) 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% of one or more **borated compounds** (such as borated dispersants,

such as borated PIBSA-PAM, such as borated PIBSA-PAM derived from PIB having an Mn of 1600 or less);

b) 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% of one or more **magnesium-based detergents**, 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 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 more, such as 5000 ppm or more, such as 6000 ppm or more, such as 7000 ppm or more, such as 8000 ppm or more);

c) 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% of one or more **zinc-based antiwear agents**, such as zinc dialkyldithiophosphates where the alkyl group is derived from one or more primary alcohol(s).

[0123] In preferred embodiments, the compositions described herein (concentrates, booster packages and or lubricating oils, comprise: 1) one or more dinuclear molybdenum compounds such as molybdenum dimer, such as molybdenum dithiocarbamate, 2) one or more **borated compounds** (such as borated dispersants, such as borated PIBSA-PAM, such as borated PIBSA-PAM derived from PIB having an Mn of 1600 or less); 3) one or more **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 more, such as 5000 ppm or more); and 4) one or more **zinc-based antiwear agents**, such as zinc dialkyldithiophosphates where the alkyl group is derived from one or more primary alcohol(s).

[0124] In preferred embodiments, the compositions described herein (concentrates, booster packages and or lubricating oils, comprise: 1) one or more **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 more, such as 5000 ppm or more, such as 6000 ppm or more, such as 7000 ppm or more, such as 8000 ppm or more); and 2) one or more **zinc-based antiwear agents**, such as zinc dialkyldithiophosphates where the alkyl group is derived from one or more primary alcohol(s).

[0125] In preferred embodiments, the compositions described herein (concentrates, booster packages and or lubricating oils, comprise: 1) one or more **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 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 more, such as 5000 ppm or more, such as 6000 ppm or more, such

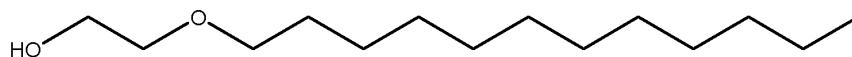
as 7000 ppm or more, such as 8000 ppm or more); and 2) one or more **sulfonate-based detergents**, such as magnesium and or calcium sulfonate detergents.

[0126] In preferred embodiments, the compositions described herein (concentrates, booster packages and or lubricating oils, comprise: 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% of one or more **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 more, such as 5000 ppm or more, such as 6000 ppm or more, such as 7000 ppm or more, such as 8000 ppm or more); and 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%, or one or more **sulfonate-based detergents**, such as magnesium and or calcium sulfonate detergents.

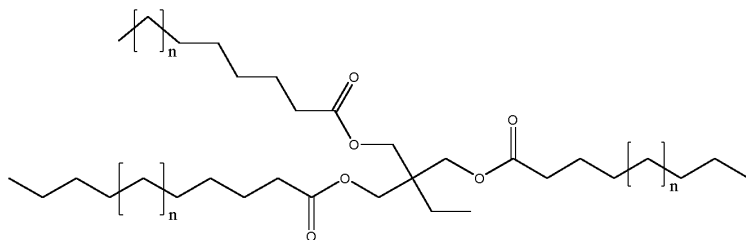
[0127] Further when combining the molten C₈ antioxidants with one or more other additive components or compositions (lubricating oil composition, concentrate compositions, antioxidant compositions, booster pack compositions, etc.), it is typically preferred to raise the temperature of the C₈ antioxidants (which are typically solids, as solid form is easier to transport) to its melting point or above (or its melting range or above), such as at least 5°C above the melting point or melting range, such as at least 10°C above the melting point or melting range, to obtain a molten material (preferably in a fluid state) that is then added in fluid (preferably molten) state to other additive components or compositions (lubricating oil composition, concentrate compositions, antioxidant compositions, booster pack compositions, etc.). For purposes of this invention and the claims thereto the molten state may contain a small amount of crystalline or solid material (such as less than 1 mass%, such as less than 0.5 mass%), but is preferably completely fluid/molten.

Polar Diluents

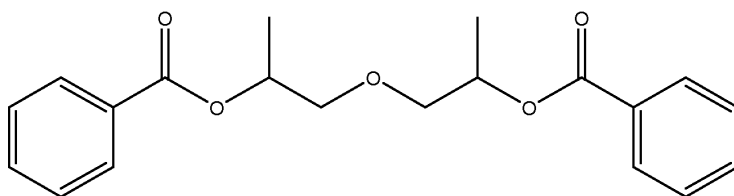
[0128] For purposes of this invention and claims thereto, when **hydrogen-bond acceptor groups** are described as being 2, 3, 4, 5, or 6 atoms (such as carbon atoms) apart, the hydrogen acceptor is not included in that count. For example, in ethoxylated lauryl alcohol (2-(dodecyloxy)ethan-1-ol), the two hydrogen-bond acceptor groups (-OH and -O-) are considered two atoms apart (specifically two carbon atoms apart).



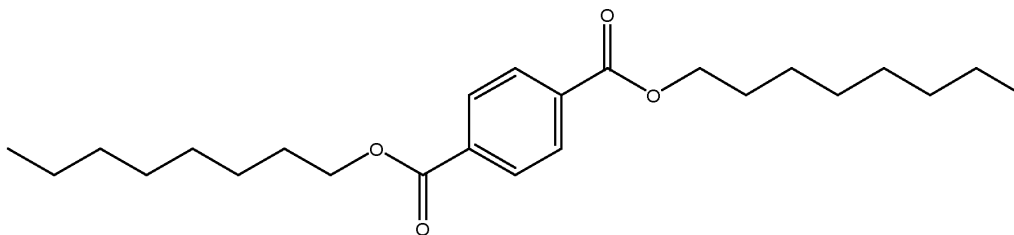
[0129] Likewise, in the C₈-C₁₀ tri-methylol propane ester formula below (n is 0, 1 or 2), the ester groups are considered three atoms apart (specifically 3 carbon atoms apart).



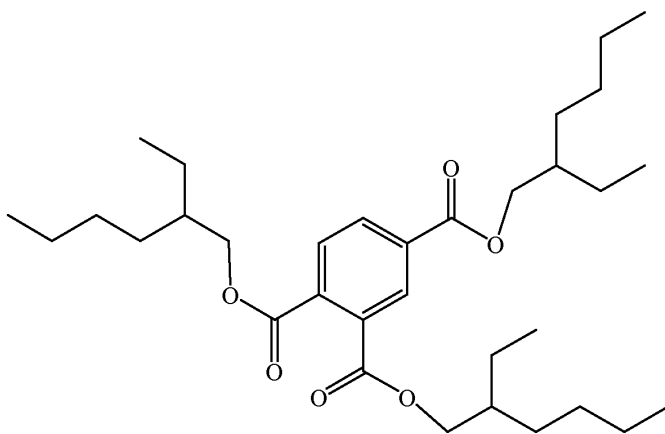
While in a (dipropylene glycol) dibenzoate formula below, the ester groups are considered two atoms apart (specifically 2 carbon atoms apart) from the "-O-" ether group.



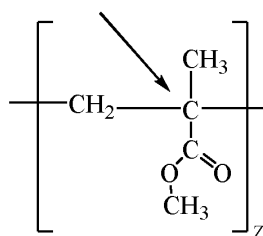
Likewise, in the dioctyl terephthalate formula below, the ester groups are considered four atoms apart (specifically 4 carbon atoms apart).



Likewise, in the trioctyl mellitate formula below, the three ester groups are considered 2, 3, and 4 four atoms apart (specifically 2, 3 and 4 carbon atoms apart) depending on which positions the ester groups occupy (e.g., ortho, meta, or para to each other).



[0130] In embodiments, the polar diluent(s) comprise two or more available hydrogen-bond acceptor groups. An available hydrogen acceptor group is defined to be a group containing a moiety (such as an oxygen containing group, such as an ester, ether or alcohol group) capable of participating in a hydrogen bond with the positively charged hydrogen atom from the amine functionality of the di(C₈-alkyl substituted phenyl) amine. Sterically hindered groups (such as a sterically hindered oxygen containing group, such as a sterically hindered ester, sterically hindered ether or sterically hindered alcohol group) that are not capable of participating in a hydrogen bond with the positively charged hydrogen atom from the amine functionality of the di(C₈-alkyl substituted phenyl) amine are not considered available. In particular, in embodiments, the polar diluent comprises two or more hydrogen-bond acceptor groups that are 2, 3, 4, 5, or 6 atoms apart where the hydrogen-bond acceptor groups do not have one or more adjacent quaternary sp³ carbons. For example, in the homopolymethylmethacrylate formula below (z is the number of repeat units, such as 2 to 10,000) the ester group is bound to an adjacent quaternary sp³ carbon (identified by the arrow) and thus is considered sterically hindered.



[0131] In embodiments, the polar diluent has an aniline point of 25°C or less, such as about 20 °C or less, such as about 15 °C or less, such as about 10 °C or less, such 5 °C or less, such as 0 °C or less.

[0132] In embodiments, the polar diluent has at 2, 3, 4 or 5 available hydrogen-bond acceptor groups (such as more ester, ether or alcohol groups) that are 2, 3, 4, 5, or 6 carbon atoms (such as 2, 3, or 4 carbon atoms) apart.

[0133] In embodiments, the polar diluent(s) are one or more diluent(s) selected from the group consisting of:

- i) di-esters derived from propylene glycol (such as di(propylene glycol)dibenzoate, and
- ii) C₈₋₁₆ alkyl triesters derived from trimethylolpropane (such as C₈-C₁₀ tri-methylol propane ester),
- iii) ethoxylated C₁₀₋₂₄ alcohols (such as ethoxylated C₁₂₋₁₈ alcohols, such as ethoxylated lauryl alcohol), and
- iv) phthalates, terephthalates, isophthalates, trimellitates and pyromellitates (such as C₆ to C₂₄ dialkyl terephthalates, such as C₈ to C₁₆ dialkyl terephthalates, such as dioctyl terephthalate, such as C₆ to C₂₄ dialkyl isophthalates, C₆ to C₂₄ dialkyl phthalates, and C₆ to C₂₄ trialkyl trimellitate, and C₆ to C₂₄ tetraalkyl pyromellitate).

Stable Antioxidant compositions

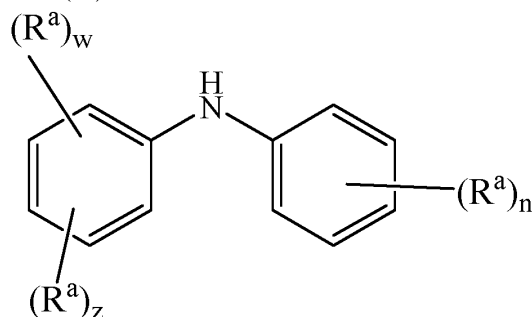
[0134] This invention further relates to stable antioxidant compositions comprising C₈-diphenylamine antioxidant comprising:

a) from 0 to less than 15 mass% (such as less than 10 mass, such as 0.1 to 5 mass%, such as 0.05 to 1 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 less than 0.3 mass%, such as less than 0.1 mass%, such as 0 mass%) mono-C₈-alkyl substituted diphenylamine represented by the Formula (III) where n is 1, w is 0, and z is 0,

b) 85 mass% or more (such as 90 mass% or more, 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 di-C₈-alkyl substituted diphenylamine represented by Formula (III), where n is 1, w is 0, and z is 1, and

c) from 0 to less than 10 mass% (such 0.1 to 5 mass%, such as 0.05 to 1 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 less than 0.3 mass%, such as less than 0.1 mass%, such as 0 mass%) tri-C₈-alkyl substituted diphenylamine represented by Formula (III), where n is 1, w is 1 and z is 1,

based upon the total weight of the diphenylamines of a), b), and c) present in the diphenylamine antioxidant, where Formula (III) is:



Formula (III)

where each R^a is independently a linear C₈ alkyl group or branched C₈ alkyl group, n is 1 or 0, z is 0 or 1, and w is 0 or 1, where the branched C₈ alkyl group may be singly, doubly or triply branched at one, two, three, four or more carbons, and may be symmetrically branched or asymmetrically branched.

[0135] C₈-alkyl substituted diphenylamine anti-oxidants useful herein are described in more detail in the section "**B. Antioxidants**" below, and are incorporated by reference in the instant description of stable antioxidant compositions.

[0136] This invention further relates to a stable antioxidant compositions (that may optionally be homogeneous or heterogeneous (such as a solution, a dispersion, a slurry, a colloid, and the like), comprising:

a) diphenylamine antioxidant comprising: 1) di(C₈-alkyl substituted phenyl) amine and 2) less than 10 mass% (such as less than 5 mass%, such as less than 1 mass%, such as less than 0.3 mass%, such as less than 0.1 mass%) of mono-C₈-alkyl substituted diphenylamine (based upon the

weight of mono- C₈-alkyl substituted phenylamines, di- C₈-alkyl substituted phenylamines, and tri- C₈-alkyl substituted phenylamines present in the lubricating oil composition); and

- b) polar diluent having an aniline point of 25°C or less, and at least two available hydrogen-bond acceptor groups (such as one or more an ester, ether and/or alcohol groups) that are 2, 3, 4, 5, or 6 atoms apart,

wherein the combination of the polar diluent of b) combined with the diphenylamine antioxidant of a) is clear after 96 hours at 20 °C in a clear glass container without agitation (such as a combination of 75 mass% of the polar diluent of b) combined with 25 mass% of the diphenylamine antioxidant of a) is clear after 96 hours at 20 °C).

[0137] In embodiments, 1 to 50 mass% (such as 10 to 40 mass%, such as 15 to 30 mass%, such as about 20 to 25 about mass%) of the diphenylamine antioxidant is combined with from 50 to 99 mass% (such as 60 to 90 mass%, such as 70 to 85 mass%, such as about 75 to about 80 mass%) of polar diluent.

[0138] In embodiments, the polar diluent(s) in the stable antioxidant composition, comprise polar diluent as described here, and typically comprise two or more hydrogen-bond acceptor groups. A hydrogen acceptor group is defined to be a group containing a moiety (such as an oxygen containing group, such as an ester, ether or alcohol group) capable of participating in a hydrogen bond with the positively charged hydrogen atom from the amine functionality of the di(C₈-alkyl substituted phenyl) amine.

[0139] In embodiments, the polar diluent(s) comprise one or more diluent selected from the group consisting of:

- i) di- and tri-esters derived from propylene glycol (such as di(propylene glycol)dibenzoate),
- ii) C₈₋₁₆ alkyl triesters derived from trimethylolpropane, such as C₈-C₁₀ tri-methylol propane ester),
- iii) ethoxylated C₁₀₋₂₄ alcohols, such as ethoxylated C₁₂₋₁₈ alcohols, such as ethoxylated lauryl alcohol, and
- iv) C₆ to C₂₄ dialkyl terephthalates, such as C₈ to C₁₆ dialkyl terephthalates, such as dioctyl terephthalate.

[0140] The stable antioxidant compositions may also comprise detergent, such as carboxylate detergent, such as salicylate detergent, such as calcium and or magnesium salicylate detergent.

[0141] The stable antioxidant compositions may also comprise detergent, such as sulfonate detergent, such as sulfonate detergent, such as calcium and or magnesium sulfonate detergent.

[0142] The stable antioxidant compositions may also comprise combinations of detergent, such as carboxylate detergent and sulfonate detergents, such as salicylate detergent and sulfonate detergent, such as calcium salicylate and magnesium sulfonate detergent.

[0143] The detergent may be present in the stable anti-oxidant composition at 1 mass% or more, such as 10 mass% or more, such as 25 mass% or more, such as 50 mass% or more, such as 75 mass% or more, based upon the weight of the stable antioxidant composition.

[0144] In embodiments, the stable anti-oxidant composition comprises:

- i) 1 to 98 mass% (such as 10 to 75 mass%, such as 20 to 50 mass%, such as about 20 to 25 about mass%) of the diphenylamine antioxidant;

- ii) 1 to 90 mass% (such as 10 to 80 mass%, such as 25 to 75 mass%, such as about 50 to about 70 mass%) of polar diluent, and
- iii) 8 to 98 mass% (such as 10 to 60 mass%, such as 20 to 50 mass%, such as about 20 to 25 about mass%) of detergent, such as carboxylate detergent, such as salicylate detergent,
- iv) optional additional components, antioxidants (other than i) above), pour point depressants, anti-foam agents, viscosity modifiers, corrosion inhibitors, anti-wear 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.

Stable Concentrate Compositions

[0145] A concentrate, also referred to as an additive package, adpak, or addpack, is a composition having: 1) 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%, such as from 0.1 to 20 mass%, such as 0.5 to 10 mas%, such as 1 to 5 mass%) base oil, and 2) lubricant composition additives (such as described herein), based upon the weight of the concentrate, which is typically then further blended with additional base oil to form a lubricating oil product.

[0146] This invention further relates to a stable concentrate composition comprising:

- i) an antioxidant composition (that may optionally be homogeneous or heterogeneous (such as a solution, a dispersion, a slurry, a colloid and the like), comprising:
 - a) diphenylamine antioxidant comprising:
 - 1) di(C₈-alkyl substituted phenyl) amine (such as 80 mass% or more, such as 90 mass% or more, such as 95 mass% or more, such as 96 mass% or more, such as 97 mass% or more, such as 98.5 mass% or more, such as 99 mass% or more),
 - 2) less than 10 mass% (such as less than 5 mass%, such as less than 1 mass%, such as less than 0.3 mass%, such as less than 0.1 mass%) of mono-C₈-alkyl substituted diphenylamine, and
 - 3) less than 10 mass% (such as less than 5 mass%, such as less than 1 mass%, such as less than 0.3 mass%, such as less than 0.1 mass%) of mono-C₈-alkyl substituted diphenylamine,
- based upon the weight of the mono-C₈-alkyl substituted phenylamines, di- C₈-alkyl substituted phenylamines and tri- C₈-alkyl substituted phenylamines present in the lubricating oil composition); and
- b) polar diluent having an aniline point of 25°C or less, such as 20°C or less, and at least 2 available hydrogen-bond acceptor groups (such as ester, ether or alcohol group) that are 2, 3, 4, 5, or 6 atoms apart (such as 1, 2 3, or 4 atoms apart, such as 2, 3 or 4 atoms apart),

wherein the combination of the polar diluent of b) combined with the diphenylamine antioxidant of a) is clear after 96 hours at 20 °C in a clear glass container without agitation (such as a combination of 75 mass% of the polar diluent of b) combined with 25 mass% of the diphenylamine antioxidant of a) is clear after 96 hours at 20°C);

- ii) detergent (such as salicylate and or sulfonate detergent, such as calcium and or magnesium salicylate and or sulfonate detergent, such as calcium salicylate and magnesium sulfonate detergent, such as calcium and magnesium salicylate detergent, such as magnesium sulfonate detergent, such as calcium salicylate detergent);
- iii) base oil (such as one or more of Group I, II, III, IV and or IV base oils, such as Group I, II and or III base oils, such as Group III oils);
- iv) optionally one or more dispersants, friction modifiers; antioxidants, other than the antioxidants of a), pour point depressants, anti-foaming agents, viscosity modifiers, corrosion inhibitors, antirust agents, and/or anti-wear agents.

[0147] This invention further relates to a stable concentrate composition comprising:

- i) an antioxidant composition (that may optionally be homogeneous or heterogeneous (such as a solution, a dispersion, a slurry, a colloid and the like), comprising:

- a) diphenylamine antioxidant comprising:

- 1) di(C₈-alkyl substituted phenyl) amine (such as 80 mass% or more, such as 90 mass% or more, such as 95 mass% or more, such as 96 mass% or more, such as 97 mass% or more, such as 98.5 mass% or more, such as 99 mass% or more),
- 2) less than 10 mass% (such as less than 5 mass%, such as less than 1 mass%, such as less than 0.3 mass%, such as less than 0.1 mass%) of mono-C₈-alkyl substituted diphenylamine, and
- 3) less than 10 mass% (such as less than 5 mass%, such as less than 1 mass%, such as less than 0.3 mass%, such as less than 0.1 mass%) of mono-C₈-alkyl substituted diphenylamine,

based upon the weight of the mono-C₈-alkyl substituted phenylamines, di- C₈-alkyl substituted phenylamines and tri- C₈-alkyl substituted phenylamines present in the lubricating oil composition); and

- b) polar diluent having an aniline point of 25°C or less, such as 20°C or less, and at least 2 available hydrogen-bond acceptor groups (such as ester, ether or alcohol group) that are 2, 3, 4, 5, or 6 atoms apart (such as 1, 2 3, or 4 atoms apart, such as 2, 3 or 4 atoms apart),

wherein the combination of the polar diluent of b) combined with the diphenylamine antioxidant of a) is clear after 96 hours at 20 °C in a clear glass container without agitation (such as a combination of 75 mass% of the polar diluent of b) combined with 25 mass% of the diphenylamine antioxidant of a) is clear after 96 hours at 20°C);

- ii) detergent (such as salicylate and or sulfonate detergent, such as calcium and or magnesium salicylate and or sulfonate detergent, such as calcium salicylate and magnesium sulfonate detergent, such as calcium and magnesium salicylate detergent, such as magnesium sulfonate detergent, such as calcium salicylate detergent);
- iii) base oil (such as one or more of Group I, II, III, IV and or IV base oils, such as Group I, II and or III base oils, such as Group III oils);

iv) one or more dispersants, friction modifiers; antioxidants, other than the antioxidants of a), pour point depressants, anti-foaming agents, viscosity modifiers, corrosion inhibitors, antirust agents, and/or anti-wear agents,

wherein the antioxidant composition is combined with the detergent at a temperature of about 40 °C or more, such as about 50°C or more, such as about 55°C or more, such as about 60 °C or more.

[0148] This invention further relates to a stable concentrate composition comprising:

i) an antioxidant composition (that may optionally be homogeneous or heterogeneous (such as a solution, a dispersion, a slurry, a colloid and the like), comprising:

a) diphenylamine antioxidant comprising: 1) di(C₈-alkyl substituted phenyl) amine and 2) less than 10 mass% of mono-C₈-alkyl substituted diphenylamine (based upon the weight of the mono-C₈-alkyl substituted phenylamines and di- C₈-alkyl substituted phenylamines present in the lubricating oil composition); and

b) optionally, polar diluent having an aniline point of 25°C or less, such as 20°C or less, and at least 2 available hydrogen-bond acceptor groups (such as ester, ether or alcohol group) that are 2, 3, 4, 5, or 6 atoms apart (such as 1, 2 3, or 4 atoms apart, such as 2, 3 or 4 atoms apart), wherein, if polar diluent is present, then the combination of the polar diluent of b) combined with the diphenylamine antioxidant of a) is clear after 96 hours at 20 °C in a clear glass container without agitation (such as a combination of 75 mass% of the polar diluent of b) combined with 25 mass% of the diphenylamine antioxidant of a) is clear after 96 hours at 20 °C);

ii) detergent (such as salicylate and or sulfonate detergent, such as calcium and or magnesium salicylate and or sulfonate detergent, such as calcium salicylate and magnesium sulfonate detergent, such as calcium and magnesium salicylate detergent, such as magnesium sulfonate detergent, such as calcium salicylate detergent);

iii) base oil (such as one or more of Group I, II, III, IV and or IV base oils, such as Group I, II and or III base oils, such as Group III oils);

iv) optionally one or more dispersants, friction modifiers; antioxidants, other than the antioxidants of a), pour point depressants, anti-foaming agents, viscosity modifiers, corrosion inhibitors, antirust agents, and/or anti-wear agents;

wherein the antioxidant composition is combined with the detergent at a temperature of 70 °C or more, such as 75°C or more, such as 80°C or more, such as 85°C or more.

[0149] This invention further relates to a stable concentrate composition comprising:

i) an antioxidant composition (that may optionally be homogeneous or heterogeneous (such as a solution, a dispersion, a slurry, a colloid and the like), comprising:

a) diphenylamine antioxidant comprising:

- 1) di(C₈-alkyl substituted phenyl) amine (such as 80 mass% or more, such as 90 mass% or more, such as 95 mass% or more, such as 96 mass% or more, such as 97 mass% or more, such as 98.5 mass% or more, such as 99 mass% or more),
- 2) less than 10 mass% (such as less than 5 mass%, such as less than 1 mass%, such as less than 0.3 mass%, such as less than 0.1 mass%) of mono-C₈-alkyl substituted diphenylamine, and
- 3) less than 10 mass% (such as less than 5 mass%, such as less than 1 mass%, such as less than 0.3 mass%, such as less than 0.1 mass%) of mono-C₈-alkyl substituted diphenylamine,

based upon the weight of the mono-C₈-alkyl substituted phenylamines, di- C₈-alkyl substituted phenylamines and tri-C₈-alkyl substituted phenylamines present in the lubricating oil composition); and

- b) optionally, polar diluent having an aniline point of 25°C or less, such as 20°C or less, and at least 2 available hydrogen-bond acceptor groups (such as ester, ether or alcohol group) that are 2, 3, 4, 5, or 6 atoms apart (such as 1, 2 3, or 4 atoms apart, such as 2, 3 or 4 atoms apart), wherein, if polar diluent is present, then the combination of the polar diluent of b) combined with the diphenylamine antioxidant of a) is clear after 96 hours at 20 °C in a clear glass container without agitation (such as a combination of 75 mass% of the polar diluent of b) combined with 25 mass% of the diphenylamine antioxidant of a) is clear after 96 hours at 20 °C);

ii) detergent (such as salicylate and or sulfonate detergent, such as calcium and or magnesium salicylate and or sulfonate detergent, such as calcium salicylate and magnesium sulfonate detergent, such as calcium and magnesium salicylate detergent, such as magnesium sulfonate detergent, such as calcium salicylate detergent);

iii) base oil (such as one or more of Group I, II, III, IV and or IV base oils, such as Group I, II and or III base oils, such as Group III oils);

iv) optionally one or more dispersants, friction modifiers; antioxidants, other than the antioxidants of a), pour point depressants, anti-foaming agents, viscosity modifiers, corrosion inhibitors, antirust agents, and/or anti-wear agents;

wherein:

- 1) the antioxidant composition is heated to a molten state (such as to 100 °C or more) and is optionally combined with one or more detergents at a temperature of 70 °C or more, such as 75°C or more, such as 80°C or more (optionally the antioxidant composition and one or more salicylate detergents are combined at a temperature of 70 °C or more, such as 75°C or more, such as 80°C or more);
- 2) the temperature of the combination of antioxidant composition and optional detergent is optionally reduced to a temperature of from 45 °C to less than 70 °C; and
- 3) the combination of antioxidant composition and optional detergent is optionally combined with one or more detergents, dispersants, friction modifiers; antioxidants, other than the antioxidants of a), pour point depressants, anti-foaming agents, viscosity modifiers, corrosion inhibitors, antirust agents, and/or anti-wear agents.

[0150] In embodiments, polar diluent (such as TMP ester) may be added to the concentrate composition in the same blending stage as the molten C₈ diphenylamine antioxidant (as opposed to pre-blending a polar diluent and C₈ diphenylamine antioxidant before adding to the concentrate blend), optionally before polar amines (such as dispersants, PIBSA, etc.) are added to the concentrate.

[0151] Likewise, other polar materials (such as OSA-TEPA), which did not necessarily perform well in the stability test for a simple blend with C₈ diphenylamine antioxidant, perform well when added to the concentrate with molten C₈ diphenylamine in the same stage (such as before the dispersants are added to a concentrate blend) enhancing the stability of the concentrate and the lubricating oil compositions made with the concentrate.

[0152] Further, one or more triazole corrosion inhibitors may be added at the same concentrate blending stage as the molten C₈ diphenylamine antioxidant (as opposed to pre-blending a polar diluent and C₈ diphenylamine antioxidant before adding to the concentrate blend), optionally before polar amines (such as dispersants, PIBSA, etc.) are added to the blending stage enhancing the stability of the concentrate and the lubricating oil composition made with the concentrate.

[0153] Alternately, dialkyl fumarate/vinyl acetate copolymers (such as one or more C₈ to C₂₀ dialkyl fumarate/vinyl acetate copolymers, such as one or more C₈ to C₁₈ dialkyl fumarate/vinyl acetate copolymers, such as one or more C₁₂ to C₁₈ dialkyl fumarate/vinyl acetate copolymers) optionally having a pour point (ASTM D97) of – 10°C or less (such as -15°C or less, such as -20°C or less, such as -25 °C or less, such as -30 °C or less) may be added at the same concentrate blending stage as the molten C₈ diphenylamine antioxidant (as opposed to pre-blending a polar diluent and C₈ diphenylamine antioxidant before adding to the concentrate blend), optionally before polar amines (such as dispersants, PIBSA, etc.) are added to the concentrate to enhance the stability of the concentrate and the lubricating oil compositions made with the concentrate.

[0154] This invention further relates to a stable concentrate composition comprising:

- i) an antioxidant composition (that may optionally be homogeneous or heterogeneous (such as a solution, a dispersion, a slurry, a colloid and the like), comprising:
 - a) diphenylamine antioxidant comprising:
 - 1) di(C₈-alkyl substituted phenyl) amine (such as 80 mass% or more, such as 90 mass% or more, such as 95 mass% or more, such as 96 mass% or more, such as 97 mass% or more, such as 98.5 mass% or more, such as 99 mass% or more),
 - 2) less than 10 mass% (such as less than 5 mass%, such as less than 1 mass%, such as less than 0.3 mass%, such as less than 0.1 mass%) of mono-C₈-alkyl substituted diphenylamine, and
 - 3) less than 10 mass% (such as less than 5 mass%, such as less than 1 mass%, such as less than 0.3 mass%, such as less than 0.1 mass%) of mono-C₈-alkyl substituted diphenylamine,based upon the weight of the mono-C₈-alkyl substituted phenylamines, di- C₈-alkyl substituted phenylamines and tri- C₈-alkyl substituted phenylamines present in the lubricating oil composition); and

- ii) optionally, detergent (such as salicylate and or sulfonate detergent, such as calcium and or magnesium salicylate and or sulfonate detergent, such as calcium salicylate and magnesium sulfonate detergent, such as calcium and magnesium salicylate detergent, such as magnesium sulfonate detergent, such as calcium salicylate detergent);
- iii) base oil (such as one or more of Group I, II, III, IV and or IV base oils, such as Group I, II and or III base oils, such as Group III oils);
- iv) optionally one or more dispersants, friction modifiers; antioxidants, other than the antioxidants of a), pour point depressants, anti-foaming agents, viscosity modifiers, corrosion inhibitors, antirust agents, and/or anti-wear agents;

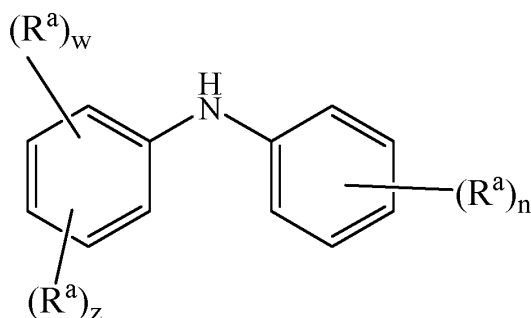
wherein:

- 1) the antioxidant composition is provided to the concentrate as a solid at a temperature of 100 °C or more;
- 2) the temperature of the combination of antioxidant composition and optional detergent is optionally reduced to a temperature of from 45 °C to less than 70 °C; and
- 3) the antioxidant composition and optional detergent are optionally combined with one or more detergents, dispersants, friction modifiers; antioxidants, other than the antioxidants of a), pour point depressants, anti-foaming agents, viscosity modifiers, corrosion inhibitors, antirust agents, and/or anti-wear agents.

[0155] This further 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 diphenylamine antioxidant comprising:
 - 1) one or more **di-C₈-alkyl substituted diphenylamine** represented by 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-C₈-alkyl substituted diphenylamine** represented by Formula (III), where n is 1, z is 0 and w is 0), and

3) 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 **tri-C₈-alkyl substituted diphenylamine** represented by Formula (III), where n is 1, z is 1 and w is 1), based upon the weight of the mono-, di-, and tri- C₈-alkyl substituted diphenylamines:



Formula (III) is:

where: the branched C₈H₁₈ 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 C₈ alkyl or branched C₈ alkyl group, where 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, anti-wear 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.

[0156] In embodiments, the concentrate composition may optionally be absent solvent (such as aliphatic or aromatic solvent) and/or absent functionalized base oil.

[0157] 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 40 mass% (in particular, 0.10 to 35 mass%, alternately 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-C₈-alkyl substituted diphenylamine** represented by Formula (III), where n is 1, w is 0, and z is 1, and optionally hindered phenol antioxidants, where: 1) **mono-C₈-alkyl substituted diphenylamine** 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 and 2) **tri-C₈-alkyl substituted diphenylamine** represented by Formula (III), where n is 1, z is 1 and w is 1) are absent or present at less 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%) 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, such as salicylate and or sulfonate detergent, such as calcium and or magnesium salicylate and or sulfonate detergent, such as calcium salicylate and magnesium sulfonate detergent, such as calcium and magnesium salicylate detergent, such as magnesium sulfonate detergent, such as calcium salicylate detergent);
- 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 0.75 mass%), based on total weight of the concentrate composition, of one or more **friction modifier(s)** (such as organic friction modifiers, such as glycerol monooleate);
- 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 60 mass% (in particular, 0.01 to 40 mass%, alternately 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 0.75 mass%), based on total weight of the concentrate composition, of one or more **anti-wear agents** (such as blends of anti-wear agents, such as ZDDP).
- [0158] 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.
- [0159] Optionally, the concentrate may be absent functionalized oil.
- [0160] In embodiments, the concentrate composition may optionally be absent solvent (such as aliphatic or aromatic solvent) and/or absent functionalized base oil.
- [0161] Optionally, the concentrate may be absent phenolic antioxidant.
- [0162] 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.
- [0163] 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.

[0164] 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.

[0165] In embodiments, the concentrate may be substantially free of or absent block copolymer, such as block, star, random, and/or tapered block copolymer.

[0166] 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).

[0167] In embodiments, the concentrate may be substantially free of or absent styrenic copolymer, such as block, star, random, and/or tapered styrenic block copolymer).

[0168] 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.

[0169] In embodiments, the concentrate may be substantially free of or absent functionalized diluent, such as functionalized oil.

[0170] 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.

Lubricating Oil Compositions

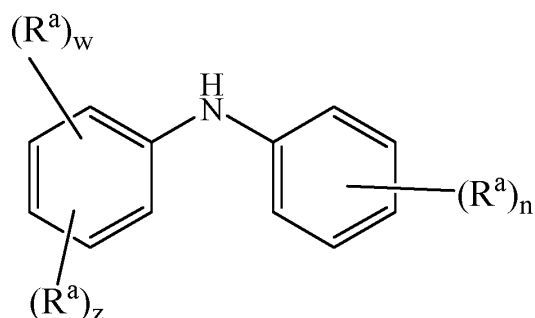
[0171] This invention further relates to stable lubricating oil compositions (also referred to as "LOC", "lubricant compositions", "lubricating compositions", or "lubricant oil compositions") comprising or resulting from the admixing of:

- (i) at least 50 mass% of one or more base oils, based upon the weight of the lubricating oil composition; and
- (ii) a stable antioxidant composition and or a stable concentrate and or stable booster as described herein.

[0172] This disclosure relates to stable 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%) 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 diphenylamine antioxidants represented by Formula (III), where w is 0, n is 1 and z is 1, and from 0 to 0.3 mass% of diphenylamine antioxidants represented by Formula (III) where n is 1 and z is 0 (such as 0 to 0.1 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:



where each R^a and R^b is independently linear C_8 alkyl or branched C_8 alkyl group and w is 0, n is 1 and z is 0 or 1, and where the branched C_8 alkyl may be singly, doubly or triply branched at one, two, three, four or more carbons, and may be symmetrically branched or asymmetrically branched;

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 C_8 diphenylamine antioxidant has been replaced with the same amount of C_9 diphenylamine antioxidant having:

- 1) about 68 mass% di- C_9 -alkyl diphenylamine,
- 2) about 29 mass% of mono- C_9 -alkyl diphenylamine, and
- 3) about 3 mass% of tri- C_9 -alkyl diphenylamine, based on the weight of 1), 2) and 3), as

determined by UPLC in 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 25% less) than the percent viscosity increase of **Comparative Formulation A**.

[0173] Note that **Comparative Formulation A** is C_9 -alkyl diphenylamine not a C_8 -alkyl diphenylamine. C_9 -alkyl diphenylamine was selected as the comparison as C_9 -alkyl diphenylamine performance is generally considered superior to typical C_8 -alkyl diphenylamine performance. Hence C_9 -alkyl diphenylamine is a more relevant comparison.

[0174] 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-C₈-alkyl substituted diphenylamines represented by Formula (III) where w is 0, n is 1 and z is 0), based upon the weight of the lubricating oil composition.

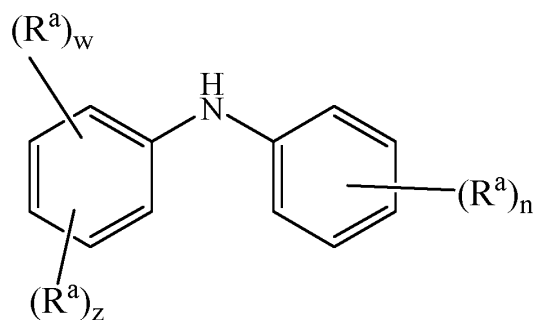
[0175] In embodiments, the lubricating oil composition may comprise 0.1 mass% or more (or 0.2 mass% or more, or 0.3 mass% or more, or 0.4 mass% or more, or 0.5 mass% or more, or 0.6 mass% or more, or 0.7 mass% or more, or 0.8 mass% or more, or 0.9 mass% or more, or 1.0 mass% or more, or 1.5 mass% or more, or 2.0 mass% or more, or 3.0 mass% or more, 4.0 mass% or more) of di-C₈-alkyl substituted diphenylamines represented by Formula (III), preferably di-C₈-alkyl substituted diphenylamines represented by Formula (III), where w is 0, n is 1 and z is 1, based upon the weight of the phenylamine antioxidant composition.

[0176] 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 **diphenylamine antioxidant** comprising (or consisting essentially of, or consisting of):

- i) one or more di-C₈-alkyl substituted diphenylamine 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- C₈-alkyl substituted diphenylamines 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- C₈-alkyl substituted diphenylamines 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:



where each R^a is independently a linear C_8 alkyl or branched C_8 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 **anti-wear agents** (such as blends of anti-wear 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 C₁₂-C₆₀ hydrocarbons** (such as C₁₂-C₂₄ linear alpha-olefins (LAOs), oligomers/polymers of polyisobutylenes, and/or blends thereof).

[0177] 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.

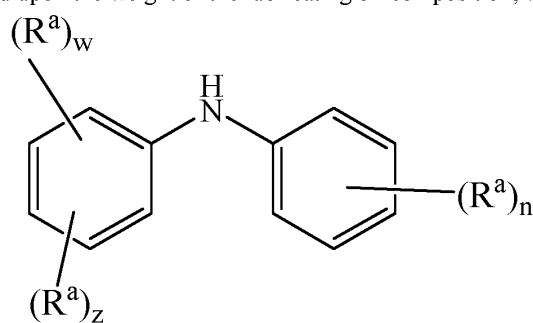
[0178] In embodiments, all of elements D, F, G, H, I, J, K, M, and O are present in addition to the base oil, detergent, and the one or more functionalized polymers described herein.

[0179] In embodiments, elements D, F, G, H, I, and J are present in addition to the base oil, detergent, and the one or more functionalized polymers described herein.

[0180] In embodiments, elements I, F, and G are present in addition to the base oil, detergent, and the one or more functionalized polymers described herein.

[0181] In embodiments, element K is present in addition to the base oil, detergent, and the one or more functionalized polymers described herein.

[0182] This invention further relates to a lubricating oil composition comprising antioxidants, where mono- C₈-alkyl substituted diphenylamines 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:



where each R^a is independently a linear C₈ alkyl or branched C₈ alkyl group, n is 1, z is 0 or 1, and w is 0 or 1.

[0183] 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-C₈-alkyl substituted diphenylamine as represented by Formula (III) where n is 1, z is 1 and w is 0, above, and
- 2) optionally, one or more additional antioxidants (such as diphenylamines 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 (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.

[0184] This invention further relates to a lubricating oil composition wherein di-C₈-alkyl substituted diphenylamine 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-C₈-alkyl substituted diphenylamine 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.

[0185] In embodiments, the lubricating oil composition may further comprising zinc dialkyldithiophosphate.

[0186] In embodiments, the lubricating oil composition may further comprises hindered phenolic antioxidant.

[0187] 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.

[0188] In embodiments, the lubricating oil composition may further comprises additional antioxidant comprising oil-soluble or oil-dispersible sulfur-containing antioxidant(s), sulfurized aliphatic (C₇ to C₂₉) hydrocarbyl fatty acid ester(s), sulfur-containing organo-molybdenum compound(s), and combinations thereof.

[0189] In embodiments, the lubricating oil composition may further comprise ethoxylated alcohol.

[0190] In embodiments, the detergent in the lubricating oil composition comprises one or more carboxylate detergent, such as one or more salicylate detergent, such as one or more alkaline earth metal salicylate detergent, such as calcium and or magnesium salicylate detergent, optionally said detergent having a TBN of up to 700 mgKOH/g, such as 50 to 500 mgKOH/g, such as 100 to 450 mgKOH/g. In embodiments detergents having a TBN of 100 or more (such as 200 mgKOH/g or more) can be used in combination with detergents having a TBN less than 100 mgKOH/g.

[0191] In embodiments, the detergent in the lubricating oil composition comprises one or more carboxylate detergent, such as one or more salicylate detergents, such as one or more alkaline earth metal salicylate detergent, such as calcium and or magnesium salicylate detergent, said detergent providing from 1 to 500 mmol/kg soap, such as 5 to 400 mmol/kg soap to the lubricating oil composition.

[0192] In embodiments, the detergent in the lubricating oil composition comprises one or more carboxylate detergent, such as one or more salicylate detergent, such as one or more alkaline earth metal salicylate detergent, such as calcium and or magnesium salicylate detergent, said detergent having: 1) having a TBN of 50 to 700 mgKOH/g, such as 60 to 400 mgKOH/g (such as a combination of detergents such as a detergent having a TBN over 100 mgKOH/g and a second detergent having a TBN less than 100 mgKOH/g); and 2) providing from 1 to 500 mmol/kg soap, such as 5 to 400 mmol/kg soap to the lubricating oil composition.

[0193] 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 diphenylamine antioxidant has been replaced with the same amount of diphenylamine antioxidant having:

- 1) about 68 mass% di-C₉-alkyl diphenylamine,
- 2) about 29 mass% of mono-C₉-alkyl diphenylamine, and
- 3) about 3 mass% of tri-C₉-alkyl diphenylamine, based on the weight of 1), 2) and 3), as

determined by UPLC in Experimental section].

[0194] 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 15% less, such as at least 20% less, such as at least 30% less) than the percent viscosity increase of **Comparative Formulation A**.

[0195] 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 organic friction modifiers (such as glycerol mono-oleate), 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, while maintaining good viscosity control.

[0196] 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 at least 0.5 WPD merits higher (such as at least 0.8 WPD merits higher, such as at least 0.85 WPD merits higher, such as at least 0.90 WPD merits higher, such as at least 0.95 WPD merits higher, such as at least 1.0 WPD merits higher, such as at least 1.10 WPD merits higher, such as at least 1.20 WPD merits 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 10% less (such as at least 20% less, such as at least 30% less, such as at least 40% 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 73% less), as compared to **Comparative Formulation A**.

[0197] This invention further relates to a lubricating oil composition where the lubricating oil composition exhibits a Sequence IIIH (ASTM D8111) weighted piston deposits merits of 4.6 or more (such as 4.7 or more WPD merits, such as 4.8 or more WPD merits, such as 4.9 or more WPD merits, such as 5.0 or more WPD merits, such as 5.1 or more WPD merits, such as 5.2 or more WPD merits, such as 5.3 or more WPD merits, such as 5.4 or more WPD merits, such as 5.5 or more WPD merits).

[0198] 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.

[0199] 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.

[0200] 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.

[0201] 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.

[0202] 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.

[0203] 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).

[0204] 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).

[0205] 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).

[0206] 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. Preferably, the lubricating composition of the present disclosure may be a multigrade oil identified by the viscometric descriptor 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. 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 April 2021 by SAE International, formerly known as Society of Automotive Engineers).

[0207] Optionally, the lubricating oil composition containing diphenylamine antioxidants described herein may be absent phenolic antioxidant.

[0208] 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.

[0209] 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.

[0210] 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.

[0211] 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.

[0212] 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.

[0213] 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 C₄₋₅ 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)

[0214] 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.

[0215] 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.

[0216] 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.)

[0217] In embodiments, the lubricating compositions of the present disclosure may be a passenger car motor oil.

[0218] In embodiments, the lubricating compositions of the present disclosure may be a passenger car diesel oil.

[0219] 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 a dispersant viscosity modifier such as an amide, imide, and/or ester functionalized partially or fully saturated polymer comprising C₄₋₅ olefins as described in United States serial number USSN 18/480,571, filed October 4, 2023; 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%.

[0220] The lubricating compositions disclosed herein may have a kinematic viscosity as measured by ASTM D-445 at 100° C of 3 cSt (mm²/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.

[0221] 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.

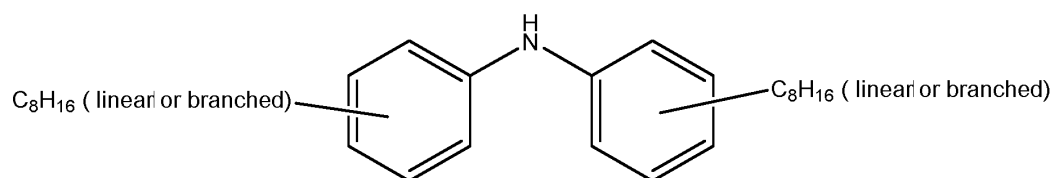
[0222] The lubricating composition disclosed herein may have a SAE viscosity grade of 0W-Y, wherein Y may be 12, 16, or 20. In an embodiment, the lubricating composition has an SAE viscosity grade of 0W-12.

Concentrates

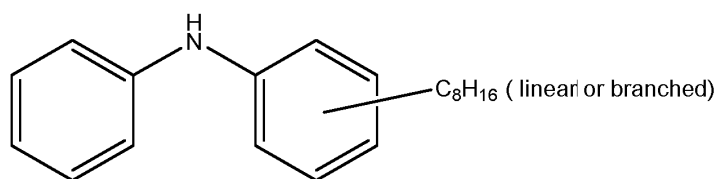
[0223] A concentrate, also referred to as a concentrated additive package, additive package, adpak, or addpack, is a composition having less than 50 mass% (such as less than 40 mass%, such as less than 30 mass%, such as less than 25 mass%, such as less than 20 mass%) base oil, 50 mass% or more, such as 80 mass% or more lubricant composition additives (such as described herein) which is typically then further blended with additional base oil to form a lubricating oil product.

[0224] This disclosure relates to concentrate compositions comprising or resulting from the admixing of:

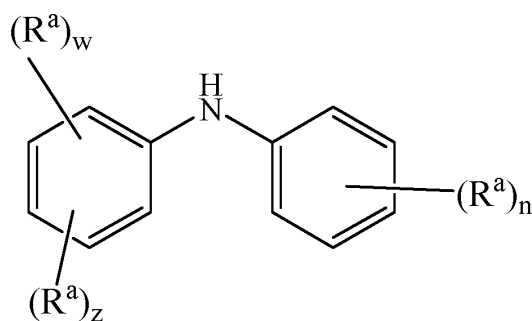
- (i) from 1 to less than 50 mass% (alternately 5 to 45 mass%, alternately 7 to 40 mass%, alternately 10 to 35 mass%, alternately 10 to 25 mass%), based upon the weight of the composition, of one or more **base oil(s)**;
- (ii) optionally, from 0.10 to 20 mass% (in particular 0.15 to 10 mass%, alternately 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 composition, of diphenyl amine antioxidant comprising: 1) one or more **di-C₈-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-C₈-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):

where: the branched C_8H_{16} 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_8 alkyl or branched C_8 alkyl group, n is 1, z is 0 or 1, and w is 0 or 1; and

(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.

[0225] In embodiments, the concentrate composition may optionally be absent solvent (such as aliphatic or aromatic solvent) and/or absent functionalized base oil.

[0226] 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_8 -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_8 -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) optionally, 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 0.75 mass%), based on total weight of the concentrate composition, of one or more **friction modifier(s)** (such as organic friction modifiers, such as glycerol monooleate);
- 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 0.75 mass%), based on total weight of the lubricating composition, of one or more **antiwear agents** (such as blends of antiwear agents, such as ZDDP, such as ZDDP derived from primary alcohol(s)).

[0227] Concentrates may be present in the lubricating oil composition at from 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.

[0228] Optionally, the concentrate may be absent functionalized oil.

[0229] In embodiments, the concentrate composition may optionally be absent solvent (such as aliphatic or aromatic solvent) and/or absent functionalized base oil.

[0230] Optionally, the concentrate may be absent phenolic antioxidant.

[0231] 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.

[0232] 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 3,000 g/mol. In embodiments, the concentrate 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.

[0233] 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.

[0234] In embodiments, the concentrate may be substantially free of or absent block copolymer, such as block, star, random, and/or tapered block copolymer.

[0235] 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).

[0236] In embodiments, the concentrate may be substantially free of or absent styrenic copolymer, such as block, star, random, and/or tapered styrenic block copolymer).

[0237] 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.

[0238] In embodiments, the concentrate may substantially free of or absent functionalized diluent, such as functionalized oil.

[0239] 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.

[0240] 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.

[0241] 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.

[0242] The invention also includes concentrates comprising: 1) enhanced aminic antioxidant (such as antioxidant comprising 90 mass% or more of bis(octylphenyl)amine and 10 mass% or less of (octylphenyl)(phenyl)amine based on the weight of the bis(octylphenyl)amine and (octylphenyl)(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).

[0243] 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, 4, or more) components (such as detergents, dispersants,

ZDDP's, molybdenum components, such as MoDTC dimers and or trimers, etc. antioxidants, such as the 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 then uses the concentrate to form a lubricating composition. Booster packages can also be provided separately for a customer to addition to a concentrate or lubricating oil composition later. The invention also includes booster packages comprising: 1) enhanced aminic antioxidant (such as antioxidant comprising 90 mass% or more of bis(octylphenyl)amine and 10 mass% or less of (octylphenyl)(phenyl)amine based on the weight of the bis(octylphenyl)amine and (octylphenyl)(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 dialkyldithiophosphates 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.

[0244] This disclosure also relates to stable booster package 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 booster composition, of one or more **base oil(s)**;
- B) from 0.10 to 40 mass% (in particular, 0.10 to 35 mass%, alternately 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-C₈-alkyl substituted diphenylamine** represented by Formula (III), where n is 1, w is 0, and z is 1, and optionally hindered phenol antioxidants, where: 1) **mono-C₈-alkyl substituted diphenylamine** 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 and 2) **tri-C₈-alkyl substituted diphenylamine** represented by Formula (III), where n is 1, z is 1 and w is 1) are absent or present at less 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%) based upon the weight of the booster);
- C) optionally, from 0.1 to 20 mass% (in particular 0.5 to 10 mass%, alternately 2 to 6 mass%), based on total weight of the booster composition, of one or more **detergent(s)** (such as blends of detergents, such as salicylate and or sulfonate detergent, such as calcium and or magnesium salicylate and or sulfonate

detergent, such as calcium salicylate and magnesium sulfonate detergent, such as calcium and magnesium salicylate detergent, such as magnesium sulfonate detergent, such as calcium salicylate detergent);

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 0.75 mass%), based on total weight of the booster composition, of one or more **friction modifier(s)** (such as organic friction modifiers, such as glycerol monooleate);

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 booster 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 booster 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 booster composition, of one or more **anti-foam agents** (such as blends of anti-foam agents);

I) optionally, from 0.01 to 60 mass% (in particular, 0.01 to 40 mass%, alternately 0.1 to 30 mass%, alternately 1 to 20 mass%), based on total weight of the booster 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 0.75 mass%), based on total weight of the booster, of one or more **anti-wear agents** (such as blends of anti-wear agents, such as ZDDP).

A. Base Oil

[0245] 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.

[0246] 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.

[0247] 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.

[0248] 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.

[0249] 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, 22nd 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 C₈ to C₂₀ alkenes, homo- or co-polymers of C₈, and/or C₁₀, and/or C₁₂ alkenes, C₈/C₁₀ copolymers, C₈/C₁₀/C₁₂ copolymers, and C₁₀/C₁₂ copolymers, and the derivatives, analogues and homologues thereof.

[0250] 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.

[0251] In another embodiment polyalphaolefin oligomers useful in the present disclosure may comprise C₂₀ to C₁₅₀₀ paraffins, preferably C₄₀ to C₁₀₀₀ paraffins, preferably C₅₀ to C₇₅₀ paraffins, preferably C₅₀ to C₅₀₀ paraffins. The PAO oligomers are dimers, trimers, tetramers, pentamers, *etc.*, of C₅ to C₁₄ alpha-olefins in one embodiment, and C₆ to C₁₂ alpha-olefins in another embodiment, and C₈ to C₁₂ 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).

[0252] 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.

[0253] 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.

[0254] Another useful 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, sebacic 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.

[0255] Esters useful as synthetic base oils herein also include those made from C₅ to C₁₂ monocarboxylic acids and polyols, and polyol ethers such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol, and tripentaerythritol.

[0256] Desirable ester base oils are commercially available as Esterex™ Esters (ExxonMobil Chemical Company, Houston, Texas).

[0257] Ester base oils can be used in smaller quantities as polar diluent herein. Preferably ester base oil is present at less than 50 mass %, based upon the weight of the lubricating oil composition, such as less than 40 mass%, such as less 30 mass%, such as less than 20 mass%, such as less than 10 mass%, such as less than 5 mass% or less, such as 3 mass% or less, such as 1 mass% or less such as 0.1 mass% or less, such as at 0 mass%. Preferably ester base oil is present at less than 50 mass %, based upon the weight of the antioxidant composition (*e.g.*, a composition of antioxidant and polar diluent), such as less than 40 mass%, such as less 30 mass%, such as less than 20 mass%, such as less than 10 mass%, such as less than 5 mass% or less, such as 3 mass% or less, such as 1 mass% or less such as 0.1 mass% or less, such as at 0 mass%.

[0258] 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.

[0259] 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.

[0260] 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.

[0261] 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).

[0262] 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 unrefined and or 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).

[0263] 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 may have viscosity index properties falling in API Groups II and or III, and thus for purposes of this invention and claims thereto renewable oils include Group II or Group III base oils (API EOLCS 1509 definition (American Petroleum Institute Publication 1509, see section E.1.3, 22nd edition, October 2023, www.API.org)).

[0264] 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, 22nd edition,

October 2023, 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 include polyalphaolefins (PAO), polybutylene, and other synthesized base stocks. 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).

[0265] 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.

[0266] The base oil useful herein may be selected from any of the synthetic, natural, refined, 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.

[0267] In embodiments, the base oil useful herein is not a Group V base oil. In embodiments, the base oil useful herein is not ester base oil, such as those described in Chemistry and Technology of Lubricants, 3rd edition, Mortier, Fox, Orszulik, ed. Springer New York, 2010, pages 54 to 61.

[0268] 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 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.

[0269] 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 90 mass% as determined by ASTM D2007.

[0270] 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.

[0271] 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.

[0272] 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).

[0273] 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.

[0274] 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.

[0275] 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.

[0276] 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 60 to 95 mass%, alternately 70 to 95 mass%, based upon the weight of the lubricating composition.

[0277] The base oils and blends thereof described above are also useful for making concentrates as well as for making lubricants therefrom.

[0278] 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.

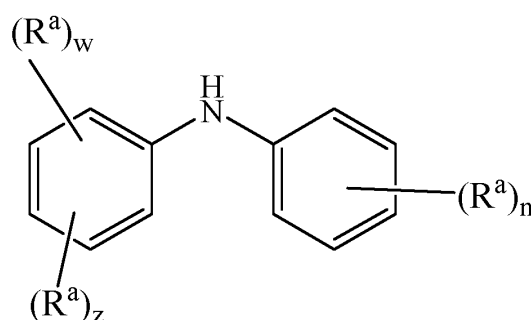
[0279] Typically, one or more base oils are present in the concentrate composition in an amount of 50 mass% or less, alternately 40 mass% or less, alternately 30 mass% or less, alternately 20 mass% or less, based on the total weight of the concentrate composition. Typically, one or more base oils are present in the concentrate composition at an amount of 0.1 to 49 mass%, alternately 5 to 40 mass%, alternately 10 to 30 mass%, alternately 15 to 25 mass%, based upon the weight of the concentrate composition.

B. Antioxidants

[0280] 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 **diphenylamine antioxidant** and optionally one or more additional antioxidants and/or optionally one or more carboxylate detergents, where **mono-C₈-alkyl substituted diphenylamines** are absent or present at less than 15 mass% (such as less than 10 mass%), based upon the weight of the **diphenylamine antioxidant**, to provide enhanced oxidative performance. The enhanced performance is a result of a previously unknown synergy 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.

[0281] 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 **diphenylamine anti-oxidants** 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-C₈-alkyl substituted diphenylamine** 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-C₈-alkyl substituted diphenylamine** are present, based upon the weight of the mono- and di- C₈-alkyl substituted diphenylamines.

[0282] 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 C₈ alkyl or branched C₈ 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 C₈ alkyl groups (C₈ alkyl groups) useful herein include, isooctyl, methylheptyl, dimethylhexyl, ethylhexyl, trimethylpentyl, methylethylpentyl, dimethylethylbutyl, diethylbutyl, methylpropylbutyl, and the like.

[0283] In embodiments, R^a comprises branched alkyl groups, such as 2,4,4-trimethylpentan-2-yl.

[0284] In embodiments the primary antioxidants employed in the lubricating oil of the present invention comprise less than a) 10 mass% N-phenyl-4-(2,4,4-trimethylpentan-2-yl)aniline, b) more than 80 mass% of bis(4-(2,4,4-trimethylpentan-2-yl)phenyl)amine, and c) less than 10 mass% of tri 2,4-bis(2,4,4-trimethylpentan-2-yl)-N-(4-(2,4,4-trimethylpentan-2-yl)phenyl)aniline, based upon the weight of a), b) and c).

[0285] In embodiments, the diphenylamine 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-C₈-alkyl substituted diphenylamines represented by Formula (III), where w is 0, n is 1 and z is 0), based upon the weight of the diphenylamine antioxidant composition.

[0286] In embodiments, the diphenylamine 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-C₈-alkyl substituted diphenylamines represented by Formula (III), where n is 1, w is 0, and z is 1, based upon the weight of the diphenylamine antioxidant composition.

[0287] 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-C₈-alkyl substituted diphenylamine 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 diphenylamines 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

diphenylamine antioxidant composition.

[0288] In embodiments, the di-C₈-alkyl substituted diphenylamine (such as represented by Formula (III) where n is 1 and z is 1 and w is 0), has:

- i) more than 90% (such as 95% or more, such as 99% or more, such as 100%) of the alkyl groups in the para position (i.e., para to the bond to the phenylamine);
- (ii) optionally less than 10%, such as 5% 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-C₈-alkyl substituted diphenylamine.

[0289] This invention further relates to diphenylamine antioxidant comprising:

- 1) di(C₈-alkyl substituted phenyl) amine, and
- 2) from 0 to less than 10 mass% mono-C₈-alkyl substituted diphenylamine, based upon the weight of the mono- and di-phenylamines present.

[0290] This invention further relates to diphenylamine antioxidant comprising:

- 1) 90 mass% or more of di(C₈-alkyl substituted phenyl) amines,
- 2) from 0, such as 1, 2, 3, or 5 to less than 10 mass% of mono-C₈-alkyl substituted diphenylamine, and
- 3) from 0 to less than 10 mass% of tri-C₈-alkyl substituted diphenylamine, based upon the weight of 1), 2) and 3).

[0291] This invention further relates to diphenylamine antioxidant composition comprising:

- a) from 0 to less than 10 mass% mono-C₈-alkyl substituted diphenylamine represented by the Formula (III) where n is 1, w is 0, and z is 0,
- b) 90 mass% or more of di(C₈-alkyl substituted phenyl) 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-C₈-alkyl substituted diphenylamines represented by Formula (III), where $w + n + z = 3$,
- d) from 0 to 1 mass% of unsubstituted diphenylamine represented by Formula (III) where n is 0 and z is 0,

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

[0292] This invention further relates to diphenylamine antioxidant composition comprising:

- a) from 0 to less than 5 mass% mono-C₈-alkyl substituted diphenylamines represented by the Formula (III) where n is 1, w is 0, and z is 0,
- b) 90 mass% or more of di-C₈-alkyl substituted diphenylamines represented by Formula (III), where w is 0, n is 1 and z is 1
- c) 5 mass% or less of tri-C₈-alkyl substituted diphenylamines represented by Formula (III), where $w + n + z = 3$,
- d) 1 mass% or less of unsubstituted diphenylamines represented by Formula (III) where n is 0, w is 0, and z is 0,

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

[0293] This invention further relates to diphenylamine antioxidant composition comprising:

- a) from 0 to less than 3 mass% mono-C₈-alkyl substituted diphenylamines represented by the Formula (III) where w is 0, n is 1 and z is 0,

- b) 95 mass% or more of di-C₈-alkyl substituted diphenylamines represented by Formula (III), where w is 0, n is 1 and z is 1,
- c) 5 mass% or less of tri-C₈-alkyl substituted diphenylamines represented by Formula (III), where w + n + z = 3,
- d) from 0 to 0.5 mass% or less of unsubstituted diphenylamines represented by Formula (III) where z is 0, w is 0, and n is 0,

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

[0294] This invention further relates to diphenylamine antioxidant composition comprising:

a) 0 to less than 1 mass% of mono-C₈-alkyl substituted diphenylamines (represented by Formula (III), where n is 1, z is 0, and w is 0); and

b) more than 99 mass% of di-C₈-alkyl substituted diphenylamines represented by Formula (III), where w is 0, n is 1 and z is 1, based upon the total weight of the diphenylamine antioxidants of a) and b) present in the lubricating oil composition.

[0295] In embodiments, the di-C₈-alkyl substituted diphenylamines represented by Formula (III) comprise di(p-octylphenyl)amine.

[0296] 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, recrystallization, chromatography, and the like. The isomer content may be determined by mass spectrometry as described in the Experimental Section.

[0297] The di-C₈-alkyl substituted diphenylamines described herein are typically synthesized by reaction of diisobutylene with diphenylamine in the presence of Lewis acid catalyst. Further, di-C₈-alkyl substituted diphenylamines may also be synthesized by a reaction of para-octyl 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).

[0298] 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%.

[0299] 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

[0300] 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%.

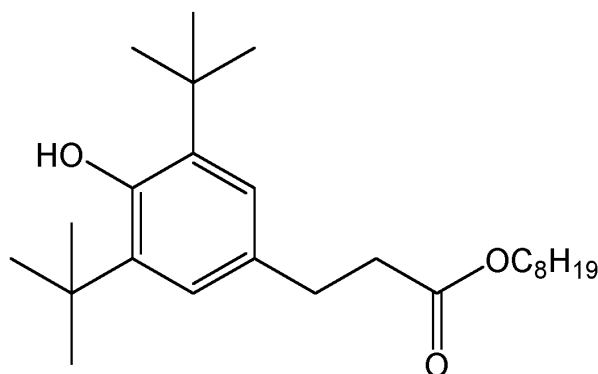
[0301] When present in a concentrate, the additional antioxidant may be present at about 0.01 mass% to about 30 mass% of the concentrate, such as from about 0.025 mass% to about 20 mass%, such as from about 0.05 mass% to about 15 mass%, 0.1 mass% to about 10 mass%, 0.5 mass% to about 8 mass%, or 1 mass% to about 5 mass%.

[0302] A number of additional antioxidants are compatible with the present invention. Examples of additional antioxidants include hindered phenols, molybdenum succinimides, and dithiocarbamates (such as Zn or Mo-dialkyldithiocarbamates). These oil-soluble components are generally known.

[0303] 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 C₆₊ 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 propionic ester derivatives, such as C₇-C₉-(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-butyl-phenol). 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).

[0304] 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 C₇-C₉-(branched)-alkyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propanoate).

[0305] A preferred hindered phenol may be represented by the formula:



[0306] 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.

[0307] Non-phenolic oxidation inhibitors, which may be used include aromatic amine antioxidants (other than those represented by Formula (III) 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.

[0308] 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.

[0309] 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 C₄ to C₂₅ olefin(s), sulfurized aliphatic (C₇ to C₂₉) 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).

[0310] 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.

[0311] 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(dialkylthiocarbamate), ethylenebis(dialkylthiocarbamate), and isobutyl disulfide-2, 2'-bis(dialkylthiocarbamate) where the alkyl groups of the dialkylthiocarbamate can preferably have from 1 to 6 carbon atoms. Examples of preferred ashless dithiocarbamates are methylenebis(dibutylthiocarbamate), ethylenebis(dibutylthiocarbamate) and isobutyl disulfide-2, 2'-bis(dibutylthiocarbamate).

[0312] 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.

[0313] 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.

[0314] 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 anti-wear 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.

[0315] 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, anti-wear 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

[0316] 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 150 mgKOH/g or more, 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.

[0317] 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.

[0318] 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. In embodiments, the sulfonate is added with other detergents, such as salicylates and or phenates. In other embodiments, the sulfonates are added separately from salicylates or phenates, for example embodiments, the sulfonates are added in a different blend stage. A blend stage is a step in the blending process separated from another step by time or temperature. For example, blending salicylate detergent and liquid C₈ diphenylamine antioxidant together at 65 °C for 15 minutes then adding dispersant and blending for a further 30 minutes would be two blend stages.

[0319] 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.

[0320] 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.

[0321] 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.

[0322] 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.

[0323] 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.

[0324] 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.

[0325] Alternately, the detergent additive(s) is a combination of magnesium salicylate and magnesium sulfonate.

[0326] The magnesium detergent typically provides the lubricating composition thereof with 200 ppm or more of magnesium atoms, suitably from 200-4000 ppm of magnesium atoms, suitably from 200-2000 ppm of magnesium atoms, suitably from 300 to 1500 of magnesium atoms or from 450-1200 ppm of magnesium atoms (ASTM D5185).

[0327] The detergent composition may comprise a combination of one or more magnesium sulfonate detergents and one or more calcium salicylate detergents.

[0328] In embodiments, the magnesium-based detergents provide high amounts of Mg to compositions described herein, such as providing at least 400 ppm (such as 400 ppm to 20,000 ppm, such as 450 to 10,000 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 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.

[0329] 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.

[0330] 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.

[0331] The detergent composition may comprise (or consist of) a combination of one or more magnesium sulfonate detergents and one or more calcium salicylate detergents.

[0332] 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).

[0333] 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.

[0334] 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.

[0335] 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.

[0336] 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.

[0337] 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).

[0338] 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 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 2100 ppm or more, such as 3000 ppm or more, such as 4000 ppm or more, such as 5000 ppm or more) of calcium atoms (ASTM D5185) to the composition (booster pack, concentrate, lubricating oil composition, etc.).

[0339] Suitably the total atomic amount of metal from detergent in the lubrication composition according to all aspects of the disclosure is no more than 5000 ppm, preferably no more than 4000 ppm and more preferably no more 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).

[0340] 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.

[0341] 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.

[0342] Carboxylate detergents, *e.g.*, salicylates, can be prepared by reacting an aromatic carboxylic acid (such as a C₅₋₁₀₀, C₉₋₃₀, C₁₀₋₃₀, C₁₀₋₂₆, C₁₄₋₂₄, C₁₀₋₂₀, 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.

[0343] 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.

[0344] 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.

[0345] 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.

[0346] 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).

[0347] 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.

[0348] 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.

[0349] 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.

[0350] 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.

[0351] 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.

[0352] 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.

[0353] 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.

[0354] 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.

[0355] 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

[0356] 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.

[0357] 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.

[0358] Other known friction modifiers comprise oil-soluble organo-molybdenum compounds. Such organo-molybdenum friction modifiers may also provide antioxidant and anti-wear 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.

[0359] 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_4 , MoO_2Br_2 , $\text{Mo}_2\text{O}_3\text{C}_{16}$, molybdenum trioxide or similar acidic molybdenum compounds.

[0360] Among the molybdenum compounds useful in the compositions of this disclosure are organo-molybdenum compounds of the formula $\text{Mo}(\text{R}''\text{OCS}_2)_4$ and $\text{Mo}(\text{R}''\text{SCS}_2)_4$, 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.

[0361] Another group of organo-molybdenum compounds useful in the lubricating compositions of this disclosure are trinuclear molybdenum compounds, especially those of the formula $\text{Mo}_3\text{S}_k\text{L}_n\text{Q}_z$ 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.

[0362] 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).

[0363] 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 C₆ to C₁₄ alkyl groups, and may be selected from C₁₀-C₁₄ and C₆-C₁₂ alkyl groups, such as hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, or isomers thereof).

[0364] 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).

[0365] 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%.

[0366] Illustrative friction modifiers useful in the lubricating compositions described herein include, for example, alkoxyated fatty acid esters, alkanolamides, polyol fatty acid esters, borated glycerol fatty acid esters, fatty alcohol ethers, and mixtures thereof.

[0367] Illustrative alkoxyated fatty acid esters include, for example, polyoxyethylene stearate, fatty acid polyglycol ester, and the like. These can include polyoxypropylene stearate, polyoxybutylene stearate, polyoxyethylene isostearate, polyoxypropylene isostearate, polyoxyethylene palmitate, and the like.

[0368] Illustrative alkanolamides include, for example, lauric acid diethylalkanolamide, palmitic acid diethylalkanolamide, and the like. These can include oleic acid diethylalkanolamide, stearic acid diethylalkanolamide, oleic acid diethylalkanolamide, polyethoxylated hydrocarbylamides, polypropoxylated hydrocarbylamides, and the like.

[0369] Illustrative polyol fatty acid esters include, for example, glycerol monooleate, saturated mono-, di-, and tri-glyceride esters, glycerol monostearate, and the like. These can include polyol esters, hydroxyl-containing polyol esters, and the like.

[0370] Illustrative borated glycerol fatty acid esters include, for example, borated glycerol monooleate, borated saturated mono-, di-, and tri-glyceride esters, borated glycerol monostearate, 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 monooleates, 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.

[0371] Illustrative fatty alcohol ethers include, for example, stearyl ether, myristyl ether, and the like. Alcohols, including those that have carbon numbers from C₃ to C₅₀, can be ethoxylated, propoxylated, or butoxylated to form the corresponding fatty alkyl ethers. The underlying alcohol portion can preferably be stearyl, myristyl, C₁₁-C₁₃ hydrocarbon, oleyl, isosteryl, and the like.

[0372] Useful concentrations of friction modifiers may range from 0.01 mass% to 5 mass%, or about 0.01 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

[0373] Conventional pour point depressants (also known as lube oil flow improvers or “LOFI’s”) 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. Particularly useful PPD’s include dialkyl fumarate/vinyl acetate copolymers (such as one or more C₈ to C₂₀ dialkyl fumarate/vinyl acetate copolymers, such as one or more C₁₂ to C₁₈ dialkyl fumarate/vinyl acetate copolymers). 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 10 mass%, such as 0.01 to 5 mass%, such as 0.5 to 3 mass%, such as about 0.05 to 1.5 mass%, based upon the weight of the lubricating composition.

G. Anti-Foam Agents

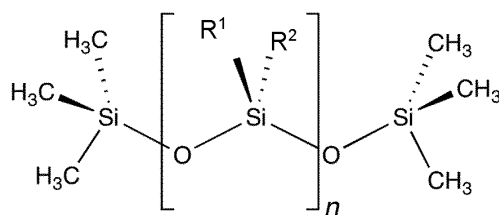
[0374] Anti-foam agents may advantageously be added to lubricant compositions described herein. These agents prevent or retard the formation of stable foams. Silicones, fluoro-silicones, and/organic polymers are typical anti-foam agents. For example, polysiloxanes, such as silicon oil or polydimethyl siloxane, provide anti-foam properties.

[0375] 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.

[0376] 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 C₁-C₁₀ 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.

[0377] 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-propyleneoxide 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

[0378] 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.

[0379] 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.

[0380] 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 PXTM3841 (*i.e.*, an alkyl acrylate polymer), commercially available from Dorf Ketyl, also referred to as MobiladTMC402.

[0381] 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

[0382] 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.

[0383] 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.

[0384] 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™".

[0385] Polymers useful as viscosity modifiers herein include polymethacrylate or polyacrylate polymers, such as linear polymethacrylate or polyacrylate polymers, such as those available from Evnolk 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).

[0386] 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).

[0387] 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.).

[0388] Dispersant viscosity modifiers useful herein include the amide, imide, and/or ester functionalized partially or fully saturated polymers comprising C₄₋₅ olefins as described in United States application USSN 18/480,571, filed October 4, 2023, which is herein incorporated by reference in its entirety. Preferred DVM's include polymers referred to as "functionalized polymers" described in USSN 18/480,571, and preferably are a functionalized hydrogenated polyisoprene family of polymers for use in lubricating oil compositions. In an advantageous form, the lubricating oil composition described herein further optionally includes one or more functionalized polymers described in 18/480,571 as dispersant viscosity modifiers 's 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 lubricating oil composition, where the functionalized polymers comprises an amide, imide, and/or ester functionalized partially or fully saturated polymer comprising C₄₋₅ 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, optionally 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 performed as set out in United States Patent Application USSN 18/480,571, filed October 4, 2023). For the functionalized polymer described in 18/480,571 useful herein, 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. The functionalized polymers described in 18/480,571 useful herein may include at least 50 %, or at least 60%, or at least 70% of 1,4-insertions of monomer, such as isoprene monomer. Furthermore, the functionalized polymers described in 18/480,571 useful herein 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. The functionalized polymers described in 18/480,571 useful herein may be absent of styrene repeat units, or absent of butadiene repeat units, or is not a homopolyisobutylene, or is not a copolymer of isoprene and butadiene.

[0389] Other useful DVM's include functionalized olefin copolymers (such as amine functionalized ethylene propylene copolymers).

[0390] 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.

[0391] 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

[0392] 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.

[0393] 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

[0394] 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 Patent Nos. 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.

[0395] 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 as from about 2100 to 2500 g/mol, and such as from about 2200 to about 2400 g/mol.

[0396] 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), pentaethylenhexamine (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.

[0397] 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.

[0398] 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.

[0399] 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.

[0400] 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 naphthylloxy ethanol (*i.e.*, 2-hydroxyethyl-1-naphthol ether (or hydroxy-terminated ethylene oxide oligomer ether of naphthol) are useful herein.

[0401] 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.

[0402] 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.

[0403] 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.

[0404] 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.

[0405] 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.

[0406] 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.

[0407] 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-borated dispersant may be 1:10 to 10:1 (weight:weight) or 1:5 to 3:1 or 1:3 to 2:1.

[0408] 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 polyisobutylene (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.

[0409] The dispersant may comprise one or more borated or unborated poly(alkenyl)succinimides, where the polyalkenyl is derived from polyisobutylene and the imide is derived from a polyamine ("PIBSA-PAM").

[0410] The dispersant may comprise one or more PIBSA-PAMs, where the PIB is derived from polyisobutylene having an Mn of from 600 to 5000 g/mol, such as from 700 to 4000 g/mol, such as from 800 to 3000 g/mol, 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), pentaethylenhexamine (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 and 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.

[0411] The dispersant may comprise one or more borated and one or more non-borated PIBSA-PAM's. 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).

[0412] 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.

[0413] 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).

[0414] 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.

[0415] The dispersant may comprise one or more borated and one or more non-borated PIBSA-PAM's.

[0416] 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.

[0417] 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

[0418] 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

[0419] 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.

[0420] 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.

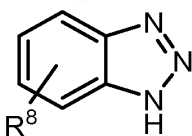
[0421] For further information on dispersants useful herein, please see US Patent No. 10,829,712, col 13, ln 36 to col 16, ln 67 and US Patent No. 7,485,603, col 2, ln 65 to col 6, ln 22, col 8, ln 25 to col 14, ln 53, and col 23, ln 40 to col 26, ln 46.

[0422] 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

[0423] 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.

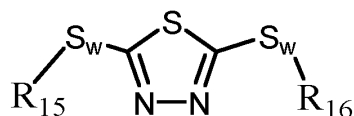
[0424] Suitable corrosion inhibitors may include nitrogen and/or sulfur-containing heterocyclic compounds such as triazoles (*e.g.*, benzotriazoles), substituted thiadiazoles, imidazoles, thiazoles, tetrazoles, hydroxyquinolines, oxazolines, imidazolines, thiophenes, indoles, indazoles, quinolines, benzoxazines, 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. Preferred corrosion inhibitors may comprise or be benzotriazole and/or tolyltriazole. Preferred corrosion inhibitor may comprise one or more of 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).

[0425] Additionally, or alternatively, the corrosion inhibitor may include one or more substituted thiadiazoles represented by the structure:



wherein R₁₅ and R₁₆ 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.

[0426] Further, additionally or alternatively, the corrosion inhibitor may include one or more other derivatives of DMTD, such as a carboxylic ester in which R₁₅ and R₁₆ 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 R₁₅ and R₁₆ are HOOC-CH(R₁₉)-(R₁₉ being a hydrocarbyl group). DMTD derivatives further produced by amidation or esterification of these terminal carboxylic acid groups may also be useful.

[0427] The preparation of 2-hydrocarbyldithio-5-mercapto-1,3,4-thiadiazoles is described, for example, in US Patent No. 3,663,561.

[0428] 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.

[0429] The preparation of 2-hydrocarbyldithio-5-mercapto-1,3,4-thiadiazoles is described, for example, in US Patent No. 3,663,561.

[0430] Still further, additionally or alternatively, the corrosion inhibitor may include a trifunctional borate having the structure, B(OR₄₆)₃, in which each R₄₆ may be the same or different. As the borate may typically be desirably compatible with the non-aqueous medium of the composition, each R₄₆ may, in particular, comprise or be a hydrocarbyl C₁-C₈ 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 C₄. 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.

[0431] When used, a corrosion inhibitor may comprise a substituted thiadiazole, a substituted benzotriazole, a substituted triazole, a trisubstituted borate, or a combination thereof.

[0432] 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.

[0433] In some embodiments, 3,4-oxy pyridinone-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.

[0434] 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. Anti-wear Agents

[0435] The lubricating oil composition of the present disclosure can contain one or more anti-wear agents that can reduce friction and excessive wear. Any anti-wear agent known by a person of ordinary skill in the art may be used in the lubricating oil composition. Non-limiting examples of suitable anti-wear agents include zinc dithiophosphate, metal (*e.g.*, Pb, Sb, Mo, and the like) salts of dithiophosphates, metal (*e.g.*, Zn, Pb, Sb, Mo, and the like), salts of dithiocarbamates, metal (*e.g.*, Zn, Pb, Sb, and the like) salts of fatty acids, boron compounds, phosphate esters, phosphite esters, amine salts of phosphoric acid esters or thiophosphoric acid esters, reaction products of dicyclopentadiene and thiophosphoric acids and combinations thereof. The amount of the anti-wear agent may vary from about 0.01 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.

[0436] In embodiments, the anti-wear agent is or comprises a dihydrocarbyl dithiophosphate metal salt, such as zinc dialkyl dithiophosphate compounds. The metal of the dihydrocarbyl dithiophosphate metal salt may be an alkali or alkaline earth metal, or aluminum, lead, tin, molybdenum, manganese, nickel, or copper. In some embodiments, the metal is zinc. In other 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,

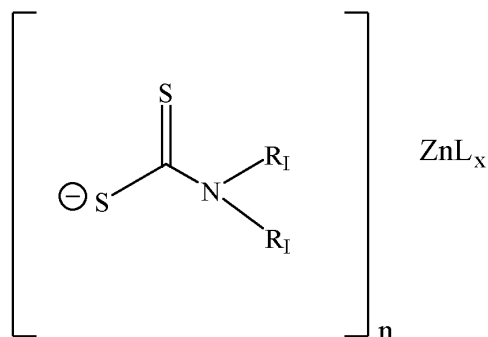
from about 3 to about 12 carbon atoms, or from about 3 to about 8 carbon atoms. In further embodiments, the alkyl group is linear or branched.

[0437] Useful anti-wear 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.

[0438] 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 $\text{Zn}[\text{SP}(\text{S})(\text{OR}_1)(\text{OR}_2)]_2$ 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. 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 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.

[0439] Useful zinc dithiophosphates include secondary zinc dithiophosphates such as those available from The Lubrizol Corporation under the trade designations "LZTM 677A", "LZTM 1095" and "LTMZ 1371", from Chevron Oronite under the trade designation "OLOATM 262" and from Afton Chemical under the trade designation "HiTECTM 7169".

[0440] In embodiments, the zinc compound can be a zinc dithiocarbamate complex, such as the zinc dithiocarbamates represented by the formula:



where each R_1 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.

[0441] The anti-wear 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 anti-wear 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.

[0442] Anti-wear 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.

[0443] Compositions according to the present disclosure may contain an additive having a different enumerated function that also has secondary effects as an anti-wear agent (for example, Component B described above, may also have anti-wear effects). These additives are not included as anti-wear agents for purposes of determining the amount of anti-wear agents in a lubricating oil composition or concentrate herein.

L. Demulsifiers

[0444] 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

[0445] 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

[0446] 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

[0447] 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 C₁₂-C₆₀ hydrocarbons (such as C₁₂-C₄₈ hydrocarbons, C₁₂-C₃₆ hydrocarbons, C₁₂-C₃₀ hydrocarbons, or C₁₂-C₂₄ 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.

[0448] 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.

[0449] 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

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 ₈ -alkyl substituted diphenylamine	0.01 - 20	0.1 - 8	1 to 5

Additional Antioxidant that is not di-C ₈ -alkyl substituted diphenylamine, such as hindered phenolic antioxidants	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
Anti-wear 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
Basestock	Balance (such as 50 to 95 %)	Balance	Balance

[0450] Typical Amounts of Lubricating Oil Components in LOC (Continued)

ADDITIVE FORMULATIONS	D (mass%)	E (mass%)	F (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 ₈ -alkyl substituted diphenylamine	0.1 - 15	0.5 - 5	1 to 5
Amine (other than di-C ₈ -alkyl substituted diphenylamine) 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
Anti-foaming 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

[0451] Typical Amounts of Lubricating Oil Components in LOC (Continued)

ADDITIVE FORMULATIONS	G (mass%)	H (mass%)	I (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 ₈ -alkyl substituted diphenylamine	0.1 - 15	0.5 - 5	0.5 to 3
Amine (other than di-C ₈ -alkyl substituted diphenylamine) 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
Anti-foaming 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
Basestock (50 to 99 mass%)	Balance	Balance	Balance

[0452] 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

[0453] This disclosure also relates to a method of lubricating an internal combustion engine during operation of the engine comprising:

- (i) Providing the lubricating composition described herein to a crankcase of the internal combustion engine;
- (ii) providing fuel, such as a hydrocarbon fuel, ammonia fuel, hydrogen fuel, in the automotive internal combustion engine; and
- (iii) combusting the fuel in the internal combustion engine.

[0454] This disclosure also relates to a method of lubricating an automotive internal combustion engine (such as an automotive internal combustion engine) during operation of the engine comprising:

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

[0455] 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.

[0456] The renewable fuel component is typically produced from vegetable oil (such as palm oil, coconut, 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

[0457] 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 heavy-duty diesel engine lubricants, but can be powertrain or other lubricants used in power transmission.

[0458] 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 or a light duty diesel engine, marine engines, standing engines and the like.

[0459] 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.

[0460] In embodiments, the lubricating oils of this disclosure are used in spark-assisted high compression internal combustion engines.

[0461] 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.)

[0462] In embodiments, the lubricating compositions of the present disclosure are suitably used in the lubrication of the crankcase of a passenger car diesel engine.

[0463] 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.

[0464] In particular, lubricating oil formulations of this disclosure are particularly useful in powertrain lubrication, such as in electric and or hybrid vehicles.

[0465] Also, the lubricating compositions of the invention may be useful as lubricants for hydrogen engines, ammonia engines and the like [*e.g.*, hydrogen (or hydrogen combined with natural gas) and or ammonia (or ammonia combined with hydrocarbon fuel, such as gasoline or diesel fuel) is all or part of the fuel the engines utilize.

[0466] 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 a lubricating composition described herein to a crankcase of the internal combustion engine;
- (ii) providing a hydrocarbon fuel and or biofuel the internal combustion engine; and
- (iii) combusting the fuel in the internal combustion engine.

[0467] 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.

[0468] This disclosure further relates to:

1. A stable antioxidant composition, comprising:
 - a) diphenylamine antioxidant comprising: 1) di(C₈-alkyl substituted phenyl) amine and 2) less than 15 mass% of mono-C₈-alkyl substituted diphenylamine (based upon the weight of mono- C₈-alkyl substituted phenylamines, di- C₈-alkyl substituted phenylamines, and any tri- C₈-alkyl substituted phenylamines present in the antioxidant composition), such as 5 to less than 15 mass% mass%, such as 5 to 10 mass%, such as 5 to 7 mass%, of mono-C₈-alkyl substituted diphenyl amine; and
 - b) polar diluent having an aniline point of 25°C or less, and at least 2 available hydrogen-bond acceptor groups (such as ester, ether or alcohol groups) that are 2, 3, 4, 5, or 6 atoms apart, wherein the combination of the polar diluent of b) combined with the diphenylamine antioxidant of a) is clear after 96 hours at 20 °C in a clear glass container without agitation according to the Antioxidant Blend Stability Test Method, where the polar diluent is optional when the di(C₈-alkyl substituted phenyl) amine is in molten or liquid crystal form; and optionally wherein the ratio of polar diluent to diphenylamine antioxidant is less than 7:1 (such as 5:1 or less, such as 4:1 or less, such as 3:1 or less, such as 2:1 or less, such as 1:1 or less, such as 0.75:1 to 0.5:1) and wherein polar diluent is optionally not diioshexylphthalate, and or optionally is not a phthalate.
2. The stable antioxidant composition of paragraph 1, further comprising detergent.
3. The stable antioxidant composition of paragraph 1, further comprising detergent, where the detergent is combined with the diphenylamine antioxidant at a temperature of at least 70 °C.
4. The stable antioxidant composition of paragraph 1, further comprising one or more base oils, dispersants, friction modifiers; antioxidants, other than the antioxidants of a), pour point depressants, anti-foaming agents, viscosity modifiers, corrosion inhibitors, antirust agents, and/or anti-wear agents.
5. The stable antioxidant composition of paragraph 1, further comprising carboxylate and or sulfonate detergent.
6. The stable antioxidant composition of paragraph 1, wherein the polar diluent(s) are one or more diluent(s) selected from the group consisting of:
 - i) di- and tri-esters derived from propylene glycol,
 - ii) C₈₋₁₆ alkyl triesters derived from trimethylolpropane,
 - iii) ethoxylated C₁₀₋₂₄ alcohols, and
 - iv) phthalates, terephthalates, isophthalates, trimellitates and pyromellitates (such as C₆ to C₂₄ dialkyl terephthalates, such as C₈ to C₁₆ dialkyl terephthalates, such as dioctyl terephthalate, such as C₆ to C₂₄ dialkyl isophthalates, C₆ to C₂₄ dialkyl phthalates, and C₆ to C₂₄ trialkyl trimellitate, and C₆ to C₂₄ tetraalkyl pyromellitate).

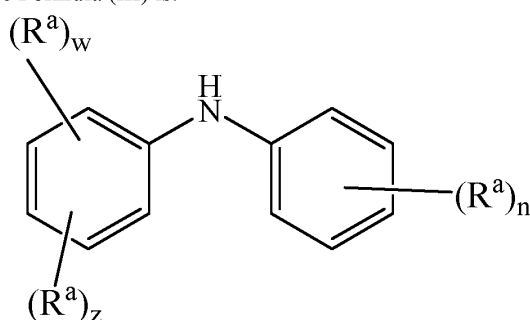
7. The stable antioxidant composition of paragraph 1, wherein the polar diluent comprises one or more of ethoxylated lauryl alcohol, C₈-C₁₀ tri-methylol propane ester, dipropylene glycol dibenzoate, dioctyl terephthalate, and/or trioctyl mellitate.
8. The stable antioxidant composition of paragraph 1, where the stable antioxidant composition comprises:
- 1 to 98 mass% of the diphenylamine antioxidant;
 - 1 to 98 mass% of polar diluent,
 - 8 to 98 mass% of detergent,
- based upon the weight of the stable antioxidant composition, and
- optional additional components comprising one or more of antioxidants, other than i) above, pour point depressants, anti-foam agents, viscosity modifiers, corrosion inhibitors, anti-wear agents, extreme pressure additives, demulsifiers, seal compatibility agents, additive diluent base oils, friction modifier(s).
9. A stable antioxidant composition comprising
- diphenylamine antioxidant comprising: 1) di(C₈-alkyl substituted phenyl) amine and 2) less than 15 mass% of mono-C₈-alkyl substituted diphenylamine (based upon the weight of mono- C₈-alkyl substituted phenylamines, di- C₈-alkyl substituted phenylamines, and any tri- C₈-alkyl substituted phenylamines present in the antioxidant composition); and
 - optional polar diluent having an aniline point of 25°C or less, and at least 2 available hydrogen-bond acceptor groups (such as ester, ether or alcohol groups) that are 2, 3, 4, 5, or 6 atoms apart,
- wherein the combination of the polar diluent of b) combined with the diphenylamine antioxidant of a) is clear after 96 hours at 20 °C in a clear glass container without agitation; and
- wherein the diphenylamine antioxidant is heated to a temperature of at least 90 °C prior to addition to a concentrate or a lubricating oil composition.
10. A stable concentrate composition comprising:
- the stable antioxidant composition of any of paragraphs 1 to 9;
 - detergent;
 - from 1 to less than 50 mass% base oil, based upon the weight of stable concentrate;
 - optionally one or more dispersants, friction modifiers; antioxidants, other than the antioxidants of i), pour point depressants, anti-foaming agents, viscosity modifiers, corrosion inhibitors, antirust agents, and/or anti-wear agents.
11. The stable concentrate composition of paragraph 10, wherein the antioxidant composition is combined with the detergent at a temperature of about 50°C or more prior to being combined with optional dispersants, friction modifiers; antioxidants, other than the antioxidants of i), pour point depressants, anti-foaming agents, viscosity modifiers, corrosion inhibitors, antirust agents, and/or anti-wear agents.
12. The stable concentrate composition of paragraph 10, wherein the antioxidant composition is combined with the detergent at a temperature of about 70°C or more prior to being combined with optional

dispersants, friction modifiers; antioxidants, other than the antioxidants of i), pour point depressants, anti-foaming agents, viscosity modifiers, corrosion inhibitors, antirust agents, and/or anti-wear agents.

13. The stable concentrate composition of paragraph 10, wherein
 - 1) the antioxidant composition is heated to a molten state and is combined with detergent at a temperature of 70 °C or more;
 - 2) the temperature of the combined antioxidant composition and detergent is optionally reduced to 45 °C to less than 70 °C; and
 - 3) the combined antioxidant composition and detergent is optionally further combined with one or more dispersants, friction modifiers; antioxidants, other than the antioxidants of 1), pour point depressants, anti-foaming agents, viscosity modifiers, corrosion inhibitors, antirust agents, and/or anti-wear agents.
14. A stable concentrate composition comprising a stable antioxidant composition, comprising:
 - a) diphenylamine antioxidant comprising: 1) di(C₈-alkyl substituted phenyl) amine and 2) less than 15 mass% of mono-C₈-alkyl substituted diphenylamine (based upon the weight of mono- C₈-alkyl substituted phenylamines, di- C₈-alkyl substituted phenylamines, and any tri- C₈-alkyl substituted phenylamines present in the antioxidant composition); and
 - b) optional polar diluent having an aniline point of 25°C or less, and at least 2 available hydrogen-bond acceptor groups (such as ester, ether or alcohol groups) that are 2, 3, 4, 5, or 6 atoms apart,wherein:
 - 1) solid antioxidant composition is optionally combined with detergent at a temperature of 90°C or more;
 - 2) the temperature of the combination of antioxidant composition and optional detergent is optionally reduced to 45 °C to less than 70 °C; and
 - 3) the combination of antioxidant composition and optional detergent is optionally combined with one or more detergents, dispersants, friction modifiers; antioxidants, other than the antioxidants of a), pour point depressants, anti-foaming agents, viscosity modifiers, corrosion inhibitors, antirust agents, and/or anti-wear agents.
15. The stable concentrate composition of paragraph 14, wherein the concentrate comprises:
 - 1) 85 mass% or more, such as 95 mass% or more of diphenylamine antioxidant comprising:
 - a) di-C₈-alkyl substituted diphenylamine (such as greater than 85 mass%, such as greater than 90 mass%, such as 85 to 95 mass%, such as 90 to 95 mass%, such as 93 to 95 mass% of di-C₈-alkyl substituted diphenylamine), and
 - b) from 0 to less than 15 mass% of mono-C₈-alkyl substituted diphenylamine (such as less than 10 mass%, such as 5 to 15 mass%, such as 5 to 10 mass%, such as 5 to 7 mass%) of mono-C₈-alkyl substituted diphenyl amine), based upon the weight of the mono- and di-phenylamines present in the concentrate; and
 - 2) salicylate detergent.

16. Stable antioxidant compositions, stable concentrate compositions and or stable lubricating oil compositions wherein the composition comprises:

- a) from 0 to less than 10 mass% mono- C_8 -alkyl substituted diphenylamine represented by the Formula (III) where n is 1, w is 0, and z is 0,
- b) 90 mass% or more of di- C_8 -alkyl substituted diphenylamine 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_8 -alkyl substituted diphenylamine represented by Formula (III), where n is 1, w is 1 and z is 1,
- d) 1 mass% or less of unsubstituted diphenylamines represented by Formula (III) where n is 0, w is 0, and z is 0, based upon the total weight of the diphenylamines of a), b), c) and d) present in the composition where Formula (III) is:

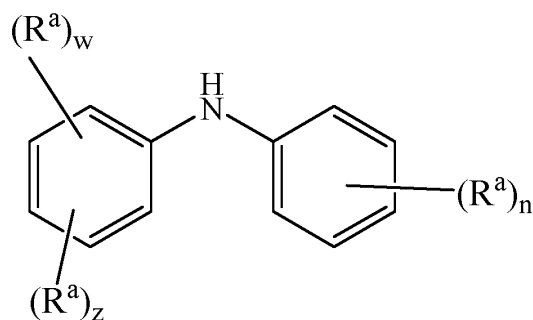


Formula (III)

where each R^a is independently a linear C_8 alkyl group or branched C_8 alkyl group, n is 1 or 0, z is 0 or 1, and w is 0 or 1, where the branched C_8 alkyl group may be singly, doubly or triply branched at one, two, three, four or more carbons, and may be symmetrically branched or asymmetrically branched.

17. A stable 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, optionally the base oil is less than 15 wt% ester base oil (such as less than 10 wt% ester base oil, such as less than 5 mass % ester base oil, such as 5, such as less than 1 mass % ester base oil, such as 0 mass % ester base oil), based on weight of base oils present;
 - (ii) the stable antioxidant composition and or a stable concentrate of any paragraphs 1 to 16.
18. Stable lubricating oil compositions 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 having from 1 to 500 mmol/kg soap (based upon the weight of the detergent);
 - (iv) optionally, one or more antioxidants not represented by Formula III, such as hindered phenolic antioxidants,

where Formula (III) is:



Formula (III)

where each R^a is independently a linear C_8 alkyl group or branched C_8 alkyl group, n is 1 or 0, z is 0 or 1, and w is 0 or 1, where the branched C_8 alkyl group may be singly, doubly or triply branched at one, two, three, four or more carbons, and may be symmetrically branched or asymmetrically branched;

- (v) optionally one or more Mo containing compounds; and
- (vi) optionally one or more fatty acid esters, such as sulfated fatty acid methyl esters;
- (vii) antioxidant composition, comprising:
 - a) diphenylamine antioxidant comprising: 1) di(C_8 -alkyl substituted phenyl) amine and 2) less than 15 mass% of mono- C_8 -alkyl substituted diphenylamine (based upon the weight of mono- C_8 -alkyl substituted phenylamines, di- C_8 -alkyl substituted phenylamines, and any tri- C_8 -alkyl substituted phenylamines present in the antioxidant composition); and
 - b) optional polar diluent having an aniline point of 25°C or less, and at least 2 available hydrogen-bond acceptor groups (such as ester, ether or alcohol groups) that are 2, 3, 4, 5, or 6 atoms apart.

19. The lubricating oil composition of paragraph 17, having higher Sequence IIIH weighted piston deposits merits at least 0.5 WPD merits higher as compared to the same lubricating oil composition except that the diphenylamine antioxidant has been replaced with the same amount of diphenylamine antioxidant having:

- 1) about 68 mass% di- C_9 -alkyl substituted diphenylamine,
- 2) about 29 mass% of mono- C_9 -alkyl substituted diphenylamine, and
- 3) about 3 mass% of tri- C_9 -alkyl substituted diphenylamine, based upon the weight of 1), 2) and

3), as determined by UPLC.

20. The lubricating oil composition of paragraph 17, 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 diphenylamine antioxidant has been replaced with the same amount of diphenylamine antioxidant having:

- 1) about 68 mass% di- C_9 -alkyl substituted diphenylamine,
- 2) about 29 mass% of mono- C_9 -alkyl substituted diphenylamine, and

- 3) about 3 mass% of tri-C₉-alkyl substituted diphenylamine, based upon the weight of 1), 2) and 3), as determined by UPLC.
21. The lubricating oil composition of paragraph 17, wherein the amount of mono-C₈-alkyl substituted diphenylamine present in the lubricating oil composition is less than 0.1 mass%, based upon the weight of the lubricating oil composition.
22. The lubricating oil composition of paragraph 17, having higher Sequence IIH weighted piston deposits merits of 4.6 or more.
23. The lubricating oil composition of paragraph 17, wherein the oxidation (FTIR, CEC-L-109-14 Oxidation Test) of the lubricating oil composition is less than or within 10 % more than the oxidation of the same lubricating oil composition except that the diphenylamine antioxidant has been replaced with the same amount of diphenylamine antioxidant having:
- 1) about 68 mass% di-C₉-alkyl diphenylamine,
 - 2) about 29 mass% of mono-C₉-alkyl diphenylamine, and
 - 3) about 3 mass% of tri-C₉-alkyl diphenylamine, based upon the weight of 1), 2) and 3), as determined by UPLC.
24. The lubricating oil composition of paragraph 17, further comprising zinc dialkyldithiophosphate, hindered phenolic antioxidant, and or molybdenum containing compound.
25. The lubricating oil composition of paragraph 17, wherein the lubricating oil composition further comprises additional antioxidant comprising oil-soluble or oil-dispersible sulfur-containing antioxidant(s), sulfurized aliphatic (C₇ to C₂₉) hydrocarbyl fatty acid ester(s), sulfur-containing organo-molybdenum compound(s), and combinations thereof.
26. The lubricating composition of paragraph 17, 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);
 - 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.
27. The lubricating composition of paragraph 26, wherein the viscosity modifier is a dispersant viscosity modifier comprising one or more functionalized polymers comprising an amide, imide, and/or ester functionalized partially or fully saturated polymer comprising C₄₋₅ 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.

28. The concentrate composition of paragraph of any of paragraphs 10 to 16, wherein the concentrate comprises:

1) diphenylamine antioxidant comprising:

a) di-C₈-alkyl substituted diphenylamine and b) from 0 to less than 5 mass% of mono-C₈-alkyl substituted diphenylamine, based upon the weight of the mono- and di-phenylamines present in the concentrate and b) 1 polar diluent having an aniline point of 25°C or less, and at least 2 available hydrogen-bond acceptor groups (such as ester, ether or alcohol groups) that are 2, 3, 4, 5, or 6 atoms apart; and

2) one or more of magnesium salicylate detergent, magnesium sulfonate detergent, calcium salicylate detergent, and calcium sulfonate detergent,

3) optional zinc dialkyldithiophosphate, at least a portion of which is derived from primary alcohol, secondary alcohol, or a combination of primary and secondary alcohol,

4) optional organic friction modifier, such as glycerol monooleate.

29. The concentrate composition of paragraph 28 wherein at least a portion of the zinc dialkyldithiophosphate is derived from iso-octanol and/or 4-methyl-pentan-2-ol and/or 2-butanol.

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

(i) providing to the internal combustion engine the lubricating composition of any of paragraphs 17 to 27;

(ii) providing a fuel in the internal combustion engine; and

(iii) combusting the fuel in the internal combustion engine.

31. The use of lubricating composition of any of paragraphs 17 to 27 in an internal combustion engine, where the oil sump temperature is greater than 100 °C.

32. The use of lubricating composition of any of paragraphs 17 to 27 in an internal combustion engine, where the oil sump temperature is greater than 120 °C.

33. A boosterpack comprising:

1) 1 to 99 mass% of diphenylamine antioxidant composition comprising:

a) di-C₈-alkyl substituted diphenylamine and b) from 0 to less than 5 mass% of mono-C₈-alkyl substituted diphenylamine, based upon the weight of the mono- and di-phenylamines present in the concentrate;

b) optionally, polar diluent having an aniline point of 25°C or less, and at least 2 available hydrogen-bond acceptor groups (ester, ether or alcohol group) that are 2, 3, 4, 5, or 6 atoms apart, wherein, if polar diluent is present, then the combination of polar diluent of b) combined with the diphenylamine antioxidant of a) is clear after 96 hours at 20 °C in a clear glass container without agitation; and

2) 1 to 99 mass% of detergent.

34. A boosterpack comprising:

1) the stable antioxidant composition of any of paragraphs 1 to 9;

2) 1 to 99 mass% of detergent; and

3) optionally one or more of the following components.

D) optionally, one or more friction modifiers;

E) optionally, one or more antioxidants, other than the antioxidants of 1) above;

- F) optionally, one or more pour point depressants;
- G) optionally, one or more anti-foaming agents;
- H) optionally, one or more viscosity modifiers;
- I) optionally, one or more dispersants;
- J) optionally, one or more inhibitors and/or antirust agents; and/or
- K) optionally, one or more anti-wear agents.

35. A method to prepare a stable concentrate composition comprising:

1) heating an antioxidant composition to a molten state and combining the antioxidant composition with detergent at a temperature of 70 °C or more;

2) optionally, reducing the temperature of the combination of antioxidant composition and detergent to 45 °C to less than 70 °C; and

3) combining the combination of antioxidant composition and detergent with dispersant,

4) optionally combining with one or more friction modifiers; antioxidants, other than the antioxidants of a), pour point depressants, anti-foaming agents, viscosity modifiers, corrosion inhibitors, antirust agents, and/or anti-wear agents,

wherein the antioxidant composition comprises:

a) di-C₈-alkyl substituted diphenylamine and b) from 0 to less than 15 mass% of mono-C₈-alkyl substituted diphenylamine, based upon the weight of the mono- and di-phenylamines present in the concentrate; and

b) optionally, polar diluent having an aniline point of 25°C or less, and at least 2 available hydrogen-bond acceptor groups (ester, ether or alcohol group) that are 2, 3, 4, 5, or 6 atoms apart, wherein, if polar diluent is present, then the combination of polar diluent of b) combined with the diphenylamine antioxidant of a) is clear after 96 hours at 20 °C in a clear glass container without agitation.

36. A method to prepare a stable concentrate composition comprising:

1) heating an antioxidant composition to a fluid (such as a melt and or a liquid crystal) state and optionally combining the antioxidant composition with detergent at a temperature of 70 °C or more;

2) optionally, reducing the temperature of the combination of antioxidant composition and detergent is to 45 °C to less than 70 °C; and

3) combining the combination of antioxidant composition and optional detergent with dispersant,

4) optionally combining with one or more friction modifiers; antioxidants, other than the antioxidants of a), pour point depressants, anti-foaming agents, viscosity modifiers, corrosion inhibitors, antirust agents, and/or anti-wear agents,

wherein the antioxidant composition comprises:

a) di-C₈-alkyl substituted diphenylamine and b) from 0 to less than 5 mass% of mono-C₈-alkyl substituted diphenylamine, based upon the weight of the mono- and di-phenylamines present in the concentrate; and

b) optionally, polar diluent having an aniline point of 25°C or less, and at least 2 available hydrogen-bond acceptor groups (ester, ether or alcohol group) that are 2, 3, 4, 5, or 6 atoms apart, wherein, if

polar diluent is present, then the combination of polar diluent of b) combined with the diphenylamine antioxidant of a) is clear after 96 hours at 20 °C in a clear glass container without agitation.

37. A method of improving viscometric growth, as determined by **CEC-L-109-14**, of a lubricating oil in an internal combustion engine, the method comprising: supplying a lubricating oil composition to the internal combustion engine, where the lubricating oil composition comprises an antioxidant composition, comprising:

a) fluid diphenylamine antioxidant comprising: 1) di(C₈-alkyl substituted phenyl) amine and 2) less than 15 mass% of mono-C₈-alkyl substituted diphenylamine (based upon the weight of mono-C₈-alkyl substituted phenylamines, di- C₈-alkyl substituted phenylamines, and any tri- C₈-alkyl substituted phenylamines present in the antioxidant composition); and

b) optional polar diluent having an aniline point of 25°C or less, and at least 2 available hydrogen-bond acceptor groups (such as ester, ether or alcohol groups) that are 2, 3, 4, 5, or 6 atoms apart,

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 10 % (such as at least 15%, or such as at least 20%, or such as at least 30% or such as at least 35%, or such as at least 40%, or such as at least 45%, or such as at least 50%, or such as at least 55%, or such as at least 60%, or such as at least 65%, or such as at least 70%, or such as at least 75%, or such as at least 80%, or such as at least 85%) less than or within 10 % more than the percent viscosity increase of the same lubricating oil composition except that the diphenylamine antioxidant has been replaced with the same amount of diphenylamine antioxidant having:

1) about 68 mass% di-C₉-alkyl substituted diphenylamine, 2) about 29 mass% of mono-C₉-alkyl substituted diphenylamine, and 3) about 3 mass% of tri-C₉-alkyl substituted diphenylamine, based upon the weight of 1), 2) and 3), as determined by UPLC.

38. The stable antioxidant compositions, booster compositions, stable concentrates and or stable lubricating oil compositions of paragraphs 1 to 29 and 33 wherein the composition comprises: trinuclear molybdenum compound such as molybdenum trimer, such as molybdenum dithiocarbamate trimer.

39. The stable antioxidant compositions, stable concentrates and or stable lubricating oil compositions of paragraphs 1 to 29, 33 and 38 wherein the composition comprises: dinuclear molybdenum compound such as molybdenum dimer, such as molybdenum dithiocarbamate dimer, and optionally one, two, or three of:

a) one or more **borated compounds** (such as borated dispersants, such as borated PIBSA-PAM, such as borated PIBSA-PAM derived from PIB having an Mn of 1600 or less);

b) **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 540 ppm to 8500 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 more, such as 5000 ppm or more, such as 6000 ppm or more, such as 7000 ppm or more, such as 8000 ppm or more); and

c) **zinc-based antiwear agents**, such as zinc dialkyldithiophosphates where the alkyl group is derived from one or more primary alcohol(s).

40. The stable antioxidant compositions, stable concentrates and or stable lubricating oil compositions of paragraphs 1 to 29, 33, 38 and 39 wherein the composition further comprises one 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 30 mass%, such as 0.1 to 20 mass%, such as 0.1 to 10 mass%, such as 0.1 to 5 mass%, of **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 30 mass%, such as 0.1 to 20 mass%, such as 0.1 to 10 mass%, such as 0.1 to 5 mass%, of **calcium-based detergents**, such as calcium sulfonate and or carboxylate (salicylate) detergents;
 - 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% of one or more **borated compounds** (such as borated dispersants, such as borated PIBSA-PAM, such as borated PIBSA-PAM derived from PIB having an Mn of 1600 or less);
 - 5) 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;
 - 6) 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 450 ppm to 9000 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 more, such as 5000 ppm or more, such as 6000 ppm or more, such as 7000 ppm or more, such as 8000 ppm or more, such as 9000 ppm or more);
 - 7) 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 dialkyldithiophosphates where the alkyl group is derived from one or more primary alcohol(s);
 - 8) 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 800 ppm, 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 more, such as 5000 ppm or more, such as 6000 ppm or more, such as 7000 ppm or more, such as 8000 ppm or more, such as 10,000 ppm or more such as 15,000 ppm or more, such as 20,000 ppm or more); and

9) 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% of **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)).

41. The stable antioxidant compositions, stable concentrates and or stable lubricating oil compositions of paragraphs 1 to 29, 33 and 38 to 40, further comprising: one or more friction modifiers such as isomerized octadecenylsuccinicanhydride-tetraethylenepentamine), one or more flow improvers (such as dialkyl fumarate/vinyl acetate copolymer (such as C₈-C₁₈ dialkyl fumarate/vinyl acetate copolymer, such as C₁₂-C₁₈ dialkyl fumarate/vinyl acetate copolymer), such as methacrylate polymers); and or one or more corrosion inhibitors (such as one or more triazoles (such as H-1,2,4-triazole-1-methanamine, N,N-bis(2-ethylhexyl) Irgamet™ 30) or benzotriazoles (such as N,N-Bis(2-ethylhexyl)-4-methyl-1h-benzotriazole-1-methanamine, Irgamet™ 39)).

42. A stable concentrate comprising:

(i) an antioxidant composition (that may optionally be homogeneous (such as a solution) or heterogeneous (such as a dispersion, a slurry, a colloid and the like)), comprising:

- a) diphenylamine antioxidant comprising: 1) di(C₈-alkyl substituted phenyl) amine and 2) less than 15 mass% (such as 10 mass% or less) of mono-C₈-alkyl substituted diphenylamine (based upon the weight of mono- C₈-alkyl substituted phenylamines, di- C₈-alkyl substituted phenylamines, and tri- C₈-alkyl substituted phenylamines present in the concentrate composition); and
- b) optionally, polar diluent having an aniline point of 25°C or less, and at least 2 available hydrogen-bond acceptor groups (ester, ether or alcohol group) that are 2, 3, 4, 5, or 6 atoms apart, wherein, if polar diluent is present, then the combination of polar diluent of b) combined with the diphenylamine antioxidant of a) is clear after 96 hours at 20 °C without agitation (such as a combination of 75 mass% of the polar diluent of b) combined with 25 mass% of the diphenylamine antioxidant of a) is clear after 96 hours at 20 °C); and

(ii) one or more components selected from the group consisting of **detergents** (such as sulfonate detergents, salicylate detergents, calcium detergents and or magnesium detergents), **dispersants** (such as borated dispersants, such as PIBSA-PAM derived from a polymer (such as polyisobutylene) having an Mn of 1600 g/mol or less), **zinc-based antiwear agents** (such as zinc dialkyldithiophosphates where the alkyl group is derived from one or more primary alcohol(s)); and

(iii) base oil (such as renewable base oil and or Group II base oil); and

- (iv) optionally, one or more components selected from friction modifiers; antioxidants, other than the antioxidants of a), pour point depressants, anti-foaming agents, lube oil flow improvers, corrosion inhibitors, antirust agents, and/or anti-wear agents;
- wherein:
- 1) the antioxidant composition (i) is heated to a fluid state (such as molten state or a liquid crystal state) (such as heating to 98 °C or more) and is combined with the component(s) (ii) and base oil (iii) at a temperature of 70 °C or more, such as 75°C or more, such as 80°C or more, such as 90°C or more, such as 100°C or more;
 - 2) the temperature of the combination of the composition of step 1) is optionally reduced to 45 °C to less than 70 °C; and
 - 3) the combination of the composition of step 1) or step 2) is optionally combined with one or more **detergents** (such as sulfonate detergents, salicylate detergents, calcium detergents and or magnesium detergents); **dispersants** (such as borated dispersants, and or dispersants (such as PIBSA-PAM) derived from a polymer (such as polyisobutylene) having an Mn of 1600 g/mol or less); **zinc-based antiwear agents** (such as zinc dialkyldithiophosphates where the alkyl group is derived from one or more primary alcohol(s)); **friction modifiers** (such as **glycerol-based friction modifiers**, such as glycerol mono-oleate); **antioxidants**, other than the antioxidants of a); **pour point depressants**; **anti-foaming agents**; **viscosity modifiers**; **lube oil flow improvers**; **corrosion inhibitors/antirust agents** (such as triazoles); and/or **anti-wear agents**, other than zinc-based antiwear agents.
43. A stable 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) the stable concentrate of paragraph 42.
44. The stable concentrates and or stable lubricating oil compositions of paragraphs 1 to 29, 33 and 38 to 43 wherein the composition comprises: dinuclear molybdenum compound such as molybdenum dimer, such as molybdenum dithiocarbamate dimer, and optionally one, two, or three of:
- a) one or more **borated compounds** (such as borated dispersants, such as borated PIBSA-PAM, such as borated PIBSA-PAM derived from PIB having an Mn of 1600 or less);
 - b) **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 8500 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 more, such as 5000 ppm or more, such as 6000 ppm or more, such as 7000 ppm or more, such as 8000 ppm or more, such as 9,000 ppm or more); and
 - c) **zinc-based antiwear agents**, such as zinc dialkyldithiophosphates where the alkyl group is derived from one or more primary alcohol(s).
45. The stable concentrates and or stable lubricating oil compositions of paragraphs 1 to 29, 33 and 38 to 44 wherein the composition further comprises one 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%, of **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 0.1 to 10 mass%, such as 0.1 to 5 mass%, of **calcium-based detergents**, such as calcium sulfonate and or carboxylate (salicylate) detergents;
- 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% of one or more **borated compounds** (such as borated dispersants, such as borated PIBSA-PAM, such as borated PIBSA-PAM derived from PIB having an Mn of 1600 or less);
- 5) 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;
- 6) 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 more, such as 5000 ppm or more, such as 6000 ppm or more, such as 7000 ppm or more, such as 8000 ppm or more);
- 7) 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 dialkyldithiophosphates where the alkyl group is derived from one or more primary alcohol(s);
- 8) 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 more, such as 5000 ppm or more); and
- 9) 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% of **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)).

46. The stable antioxidant compositions, stable concentrates and or stable lubricating oil compositions of paragraphs 1 to 29, 33 and 38 to 45, further comprising: one or more friction modifiers such as isomerized octadecenylsuccinicanhydride-tetraethylenepentamine), one or more flow improvers (such as dialkyl fumarate/vinyl acetate copolymer (such as C₈-C₁₈ dialkyl fumarate/vinyl acetate copolymer, such as C₁₂-C₁₈ dialkyl fumarate/vinyl acetate copolymer), such as methacrylate polymers); and or one or more corrosion inhibitors (such as one or more triazoles (such as H-1,2,4-triazole-1-methanamine, N,N-bis(2-ethylhexyl) Irgamet™ 30) or benzotriazoles (such as N,N-Bis(2-ethylhexyl)-4-methyl-1h-benzotriazole-1-methanamine, Irgamet™ 39)).
47. A method to prepare a stable concentrate composition comprising C₈ antioxidant and one or more additive components, said method comprising:
- 1) heating an antioxidant composition to a fluid state (such as a liquid, molten or liquid crystal state) and combining the antioxidant composition with an additive component for the concentrate at a temperature of 70 °C or more;
 - 2) optionally, reducing the temperature of the combination of antioxidant composition and additive component to 45 °C to less than 70 °C; and
 - 3) optionally, combining the combination of antioxidant composition and additive component with one or more additional additive components;

wherein the antioxidant composition comprises:

- a) di-C₈-alkyl substituted diphenylamine and b) from 0 to less than 15 mass% (such as 5 to less than 15 mass%, such as 90 to 95 mass%) of mono-C₈-alkyl substituted diphenylamine, based upon the weight of the mono- and di-phenylamines present in the concentrate; and
- b) optionally, polar diluent having an aniline point of 25°C or less, and at least 2 available hydrogen-bond acceptor groups (ester, ether or alcohol group) that are 2, 3, 4, 5, or 6 atoms apart, wherein, if polar diluent is present, then the combination of polar diluent of b) combined with the diphenylamine antioxidant of a) is clear after 96 hours at 20 °C in a clear glass container without agitation;

and wherein the additive components are selected from:

- A) base oils;
- C) detergents,
- D) friction modifiers;
- E) antioxidants, other than the antioxidants of a) above;
- F) pour point depressants;
- G) anti-foaming agents;
- H) viscosity modifiers;
- I) dispersants;
- J) corrosion inhibitors and/or antirust agents;
- K) anti-wear agents; and

variations and combinations thereof.

48. A method of lubricating an internal combustion engine, the method comprising: supplying a lubricating oil composition to the internal combustion engine, where the lubricating oil composition comprises:
- 1) base oil, optionally comprising renewable base oil and or Group II base oil;
 - 2) an antioxidant composition, comprising:
 - a) diphenylamine antioxidant comprising: 1) di(C₈-alkyl substituted phenyl) amine and 2) less than 15 mass% of mono-C₈-alkyl substituted diphenylamine (based upon the weight of mono- C₈-alkyl substituted phenylamines, di- C₈-alkyl substituted phenylamines, and any tri- C₈-alkyl substituted phenylamines present in the antioxidant composition); and
 - b) optional polar diluent having an aniline point of 25°C or less, and at least 2 available hydrogen-bond acceptor groups (such as ester, ether or alcohol groups) that are 2, 3, 4, 5, or 6 atoms apart; and
 - 3) one, two, three, four, five, six, seven, eight, nine or more components 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) **calcium-based detergents**, such as calcium sulfonate and or carboxylate (salicylate) detergents;
 - 4) **borated compounds** (such as borated dispersants, such as borated PIBSA-PAM, such as borated PIBSA-PAM derived from PIB having an Mn of 1600 or less);
 - 5) **organomolybdenum-based friction modifier**, such as molybdenum dithiocarbamate dimers and or trimers;
 - 6) **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 Mg);
 - 7) **zinc-based antiwear agents**, such as zinc dialkyldithiophosphates where the alkyl group is derived from one or more primary alcohol(s);
 - 8) **salicylate-based detergent**, optionally providing high amounts of Ca and or Mg to the composition (such as 40 ppm to 5000 ppm);
 - 9) **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); and combinations and variations thereof.
49. The method of paragraph 48, wherein the antioxidant composition is prepared by: 1) heating the diphenylamine antioxidant comprising: 1) di(C₈-alkyl substituted phenyl) amine and 2) less than 15 mass% of mono-C₈-alkyl substituted diphenylamine (based upon the weight of mono- C₈-alkyl substituted phenylamines, di- C₈-alkyl substituted phenylamines, and any tri- C₈-alkyl substituted phenylamines present in the antioxidant composition) to a fluid state (such as a liquid or molten

state) and combining the fluid antioxidant with one or more additive components at a temperature of 50°C or more, 60°C or more 70°C or more, where the additive components are selected from:

- A) base oils,
- C) detergents,
- D) friction modifiers,
- E) antioxidants, other than the antioxidants of 1) above,
- F) pour point depressants,
- G) anti-foaming agents,
- H) viscosity modifiers,
- I) dispersants,
- J) corrosion inhibitors and/or antirust agents,
- K) anti-wear agents, and variations and combinations thereof;

2) optionally, reducing the temperature of the combination of antioxidant composition and additive component(s) to 45 °C to less than 70 °C; and

3) optionally, combining the combination of antioxidant composition and additive component(s) with one or more additional additive components.

50. The method of paragraph 48 or 49, 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 5 % less (such as at least 10 %, such as at least 15%, or 20%, or 30% or 35%, of 40%, or 45%, or 50%, or 55%, or 60%, or 65%, or 70%, or 75%, or 80%, or 85%, or 95%, or 100%, or 105%) less than the percent viscosity increase of the same lubricating oil composition except that the diphenylamine antioxidant has been replaced with the same amount of diphenylamine antioxidant having: 1) about 68 mass% di-C₉-alkyl substituted diphenylamine, 2) about 29 mass% of mono-C₉-alkyl substituted diphenylamine, and 3) about 3 mass% of tri-C₉-alkyl substituted diphenylamine, based upon the weight of 1), 2) and 3), as determined by UPLC.
51. The method of paragraph 49, wherein one or more polar diluents, octadecenylsuccinic anhydride-tetraethylenepentamine, one or more triazole corrosion inhibitors, and or one or more dialkyl fumarate/vinyl acetate copolymers are added to the concentrate in the same blending stage as one or more molten C₈ diphenylamine antioxidant are added to the concentrate.
52. The method of paragraph 49, wherein one or more C₈-C₁₀ tri-methylol propane esters, octadecenylsuccinic anhydride-tetraethylenepentamine, one or more triazole and or benzotriazole corrosion inhibitors, and or one or more C₈ to C₁₈ dialkyl fumarate/vinyl acetate copolymers are added to the concentrate in the same blending stage as one or more molten C₈ diphenylamine antioxidant are added to the concentrate.
53. The method of paragraph 51 or 52 wherein the one or more dialkyl fumarate/vinyl acetate copolymers each have a pour point (ASTM D97) of -10°C or less (such as -15°C or less, such as -20°C or less, such as -25 °C or less, such as -30 °C or less) are added at the same concentrate blending stage as the molten C₈ diphenylamine antioxidant.

54. The method of paragraph 49, wherein one or more friction modifiers such as isomerized octadecenylsuccinic anhydride-tetraethylenepentamine), one or more flow improvers (such as dialkyl fumarate/vinyl acetate copolymer (such as C₈-C₁₈ dialkyl fumarate/vinyl acetate copolymer, such as C₁₂-C₁₈ dialkyl fumarate/vinyl acetate copolymer), such as methacrylate polymers); and or one or more corrosion inhibitors (such as one or more triazoles (such as H-1,2,4-triazole-1-methanamine, N,N-bis(2-ethylhexyl) Irgamet™ 30) or benzotriazoles (such as N,N-Bis(2-ethylhexyl)-4-methyl-1h-benzotriazole-1-methanamine, Irgamet™ 39)) are added at the same concentrate blending stage as the molten C₈ diphenylamine antioxidant.
55. A stable concentrate composition comprising: a) diphenylamine antioxidant comprising: 1) di(C₈-alkyl substituted phenyl) amine and 2) less than 15 mass% of mono-C₈-alkyl substituted diphenyl amine, based upon the weight of mono- C₈-alkyl substituted phenylamines, di- C₈-alkyl substituted phenylamines, and any tri-C₈-alkyl substituted phenylamines present in the antioxidant composition, (such as 5 to less than 15 mass% mass%, such as 5 to 10 mass%, such as 5 to 7 mass%, of mono-C₈-alkyl substituted diphenyl amine), and b) one or more polar diluents, octadecenylsuccinic anhydride-tetraethylenepentamine, one or more triazole corrosion inhibitors, and or one or more dialkyl fumarate/vinyl acetate copolymers

wherein the one or more polar diluents, octadecenylsuccinic anhydride-tetraethylenepentamine, one or more triazole corrosion inhibitors, and or one or more dialkyl fumarate/vinyl acetate copolymers are added to the concentrate in the same blending stage as one or more molten C₈ diphenylamine antioxidant are added to the concentrate.

56. A method to prepare a stable concentrate composition comprising:
- 1) heating an antioxidant composition comprising:
 - a) diphenylamine antioxidant comprising: 1) di(C₈-alkyl substituted phenyl) amine and 2) less than 15 mass% of mono-C₈-alkyl substituted diphenyl amine, based upon the weight of mono- C₈-alkyl substituted phenylamines, di- C₈-alkyl substituted phenylamines, and any tri-C₈-alkyl substituted phenylamines present in the antioxidant composition, (such as 5 to less than 15 mass% mass%, such as 5 to 10 mass%, such as 5 to 7 mass%, of mono-C₈-alkyl substituted diphenyl amine),
- to a fluid state (such as a liquid or molten state) at a temperature of 70 °C or more;
- 2) optionally, reducing the temperature of the combination of antioxidant composition to 45 °C to less than 70 °C; and
 - 3) combining the antioxidant composition with detergent and or dispersant;
 - 4) optionally combining the antioxidant composition with one or more friction modifiers; antioxidants, other than the antioxidants of a), pour point depressants, anti-foaming agents, viscosity modifiers, corrosion inhibitors, antirust agents, and/or anti-wear agents;

wherein the antioxidant composition does not comprise solid di-C₈-alkyl substituted diphenylamine.

57. The method of paragraph 56, where the stable concentrate composition is absent polar diluent.

58. The method of paragraph 56, wherein one or more C₈-C₁₀ tri-methylol propane esters, octadecenylsuccinic anhydride-tetraethylenepentamine, one or more triazole and or benzotriazole corrosion inhibitors, and or one or more C₈ to C₁₈ dialkyl fumarate/vinyl acetate copolymers are added to the concentrate in the same blending stage as one or more fluid C₈ diphenylamine antioxidants are added to the concentrate.
59. The method of paragraph 56, wherein one or more friction modifiers such as isomerized octadecenylsuccinic anhydride-tetraethylenepentamine), one or more flow improvers (such as dialkyl fumarate/vinyl acetate copolymer (such as C₈-C₁₈ dialkyl fumarate/vinyl acetate copolymer, such as C₁₂-C₁₈ dialkyl fumarate/vinyl acetate copolymer), such as methacrylate polymers); and or one or more corrosion inhibitors (such as one or more triazoles (such as H-1,2,4-triazole-1-methanamine, N,N-bis(2-ethylhexyl) Irgamet™ 30) or benzotriazoles (such as N,N-Bis(2-ethylhexyl)-4-methyl-1h-benzotriazole-1-methanamine, Irgamet™ 39)) are added at the same concentrate blending stage as the molten C₈ diphenylamine antioxidant.
60. A method of reducing friction, as determined by HFRR Average Friction Coefficient at 140 °C, of a lubricating oil composition in an internal combustion engine, the method comprising: supplying a lubricating oil composition to the internal combustion engine, where the lubricating oil composition comprises an antioxidant composition comprising:
 - a) fluid diphenylamine antioxidant comprising: 1) di(C₈-alkyl substituted phenyl) amine and 2) less than 15 mass% of mono-C₈-alkyl substituted diphenylamine (based upon the weight of mono- C₈-alkyl substituted phenylamines, di- C₈-alkyl substituted phenylamines, and any tri- C₈-alkyl substituted phenylamines present in the antioxidant composition)
 wherein the lubricating oil composition has an HFRR average Friction Coefficient at 140 °C of at least five percent 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) than the HFRR average Friction Coefficient at 140 °C of the same lubricating oil composition except that the fluid diphenylamine antioxidant has been replaced with the same amount of diphenylamine antioxidant having:
 - 1) about 68 mass% di-C₉-alkyl substituted diphenylamine,
 - 2) about 29 mass% of mono-C₉-alkyl substituted diphenylamine, and
 - 3) about 3 mass% of tri-C₉-alkyl substituted diphenylamine, based upon the weight of 1), 2) and 3), as determined by UPLC.
61. A method of reducing wear, as determined by MTM-R Wear Scar Volume, μm³, of a lubricating oil composition in an internal combustion engine, the method comprising: supplying a lubricating oil composition to the internal combustion engine, where the lubricating oil composition comprises an antioxidant composition comprising:
 - a) fluid diphenylamine antioxidant comprising: 1) di(C₈-alkyl substituted phenyl) amine and 2) less than 15 mass% of mono-C₈-alkyl substituted diphenylamine (based upon the weight of mono- C₈-alkyl

substituted phenylamines, di- C₈-alkyl substituted phenylamines, and any tri- C₈-alkyl substituted phenylamines present in the antioxidant composition)

wherein the lubricating oil composition has an at least a 15% reduction (such as at least a 25% reduction, such as at least a 35% reduction, such as at least a 45 % reduction, such as at least a 55% reduction, such as at least a 65 % reduction, such as at least a 75% reduction, such as at least an 85% reduction) in wear scar volume, μm^3 , as compared to the same lubricating oil composition except that the fluid diphenylamine antioxidant has been replaced with the same amount of diphenylamine antioxidant having:

- 1) about 68 mass% di-C₉-alkyl substituted diphenylamine,
- 2) about 29 mass% of mono-C₉-alkyl substituted diphenylamine, and
- 3) about 3 mass% of tri-C₉-alkyl substituted diphenylamine, based upon the weight of 1), 2) and 3), as determined by UPLC; and or

wherein the lubricating oil composition has an at least a 15% reduction (such as at least a 25% reduction, such as at least a 35% reduction, such as at least a 45 % reduction, such as at least a 55% reduction, such as at least a 65 % reduction, such as at least a 75% reduction, such as at least an 85% reduction, such as at least a 95% reduction, such as at least a 99% reduction, such as at least a 99.4% reduction) in wear scar volume, μm^3 , as compared to the same lubricating oil composition except that the fluid diphenylamine antioxidant has been replaced with a 1:1 blend of solid diphenylamine antioxidant and TMP ester providing the same amount of diphenylamine antioxidant to the lubricating oil composition.

62. A method of reducing piston deposits, as determined by MHT4 TEOST, mg, of a lubricating oil composition in an internal combustion engine, the method comprising: supplying a lubricating oil composition to the internal combustion engine, where the lubricating oil composition comprises an antioxidant composition comprising:

- a) fluid diphenylamine antioxidant comprising: 1) di(C₈-alkyl substituted phenyl) amine and
- 2) less than 15 mass% of mono-C₈-alkyl substituted diphenylamine (based upon the weight of mono- C₈-alkyl substituted phenylamines, di- C₈-alkyl substituted phenylamines, and any tri- C₈-alkyl substituted phenylamines present in the antioxidant composition) , and
- b) one or more polar diluents, octadecenylsuccinic anhydride-tetraethylenepentamine, one or more triazole corrosion inhibitors, and or one or more dialkyl fumarate/vinyl acetate copolymers,

wherein the lubricating oil composition has an at least a 15% reduction (such as at least a 25% reduction, such as at least a 35% reduction, such as at least a 45 % reduction, such as at least a 55% reduction, such as at least a 65 % reduction, such as at least a 70% reduction) in deposits, mg, as compared to the same lubricating oil composition except that the fluid diphenylamine antioxidant has been replaced with the same amount of diphenylamine antioxidant having:

- 1) about 68 mass% di-C₉-alkyl substituted diphenylamine,
- 2) about 29 mass% of mono-C₉-alkyl substituted diphenylamine, and

3) about 3 mass% of tri-C₉-alkyl substituted diphenylamine, based upon the weight of 1), 2) and 3), as determined by UPLC.

63. A method of reducing piston deposits, as determined by MHT4 TEOST, mg, of a lubricating oil composition in an internal combustion engine, the method comprising: supplying a lubricating oil composition to the internal combustion engine, where the lubricating oil composition comprises an antioxidant composition comprising:
- a) diphenylamine antioxidant comprising: 1) di(C₈-alkyl substituted phenyl) amine and 2) less than 15 mass% of mono-C₈-alkyl substituted diphenylamine (based upon the weight of mono- C₈-alkyl substituted phenylamines, di- C₈-alkyl substituted phenylamines, and any tri- C₈-alkyl substituted phenylamines present in the antioxidant composition)
- wherein the lubricating oil composition has an at least a 15% reduction (such as at least a 25% reduction, such as at least a 35% reduction, such as at least a 45 % reduction, such as at least a 55% reduction, such as at least a 65 % reduction) in wear scar volume, μm^3 , as compared to the same lubricating oil composition except that the fluid diphenylamine antioxidant has been replaced with a 1:1 blend of solid diphenylamine antioxidant and TMP ester providing the same amount of diphenylamine antioxidant to the lubricating oil composition.
64. A lubricating oil composition comprising fluid diphenylamine antioxidant comprising: 1) di(C₈-alkyl substituted phenyl) amine and 2) less than 15 mass% of mono-C₈-alkyl substituted diphenylamine (based upon the weight of mono- C₈-alkyl substituted phenylamines, di- C₈-alkyl substituted phenylamines, and any tri- C₈-alkyl substituted phenylamines present in the antioxidant composition).
65. A lubricating oil composition comprising base oil and molten diphenylamine antioxidant comprising: 1) di(C₈-alkyl substituted phenyl) amine and 2) less than 15 mass% of mono-C₈-alkyl substituted diphenylamine (based upon the weight of mono- C₈-alkyl substituted phenylamines, di- C₈-alkyl substituted phenylamines, and any tri- C₈-alkyl substituted phenylamines present in the antioxidant composition).
66. A lubricating oil composition comprising molten diphenylamine antioxidant comprising: 1) di(C₈-alkyl substituted phenyl) amine and 2) less than 15 mass% of mono-C₈-alkyl substituted diphenylamine (based upon the weight of mono- C₈-alkyl substituted phenylamines, di- C₈-alkyl substituted phenylamines, and any tri- C₈-alkyl substituted phenylamines present in the antioxidant composition).
67. A method to prepare a lubricating oil composition comprising combining one or more components with base oil and thereafter combining the base oil and one or more components with molten diphenylamine antioxidant comprising: 1) di(C₈-alkyl substituted phenyl) amine and 2) less than 15 mass% of mono-C₈-alkyl substituted diphenylamine (based upon the weight of mono- C₈-alkyl substituted phenylamines, di- C₈-alkyl substituted phenylamines, and any tri- C₈-alkyl substituted phenylamines present in the antioxidant composition), where the components optionally comprise one or more of: B) one or more detergents; D) one or more friction modifiers; E) one or more

- antioxidants, other than the antioxidants of 1) above; F) one or more pour point depressants; G) one or more anti-foaming agents; H) one or more viscosity modifiers; I) one or more dispersants; J) one or more inhibitors and/or antirust agents; and/or K) one or more anti-wear agents.
68. A method to prepare a lubricating oil composition comprising combining a concentrate with base oil and thereafter combining the base oil and concentrate with molten diphenylamine antioxidant comprising: 1) di(C₈-alkyl substituted phenyl) amine and 2) less than 15 mass% of mono-C₈-alkyl substituted diphenylamine (based upon the weight of mono- C₈-alkyl substituted phenylamines, di- C₈-alkyl substituted phenylamines, and any tri- C₈-alkyl substituted phenylamines present in the antioxidant composition), where the concentrate optionally comprises one or more of: B) one or more detergents; D) one or more friction modifiers; E) one or more antioxidants, other than the antioxidants of 1) above; F) one or more pour point depressants; G) one or more anti-foaming agents; H) one or more viscosity modifiers; I) one or more dispersants; J) one or more inhibitors and/or antirust agents; and/or K) one or more anti-wear agents.
69. A method to prepare a lubricating oil composition comprising combining base oil with molten diphenylamine antioxidant comprising: 1) di(C₈-alkyl substituted phenyl) amine and 2) less than 15 mass% of mono-C₈-alkyl substituted diphenylamine (based upon the weight of mono- C₈-alkyl substituted phenylamines, di- C₈-alkyl substituted phenylamines, and any tri- C₈-alkyl substituted phenylamines present in the antioxidant composition) and thereafter combining the base oil and molten diphenylamine with a concentrate, optionally thereafter combining the base oil, molten diphenylamine and concentrate with and at least one additional component, such as one or more of: B) one or more detergents; D) one or more friction modifiers; E) one or more antioxidants, other than the antioxidants of 1) above; F) one or more pour point depressants; G) one or more anti-foaming agents; H) one or more viscosity modifiers; I) one or more dispersants; J) one or more inhibitors and/or antirust agents; and/or K) one or more anti-wear agents.
70. A booster package comprising molten diphenylamine antioxidant comprising: 1) di(C₈-alkyl substituted phenyl) amine and 2) less than 15 mass% of mono-C₈-alkyl substituted diphenylamine (based upon the weight of mono- C₈-alkyl substituted phenylamines, di- C₈-alkyl substituted phenylamines, and any tri- C₈-alkyl substituted phenylamines present in the antioxidant composition), and at least one other component, such as one or more of: B) one or more detergents; D) one or more friction modifiers; E) one or more antioxidants, other than the antioxidants of 1) above; F) one or more pour point depressants; G) one or more anti-foaming agents; H) one or more viscosity modifiers; I) one or more dispersants; J) one or more inhibitors and/or antirust agents; and/or K) one or more anti-wear agents.

[0469] The following non-limiting examples are provided to illustrate the disclosure.

Experimental

[0470] All molecular weights are number average molecular weights (M_n) 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. APK means additive package.

Testing Procedures

[0471] **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.

[0472] **KV100** and **KV40** are Kinematic viscosity measurements at 100°C and 40°C respectively, according to ASTM D445-19a.

[0473] **Aniline point** is determined according to ASTM 611, Method A.

[0474] **Antioxidant Blend Stability Test Method:** Solid C₈-alkyl diphenylamine (1.5 g) and the test component(s) (1.5 g) were placed in a clear glass container (Fisherbrand™ Glass Screw Neck Specimen Vials, 28 mL), and heated together to 100°C. Upon melting the mixture was stirred for 30 mins, then cooled to 20°C and sealed with a polypropylene screw top cap. Sample clarity is determined by allowing the blend to sit without agitation for a specified number of hours (96 hours, unless otherwise indicated) at a specified temperature (20°C, unless otherwise indicated), then visually observing the blend after the specified number of hours for crystallization, precipitation or cloudiness. An observation of "clear" means that the blend is observed under natural light (~2,000 lux) to have no crystallization, precipitation, or cloudiness after X hours of being held at Y °C temperature in a clear glass container with no agitation. A sample is considered stable after X hours of being held at Y °C temperature if the sample is clear.

[0475] **Additive Package Stability Study Procedure:** Unstable solutions of additives, or incompatibility between components in additive packages may lead to separation and/or formation of gels, sediment or crystalline material. This procedure is intended to identify likely problems with storage or handling of new and existing additives in additive package formulations.

[0476] The additive package containing the test component is poured into a graduated glass centrifuge tube (as detailed in ASTM D96-88, section 5) until it reaches the tube's 100 ml capacity. The graduations should be clear, and the tube should be clean. The sample tube is stoppered, supported vertically and stored in a calibrated temperature-controlled oven ($\pm 5^\circ\text{C}$). At regular intervals (over 480 hours if not otherwise stated) the centrifuge tube with sample is observed, firstly under natural light and then with a lamp light source (60 watts). The volumetric markings on the tube must face the light source, and impairment of their visibility through the tube due to haze allows for the severity of the instability to be established. Phenomena such as suspensions, crystal formation, gels and phase separation are also reported and are signs of package instability.

[0477] An additive packages (also referred to as a "concentrates" or a "concentrated additive packages") are considered stable if they are determined to be one of the following:

[0478] - "clear and bright", if they have no suspensions, crystal formation, gels or phase separation and the volumetric markings are visible under natural light (~2,000 lux) through the tube. A small amount of sediment (0.5 vol% or less, preferably 0.2 vol% or less) is permissible in the tube.

[0479] - “clear and dark”, if they have no suspensions, crystal formation, gels or phase separation and the volumetric markings are only visible under lamp light source (60 watts) through the tube. A small amount of sediment (0.5 vol% or less, preferably 0.2 vol% or less) is permissible in the tube.

[0480] - “slight haze”, if they have no suspensions, crystal formation, gels or phase separation, other than a slight haze that is not visible under natural light (~2,000 lux), but visible under lamp light source (60 watts) through the tube. A small amount of sediment (0.5 vol% or less, preferably 0.2 vol% or less) is permissible in the tube. A small amount of sediment (0.5 vol% or less) is permissible in the tube.

[0481] **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.

[0482] **Renault TOC4** (Catalysed Oxidation Test – type 4, RNES-B-00023) is a blown air oxidation test run at 170°C with 360 ppm of iron catalyst with air bubbled through the heated sample at 10 L/h for 168 hours. The oxidation of the aged oil at 120 hours is determined by infrared absorbance (IR) and reported in units of absorbance per centimeter, DIN 51453. Kinematic viscosity at 40°C (ASTM D445) is measured at the initiation of the test and at 120 hours and the percentage change in viscosity is calculated.

[0483] **Component analysis:** The relative amounts of mono-, di- and tri-C₈ and mono-, di- and tri-C₉ alkylated diphenylamine are determined using **Ultra-Performance Liquid Chromatography** (UPLC) with UV and mass spectrometer detectors using either **Method 1** detailed in Table A; or, **Method 2**, detailed in Table B. The mass spectrometer chromatograms were used to confirm identity of the mono-, di and tri-C₈ alkyl substituted diphenylamine and the mono-, di- and tri-C₉ alkyl substituted diphenylamines. The UV chromatograms were used to establish the relative % of each C₈-substituted diphenylamine by comparing the area under the curve for each constituent. The UV chromatograms were used to establish the relative % of each C₉-substituted diphenylamine by comparing the area under the curve for each constituent. For the purposes of the examples below, the area under the curve is equated to mass%.

[0484] Table A. UPLC method to analyse octylated diphenylamines and nonylated diphenylamines.

Ultra-performance liquid chromatograph	Agilent Infinite II 1260
Sample concentration	0.4 mg/mL in acetonitrile
Injection volume	1 µL
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

Table B. UPLC method to analyse octylated diphenylamines.

Ultra-performance liquid chromatograph	Agilent Infinite II 1260
Sample concentration	0.5 mg/mL in acetonitrile
Injection volume	5 µL
Flow rate	0.5 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: 60-40% phase A, 40-60% phase B over 2.5 mins Stage 3: 40% phase A, 60% phase B over 0.5 mins Stage 4: 40-0% phase A, 60-100% phase B for 1 mins Stage 5: 0% phase A, 100% phase B for 5.0 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

[0485] In event of conflict between UPLC Method 1 and UPLC Method 2, UPLC Method 1 shall control.

[0486] **Sequence IIH** test for control of viscosity and piston deposits was carried out in a 2014 Chrysler Pentastar port fuel-injected gasoline engine according to test procedure ASTM D8111. The Sequence IIH 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 (ASTM D445-19a), 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 D4739). 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 IIH test is an industry standard test used to evaluate protection against oil thickening and piston deposits by internal combustion engine lubricating compositions.

[0487] **MHT-4-TEOST:** Moderately high temperature deposit test was performed according to ASTM D7097-19.

[0488] **33C-TEOST:** The test evaluates the deposit tendency of a lubricant under high temperature conditions by flowing lubricant through a heated rod and subsequently measures the deposit amount by weight according to ASTM D6335-19.

[0489] **MTM-R Test:** Each oil was tested using a Mini-Traction Machine with reciprocating function (MTM-R) available from PCS Instruments, London, UK. This machine employs an 0.75 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 $<0.02 \mu\text{mRa}$ and surface hardness = 800-920 Hv. The disc was made from AISI52100 grade steel and was uncoated, with surface roughness $<0.02 \mu\text{mRa}$ 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 Zometrics 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.

[0490] MTM TEST: Each oil was tested using a Mini-Traction Machine (MTM) available from PCS Instruments, London, UK. This machine employs a 0.75 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 $<0.02 \mu\text{mRa}$ and surface hardness = 800-920 Hv. The disc was made from AISI52100 grade steel and was uncoated, with surface roughness $<0.02 \mu\text{mRa}$ 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. The mean Stribeck co-efficient of friction of the contact at 135°C was recorded at the end of each test.

[0491] High-Frequency Reciprocating Rig (HFRR): An HFRR device commercially available from PCS Instruments, London, UK (AUTOHFR software, v2.0 PCS4 user manual) was used. This device employs a $\sim 6\text{mm}$ diameter ball as an upper specimen which is reciprocated under an applied load against a lower specimen in the form of a $\sim 10\text{mm}$ diameter x $\sim 3\text{mm}$ 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 $\sim 40\text{Hz}$; stroke length $\sim 1\text{mm}$; applied load $\sim 400\text{g}$; and contact pressure $\sim 1\text{GPa}$. Samples are analyzed at temperatures ranging from $\sim 40^\circ\text{C}$ to $\sim 140^\circ\text{C}$. Sample runs commence when a sample is held at $\sim 40^\circ\text{C}$ for $\sim 1\text{min}$, subject to test conditions for $\sim 5\text{mins}$, ramped at $\sim 5\text{-}15^\circ\text{C/min}$ up another $\sim 20^\circ\text{C}$, held at that increased temperature for $\sim 1\text{min}$, and the cycle repeated every $\sim 20^\circ\text{C}$ up to $\sim 140^\circ\text{C}$, after which the temperature is ramped down to room temperature ($\sim 20\text{-}25^\circ\text{C}$). 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**

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
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
PIBSA-Ester Dispersant	PIBSA ester of hydrocarbyl-bridged naphthyloxy alcohol in oil, See US Patent No. 7,485,603.
Mg Salicylate	Magnesium Salicylate Detergent in oil (TBN 340)
Ca Salicylate	Calcium Salicylate Detergent (200 to 400 TBN) in oil
Ca Salicylate (low TBN)	Calcium Salicylate Detergent (less than 100 TBN) in oil
Ca sulfonate	Calcium sulfonate detergent in oil 300 TBN
Mg sulfonate	Magnesium sulfonate detergent in oil 400 TBN
ZDDP	ZDDP (derived from primary and secondary alcohols) in oil
1° ZDDP	ZDDP derived from primary alcohols in oil
Phenolic antioxidant	Hindered phenol antioxidant, Irganox™ L135
C ₉ -alkyl diphenylamine (C9 DPA)	Di(nonylphenyl)amine antioxidant (such as Naugalube™438L)
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	Polydimethyldisiloxane (PDMS) silicone anti-foamant
Olefin Copolymer VM	Ethylene propylene olefin copolymer in oil
LOFI	Lube oil flow improver - C ₈₋₁₈ dialkylfumarate/vinyl acetate copolymer in 44 m% oil
PMA-LOFI	Lube oil flow improver - Polymethacrylate copolymer in ~ 40 m% oil
Fumarate/PVA – LOFI 2	Lube oil flow improver – C ₁₂₋₁₈ fumarate/vinyl acetate copolymer in 44m% oil, KV100 < 125 cSt
Fumarate/PVA – LOFI 3	Lube oil flow improver – C ₁₂₋₁₈ fumarate/vinyl acetate copolymer in 41m% oil, KV100 > 250 cSt
Star H-SD block copol	Hydrogenated styrene-diene star block copolymer viscosity modifier in oil
PAO	Polyalphaolefin base oil, VI 120-140, KV100 4-6 cSt
diluent	Group I base oil (also referred to as Group I diluent oil)
Ethoxylated lauryl alcohol	Berol™ 1214, Nouryon, Stenungsund, Sweden.
(Dipropylene glycol) dibenzoate	Sigma-Aldrich, Gillingham, UK.
Dodecanol	Sigma-Aldrich, Gillingham, UK.
TMP ester	C ₈ -C ₁₀ Tri-methylol propane ester, Priolube™ 3970, Croda Chemical, Gouda, The Netherlands.
Alkylated naphthalene	Synesstic™ 5 ExxonMobil Chemical, Baton Rouge Louisiana, USA.

Trioctyl trimellitate	Sigma-Aldrich, Gillingham, UK.
Dioctyl terephthalate	Sigma-Aldrich, Gillingham, UK.
C ₁₂ -C ₃₂ Alkylated benzene	Infineum, Notre-Dame-de-Gravenchon, France.
OSA-TEPA	Isomerized octadecenylsuccinic anhydride-tetraethylenepentamine friction modifier (Dixie Chemical, Pasadena, Texas, USA) in ~ 86 m% oil
Alkyl benzene sulfonic acid	Infineum, Notre-Dame-de-Gravenchon, France.
Group II base oil	Group II base oil, ~5 cSt
NEXBASE4PLUS™	NEXBASE4PLUS™ -Group III Basestock, approx 2:1 mix of SynNova 4: Nexbase3043; KV100 ~ 4 cSt
Group III base oil	Group III base oil ~4 cSt

[0492] C₈-alkyl diphenylamine Naugalube™ 438 (reaction product of diphenylamine and 2,4,4-trimethylpentene) from Lanxess (Batch 1, 2 & 3), contains isomers of: mono-C₈-alkyl diphenylamine, tri-C₈-alkyl substituted diphenylamine, and di-C₈-substituted diphenylamine as shown in the table below (isomer content determined by UPLC, Method 1 or 2, as indicated). Irganox™ L01, (bis(4-(1,1,3,3-tetramethylbutyl)phenyl)amine) C₈-alkyl diphenylamine has a lower level of mono-C₈-alkyl diphenylamine as shown in the table below as Batch 4.

C ₈ -alkyl diphenylamine	Batch 1 (*mass%)	Batch 2 (*mass%)	Batch 3 (*mass%)	Batch 4 (*mass%)	Batch 5 (*mass%)
Mono-substituted	8.0	9.6	8.3	0.3	10.4
Di-substituted	89.2	87.0	89.1	99.0	89.0
Tri-substituted	2.8	3.4	2.0	Not detected	0.6

* Determined using UPLC Method 1, based upon the combined weight of the mono-, di-, and tri-substituted isomers.

** Determined using UPLC Method 2, based upon the combined weight of the mono-, di-, and tri-substituted isomers.

Pre-blending Method 1 - Binary Mixtures using Antioxidant Blend Stability Test Method

[0493] C₈-alkyl diphenylamine (Batch 2) and the test component were heated together to 100°C. Upon melting the mixture was stirred for 30 mins, then cooled to 20°C (clear glass container, no agitation after cooling to 20 °C). The time it took for crystallization to occur was observed and recorded (Antioxidant Blend Stability Test Method), the results are given in the table below.

Component	Aniline Point (°C) ASTM D611, Method A	Neat C ₈ -alkyl diphenylamine (Batch 2) to component mass%	Time to crystallization (hours) (except as noted below#, samples were clear/stable until crystallization observed.)
C ₈ -alkyl diphenylamine (Batch 2)		100	4.9
Batch 2 plus component below			
Ethoxylated lauryl alcohol	<0*	50:50	1.2
Ethoxylated lauryl alcohol	<0*	25:75	264
Lauryl alcohol	<0*	50:50	0.5
Lauryl alcohol	<0*	25:75	1.2
(Dipropylene glycol) dibenzoate	< -20**	50:50	24-96 [#]

(Dipropylene glycol) dibenzoate	< -20**	25:75	150
TMP ester	<0*	50:50	5.1
TMP ester	<0*	25:75	264
Alkylated naphthalene	31	50:50	3.4
Alkylated naphthalene	31	25:75	5.2
Trioctyl trimellitate	< -20**	50:50	6.3
Trioctyl trimellitate	< -20**	25:75	24-96 [#]
Dioctyl terephthalate	< -20**	50:50	5.2
Dioctyl terephthalate	< -20**	25:75	264
C ₁₂ -C ₃₂ Alkylated benzene	37.2	50:50	4.4
C ₁₂ -C ₃₂ Alkylated benzene	37.2	25:75	4.7
Group I base oil ~ 5 cSt KV100	100	50:50	0.8
Group I base oil ~ 5 cSt KV100	100	25:75	1.9
OSA-TEPA		90:10	4.6
OSA-TEPA		75:25	1.1
Alkyl benzene sulfonic acid		90:10	5.6
Alkyl benzene sulfonic acid		75:25	3.1
PIBSA-PAM 2300 Mn in ~ 66 m% oil		50:50	4.5
PIBSA-PAM 2300 Mn in ~ 66 m% oil		25:75	24-96 [#]
PMA-LOFI		99:10	5.7
PMA-LOFI		90:10	4.6
PMA-LOFI		75:25	2.0

[#] = clear after 24 hours, but precipitate present at 96 hours.

* = measured to be less than 0 °C, limit of the test performed in the lab.

** = measured to be less than -20 °C, limit of the test performed in the lab.

[0494] Neat C₈-alkyl diphenylamine took less than 5 hours to start to crystallize out at 20°C from a molten state. The time to crystallization of C₈-alkyl diphenylamine was extended to up to 96 hours and more than 96 hours at 25 mass% A.I. with PIBSA-PAM and ethoxylated lauryl alcohol, respectively. However, fluids with higher aniline points like the Group I base oil, did not extend the time to crystallisation at 20°C beyond 5 hours at any A.I. dilution tested. Fluids that have lower aniline points than alkylated naphthalene, e.g. TMP ester, are able to extend the time to crystallisation at both 25 and 50 mass% A.I. at 20°C.

[0495] A 1:1 mixture by mass of C₈-alkyl diphenylamine and TMP ester was used to demonstrate stability of the C₈-alkyl diphenylamine in additive packages and finished oils. The finished oils have demonstrated improved viscosity and deposits control as compared to equivalent engine oils with commonly used diphenylamine antioxidant, di(C₉-alkylphenyl) amine (Nauvalube 438L, Lanxess), at equal A.I. by mass%.

Preblend Method 2 - Ternary mixtures using Antioxidant Blend Stability Test Method

[0496] A combination of C₈-alkyl diphenylamine (Batch 2) with TMP ester (1:1 mixture by mass) and the test component were heated together to 100°C. On melting, the mixture was stirred for 30 mins, then cooled to 20°C (clear glass container, no agitation after cooling to 20 °C). The time it took for crystallization to occur was recorded (Antioxidant Blend Stability Test Method). The results are given in the table below.

	Mass% A.I.	Time to crystallization (hours)

1:3 mixture by mass of C ₈ -alkyl diphenylamine (Batch 2) and TMP ester	25	264
1:1 mixture by mass of C₈-alkyl diphenylamine and TMP ester plus components below	50	
Group I Basestock	25	5-24
Group III Basestock	25	5-24
Borated-PIBSA-PAM	25	<5
PIBSA-PAM	25	5-24
Calcium Salicylate Detergent (TBN 225)	25	>450
Calcium Salicylate Detergent (TBN 64)	25	96-125

[0497] Note, the high TBN calcium salicylate detergent was able to retain C₈-alkyl diphenylamine as a liquid for longer (>180 hours) compared to the reference, C₈-alkyl diphenylamine in TMP ester at 25 mass% active ingredient. The low TBN calcium salicylate detergent mixture remained liquid for up to 5 days, but the dispersants and base oils did not appear to impact retaining the C₈-alkyl diphenylamine in the liquid state.

Additive Package Stability Test

[0498] **Component 1** is a 1:1 mixture of equal masses of C₈-alkyl diphenylamine (Batch 1) and TMP ester that were blended together using Preblend Method 1 from above to give a viscous yellow liquid. The stability of Component 1 in various additive packages is exemplified in the stability testing section below. **Component 2** is C₉-alkyl diphenylamine (the C₉-alkyl diphenylamine has about 68 mass% of di(C₉-alkyl) diphenylamine, about 29 mass% of mono(C₉-alkyl) diphenylamine and about 3 mass% of tri(C₉-alkyl) diphenylamine, based upon the weight of the C₉-alkylated diphenylamines - Isomer content determined by UPLC Method 1). Note that **Component 2** is C₉-alkyl diphenylamine not a C₈-alkyl diphenylamine. C₉-alkyl diphenylamine was selected as the comparison as C₉-alkyl diphenylamine performance is generally considered superior to typical C₈-alkyl diphenylamine performance due to the component crystallizing out of solution, among other things. Hence C₉-alkyl diphenylamine is a more relevant comparison.

Concentrated Additive Package Stability Test 1

[0499] The concentrated additive packages APK A, APK B and APK C were blended at equal mass% A.I with **Component 1 (1:1 Mixture of C₈-alkyl diphenylamine and TMP ester)**, molten C₈-alkyl diphenylamine (melted at 100°C) and solid C₈-alkyl diphenylamine, respectively as in Table 1 below. Two blending methods were used to make the concentrated additive packages:

- Blend Method 1: The C₈-alkyl diphenylamine was blended into the concentrated additive package at the same temperature as the other components, i.e. 55-60°C.
- Blend Method 2: The C₈-alkyl diphenylamine was blended at 80°C with the salicylate detergent, anti-foamant, and diluent oil, and the remaining components were added at 55-60°C. (Note Component 1 was pre-blended with the detergent, anti-foamant, and diluent oil in this method first as a convenience. One or more additive package blend components may be utilized in different combinations for the “pre-blending” step or order of addition. As a non-limiting example, C₈-alkyl

diphenylamine may be pre-blended with one or more of detergent, ZDDP, amine (other than di-C₈-alkyl substituted diphenylamine) and or phenol based antioxidant, anti-foamant, corrosion inhibitor, pour point depressant, friction modifier, anti-wear agent, linear alpha olefins, and/or diluent oil alone or in different combinations for a “pre-blending” step.)

[0500] The concentrated additive packages (also referred to as concentrates) were stored at 20°C and 60°C for up to 12 weeks, the stability by appearance recorded and the results are shown in Table 1 (**Additive Package Stability Study Procedure**).

Table 1.

Components (Mass %)			
Additive package*	APK A	APK B	APK C
Ca Salicylate-225 TBN	16	17	17
Ca Salicylate-65 TBN	4.2	4.5	4.5
Component 1 (Batch 1, 1:1 blend with TMP ester, 50 mass% A.I.)	12		
C ₈ -Alkyl diphenylamine (Molten fluid, Batch 1)		6.4	
C ₈ -Alkyl diphenylamine (Solid, Batch 1)			6.4
Results from additive package Blending studies			
Blend Method 1: APK appearance at 480 hrs at 20°C.	Clear and dark	Clear and dark	Clear and dark
Blend Method 1: APK appearance at 480 hrs at 60°C.	Clear and dark	Clear and dark	Clear and dark
Blend Method 2: APK appearance at 480 hours at 20°C.	Clear and dark	Clear and dark	Clear and dark
Blend Method 2: APK appearance at 480 hours at 60°C.	Clear and dark	Clear and dark	Clear and dark

*each concentrated additive package contained the detergents in bold and had the same amount of PIBSA-PAM, borated PIBSA-PAM, PIBSA, ZDDP, anti-foamant and Group I diluent oil, except for APK A which has each of these components in the additive package at proportionally 0.94 compared to APK B and APK C.

[0501] The blending results in Table 1 using Blend Methods 1 and 2 showed that preblended C₈-alkyl diphenylamine with TMP ester, neat solid C₈-alkyl diphenylamine, and the melted neat C₈-alkyl diphenylamine could be blended into a concentrated additive package to give a clear and stable mixture. All three concentrated additive packages were clear and stable for at least 480 hours.

Concentrated Additive Package Stability Test 2

[0502] The concentrated additive packages APK D, APK E and APK F were blended at equal mass% A.I. with a C₈-alkyl diphenylamine (, i.e., Component 1 (1:1 Mixture of C₈-alkyl diphenylamine (Batch 1) and TMP ester), molten C₈-alkyl diphenylamine (melted at 100°C) and/or solid C₈-alkyl diphenylamine, respectively) as shown in Table 2 below. The blending methods that were used to make concentrated additive packages were:

- Blend Method 1: The C₈-alkyl diphenylamine was blended into the concentrated additive package at the same temperature as the other components, i.e. 55-60°C.

- Blend Method 2: The C₈-alkyl diphenylamine was blended into the concentrated additive package (containing Ca and Mg salicylates, diluent oil, etc.) at 80°C and the remaining components (dispersants, PIBSA) were added at 55-60°C.
- Blend Method 3: The C₈-alkyl diphenylamine was blended into the concentrated additive package (containing Ca salicylates, diluent oil, PIBSA-PAM, borated PIBSA-PAM, PIBSA, etc.) at 55 to 60°C, and the remaining components (Mg salicylate) were added at 55-60°C.
- Blend Method 4: The C₈-alkyl diphenylamine was blended into the concentrated additive package (containing Ca salicylates, diluent oil, PIBSA-PAM, borated PIBSA-PAM, PIBSA, etc.) at 95°C, and the remaining components (Mg salicylates) were added at 55-60°C.
- Blend Method 5: The C₈-alkyl diphenylamine was blended into concentrated additive package (containing Ca and Mg Salicylates, ZDDP, phenolic antioxidant, anti-foam, etc.) at 55-60°C, and the remaining components (dispersants and PIBSA) were added at 55-60°C.

[0503] The concentrated additive package was stored at 20°C and 60°C for 10 weeks, the stability by appearance recorded and the results are shown in Table 2 (Additive Package Stability Study Procedure).

Table 2.

Components (Mass %)							
Additive package***		APK D	APK E	APK E	APK E	APK E	APK F
Mg salicylate		4.1	4.5	4.5	4.5	4.5	4.5
Ca salicylate ~ 225 TBN		6.8	7.6	7.6	7.6	7.6	7.6
Ca salicylate ~ 350 TBN		2.7	3	3	3	3	3
Component 1 (Batch 1, C ₈ -alkyl diphenylamine)		20					
C ₈ -alkyl diphenylamine (Fluid/Molten, Batch 1)			11				
C ₈ -alkyl diphenylamine (Molten, Batch 5)				11			
C ₈ -alkyl diphenylamine (Fluid/Molten, Batch 4)					11		
C ₈ -alkyl diphenylamine (Fluid/Molten, Batch 3)						11	
C ₈ -alkyl diphenylamine (Solid, Batch 1)							11
Results from Blending studies							
Blend Method 1: APK appearance at 480 hrs	Stability at 20°C	Clear and dark	Antioxidant precipitated on cooling to 60°C				Antioxidant insoluble
	Stability at 60°C	Clear and dark					
Blend Method 2: APK	Stability at 20°C	Clear and dark	Crystals form at 288 hrs				Crystals form at 480 hrs

appearance at 480 hrs	Stability at 60°C	Clear and dark	Clear and dark				Clear and dark
Blend Method 3: APK appearance at 589 hrs	Stability at 20°C	-		Crystals form at 589 hrs ****			- -
Blend Method 4: APK appearance at 1176 hrs	Stability at 20°C	-		Crystals form at 1176 hrs ****	Crystals form at 48 hrs	Crystals form at point between 24 and 500 hours ^{^^}	

***each concentrated additive package contained the detergents in bold above and had the same amount of PIBSA-PAM, borated PIBSA-PAM, PIBSA, ZDDP, phenolic anti-oxidant, anti-foamant and Group I diluent oil, except for APK D which has each of these components in at proportionally 0.90 compared to APK E and APK F.

**** average of two measurements

^{^^}data not determined between 24 and 500 hours.

[0504] The results in Table 2 show at the higher treat rate used in this package that blending at 60°C with neat C₈-alkyl diphenylamine, the component is either not soluble (if it is a solid) or comes out of solution on cooling (if it is molten). However, if C₈-alkyl diphenylamine is preblended with TMP ester the concentrated additive package is clear and stable concentrate for at least 480 hours using Blend Method 1.

[0505] Blend Method 2 allows the concentrated additive package to be blended with molten or solid neat C₈-alkyl diphenylamine that is stable on storage for up to 480 hours at 60°C.

[0506] In Blend Method 3, Mg salicylate is left out of the first stage of the blending procedure and added in step 2, whilst PIBSA-PAM, borated PIBSA-PAM and PIBSA are added in the first stage. The result is that molten C₈-alkyl diphenylamine (Batch 5) remains stable in the additive package for 589 hours.

[0507] By carrying out the first blending stage at a higher temperature (95°C) in Blend Method 4, the stability of the additive package with molten neat C₈-alkyl diphenylamine (Batch 5) is increased further verses Blend Method 3.

[0508] In Table 2 the stability of the additive packages are confirmed to be sufficiently stable with molten C₈-alkyl diphenylamine batches 3, 4 and 5 using Blend Method 4, making them suitable for blending into stable finished engine oils.

[0509] Table 3 details the blending experiments using additives that suppress crystallisation using Blending Method 5 (the molten C₈-alkyl diphenylamine was blended with the Ca and Mg salicylate detergents, ZDDP, phenolic antioxidant, anti-foamant, Group 1 diluent, and one of TMP ester, OSA-TEPA, corrosion inhibitor, LOFI, LOFI-2, or LOFI-3, at 60°C for approx 30 minutes, then PIBSA-PAM, borated PIBSA-PAM, and PIBSA, were added at 60°C for approx 30 minutes). Note Blend Method 5 allows prolonged stability of the additive package with molten neat C₈-alkyl diphenylamine (Batch 3), increasing stability length by 48 hrs on storage at 20°C as compared to Blend Method 2 (see Table 2). Addition of OSA-TEPA, Corrosion Inhibitor and or LOFI greatly improved stability with the Adpack formulation remaining stable at 1008 hrs. Addition of Fumarate/PVA – LOFI 2 or Fumarate/PVA – LOFI 3 increased the stability of the Adpack formulation by 336 hrs and 168 hrs respectively vs Adpack E blend Method 5.

Table 3.

Components (Mass %)						
Additive package***	APK H	APK J	APK K	APK M	APK N	APK P
Mg salicylate	4.4	4.4	4.4	4.4	4.4	4.4
Ca salicylate ~ 225 TBN	7.4	7.4	7.4	7.4	7.4	7.4
Ca salicylate ~ 350 TBN	2.9	2.9	2.9	2.9	2.9	2.9
C ₈ -alkyl diphenylamine (Fluid/Molten, Batch 3)	11	11	11	11	11	11
TMP ester	2.8					
OSA-TEPA		2.8				
Corrosion Inhibitor			2.8			
LOFI				2.8		
Fumarate/PVA – LOFI 2					2.8	
Fumarate/PVA – LOFI 3						2.8
Results from Blending studies						
Stability at 20°C appearance at 1008 hours	Crystals form at 336 hrs	Clear and bright	Clear and bright	Clear and bright	Crystals form at 672 hrs	Crystals form at 504 hrs

***each concentrated additive package contained the detergents in bold and had the same amount of PIBSA-PAM, borated PIBSA-PAM, PIBSA, ZDDP, phenolic anti-oxidant, anti-foamant and Group I diluent oil.

Finished Oil-Blending Methods

[0510] The oils in Example 1 (Oil A and Comparative Oil B) were blended by combining LOFI and viscosity modifier in Group III base oil at 75°C, then blending in the concentrated additive package at 60°C. The concentrated additive package was prepared with Component 1 (Batch 1, 1:1 blend with TMP ester, 50 mass% A.I.) or Component 2 (C₉-alkyl diphenylamine) using Blend Method 2.

[0511] The Oils in Examples 2-7 were blended by combining Component 1 or Component 2 with LOFI and viscosity modifier in base oil at 75°C, then a concentrated additive package and organic friction modifier (Examples 4 and 5) were added at 60°C. The additive package contains the remaining components for the engine oil. The concentrated additive package was blended at 60°C by first blending the phenolic antioxidant (Examples 4 and 6), anti-foamant, Mo-friction modifier (Examples 2, 3, 5 and 7), salicylate detergent and ZDDP with diluent oil, followed by PIBSA-PAM, borated PIBSA-PAM, PIBSA-Ester dispersant (Examples 2 and 3), corrosion inhibitor (Examples 5 and 7) and PIBSA.

[0512] The oils in Example 8 (Oil S and Comparative Oil T) were blended by combining LOFI and viscosity modifier in base oil at 75°C, then blending in a concentrated additive package, some ester friction modifier and some dispersant at 60°C. The concentrated additive package was prepared with Component 1 or Component 2 combined with anti-foamant, the remaining ester friction modifier and diluent oil at 95°C, the detergent was added at 95°C and the remaining components were added at 60°C.

[0513] The oils in examples 9-15 (Oils A1 to K3) were blended by combining LOFI and viscosity modifier in base oil at 75°C, then Component 1, or Component 2 (C₉-alkyl diphenylamine) or molten C₈-alkyl diphenylamine (Batch 3) with a concentrated additive package and/or organic friction modifier and/or Mo-Dimer-FM (Examples 10, 15) were added at 60°C. The additive package contains the remaining components for the engine oil. The concentrated additive package was blended with one of two methods. Method 1 (Examples 9-10, 12-15) at 60°C by first blending the phenolic antioxidant, anti-foamant, salicylate detergent and ZDDP, diluent oil and /or Mo-friction modifier (Example 10), followed by PIBSA-PAM, borated PIBSA-PAM, and PIBSA; or Method 2 (Example 11) where anti-foamant and PIBSA-PAM are first blended at 95 °C followed by sulfonate detergent at 95 °C, followed by borated PIBSA-PAM, phenolic antioxidant, PIBSA and diluent oil at 70 °C, followed by ZDDP at 60 °C.

[0514] The formulated oils are shown in Tables 4, 6, 8, 10, 12, 14, 16, 18, 20, 21, 22, 23, 24, 25, 26(a) and 26(b) below.

Example 1

[0515] Component 1 (Batch 1) and **Component 2** were each blended into the formulation described in Table 4 to form Oil A and Comparative Oil B, respectively.

Table 4.

Components ^{^^} (Mass%)	Oil A	Comparative Oil B
Ca Salicylate Detergent TBN ~ 225	2.1	2.1
Ca Salicylate Detergent low TBN ~ 65	0.5	0.5
ZDDP	1.0	1.0
Component 2 (C ₉ -alkyl diphenylamine)		0.8
Component 1 (Batch 1, 1:1 blend with TMP ester, 50 mass% A.I.)	1.6	
Group III base oil, 4-6 cSt	70.2	71
Ash (mass%)	0.78	0.78
Elemental Analysis ICP		
B ppm	70	70
Ca (mass%)	0.18	0.18
Mg (mass%)	0.001	0.001
N (mass%)	0.10	0.10
P (mass%)	0.08	0.08
S (mass%)	0.19	0.19
Si ppm	0.09	0.09

^{^^}each oil had the same amount of PIBSA-PAM, borated PIBSA-PAM, PIBSA, anti-foamant, LOFI, Star H-SD block copol and Group I diluent oil.

[0516] Oil A was observed to be stable (no precipitate, no change in color) after 12 weeks at 0 °C, 20 °C, and 60 °C. Comparative Oil B was observed to have no precipitate and or change in color after 12 weeks at 0 °C, 20 °C, and 60 °C. 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 5.

Table 5. Results

Component (mass%)	Oil A	Comparative Oil B
Component 2 (C ₉ -alkyl diphenylamine)		0.8
Component 1 (Batch 1, 1:1 blend with TMP ester, 50 mass% AI)	1.6	
CEC-L-109-14 test result: Oxidation, FTIR (A/cm)	30.2	29.3
CEC-L-109-14 test result: % Change in K _v 100	10.7	14.5

[0517] In Table 5, the data shows that at the end of the tests, Component 1 (Batch 1) maintained high levels of oxidation control, while obtaining reduced viscosity increase (% Change in K_v100) at end of the test compared to Oil B.

Example 2

[0518] Component 1 (Batch 1) and Component 2 were each blended into the formulation as described in Table 6 to form Oils C, D, E and F and Comparative Oils G, H, I and J, respectively.

Table 6.

Components ** Mass%	C	D	E	F	C-G	C-H	C-I	C-J
Magnesium salicylate	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Calcium salicylate TBN ~225	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, 1:1 blend with TMP ester, 50 mass% A.I.)	1.0	1.5	2	2.5				
Component 2 C ₉ -alkyl diphenylamine					0.5	0.75	1	1.25
Group III base oil	78.5	78.0	77.5	77.0	79.0	78.7	78.5	78.2
Ash (mass%)	0.76	0.76	0.76	0.76	0.76	0.76	0.76	0.76
Elemental Analysis ICP								
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
Si ppm	13	13	13	13	13	13	13	13

** each oil had the same amount of Mo friction modifier, PIBSA-PAM, borated PIBSA-PAM, PIBSA, PIBSA-Ester Dispersant, anti-foamant, Group I diluent oil, LOFI, and Star H-SD block copol.

[0519] Oils C, D, E and F, and Comparative Oils G, H, I and J 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 C	Oil D	Oil E	Oil F	C-G	C-H	C-I	C-J
Component 2 C ₉ -alkyl diphenylamine						0.5	0.75	1.0	1.25
Component 1 (Batch 1, 1:1 blend with TMP ester, 50 mass% A.I.)		1.0	1.5	2	2.5				
CEC-L-109-14 test results	Oxidation FTIR (A/cm)	63.3	41.9	34.8	31.7	63.4	43.9	35.9	30.2
	% Change in K _v 100	80.7	52.0	50.4	44.6	72.9	60.3	52.7	48.2

[0520] At all treat rates the oils containing Component 1 maintained oxidation control. At 0.5 mass% active ingredient, Comparative Oil G performs better than Oil C at viscosity control. Whilst at the higher antioxidant treat rates, 0.75 mass%, 1.0 mass% and 1.25 mass%, Component 1 (Batch 1) has maintained high levels of oxidation control, while obtaining reduced viscosity increase (% Change in K_v100) at end of the test compared to Component 2 at the same respective antioxidant treat rate.

Example 3

[0521] Component 1 and Component 2 were each blended into the formulation described in Table 8 to form Oils K and Comparative Oils L, respectively.

Table 8.

Components*** Mass%	Oil K	Comparative Oil L
Mg Salicylate ~340 TBN	1.5	1.5
Ca Salicylate TBN ~350	0.2	0.2
Ca Salicylate TBN ~ 225	1.4	1.4
ZDDP	1.3	1.3
Component 1 (Batch 1, 1:1 blend with TMP ester, 50 mass% A.I.)	2.0	
Component 2 (C ₉ -alkyl diphenylamine)		1.0
Group III base oil 4-6 cSt	76.5	77.5
Ash (mass%)	1.1	1.1
Elemental Analysis ICP		
B ppm	100	100
Ca (mass%)	0.14	0.14
Mg (mass%)	0.11	0.11

Mo ppm	75	75
N (mass%)	0.13	0.13
P (mass%)	0.09	0.09
S (mass%)	0.22	0.22
Si ppm	7.3	7.3

***each oil had the same amount of Mo friction modifier, PIBSA-PAM, borated PIBSA-PAM, PIBSA, PIBSA-Ester Dispersant, anti-foamant, Group I diluent oil, LOFI, and Star H-SD block copol.

[0522] Oils K and Comparative Oils L 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 9.

Table 9.

Component Mass%		Oil K	Comparative Oil L
Component 2 (C ₉ -alkyl diphenylamine)			1.0
Component 1 (Batch 1, 1:1 blend with TMP ester, 50 mass% A.I.)		2.0	
CEC-L-109-14 test results	Oxidation FTIR (A/cm)	44.0	39.5
	% Change in K _v 100	29.4	34.5

[0523] Much like Examples 1 and 2, Oil K has better viscosity control than Comparative Oil L. In this case Oil K seems to have slightly higher oxidation than Oil L.

Example 4

[0524] Component 1 (Batch 1) and Component 2 were each blended into the formulation described in Table 10 to form Oil M and Comparative Oil N, respectively.

Table 10.

Components*** (Mass%)	Oil M	Comparative Oil N
Magnesium salicylate (340 TBN)	0.6	0.6
Ca Salicylate TBN ~350	0.4	0.4
Ca Salicylate TBN ~ 225	1.0	1.0
ZDDP	1.0	1.0
Phenolic antioxidant	0.2	0.2
Component 1 (Batch 1, 1:1 blend with TMP ester, 50 mass% A.I.)	3.0	
Component 2 (C ₉ -alkyl diphenylamine)		1.5
Group III Basestock	57.3	58.8
Ash (mass%)	0.77	0.77
Elemental Analysis ICP		
B ppm	72	72
Ca (mass%)	0.13	0.13

Mg (mass%)	0.05	0.05
N (mass%)	0.09	0.09
P (mass%)	0.08	0.08
S (mass%)	0.18	0.18
Si ppm	6.2	6.2

***each oil had the same amount of organic friction modifier, PIBSA-PAM, borated PIBSA-PAM, PIBSA, anti-foamant, PAO, Group I diluent oil, LOFI and Star H-SD block copol.

[0525] Oils M and Comparative Oil 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 11.

Table 11.

Component		Oil M	Comparative Oil N
Mass%			
Component 2(C ₉ -alkyl diphenylamine)			1.5
Component 1 (Batch 1, 1:1 blend with TMP ester, 50 mass% A.I.)		3.0	
CEC-L-109-14 test results	Oxidation FTIR (A/cm)	32.7	33.9
	% Change in K _v 100	52.0	62.6

[0526] Much like Examples 1 - 3 Oil M has better viscosity control than Comparative Oil N. In this case Oil M has slightly lower oxidation than Oil N.

Example 5

[0527] Component 1 (Batch 1) and Component 2 were each blended into the formulation described in Table 12 to form Oil O and Comparative Oil P, respectively.

Table 12.

Components* (Mass%)	Oil O	Comparative Oil P
Magnesium salicylate ~340 TBN	0.9	0.9
Calcium salicylate 225 TBN	1.3	1.3
ZDDP	0.9	0.9
Component 1 (Batch 1, 1:1 blend with TMP ester, 50 mass% A.I.)	6.0	
Component 2 (C ₉ -alkyl diphenylamine)		3.0
Group III Basestock	60.1	63.1
Ash (mass%)	0.77	0.77
Elemental Analysis ICP		
B ppm	210	210
Ca (mass%)	0.10	0.10
Mg (mass%)	0.07	0.07

Mo ppm	150	150
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, PIBSA-PAM, borated PIBSA-PAM, PAO, anti-foamant, Group I diluent oil, LOFI, and Star H-SD block copol.

[0528] Oils O and Comparative Oil P 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 13.

Table 13.

Component Mass%		Oil O	Comparative Oil P
Component 2 (C ₉ -alkyl diphenylamine)			3.0
Component 1 (Batch 1, 1:1 blend with TMP ester, 50 mass% A.I.)		6.0	
CEC-L-109-14 test results	Oxidation FTIR (A/cm)	30.8	30.9
	% Change in K _v 100	61.0	75.8

[0529] Much like Examples 1 to 4, Oil O has better viscosity control than Comparative Oil P. In this case Oil O seems to have equivalent oxidation than Oil L.

Example 6

[0530] Component 1 (Batch 1) and Component 2 were each blended into the formulation as described in Table 14 to form Oil Q and Comparative Oil R, respectively.

Table 14.

Components** (Mass%)	Oil Q	Comparative Oil R
Ca Salicylate TBN ~350	0.7	0.7
Ca Salicylate TBN ~ 225	1.2	1.2
ZDDP	0.8	0.8
Phenolic Antioxidant	0.4	0.4
Component 1 (Batch 1, 1:1 blend with TMP ester, 50 mass% A.I.)	1.6	
Component 2 (C ₉ -alkyl diphenylamine)		0.8
PAO	20.0	20.0
Group III Basestock	50.6	51.4
Ash (mass%)	0.84	0.84
Elemental Analysis ICP		
Ca (mass%)	0.18	0.18
N (mass%)	0.15	0.15

P (mass%)	0.08	0.08
S (mass%)	0.19	0.19
Si ppm	7.0	7.0

**each oil had the same amount of PIBSA-PAM, borated PIBSA-PAM, PIBSA, anti-foamant, Group I diluent oil, LOFI, and Star H-SD block copol.

[0531] Oil Q and Comparative Oil R 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 15.

Table 15.

Component (Mass%)		Oil Q	Comparative Oil R
Component 2 (C ₉ -alkyl diphenylamine)			0.8
Component 1 (Batch 1, 1:1 blend with TMP ester, 50 mass% A.I.)		1.6	
CEC-L-109-14 test results	Oxidation FTIR (A/cm)	34.8	39.0
	% Change in K _v 100	55.8	69.7

[0532] Oil Q oxidation and viscosity control was markedly better than Comparative Oil R.

Example 7

[0533] Component 1 (Batch 1) and Component 2 were each blended into the formulation described in Table 16 to form Oil S and Comparative Oil T, respectively.

Table 16.

Components*** (Mass%)	Oil S	Comparative Oil T
Mg Salicylate ~340 TBN	0.7	0.7
Ca salicylate (TBN ~ 350)	0.7	0.7
Ca salicylate, Low TBN	1.0	1.0
ZDDP	1.0	1.0
Component 1 (Batch 1, 1:1 blend with TMP ester, 50 mass% A.I.)	3.8	
Component 2 (C ₉ -alkyl diphenylamine)		1.9
Group III+ base oil	76.2	78.1
Ash (mass%)	0.71	0.71
Elemental Analysis ICP		
B ppm	65	65
Ca (mass%)	0.11	0.11
Mg (mass%)	0.05	0.05
N (mass%)	0.17	0.17
P (mass%)	0.08	0.08
S (mass%)	0.21	0.21
Si ppm	9	9

***each oil had the same amount of Mo friction modifier, PIBSA-PAM, borated PIBSA-PAM, PIBSA, corrosion inhibitor, anti-foamant, Group I diluent, LOFI, and Star H-SD block copol.

[0534] Oil S and Comparative Oil T were tested for oxidation stability and viscosity control using the test conditions detailed in Renault TOC4 test, with a test run time of 168 hours. The data are reported in Table 17.

Table 17.

Component Mass%		Oil S	Comparative Oil T
Component 2 (C ₉ -alkyl diphenylamine)			1.9
Component 1 (Batch 1, 1:1 blend with TMP ester, 50 mass% A.I.)		3.8	
Renault TOC 4 Results	Oxidation FTIR (A/cm)	281	277
	% Change in K _v 40	19.4	52.8

[0535] Much like Examples 1 – 6, Oil S has better viscosity control than Comparative Oil T.

Example 8

[0536] Component 1 (Batch 2) and Component 2 were each blended into the formulation as described in Table 18 to form Oil U and Comparative oil V, respectively.

Table 18.

Constituent (Mass%) [^]	Oil U	Comparable Oil V
Ca sulfonate	0.9	0.9
Mg sulfonate	0.5	0.5
ZDDP	0.9	0.9
Component 1 (Batch 1, 1:1 blend with TMP ester, 50 mass% A.I.)	2.0	
Component 2 (C ₉ -alkyl diphenylamine)		1.0
Group III base oil	84.9	85.9
Ash (mass%)	0.63	0.63
Elemental Analysis ICP		
Ca (mass%)	0.10	0.10
Mg (mass%)	0.04	0.04
Mo ppm	69	69
N (mass%)	0.06	0.06
P (mass%)	0.06	0.06
S (mass%)	0.20	0.20
Si ppm	9	9

[^] each oil had the same amount of PIBSA-PAM, ODSA, Mo friction modifier, Ester friction modifier, anti-foamant, Group I diluent oil, LOFI, and Star H-SD block copol.

[0537] Oil U and Comparative Oil V were tested for their ability to control viscosity increase (PVIS) and piston deposits (WPD merits) in the Seq IIIH test (ASTM D8111) as described above. The data are reported in Table 19.

Table 19.

Component	Oil U (mass%)	Comparative Oil V (mass%)
Component 2 (C ₉ -alkyl diphenylamine)		1.0
Component 1 (Batch 1, 1:1 blend with TMP ester, 50 mass% A.I.)	2.0	
Sequence IIIH PVIS (%)	3.4	76.6
Sequence IIIH WPD (merits)	5.5	4.3

[0538] The viscosity control is much better for Oil U (Component 1, Batch 2) than Comparative Oil V (Component 2), and the difference is greater than observed in blown air oxidation tests. Unexpectedly, there was also a large difference in the level of piston deposits. Comparative Oil V has weighted piston deposits (WPD merits) of 4.3 which is lower than the anticipated API GF-7 level of 4.6; however, Oil U has a WPD merits of 5.5 which represents a significant improvement in deposit control compared to Comparative Oil V and the anticipated API GF-7 specification limit for WPD.

Example 9

[0539] It is shown in the preceding examples that the aminic antioxidant with low levels of mono-C₈-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.

[0540] Component 1 (1:1 Mixture of C₈-alkyl diphenylamine and TMP ester), C₈-alkyl diphenylamine (Batch 3) and Component 2 (C₉-alkyl diphenylamine) were each blended into the formulations described in Tables 20 to 26(b) below.

[0541] In Table 20 lubricating oils are formulated with Component 1 (1:1 Mixture of C₈-alkyl diphenylamine and TMP ester), molten C₈-alkyl diphenylamine (Batch 3) and Component 2 (C₉-alkyl diphenylamine), 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 20

Constituent* (mass%)	C-Oil A1	C-Oil B1	Oil C1	Oil D1	Oil E1	Oil F1	Oil G1
Borated-PIBSA-PAM	0.6	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	0.6

Ca Salicylate	1.4	1.4	1.4	1.4	1.4	1.4	1.4
Component 2 (C ₉ -alkyl diphenylamine)	1.0	1.0					
Component 1 (Batch 2, 1:1 blend with TMP ester, 50 mass% A.I.)			2.0	2.0			2.0
C ₈ -alkyl diphenylamine (Batch 3, Molten)					1.0	1.0	
Organic Friction Modifier	0.6		0.6		0.6		0.5
Group III base oil	balance	balance	balance	balance	balance	balance	balance
Elemental Analysis ICP							
Ash (mass%)	0.77	0.77	0.77	0.77	0.77	0.77	0.77
B ppm	72	72	72	72	72	72	72
Ca (mass%)	0.13	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	0.05
N (mass%)	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
S (mass%)	0.18	0.18	0.18	0.18	0.18	0.18	0.18
Performance Data							
CEC-L-109-14 test % Change in Kv100	89.0	56.8	60.1	40.2	48.7	38.3	
MHT-4 TEOST (mg)	21.9		14.5				
TEOST 33C (mg)	27.0		21.8				
MTM: Friction Coefficient, 135°C, 0.02 m/s	0.104	0.782	0.104				0.675
HFRR: Wear Scar Diameter (μm)	197		203				
HFRR: avg Friction Coefficient at 140°C	0.136	0.151	0.128				0.134
MTM-R: Avg Traction Coefficient at 100°C	0.092	0.103	0.093				0.097
MTM-R: Wear Scar Volume/ μm ³	137770	191720	99255				192360

*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.

[0542] Oil C1, D1, E1 and F1 containing C₈-alkyl diphenylamine outperform their respective comparative oils with Component 2 (C-Oil A1 and C-Oil B1) by between 16 and 40% (See Figure 3). This is consistent with the observations made in Examples 1-6.

[0543] Due to the improved L109 viscosity control performance when using C₈-alkyl diphenylamine versus Component 2, increased treat rates of GMO can be used when formulating with C₈-alkyl diphenylamine. To calculate the amount of GMO that would be used in the inventive examples, with Component 1, to obtain the L109 viscosity performance equivalent to a comparative Component 2 blend, solve for X in the following equation (See Figure 3):

$$Y = 40.2 + 33.2X,$$

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:

$$X = (56.8 - 40.2)/33.2 = 0.5 \text{ mass\% GMO.}$$

Oil G1 was formulated with Component 1 and 0.5 mass% GMO and was compared to Comparative Oil B1 formulated with Component 2 and zero mass% GMO. The data show good reductions for Oil G1 in HFRR friction coefficient (0.134 vs 0.151) and MTM friction coefficient (0.675 vs 0.782), as well as maintaining wear performance in MTM-R. Lower friction will translate in an engine to greater fuel economy. For Comparative Oil B1 vs Oil G1, we predict that Oil G1 will have similar CEC-L-109-14 viscosity control results to Comparative Oil B1.

[0544] Oil C1 maintains similar friction performance in the MTM and MTM-R tests as Comparative Oil A1, whilst surprisingly showing lower wear scar volume in the MTM-R test (99255 vs 137770). Further note that for Comparative Oil A1 in comparison with Oil C1 (both containing 0.6 mass% GMO), Oil A1 obtains lower viscosity growth in CEC-L-109-14 (89.0% vs 60.1%) in addition to the reduced MTM-R wear scar volume.

[0545] These data indicate that the inventive antioxidant Component 1 enables higher treat rates of friction modifier GMO with maintained or 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.

[0546] Also note, Component 1 shows better deposit control in the 33C TEOST and MHT-4 TEOST (Comparative Oil A1 vs Oil C1). This is consistent with the large improvement in WPD in the Seq IIIH exemplified in Example 8.

Example 10

[0547] Table 21 shows inventive oils with Component 1 (1:1 Mixture of C₈-alkyl diphenylamine and TMP ester) or C₈-alkyl diphenylamine (Batch 3, molten) and comparative Component 2 (C₉-alkyl diphenylamine) oils blended with either trimeric MoDTC friction modifier or dimeric MoDTC friction modifier.

Table 21.

Constituent* (mass%)	C-Oil H1	C-Oil J1	Oil K1	Oil L1	Oil M1	Oil N1	C-Oil O1	C-Oil A1
Borated-PIBSA-PAM	0.6	0.6	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	0.6	0.6
Ca Salicylate	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4
Mo-friction modifier		0.9		0.9		0.9		0.0
Mo-Dimer FM	0.5		0.5		0.5		0.23	
Component 2 (C ₉ -alkyl diphenylamine)	1.0	1.0					1.0	1.0
Component 1 (Batch 2, 1:1 blend with TMP ester, 50 mass% A.I.)			2.0	2.0				

C ₈ -alkyl diphenylamine (Batch 3, molten)					1.0	1.0		
Organic Friction Modifier	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
Elemental Analysis ICP								
Ash (mass%)	0.77	0.77	0.77	0.77	0.77	0.77	0.77	0.77
B ppm	72	72	72	72	72	72	72	72
Ca (mass%)	0.13	0.13	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	0.05	0.05
Mo ppm	500	500	500	500	500	500	228	0
N (mass%)	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
S (mass%)	0.24	0.27	0.24	0.27	0.24	0.27	0.21	0.18
Performance Data								
CEC-L-109-14 % Change in Kv100	180.3	126.1	130.6	59.8	92.7	84.6		
MTM: Friction Coefficient, 135°C, 0.02 m/s			0.103	0.103			0.104	0.104
HFRR: Wear Scar Diameter μm			178	164.5			217	197
HFRR Friction Coefficient at 140°C			0.068	0.067			0.077	0.136
MTM-R: Avg Traction Coefficient at 100°C			0.04	0.034			0.039	0.092
MTM-R: Wear Scar Volume/ μm^3			35117				39716	137770

*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.

[0548] Comparative Oil O1 was formulated with Component 2 (C₉-alkyl diphenylamine) and 0.23 mass % molybdenum dithiocarbamate dimer, providing 228 ppm Mo, and compared to Oil K1 formulated with Component 1 and 0.5 mass % molybdenum dithiocarbamate dimer, providing 500 ppm Mo.

[0549] Inventive Oil K1, containing 272 ppm more Mo than Comparative Oil O1 showed lower HFRR friction coefficient (0.068 vs. 0.077) and HFRR wear scar diameter (178 vs 217 μm) and matched MTM-R traction coefficient (0.04 vs 0.039) and reduced MTM-R wear scar volume (35,117 vs 39,716 μm^3). Lower friction is expected to translate in an engine into greater fuel economy. Likewise, the higher Mo content that can be used in oil compositions because of the presence of Component 1 is expected to reduce low speed pre-ignition events. Oil K1 is expected to have a similar or better percent change in viscosity (CEC-L-109) as compared to Comparative Oil O1.

[0550] Comparative Oil A1 is expected to have a similar percent change in viscosity (CEC-L-109) as compared to Oil L1. Comparative Oil A1 was formulated with Component 2 (C₉-alkyl diphenylamine), providing 0 ppm Mo, and compared to Oil L1 formulated with Component 1 and 0.9 mass % molybdenum dithiocarbamate trimer, providing 500 ppm Mo. Note that Oil L1 shows lower HFRR friction coefficient

(0.067 vs. 0.136) and HFFR wear scar diameter (165 vs 197 μm) and reduce MTM-R traction coefficient (0.034 vs 0.092), whilst maintaining friction performance in the MTM test.

[0551] Comparative Oil H1 was formulated with Component 2 (C_9 -alkyl diphenylamine) and 0.50 mass % molybdenum dithiocarbamate dimer, providing 500 ppm Mo, and compared to inventive Oils K1 and M1 formulated with Component 1 or C_8 -alkyl diphenylamine (Batch 3) and 0.5 mass % molybdenum dithiocarbamate dimer, providing 500 ppm Mo. Note that Oils K1 and M1 have significantly reduced CEC-L-109-14 percent increase in viscosity as compared to Comparative Oil H1 (130.6% or 92.7% vs 180.3%).

[0552] Comparative Oil J1 was formulated with Component 2 (C_9 -alkyl diphenylamine) and 0.90 mass % molybdenum dithiocarbamate dimer, providing 500 ppm Mo, and compared to inventive Oils L1 and N1 formulated with Component 1 or C_8 -alkyl diphenylamine (Batch 3, molten) and 0.9 mass % molybdenum dithiocarbamate dimer, providing 500 ppm Mo. Note that Oils L1 and N1 have significantly reduced CEC-L-109-14 percent increase in viscosity as compared to Comparative Oil J1 (59.8% or 84.6% vs 126.1%).

[0553] Due to the improved L109 viscosity control performance when using C_8 -alkyl diphenylamine versus Component 2 (C_9 -alkyl diphenylamine) in the presence of 500 ppm Mo, increased treat rates of molybdenum dithiocarbamate dimer can be used when formulating with C_8 -alkyl diphenylamine. 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 blend, solve for X in the following equation:

$$Y = 89 + 0.183X,$$

where Y equals the L109 viscosity increase of the inventive Component 1 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 blend (Oil K1) solve for X in the equation above, where Y is 130.6. For our example, $X = (130.6 - 89)/0.183 = 227$ ppm Mo or 0.23 mass% of Mo-Dimer FM.

[0554] Due to the improved L109 viscosity control performance when using C_8 -alkyl diphenylamine vs Component 2 (C_9 -alkyl diphenylamine) 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 C_8 -alkyl diphenylamine. To calculate the amount of Mo (ppm) that would be used in the comparative examples to obtain equivalent L109 viscosity control to inventive Component 1 blend, the equation $Y = 0.0742X + 89$ is used where Y equals L109 viscosity increase performance of Component 1 and X equals Mo ppm from molybdenum dithiocarbamate trimer.

[0555] For example, to calculate the amount of molybdenum from dithiocarbamate trimer that would be used in the comparative example (C-Oil A1) to give equivalent L109 viscosity control with to comparative example (Oil L1), solve for X in above equation where Y is 59.8. For our example, $X = (59.8 - 89)/0.0742 < 0$ ppm Mo from molybdenum dithiocarbamate trimer.

Example 11

[0556] In Table 22 lubricating oils are formulated with Component 1 (1:1 Mixture of C₈-alkyl diphenylamine and TMP ester), molten C₈-alkyl diphenylamine Batch 3 and Component 2. For each component there is a representative oil with an all sulphonate detergent system (C-Oil P1, Oil R1, Oil T1), with low molecular weight dispersant (C-Oil Q1, Oil S1, Oil U1) and with a high magnesium all sulfonate detergent system (C-Oil V1, Oil W1, Oil X1). In each of the different formulation spaces oils blended with Component 1 (1:1 Mixture of C₈-alkyl diphenylamine and TMP ester) or molten C₈-alkyl diphenylamine Batch 3 had better viscosity control in the L-109 test than the comparative oils with Component 2.

[0557] Component 1 in an all-sulfonate detergent system (Oil R1) demonstrates better deposit control than equivalent formulations with Component 2 (C-Oils P1) in a standard industry bench test, MHT-4 TEOST, as well as maintaining performance in the 33C TEOST. On the other hand, Component 1 with low molecular weight detergent (Oil S1) demonstrates better deposit control than equivalent formulations with Component 2 (C-Oils Q1) in a standard industry bench test, 33C TEOST, as well as maintaining performance in the MHT-4 TEOST.

[0558] In a lubricating oil composition with a high magnesium sulfonate detergent system blended with molten C₈-alkyl diphenylamine Batch 3 (Oil X1) deposit control in 33C and MHT-4 TEOST was equivalent to the comparative oil with Component 2 (C-Oil V1). Surprisingly, a high magnesium sulfonate detergent system Oil W1, blended with Component 1 (1:1 Mixture of C₈-alkyl diphenylamine and TMP ester), had exceptional deposit control in the 33C and MHT-4 TEOST tests, 0.9 and 3.1 mg respectively.

[0559] The comparative and inventive antioxidants blended into oils with a high magnesium sulfonate detergent system (C-Oil V1, Oils W1 and X1) were tested for friction and wear performance in the MTM-R and HFRR tests. The inventive oils' friction/traction performance matched that of the Comparative Oil V1. Oil X1 had less measured wear than Comparative Oil V1 in the two tests.

Table 22.

Constituent* (mass%)	C-Oil P1	C-Oil Q1	Oil R1	Oil S1	Oil T1	Oil U1	C-Oil V1	Oil W1	Oil X1
LMW PIBSA-PAM		1.5		1.5		1.5			
Borated-PIBSA-PAM	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Mg Salicylate		0.6		0.6		0.6			
Ca Salicylate		1.4		1.4		1.4			
Ca sulfonate	1.1		1.1		1.1		0.7	0.7	0.7
Mg sulfonate	0.5		0.5		0.5		0.9	0.9	0.9
Component 2 (C ₉ -alkyl diphenylamine)	1.0	1.0					1.0		
Component 1 (Batch 2, 1:1 blend with TMP ester, 50 mass% A.I.)			2.0	2.0				2.0	

C ₈ -alkyl diphenylamine (Batch 3, molten)					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	0.77	0.77	0.77	0.77	0.77	0.77	0.77	0.77
B ppm	72	72	72	72	72	72	72	72	72
Ca (mass%)	0.13	0.13	0.13	0.13	0.13	0.13	0.09	0.09	0.09
Mg (mass%)	0.05	0.05	0.05	0.05	0.05	0.05	0.08	0.08	0.08
N (mass%)	0.12	0.14	0.12	0.14	0.12	0.14	0.14	0.14	0.14
P (mass%)	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08
S (mass%)	0.20	0.18	0.20	0.18	0.20	0.18	0.18	0.18	0.18
Performance Testing									
CEC-L-109-14 % Change in Kv100	63.4	68.7	53.5	53.7	44.7	42.7	172.3	65.5	97
MHT4 TEOST (mg)	38.2	22.8	14.5	23			23.9	3.1	20.6
33C TEOST (mg)	5.2	16.6	7.6	6.7			28.8	0.9	29.7
HFRR: Wear Scar Diameter μm							179.5	187	166.5
HFRR Friction Coefficient at 140°C							0.156	0.151	0.155
MTM-R: Avg Traction Coefficient at 100°C							0.093	0.089	0.087
MTM-R: Wear Scar Volume/ μm^3							50970	66243	41460

*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 12

[0560] In Table 23, compatibility of C₈-alkyl diphenylamine is demonstrated with Group II and renewable base oils. The performance of C₈-alkyl diphenylamine was evaluated in these base oils in the CEC-L109-14 test. Comparative Oil A2 was formulated with a renewable base oil, Nexbase4plus™. It was found that the enhanced viscosity control demonstrated with oils blended with C₈-alkyl diphenylamine (1:1 Mixture of C₈-alkyl diphenylamine and TMP ester, or molten C₈-alkyl diphenylamine, Batch 3) in previous examples was maintained. Similarly, in a Group II/III blend, C₈-alkyl diphenylamine in Oil D2 and Oil F2 had lower viscosity increases in the L109 test than Component 2 (Comparative Oil B2), by 22% and 29% respectively. C₈-alkyl diphenylamine can therefore successfully be used in formulations that are formulated to be lower cost or to be more sustainable.

Table 23.

Constituent* (mass%)	C-Oil A2	C-Oil B2	Oil C2	Oil D2	Oil E2	Oil F2
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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
Component 2 (C ₉ -alkyl diphenylamine)	1.0	1.0				
Component 1 (Batch 2, 1:1 blend with TMP ester, 50 mass% A.I.)			2.0	2.0		
C ₈ -alkyl diphenylamine (Batch 3, Molten)					1.0	1.0
Organic Friction Modifier	0.6	0.6	0.6	0.6	0.6	0.6
Group II		30.0		30.0		30.0
NEXBASE4PLUS™	59.3		59.3		59.3	
Group III base oil		29.3		29.3		29.3
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
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 test % Change in Kv100	79.3	81.1	55.7	59	51.6	51.7

*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 13

[0561] In Table 24, the CEC-L109-14, friction and wear performance of C₈-alkyl diphenylamine was tested varying either the detergent system or ZDDP type.

[0562] Oils blended with C₈-alkyl diphenylamine, either blended in a polar diluent (Oils C1, H2, J2, K2) or as a molten liquid (Oil E1, L2, M2, N2), performed better in the CEC-L109-14 for viscosity control than blends containing Component 2 (Oil A1, E2, F2, G2).

[0563] Comparison Oil O2 was formulated with Component 2 and 0.6 mass% magnesium detergent, 600 ppm Mg, which is calculated to give equivalent L109 viscosity increase performance to Oil J2 containing 800 ppm Mg. The performance of the two oils were compared in friction (MTM) and wear (HFRR) tests. Oil J2 had lower wear in the HFRR test and lower friction/traction in the MTM, MTM-R and HFRR tests than Comparative Oil O2. As well improving fuel economy and engine wear, higher magnesium treat rates can enable reduced low-speed pre-ignition in gasoline engines.

[0564] In formulations with all calcium sulfonate detergent systems (Oil H2 and C-Oil E2), the oil with C₈-alkyl diphenylamine had lower friction and wear in the MTM-R and HFRR tests.

[0565] Using ZDDP made from all primary alcohols gives improved performance in the MTM-R test with Component 1 compared to Component 2. Oil H2 has better traction than comparative Oil G2 (0.087 vs 0.096) and reduced wear scar volume (68337 vs 123000 μm^3).

Table 24.

Constituent* (mass%)	C-Oil A1	C-Oil E2	C-Oil F2	C-Oil G2	Oil C1	Oil H2	Oil J2	Oil K2	Oil E1	Oil L2	Oil M2	Oil N2	C-Oil O2
Borated-PIBSA-PAM	0.6	0.6	0.6	0.6	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	0.6		1.0	0.6	0.6
Ca Salicylate	1.4	2.0	1.0	1.4	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	1.0	1.0		1.0
1° ZDDP				1.1				1.1				1.1	
Component 2 (C ₉ -alkyl diphenylamine)	1.0	1.0	1.0	1.0									1.0
Component 1 (Batch 2, 1:1 blend with TMP ester, 50 mass% A.I.)					2.0	2.0	2.0	2.0					
C ₈ -alkyl diphenyl amine (Batch 3, Molten)									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	0.6	0.6	0.6	0.6
Group III base oil	balance	balance	balance	balance	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	0.77	0.86	0.74	0.77	0.67
B ppm	72	71	71	71	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	0.13	0.21	0.08	0.13	0.08
Mg (mass%)	0.05	0.0	0.08	0.05	0.05	0.0	0.08	0.05	0.05	0.0	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	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	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	0.18	0.18	0.18	0.18
Performance Testing													
CEC-L-109-14 test % Change in Kv100	89	50.3	165.9	98.8	60.1	35.3	94	53.6	48.7	34.5	89.3	50.5	
HFRR: Wear Scar Diameter μm	197	205		172.5	202.5	188.5	205.5	190.5					261
HFRR: Friction Coef. at 140°C	0.136	0.129		0.108	0.128	0.125	0.135	0.124					0.137
MTM-R: Traction	0.092	0.089		0.096	0.093	0.087	0.09	0.081					0.092

Coef. at 100°C													
MTM-R: Wear Scar Volume/ μm^3	137770	73086		123000	99255	68337		70900					

*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.

Example 14

[0566] In Table 25, Oils P2, Q2, R2 have been formulated with higher levels of Borated-PIBSA-PAM at 200 ppm of boron, compared to the baseline oils A1 and C1 at 72 ppm of boron. Increasing the Borated-PIBSA-PAM treat rate gives a reduction in viscosity control with either Component 1 or 2. Consistent with all other testing, viscosity control is better for oils blended with C₈-alkyl diphenylamine than with Component 2 in the presence of high boron.

Table 25

Constituent* (mass%)	C-Oil A1	Oil C1	C-Oil P2	Oil Q2	Oil R2	Oil S2
Borated-PIBSA-PAM	0.6	0.6	1.5	1.5	1.5	1.9
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
ZDDP	1	1	1	1	1	1
1° ZDDP						
Component 2 (C ₉ -alkyl diphenylamine)	1		1			
Component 1 (Batch 2, 1:1 blend with TMP ester, 50 mass% A.I.)		1		1		1
C ₈ -alkyl diphenylamine (Batch 3, molten)					1	
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	0.81	0.81	0.81	0.81
B ppm	72	72	200	200	200	252
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
N (mass%)	0.11	0.11	0.13	0.13	0.13	0.14
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 test % Change in Kv100	89	60.1	102	92	82.7	
MTM: Friction Coef., 135°C, 0.02 m/s	0.104	0.104	0.116			0.109
HFRR: Wear Scar Area, avg (μm^2)	197		275			270
HFRR: avg Friction Coefficient at 140°C	0.136	0.128	0.142			0.142

MTM-R: Avg Traction Coefficient at 100°C	0.092	0.093	0.103			0.088
MTM-R: Wear	137770	99255	189000			121430

[0567] Due to the improved L109 viscosity control performance when using C₈-alkyl diphenylamine versus Component 2, increased treat rates of Borated-PIBSA-PAM can be used when formulating with C₈-alkyl diphenylamine. To calculate the amount of boron in Borated-PIBSA-PAM that would be used in the inventive examples, with Component 1, to obtain the L109 viscosity performance equivalent to a comparative Component 2 blend, solve for X in the following equation (See Figure 4):

$$Y = 13.9 + 0.34X,$$

where Y equals the CEC-L-109 viscosity increase of the comparative Component 2 blend and X is equal to the boron ppm. For example, to calculate the amount of boron from Borated-PIBSA-PAM that can be added to inventive blend Oil C1 to give equivalent L109 viscosity control to the comparative Component 2 blend (C-Oil P2) the following equation is used:

$$X = (102 - 13.9)/0.34 = 259 \text{ ppm of boron, or 1.95 mass\% Borated-PIBSA-PAM.}$$

[0568] Oil S2 was formulated with Component 1 and 1.9 mass% Borated-PIBSA-PAM and was compared to Comparative Oil P2 formulated with Component 2 and 0.6 mass% PIBSA-PAM. The data show a reduction for Oil S2 in MTM friction coefficient (0.109 vs 0.116), and traction coefficient (0.088 vs 0.103) in the MTM-R relative to C-Oil P2. Oil S2 also showed an improvement in wear control compared to C-Oil P2 in the MTM-R (121,430 vs 189,000 μm^3) and in HFRR (270 vs 275 μm), as well as maintaining HFRR friction coefficient (0.142 vs 0.142). Lower friction will translate in an engine to greater fuel economy, and reduced wear which can extend the working life of an engine. For Comparative Oil P2 vs Oil S2, we predict that Oil S2 will have similar CEC-L-109-14 viscosity control results to Comparative Oil P2.

Example 15

[0569] In Table 26(a) and (b), oils blended with C₈-alkyl diphenylamine, whether blended in a polar diluent (Oils A3, B3, C3, D3, E3) or blended as a molten liquid (Oil F3, G3, H3, J3), performed better in the CEC-L109-14 for viscosity control than blends containing Component 2 (Oil T2, U2, V2, W2, X2). The exception is Oil K3 which has greater % viscosity increase than comparative Oil X2 (152.8 vs 134.7), however, the preceding data C₈-alkyl diphenylamine suggests that the Oil K3 result is an outlier and can be discounted.

[0570] The comparative analysis of oils in Tables 26(a) and (b), across a range of formulation spaces, reveals several performance improvements across the MTM, MTM-R, HFRR, 33C TEOST and MHT-4 TEOST tests. For instance, Oil A3 and Oil F3, when compared to C-Oil T2, show improved friction in the HFRR test (0.051 and 0.054 vs 0.070) and MTM test (0.077 and 0.066 vs 0.101), and equivalent traction coefficient in the MTM-R (0.033 and 0.033 vs 0.033). Oil A3, relative to C-Oil T2 also had reduced wear in HFRR test (154 vs 166) and better performance in the MHT4 TEOST. Similarly, Oil B3 and Oil G3, when

compared to C-Oil U2, exhibit improved wear in MTM-R test (42355 and 2270 vs 72083 μm^3), along with better deposit control in the TEOST 33C test.

[0571] Further comparisons show that Oil C3, when tested against C-Oil V2, provides better wear and friction in HFRR tests, and better results in the MHT4 TEOST test. Oil A3 on the other hand, when compared to C-Oil V2 provides better wear and friction in MTM-R test, and better results in the 33C TEOST test.

[0572] Oil D3, E3, J3 and K3 also show improvements in friction, wear and deposit tests when compared to their respective counterparts (C-Oil W2 and C-Oil X2). Overall, the data indicates that the changes in other components within the formulation, such as the inclusion of high boron, high magnesium, and 1° ZDDP, along with Mo dimer FM, lead to notable enhancements in oil performance across multiple testing parameters when comparing C₈-alkyl diphenylamine to Component 2.

[0573] It is impressive to note that the positive impact of the inventive components here can be demonstrated across a wide variety of compositions.

Table 26(a)

[illegible]

S (mass%)	0.24	0.24	0.18	0.24	0.24	0.18	0.24	0.24	0.18
Performance Testing									
CEC-L-109-14 % Change in Kv100	112.6	165.4	132	93.9	133.9	81.7	99.6	152.6	96.7
MTM: Friction Coefficient, 135°C, 0.02 m/s	0.1011	0.1005	0.1005	0.0768	0.0985	0.11	0.0658	0.102	0.1099
HFRR: Wear Scar Diameter μm	165.5	159.5	187	153.5	172.5	176.5	166	163.5	192
HFRR Friction Coefficient at 140°C	0.07	0.062	0.136	0.051	0.06	0.126	0.054	0.058	0.13
MTM-R: Avg Traction Coefficient at 100°C	0.0330	0.0333	0.0857	0.0334	0.0377	0.0928	0.0330	0.0389	0.0811
MTM-R: Wear Scar Volume/ μm^3		72083	59893		42355	63239		2270	33754
TEOST 33C (mg)	34.7	37.7	41.5	32.6	6.9	38.6	42.7	21.5	23.4
MHT4 TEOST (mg)	20.2	19.8	17.3	2.5	24.9	11.3	19.8	14.6	18.8

Table 26(b).

Constituent* (mass%)	C-Oil W2	C-Oil X2	Oil D3	Oil E3	Oil J3	Oil K3
Borated-PIBSA-PAM	0.6	1.5	0.6	1.5	0.6	1.5
Mg Salicylate	1	1	1	1	1	1
Ca Salicylate	1	1	1	1	1	1
ZDDP						
1° ZDDP	1.1	1.1	1.1	1.1	1.1	1.1
Mo Dimer FM	0.5	0.5	0.5	0.5	0.5	0.5
Component 2 (C ₉ -alkyl diphenylamine)	1.0	1.0				
Component 1 (Batch 2, 1:1 blend with TMP ester, 50 mass% A.I.)			2.0	2.0		
C ₈ -alkyl diphenylamine (Batch 3, Molten)					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%)	0.74	0.74	0.74	0.74	0.74	0.74
B ppm	71	200	71	200	71	200
Ca (mass%)	0.08	0.08	0.08	0.08	0.08	0.08
Mg (mass%)	0.08	0.08	0.08	0.08	0.08	0.08
N (mass%)	0.12	0.13	0.12	0.13	0.12	0.13
P (mass%)	0.08	0.08	0.08	0.08	0.08	0.08
S (mass%)	0.23	0.24	0.23	0.24	0.23	0.24
Performance Testing						
CEC-L-109-14	129.3	134.7	87.9	109.7	98	152.8

% Change in Kv100						
MTM: Friction Coefficient, 135°C, 0.02 m/s	0.1002	0.1074	0.0927	0.1204	0.1134	0.1256
HFRR:Wear Scar Diameter μm	152	149	162	180	154.5	160
HFRR Friction Coefficient at 140°C	0.069	0.058	0.072	0.057	0.071	0.058
MTM-R: Avg Traction Coefficient at 100°C	0.0266	0.0285	0.0352	0.0332	0.0317	0.0266
	16	78	57	43	98	69
MTM-R: Wear Scar Volume/ μm^3	43060	61399	264070	166800	15976	8396
TEOST 33C (mg)	29.7	25.6	32.8	34.7	33.8	34.2
MHT4 TEOST (mg)	4.4	22.9	15.1	7.1	15.2	10.2

[0574] Particular advantages to note in the compositions described herein where the inventive antioxidant composition is provided as an inventive combination of C₈ diphenylamine with a polar diluent (such as TMP ester) include:

Comparative Oil	Test Oil (using)	Description of Comparison C8 DPA is 1:1 Mixture of C ₈ -alkyl diphenylamine (Batch 2) and TMP ester), C9 DPA is Component 2	Advantages of C8 DPA CCCCC
Comparative Oil A1	Oil C1	0.6 wt% GMO present C9 DPA compared to C8 DPA	Better L109 Viscometric growth properties, better HFRR friction, better MTM-R wear, better TEOST 33C, better MHT4 teost, no negative impact on MTM friction, no negative impact on MTM-R friction
Comparative Oil B1	Oil D1	0 wt% GMO present C9 DPA compared to C8 DPA	Better L109 Viscometric growth properties
Comparative Oil B1	Oil G1	0 wt% GMO present & AO is C9 DPA vs 0.5 wt% GMO present and C8 DPA	Better MTM friction, better HFRR friction, better MTM-R friction, no negative impact on MTM wear
C-Oil H1	Oil K1	500 ppm Mo from Mo-Dimer FM present, C9 DPA compared to C8 DPA	Better L109 Viscometric growth properties
C-Oil J1	Oil L1	500 ppm Mo from Mo-friction modifier (trimer) present, C9 DPA compared to C8 DPA	Better L109 Viscometric growth properties
C-Oil O1	Oil K1	228 ppm Mo from Mo-Dimer FM & AO is C9 DPA vs 500 ppm Mo (Mo-Dimer FM) & AO is C8 DPA	Better HFRR wear, better HFRR friction, better MTM-R wear, no negative impact on MTM friction, no negative impact on MTM-R friction
Comparative Oil A1	Oil L1	0 ppm Mo & AO is C9 DPA vs 500 ppm Mo from Mo-friction modifier (trimer) and AO is C8 DPA	Better HFRR wear, better HFRR friction, better MTM-R friction, no negative impact on MTM friction
C-Oil P1	Oil R1	Sulfonate detergent present, C9 DPA compared to C8 DPA	Better L109 visc, better MHT4 TEOST, no negative impact on TEOST 33C
C-Oil Q1	Oil S1	LMW PIBSA-PAM present,	Better L109 Viscometric growth properties,

		C9 DPA compared to C8 DPA	better TEOST 33C, no negative impact on MHT4 TEOST
C-Oil V1	Oil X1	Sulfonate detergent providing 800 ppm Mg present C9 DPA compared to C8 DPA	Better L109 Viscometric growth properties, better HFRR friction, better MTM-R friction, better TEOST 33C, better MHT4 TEOST
Comparative Oil A2	Oil C2	Renewable basestock present C9 DPA compared to C8 DPA	Better L109 Viscometric growth properties
Comparative Oil B2	Oil D2	Group II basestock present, C9 DPA compared to C8 DPA	Better L109 Viscometric growth properties
C-Oil E2	Oil H2	Ca Salicylate detergents are present C9 DPA compared to C8 DPA	Better L109 Viscometric growth properties, better HFRR wear, better HFRR friction, better MTM-R wear, better MTM-R friction
C-Oil F2	Oil J2	Mg Salicylate detergent providing 800 ppm Mg is present C9 DPA compared to C8 DPA	Better L109 Viscometric growth properties
C-Oil G2	Oil K2	1° ZDDP is present C9 DPA compared to C8 DPA	Better L109 Viscometric growth properties, better MTM-R friction, better MTM-R wear
C-Oil P2	Oil Q2	200 ppm Boron present, C9 DPA compared to C8 DPA	Better L109 Viscometric growth properties
C-Oil P2	Oil S2	200 ppm B present and AO is C9 DPA vs 252 ppm B is present and AO is C8 DPA	Better MTM friction, better MTM-R friction, better MTM-R wear, no negative impact on HFRR friction, no negative impact on HFRR wear
C-Oil T2	Oil A3	200 ppm Boron and Mo Dimer FM present, C9 DPA compared to C8 DPA	Better L109 Viscometric growth properties, better HFRR wear, better HFRR friction, better MTM friction, better MHT4 TEOST, no negative impact on TEOST 33C, no negative impact on MTM-R friction
C-Oil U2	Oil B3	800 ppm Mg + Mo Dimer FM present C9 DPA compared to C8 DPA	Better L109 Viscometric growth properties, better MTM friction, better MTM-R wear, better TEOST 33C, no negative impact on HFRR friction
C-Oil V2	Oil C3	1° ZDDP and 800 ppm Mg present, C9 DPA compared to C8 DPA	Better L109 Viscometric growth properties, better HFRR wear, better HFRR friction, better MHT4 TEOST, no negative impact on TEOST 33C
C-Oil W2	Oil D3	1° ZDDP, 800 ppm Mg and Mo Dimer FM present, C9 DPA compared to C8 DPA	Better L109 Viscometric growth properties, better MTM friction
C-Oil X2	Oil E3	1° ZDDP, 800 ppm Mg, 200 ppm boron and Mo Dimer FM present C9 DPA compared to C8 DPA	Better L109 Viscometric growth properties, better MHT4 TEOST, no negative impact on HFRR friction

[0575] Particular advantages to note in the compositions described herein where the inventive antioxidant composition is provided to the additive package in fluid (such as molten or liquid crystal) form without polar diluent include:

Comparative Oil	Test Oil	Description of Comparison C8 DPA is molten C ₈ -alkyl diphenylamine (Batch 3), C9 DPA is Component 2	Advantages
Comparative Oil A1	Oil E1	0.6 wt% GMO present, C9 DPA compared to C8 DPA	Better L109 Viscometric growth properties
Comparative Oil B1	Oil F1	0 wt% GMO present, C9 DPA compared to C8 DPA	Better L109 Viscometric growth properties
C-Oil H1	Oil M1	500 ppm Mo from Mo-Dimer FM present, C9 DPA compared to C8 DPA	Better L109 Viscometric growth properties
C-Oil J1	Oil N1	500 ppm Mo from Mo-friction modifier (trimer) present, C9 DPA compared to C8 DPA	Better L109 Viscometric growth properties
C-Oil P1	Oil T1	Sulfonate detergent present, C9 DPA compared to C8 DPA	Better L109 Viscometric growth properties
C-Oil Q1	Oil U1	LMW PIBSA-PAM present, C9 DPA compared to C8 DPA	Better L109 Viscometric growth properties
C-Oil V1	Oil W1	Sulfonate detergent providing 800 ppm Mg present C9 DPA compared to C8 DPA	Better L109 Viscometric growth properties better HFRR wear, better MTM-R friction, better MTM-R wear, better TEOST 33C, no negative impact on HFRR friction, no negative impact on MHT4 TEOST
Comparative Oil A2	Oil E2	Renewable basestock present C9 DPA compared to C8 DPA	Better L109 Viscometric growth properties
Comparative Oil B2	Oil F2	Group II basestock present C9 DPA compared to C8 DPA	Better L109 Viscometric growth properties
C-Oil E2	Oil L2	Ca Salicylate detergents are present C9 DPA compared to C8 DPA	Better L109 Viscometric growth properties
C-Oil F2	Oil M2	Mg Salicylate detergent providing 800 ppm Mg is present C9 DPA compared to C8 DPA	Better L109 Viscometric growth properties
C-Oil G2	Oil N2	1° ZDDP is present C9 DPA compared to C8 DPA	Better L109 Viscometric growth properties
C-Oil P2	Oil R2	200 ppm Boron present, C9 DPA compared to C8 DPA	Better L109 Viscometric growth properties
C-Oil T2	Oil F3	200 ppm Boron and Mo Dimer FM present, C9 DPA compared to C8 DPA	Better L109 Viscometric growth properties, better MTM friction, better HFRR friction, no negative impact on HFRR wear, no negative impact on MTM-R wear, no negative impact on MTM-R friction, no negative impact on MHT4 TEOST
C-Oil U2	Oil G3	800 ppm Mg + Mo Dimer FM present	Better L109 Viscometric growth properties, better MTM-R wear,

		C9 DPA compared to C8 DPA	better TEOST 33C, better MHT4 TEOST, no negative impact on MTM friction, no negative impact on HFRR friction
C-Oil V2	Oil A3	1° ZDDP and 500 ppm Mg present, C9 DPA compared to C8 DPA	Better L109 Viscometric growth properties, better MTM-R friction, better MTM-R wear, better TEOST 33C, no negative impact on HFRR friction
C-Oil W2	Oil J3	1° ZDDP, 800 ppm Mg and Mo Dimer FM present, C9 DPA compared to C8 DPA	Better L109 Viscometric growth properties Better MTM-R wear
C-Oil X2	Oil K3	1° ZDDP, 800 ppm Mg, 200 ppm boron and Mo Dimer FM present C9 DPA compared to C8 DPA	Better MTM-R wear, better MHT4 TEOST, no negative impact on HFRR friction, no negative impact on MTM-R friction

[0576] 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

What is claimed is:

1. A stable antioxidant composition, comprising:
 - a) fluid diphenylamine antioxidant comprising: 1) di(C₈-alkyl substituted phenyl) amine and 2) less than 15 mass% of mono-C₈-alkyl substituted diphenyl amine, based upon the weight of mono- C₈-alkyl substituted phenylamines, di-C₈-alkyl substituted phenylamines, and any tri-C₈-alkyl substituted phenylamines present in the antioxidant composition, (such as 5 to less than 15 mass% mass%, such as 5 to 10 mass%, such as 5 to 7 mass%, of mono-C₈-alkyl substituted diphenyl amine); and
 - b) polar diluent having an aniline point of 25°C or less, and at least 2 available hydrogen-bond acceptor groups (such as ester, ether or alcohol groups) that are 2, 3, 4, 5, or 6 atoms apart, wherein the composition comprising the polar diluent of b) combined with the diphenylamine antioxidant of a) is clear after 96 hours at 20 °C in a clear glass container without agitation according to the Antioxidant Blend Stability Test Method, where the polar diluent is optional when the di(C₈-alkyl substituted phenyl) amine is in molten or liquid crystal form; and wherein the ratio of polar diluent to diphenylamine antioxidant is less than 7:1 (such as 5:1 or less, such as 4:1 or less, such as 3:1 or less, such as 2:1 or less, such as 1:1 or less, such as 0.75:1 to 0.5:1) and wherein polar diluent is optionally not diioshexylphthalate, and or optionally is not a phthalate.
2. The stable antioxidant composition of claim 1, further comprising:
 - 1) detergent, preferably carboxylate and or sulfonate detergent, where the detergent is optionally combined with the diphenylamine antioxidant at a temperature of at least 70 °C; and or
 - 2) one or more base oils, dispersants, friction modifiers; antioxidants, other than the antioxidants of a), pour point depressants, anti-foaming agents, viscosity modifiers, corrosion inhibitors, antirust agents, and/or anti-wear agents.
3. The stable antioxidant composition of claim 1 or claim 2, wherein the polar diluent(s) are one or more diluent(s) selected from the group consisting of:
 - i) di- and tri-esters derived from propylene glycol,
 - ii) C₈₋₁₆ alkyl triesters derived from trimethylolpropane,
 - iii) ethoxylated C₁₀₋₂₄ alcohols, and
 - iv) phthalates, terephthalates, isophthalates, trimellitates and pyromellitates.
4. The stable antioxidant composition of claim 1 or claim 2, wherein the polar diluent comprises one or more of ethoxylated lauryl alcohol, C₈-C₁₀ tri-methylol propane ester, dipropylene glycol dibenzoate, dioctyl terephthalate, and/or trioctyl mellitate.

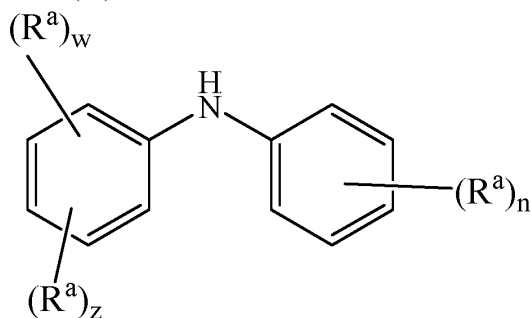
5. The stable antioxidant composition of any of claims 1 to 4 wherein the diphenylamine antioxidant is heated to a temperature of at least 90 °C prior to addition to a concentrate or a lubricating oil composition.
6. A stable concentrate composition comprising:
 - i) the stable antioxidant composition of any of claims 1 to 5;
 - ii) detergent;
 - iii) from 1 to less than 50 mass% base oil, based upon the weight of stable concentrate;
 - iv) optionally one or more dispersants, friction modifiers; antioxidants, other than the antioxidants of i), pour point depressants, anti-foaming agents, viscosity modifiers, corrosion inhibitors, antirust agents, and/or anti-wear agents.
7. The stable concentrate composition of claim 6, wherein the antioxidant composition is combined with the detergent at a temperature of about 50°C or more or 70 °C or more prior to being combined with optional dispersants, friction modifiers; antioxidants, other than the antioxidants of i), pour point depressants, anti-foaming agents, viscosity modifiers, corrosion inhibitors, antirust agents, and/or anti-wear agents.
8. The stable concentrate composition of claim 7, wherein:
 - 1) the antioxidant composition is heated to a molten state and is combined with detergent at a temperature of 70 °C or more or 90 °C or more;
 - 2) the temperature of the combined antioxidant composition and detergent is optionally reduced to 45 °C to less than 70 °C; and
 - 3) the combined antioxidant composition and detergent is optionally further combined with one or more dispersants, friction modifiers; antioxidants, other than the antioxidants of 1), pour point depressants, anti-foaming agents, viscosity modifiers, corrosion inhibitors, antirust agents, and/or anti-wear agents.
9. The stable concentrate composition of claim 7, wherein:
 - 1) solid antioxidant composition is optionally combined with detergent at a temperature of 90°C or more;
 - 2) the temperature of the combination of antioxidant composition and optional detergent is optionally reduced to 45 °C to less than 70 °C; and
 - 3) the combination of antioxidant composition and optional detergent is optionally combined with one or more detergents, dispersants, friction modifiers; antioxidants, other than the antioxidants of a), pour point depressants, anti-foaming agents, viscosity modifiers, corrosion inhibitors, antirust agents, and/or anti-wear agents.

10. The stable concentrate composition of any of claims 6 to 9 wherein the concentrate comprises:
- 1) 95 mass% or more of diphenylamine antioxidant comprising:
 - a) di-C₈-alkyl substituted diphenylamine (such as greater than 85 mass%, such as greater than 90 mass%, such as 85 to 95 mass%, such as 90 to 95 mass%, such as 93 to 95 mass% of di-C₈-alkyl substituted diphenylamine), and
 - b) from 0 to 15 mass% of mono-C₈-alkyl substituted diphenylamine, based upon the weight of the mono- and di-phenylamines present in the concentrate (such as less than 10 mass%, such as 5 to 15 mass%, such as 5 to 10 mass%, such as 5 to 7 mass%) of mono-C₈-alkyl substituted diphenyl amine); and
 - 2) salicylate detergent.
11. The stable concentrate composition of any of claims 6 to 10, wherein:
- 1) the diphenylamine antioxidant comprises:
 - a) di-C₈-alkyl substituted diphenylamine and b) from 0 to less than 5 mass% of mono-C₈-alkyl substituted diphenylamine, based upon the weight of the mono- and di-phenylamines present in the concentrate and b) polar diluent having an aniline point of 25°C or less, and at least 2 available hydrogen-bond acceptor groups (such as ester, ether or alcohol groups) that are 2, 3, 4, 5, or 6 atoms apart; and
 - 2) the detergent comprises one or more of magnesium salicylate detergent, magnesium sulfonate detergent, calcium salicylate detergent, and calcium sulfonate detergent,
 - 3) the concentrate optionally comprises zinc dialkyldithiophosphate, at least a portion of which is derived from primary alcohol, secondary alcohol, or a combination of primary and secondary alcohol,
 - 4) the concentrate optionally comprises organic friction modifier, such as glycerol mono-oleate.
12. A boosterpack comprising:
- 1) the stable antioxidant composition of any of claims 1 to 5;
 - 2) 1 to 99 mass% of detergent; and
 - 3) optionally one or more of the following components.
 - D) optionally, one or more friction modifiers;
 - E) optionally, one or more antioxidants, other than the antioxidants of 1) above;
 - F) optionally, one or more pour point depressants;
 - G) optionally, one or more anti-foaming agents;
 - H) optionally, one or more viscosity modifiers;
 - I) optionally, one or more dispersants;
 - J) optionally, one or more inhibitors and/or antirust agents; and/or
 - K) optionally, one or more anti-wear agents.

13. A stable 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, optionally the base oil is less than 15 wt% ester base oil (such as less than 10 wt% ester base oil, such as less than 5 mass % ester base oil, such as 3 mass% or less, such as less than 1 mass % ester base oil, such as 0 mass % ester base oil), based on weight of base oils present;
 - (ii) the stable antioxidant composition and or a stable concentrate of any of claims 1 to 12.
14. The lubricating oil composition of claim 13, having higher Sequence IIIH weighted piston deposits merits at least 0.5 WPD merits higher or 4.6 merits higher, as compared to the same lubricating oil composition except that the diphenylamine antioxidant has been replaced with the same amount of diphenylamine antioxidant having:
- 1) about 68 mass% di-C₉-alkyl substituted diphenylamine,
 - 2) about 29 mass% of mono-C₉-alkyl substituted diphenylamine, and
 - 3) about 3 mass% of tri-C₉-alkyl substituted diphenylamine, based upon the weight of 1), 2) and 3), as determined by UPLC.
15. The lubricating oil composition of claim 13 or 14, 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 10 %, (such as at least 15%, or 20%, or 30% or 35%, or 40%, or 45%, or 50%, or 55%, or 60%, or 65%, or 70%, or 75%, or 80%, or 85%, or 95%, or 100%, or 105%) less than or within 10 % more than the percent viscosity increase of the same lubricating oil composition except that the diphenylamine antioxidant has been replaced with the same amount of diphenylamine antioxidant having:
- 1) about 68 mass% di-C₉-alkyl substituted diphenylamine,
 - 2) about 29 mass% of mono-C₉-alkyl substituted diphenylamine, and
 - 3) about 3 mass% of tri-C₉-alkyl substituted diphenylamine, based upon the weight of 1), 2) and 3), as determined by UPLC.
16. The lubricating oil composition of claim 13, 14 or 15, further comprising zinc dialkyldithiophosphate, hindered phenolic antioxidant, and or molybdenum containing compound.
17. The lubricating composition of any of claim 13 to 16, 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);
 - F) optionally, one or more pour point depressants;
 - G) optionally, one or more anti-foaming agents;

- H) optionally, one or more viscosity modifiers;
 I) optionally, one or more dispersants;
 J) optionally, one or more inhibitors and/or antirust agents; and/or
 K) optionally, one or more anti-wear agents;

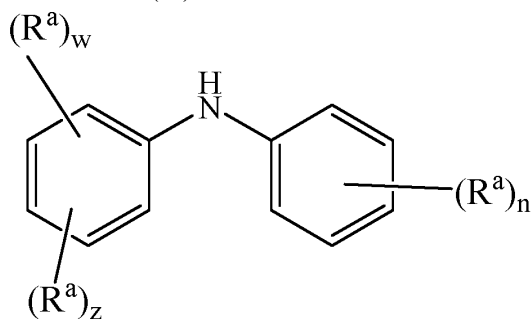
wherein where Formula (III) is:



Formula (III)

where each R^a is independently a linear C_8 alkyl group or branched C_8 alkyl group, n is 1 or 0, z is 0 or 1, and w is 0 or 1, where the branched C_8 alkyl group may be singly, doubly or triply branched at one, two, three, four or more carbons, and may be symmetrically branched or asymmetrically branched.

18. The stable antioxidant compositions, stable concentrates and or stable lubricating oil compositions of claims 1 to 17 wherein the diphenylamine antioxidant comprises:
- from 0 to less than 10 mass% mono- C_8 -alkyl substituted diphenylamine represented by the Formula (III) where n is 1, w is 0, and z is 0 (such as 5 to less than 10 mass%, such as 7 to less than 10 mass%, of mono- C_8 -alkyl substituted diphenyl amine),
 - 90 mass% or more of di- C_8 -alkyl substituted diphenylamine represented by Formula (III), where n is 1, w is 0, and z is 1,
 - from 0 to less than 10 mass% tri- C_8 -alkyl substituted diphenylamine represented by Formula (III), where n is 1, w is 1 and z is 1,
 - 1 mass% or less of unsubstituted diphenylamines represented by Formula (III) where n is 0, w is 0, and z is 0, based upon the total weight of the diphenylamines of a), b), c) and d) present in the composition where Formula (III) is:



Formula (III)

where each R^a is independently a linear C₈ alkyl group or branched C₈ alkyl group, n is 1 or 0, z is 0 or 1, and w is 0 or 1, where the branched C₈ alkyl group may be singly, doubly or triply branched at one, two, three, four or more carbons, and may be symmetrically branched or asymmetrically branched.

19. A method of lubricating an internal combustion engine during operation of the engine comprising:
 - (i) providing to an internal combustion engine the lubricating composition of any of claims 13 to 18;
 - (ii) providing a fuel in the internal combustion engine; and
 - (iii) combusting the fuel in the internal combustion engine.
20. The use of lubricating composition of any of claims 13 to 18 in an internal combustion engine, where the oil sump temperature is greater than 100 °C or greater than 120 °C.
21. A method to prepare a stable concentrate composition comprising:
 - 1) heating an antioxidant composition to a fluid state (such as a liquid or molten state) and combining the antioxidant composition with detergent at a temperature of 70 °C or more;
 - 2) optionally, reducing the temperature of the combination of antioxidant composition and detergent to 45 °C to less than 70 °C; and
 - 3) combining the combination of antioxidant composition and detergent with dispersant,
 - 4) optionally combining with one or more friction modifiers; antioxidants, other than the antioxidants of a), pour point depressants, anti-foaming agents, viscosity modifiers, corrosion inhibitors, antirust agents, and/or anti-wear agents,wherein the antioxidant composition comprises:
 - a) di-C₈-alkyl substituted diphenylamine and b) from 0 to less than 15 mass% of mono-C₈-alkyl substituted diphenylamine, based upon the weight of the mono- and di-phenylamines present in the concentrate; and
 - b) optionally, polar diluent having an aniline point of 25°C or less, and at least 2 available hydrogen-bond acceptor groups (ester, ether or alcohol group) that are 2, 3, 4, 5, or 6 atoms apart, wherein, if polar diluent is present, then the combination of polar diluent of b) combined with the diphenylamine antioxidant of a) is clear after 96 hours at 20 °C in a clear glass container without agitation.
22. The method of claim 21, wherein the fluid state is molten or liquid crystal.
23. A method of improving viscometric growth, as determined by **CEC-L-109-14**, of a lubricating oil in an internal combustion engine, the method comprising: supplying a lubricating oil composition to the internal combustion engine, where the lubricating oil composition comprises an antioxidant composition comprising:

a) fluid (such as molten or liquid crystal) diphenylamine antioxidant comprising: 1) di(C₈-alkyl substituted phenyl) amine and 2) less than 15 mass% of mono-C₈-alkyl substituted diphenylamine (based upon the weight of mono- C₈-alkyl substituted phenylamines, di- C₈-alkyl substituted phenylamines, and any tri- C₈-alkyl substituted phenylamines present in the antioxidant composition); and

b) optional polar diluent having an aniline point of 25°C or less, and at least 2 available hydrogen-bond acceptor groups (such as ester, ether or alcohol groups) that are 2, 3, 4, 5, or 6 atoms apart,

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 10 % (such as at least 15%, or 20%, or 30% or 35%, of 40%, or 45%, or 50%, or 55%, or 60%, or 65%, or 70%, or 75%, or 80%, or 85%) less than or within 10 % more than the percent viscosity increase of the same lubricating oil composition except that the diphenylamine antioxidant has been replaced with the same amount of diphenylamine antioxidant having:

- 1) about 68 mass% di-C₉-alkyl substituted diphenylamine,
- 2) about 29 mass% of mono-C₉-alkyl substituted diphenylamine, and
- 3) about 3 mass% of tri-C₉-alkyl substituted diphenylamine, based upon the weight of 1), 2) and 3), as determined by UPLC.

24. The stable antioxidant compositions, stable concentrates and or stable lubricating oil compositions of claims 1 to 18 wherein the composition comprises: trinuclear molybdenum compound such as molybdenum trimer, such as molybdenum dithiocarbamate trimer.

25. The stable antioxidant compositions, stable concentrates and or stable lubricating oil compositions of claims 1 to 18 wherein the composition comprises: dinuclear molybdenum compound such as molybdenum dimer, such as molybdenum dithiocarbamate dimer, and optionally one, two, or three of:

- a) one or more **borated compounds** (such as borated dispersants, such as borated PIBSA-PAM, such as borated PIBSA-PAM derived from PIB having an Mn of 1600 or less);
- b) **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 540 ppm to 8500 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 more, such as 5000 ppm or more, such as 6000 ppm or more, such as 7000 ppm or more, such as 8000 ppm or more); and
- c) **zinc-based antiwear agents**, such as zinc dialkyldithiophosphates where the alkyl group is derived from one or more primary alcohol(s).

26. The stable antioxidant compositions, stable concentrates and or stable lubricating oil compositions of claims 1 to 18 wherein the composition further comprises one 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 30 mass%, such as 0.1 to 20 mass%, such as 0.1 to 10 mass%, such as 0.1 to 5 mass%, of **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 30 mass%, such as 0.1 to 20 mass%, such as 0.1 to 10 mass%, such as 0.1 to 5 mass%, of **calcium-based detergents**, such as calcium sulfonate and or carboxylate (salicylate) detergents;
 - 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% of one or more **borated compounds** (such as borated dispersants, such as borated PIBSA-PAM, such as borated PIBSA-PAM derived from PIB having an Mn of 1600 or less);
 - 5) 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;
 - 6) 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 450 ppm to 9000 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 more, such as 5000 ppm or more, such as 6000 ppm or more, such as 7000 ppm or more, such as 8000 ppm or more, such as 9000 ppm or more);
 - 7) 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 dialkyldithiophosphates where the alkyl group is derived from one or more primary alcohol(s);
 - 8) 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 800 ppm, 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 more, such as 5000 ppm or more, such as 6000 ppm or more, such as 7000 ppm or more, such as 8000 ppm or more, such as 10,000 ppm or more such as 15,000 ppm or more, such as 20,000 ppm or more); and

9) 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% of **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)).

27. The stable antioxidant compositions, stable concentrates and or stable lubricating oil compositions of claims 1 to 18, further comprising: one or more friction modifiers such as isomerized octadecenylsuccinicanhydride-tetraethylenepentamine), one or more flow improvers (such as dialkyl fumarate/vinyl acetate copolymer (such as C₈-C₁₈ dialkyl fumarate/vinyl acetate copolymer, such as C₁₂-C₁₈ dialkyl fumarate/vinyl acetate copolymer), such as methacrylate polymers); and or one or more corrosion inhibitors (such as one or more triazoles (such as H-1,2,4-triazole-1-methanamine, N,N-bis(2-ethylhexyl) Irgamet™ 30) or benzotriazoles (such as N,N-Bis(2-ethylhexyl)-4-methyl-1h-benzotriazole-1-methanamine, Irgamet™ 39)).
28. A stable concentrate comprising:
- (i) an antioxidant composition (that may optionally be homogeneous (such as a solution) or heterogeneous (such as a dispersion, a slurry, a colloid and the like)), comprising:
 - a) diphenylamine antioxidant comprising: 1) di(C₈-alkyl substituted phenyl) amine and 2) less than 15 mass% (such as 10 mass% or less) of mono-C₈-alkyl substituted diphenylamine (based upon the weight of mono- C₈-alkyl substituted phenylamines, di- C₈-alkyl substituted phenylamines, and tri- C₈-alkyl substituted phenylamines present in the concentrate composition); and
 - b) optionally, polar diluent having an aniline point of 25°C or less, and at least 2 available hydrogen-bond acceptor groups (ester, ether or alcohol group) that are 2, 3, 4, 5, or 6 atoms apart, wherein, if polar diluent is present, then the combination of polar diluent of b) combined with the diphenylamine antioxidant of a) is clear after 96 hours at 20 °C without agitation (such as a combination of 75 mass% of the polar diluent of b) combined with 25 mass% of the diphenylamine antioxidant of a) is clear after 96 hours at 20 °C); and
 - (ii) one or more components selected from the group consisting of **detergents** (such as sulfonate detergents, salicylate detergents, calcium detergents and or magnesium detergents), **dispersants** (such as borated dispersants, such as PIBSA-PAM derived from a polymer (such as polyisobutylene) having an Mn of 1600 g/mol or less), **zinc-based antiwear agents** (such as zinc dialkyldithiophosphates where the alkyl group is derived from one or more primary alcohol(s)); and
 - (iii) base oil (such as renewable base oil and or Group II base oil); and
 - (iv) optionally, one or more components selected from friction modifiers; antioxidants, other than the antioxidants of a), pour point depressants, anti-foaming agents, lube oil flow improvers, corrosion inhibitors, antirust agents, and/or anti-wear agents;
- wherein:

- 1) the antioxidant composition (i) is heated to a fluid state (such as molten state or a liquid crystal state) (such as heating to 98 °C or more) and is combined with the component(s) (ii) and base oil (iii) at a temperature of 70 °C or more, such as 75°C or more, such as 80°C or more, such as 90°C or more, such as 100°C or more;
 - 2) the temperature of the combination of the composition of step 1) is optionally reduced to 45 °C to less than 70 °C; and
 - 3) the combination of the composition of step 1) or step 2) is optionally combined with one or more **detergents** (such as sulfonate detergents, salicylate detergents, calcium detergents and or magnesium detergents); **dispersants** (such as borated dispersants, and or dispersants (such as PIBSA-PAM) derived from a polymer (such as polyisobutylene) having an Mn of 1600 g/mol or less); **zinc-based antiwear agents** (such as zinc dialkyldithiophosphates where the alkyl group is derived from one or more primary alcohol(s)); **friction modifiers** (such as **glycerol-based friction modifiers**, such as glycerol mono-oleate); **antioxidants**, other than the antioxidants of a); **pour point depressants**; **anti-foaming agents**; **viscosity modifiers**; **lube oil flow improvers**; **corrosion inhibitors/antirust agents** (such as triazoles); and/or **anti-wear agents**, other than zinc-based antiwear agents.
29. A stable 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) the stable concentrate of claim 28.
30. The stable concentrates and or stable lubricating oil compositions of claim 28 or 29 wherein the composition comprises: dinuclear molybdenum compound such as molybdenum dimer, such as molybdenum dithiocarbamate dimer, and optionally one, two, or three of:
- a) one or more **borated compounds** (such as borated dispersants, such as borated PIBSA-PAM, such as borated PIBSA-PAM derived from PIB having an Mn of 1600 or less);
 - b) **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 8500 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 more, such as 5000 ppm or more, such as 6000 ppm or more, such as 7000 ppm or more, such as 8000 ppm or more, such as 9,000 ppm or more); and
 - c) **zinc-based antiwear agents**, such as zinc dialkyldithiophosphates where the alkyl group is derived from one or more primary alcohol(s).
31. The stable concentrates and or stable lubricating oil compositions of claims 28 to 30 wherein the composition further comprises one 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%, of **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 0.1 to 10 mass%, such as 0.1 to 5 mass%, of **calcium-based detergents**, such as calcium sulfonate and or carboxylate (salicylate) detergents;
- 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% of one or more **borated compounds** (such as borated dispersants, such as borated PIBSA-PAM, such as borated PIBSA-PAM derived from PIB having an Mn of 1600 or less);
- 5) 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;
- 6) 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 more, such as 5000 ppm or more, such as 6000 ppm or more, such as 7000 ppm or more, such as 8000 ppm or more);
- 7) 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 dialkyldithiophosphates where the alkyl group is derived from one or more primary alcohol(s);
- 8) 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 more, such as 5000 ppm or more); and
- 9) 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% of **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)).

32. The stable antioxidant compositions, stable concentrates and or stable lubricating oil compositions of claims 28 to 31, further comprising: one or more friction modifiers such as isomerized octadecenylsuccinicanhydride-tetraethylenepentamine), one or more flow improvers (such as dialkyl fumarate/vinyl acetate copolymer (such as C₈-C₁₈ dialkyl fumarate/vinyl acetate copolymer, such as C₁₂-C₁₈ dialkyl fumarate/vinyl acetate copolymer), such as methacrylate polymers); and or one or more corrosion inhibitors (such as one or more triazoles (such as H-1,2,4-triazole-1-methanamine, N,N-bis(2-ethylhexyl) Irgamet™ 30) or benzotriazoles (such as N,N-Bis(2-ethylhexyl)-4-methyl-1h-benzotriazole-1-methanamine, Irgamet™ 39)).
33. A method to prepare a stable concentrate composition comprising C₈ antioxidant and one or more additive components, said method comprising:
 - 1) heating an antioxidant composition to a fluid state (such as a liquid or molten state) and combining the antioxidant composition with an additive component for the concentrate at a temperature of 70 °C or more;
 - 2) optionally, reducing the temperature of the combination of antioxidant composition and additive component to 45 °C to less than 70 °C; and
 - 3) optionally, combining the combination of antioxidant composition and additive component with one or more additional additive components;
 wherein the antioxidant composition comprises:
 - a) di-C₈-alkyl substituted diphenylamine and b) from 0 to less than 15 mass% (such as 5 to less than 15 mass%, such as 90 to 95 mass%) of mono-C₈-alkyl substituted diphenylamine, based upon the weight of the mono- and di-phenylamines present in the concentrate; and
 - b) optionally, polar diluent having an aniline point of 25°C or less, and at least 2 available hydrogen-bond acceptor groups (ester, ether or alcohol group) that are 2, 3, 4, 5, or 6 atoms apart, wherein, if polar diluent is present, then the combination of polar diluent of b) combined with the diphenylamine antioxidant of a) is clear after 96 hours at 20 °C in a clear glass container without agitation;
 and wherein the additive components are selected from: A) base oils; C) detergents, D) friction modifiers; E) antioxidants, other than the antioxidants of a) above; F) pour point depressants; G) anti-foaming agents; H) viscosity modifiers; I) dispersants; J) corrosion inhibitors and/or antirust agents; K) anti-wear agents; and variations and combinations thereof.
34. The method of claim 33, wherein the fluid state is molten or liquid crystal.

35. A method of lubricating an internal combustion engine, the method comprising: supplying a lubricating oil composition to the internal combustion engine, where the lubricating oil composition comprises:
- 1) base oil, optionally comprising renewable base oil and or Group II base oil;
 - 2) a fluid antioxidant composition (such as a molten or solution antioxidant composition), comprising:
 - a) diphenylamine antioxidant comprising: 1) di(C₈-alkyl substituted phenyl) amine and 2) less than 15 mass% of mono-C₈-alkyl substituted diphenylamine (based upon the weight of mono- C₈-alkyl substituted phenylamines, di- C₈-alkyl substituted phenylamines, and any tri- C₈-alkyl substituted phenylamines present in the antioxidant composition); and
 - b) optional polar diluent having an aniline point of 25°C or less, and at least 2 available hydrogen-bond acceptor groups (such as ester, ether or alcohol groups) that are 2, 3, 4, 5, or 6 atoms apart; and
 - 3) one, two, three, four, five, six, seven, eight, nine or more components 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) **calcium-based detergents**, such as calcium sulfonate and or carboxylate (salicylate) detergents;
 - 4) **borated compounds** (such as borated dispersants, such as borated PIBSA-PAM, such as borated PIBSA-PAM derived from PIB having an Mn of 1600 or less);
 - 5) **organomolybdenum-based friction modifier**, such as molybdenum dithiocarbamate dimers and or trimers;
 - 6) **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 Mg);
 - 7) **zinc-based antiwear agents**, such as zinc dialkyldithiophosphates where the alkyl group is derived from one or more primary alcohol(s);
 - 8) **salicylate-based detergent**, optionally providing high amounts of Ca and or Mg to the composition (such as 40 ppm to 5000 ppm);
 - 9) **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); and combinations and variations thereof.
36. The method of claim 35, wherein the antioxidant composition is prepared by: 1) heating the diphenylamine antioxidant comprising: 1) di(C₈-alkyl substituted phenyl) amine and 2) less than 15 mass% of mono-C₈-alkyl substituted diphenylamine (based upon the weight of mono- C₈-alkyl substituted phenylamines, di- C₈-alkyl substituted phenylamines, and any tri- C₈-alkyl substituted

- phenylamines present in the antioxidant composition) to a fluid state (such as a liquid or molten state) and combining the fluid antioxidant with one or more additive components at a temperature of 50°C or more, 60°C or more 70°C or more, where the additive components are selected from:
- A) base oils, C) detergents, D) friction modifiers, E) antioxidants, other than the antioxidants of 1) above, F) pour point depressants, G) anti-foaming agents, H) viscosity modifiers, I) dispersants, J) corrosion inhibitors and/or antirust agents, K) anti-wear agents, and variations and combinations thereof;
- 2) optionally, reducing the temperature of the combination of antioxidant composition and additive component(s) to 45°C to less than 70°C; and
- 3) optionally, combining the combination of antioxidant composition and additive component(s) with one or more additional additive components.
37. The method of claim 35 or 36, 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 5 % less (such as at least 10 %, such as at least 15%, or 20%, or 30% or 35%, of 40%, or 45%, or 50%, or 55%, or 60%, or 65%, or 70%, or 75%, or 80%, or 85%, or 95%, or 100%, or 105%) less than the percent viscosity increase of the same lubricating oil composition except that the diphenylamine antioxidant has been replaced with the same amount of diphenylamine antioxidant having: 1) about 68 mass% di-C₉-alkyl substituted diphenylamine, 2) about 29 mass% of mono-C₉-alkyl substituted diphenylamine, and 3) about 3 mass% of tri-C₉-alkyl substituted diphenylamine, based upon the weight of 1), 2) and 3), as determined by UPLC.
38. The method of claim 36, wherein one or more polar diluents, octadecenylsuccinic anhydride-tetraethylenepentamine, one or more triazole corrosion inhibitors, and or one or more dialkyl fumarate/vinyl acetate copolymers are added to the concentrate in the same blending stage as one or more molten C₈ diphenylamine antioxidant are added to the concentrate.
39. The method of claim 36, wherein one or more C₈-C₁₀ tri-methylol propane esters, octadecenylsuccinic anhydride-tetraethylenepentamine, one or more triazole and or benzotriazole corrosion inhibitors, and or one or more C₈ to C₁₈ dialkyl fumarate/vinyl acetate copolymers are added to the concentrate in the same blending stage as one or more molten C₈ diphenylamine antioxidant are added to the concentrate.
40. The method of claim 39 wherein the one or more dialkyl fumarate/vinyl acetate copolymers each have a pour point (ASTM D97) of -10°C or less (such as -15°C or less, such as -20°C or less, such as -25 °C or less, such as -30 °C or less) are added at the same concentrate blending stage as the molten C₈ diphenylamine antioxidant.

41. The method of claim 36, wherein one or more friction modifiers such as isomerized octadecenylsuccinicanhydride-tetraethylenepentamine), one or more flow improvers (such as dialkyl fumarate/vinyl acetate copolymer (such as C₈-C₁₈ dialkyl fumarate/vinyl acetate copolymer, such as C₁₂-C₁₈ dialkyl fumarate/vinyl acetate copolymer), such as methacrylate polymers); and or one or more corrosion inhibitors (such as one or more triazoles (such as H-1,2,4-triazole-1-methanamine, N,N-bis(2-ethylhexyl) Irgamet™ 30) or benzotriazoles (such as N,N-Bis(2-ethylhexyl)-4-methyl-1h-benzotriazole-1-methanamine, Irgamet™ 39)) are added at the same concentrate blending stage as the molten C₈ diphenylamine antioxidant.
42. A stable concentrate composition comprising:
 - a) diphenylamine antioxidant comprising: 1) di(C₈-alkyl substituted phenyl) amine and 2) less than 15 mass% of mono-C₈-alkyl substituted diphenyl amine, based upon the weight of mono- C₈-alkyl substituted phenylamines, di- C₈-alkyl substituted phenylamines, and any tri-C₈-alkyl substituted phenylamines present in the antioxidant composition, (such as 5 to less than 15 mass% mass%, such as 5 to 10 mass%, such as 5 to 7 mass%, of mono-C₈-alkyl substituted diphenyl amine), and
 - b) one or more polar diluents, octadecenylsuccinic anhydride-tetraethylenepentamine, one or more triazole corrosion inhibitors, and or one or more dialkyl fumarate/vinyl acetate copolymers wherein the one or more polar diluents, octadecenylsuccinic anhydride-tetraethylenepentamine, one or more triazole corrosion inhibitors, and or one or more dialkyl fumarate/vinyl acetate copolymers are added to the concentrate in the same blending stage as one or more molten C₈ diphenylamine antioxidant are added to the concentrate.
43. A method to prepare a stable concentrate composition comprising:
 - 1) heating an antioxidant composition comprising:
 - a) diphenylamine antioxidant comprising: 1) di(C₈-alkyl substituted phenyl) amine and 2) less than 15 mass% of mono-C₈-alkyl substituted diphenyl amine, based upon the weight of mono- C₈-alkyl substituted phenylamines, di- C₈-alkyl substituted phenylamines, and any tri-C₈-alkyl substituted phenylamines present in the antioxidant composition, (such as 5 to less than 15 mass% mass%, such as 5 to 10 mass%, such as 5 to 7 mass%, of mono-C₈-alkyl substituted diphenyl amine),
 to a fluid state (such as a liquid or molten state) at a temperature of 70 °C or more;
 - 2) optionally, reducing the temperature of the combination of antioxidant composition to 45 °C to less than 70 °C; and
 - 3) combining the antioxidant composition with detergent and or dispersant;
 - 4) optionally combining the antioxidant composition with one or more friction modifiers; antioxidants, other than the antioxidants of a), pour point depressants, anti-foaming agents, viscosity modifiers, corrosion inhibitors, antirust agents, and/or anti-wear agents;

wherein the antioxidant composition does not comprise solid di-C₈-alkyl substituted diphenylamine.

44. The method of claim 43, where the stable concentrate composition is absent polar diluent.
45. The method of claim 43, wherein one or more C₈-C₁₀ tri-methylol propane esters, octadecenylsuccinic anhydride-tetraethylenepentamine, one or more triazole and or benzotriazole corrosion inhibitors, and or one or more C₈ to C₁₈ dialkyl fumarate/vinyl acetate copolymers are added to the concentrate in the same blending stage as one or more fluid C₈ diphenylamine antioxidants are added to the concentrate.
46. The method of claim 43, wherein one or more friction modifiers such as isomerized octadecenylsuccinic anhydride-tetraethylenepentamine), one or more flow improvers (such as dialkyl fumarate/vinyl acetate copolymer (such as C₈-C₁₈ dialkyl fumarate/vinyl acetate copolymer, such as C₁₂-C₁₈ dialkyl fumarate/vinyl acetate copolymer), such as methacrylate polymers); and or one or more corrosion inhibitors (such as one or more triazoles (such as H-1,2,4-triazole-1-methanamine, N,N-bis(2-ethylhexyl) Irgamet™ 30) or benzotriazoles (such as N,N-Bis(2-ethylhexyl)-4-methyl-1h-benzotriazole-1-methanamine, Irgamet™ 39)) are added at the same concentrate blending stage as the molten C₈ diphenylamine antioxidant.
47. A method of reducing friction, as determined by HFRR Average Friction Coefficient at 140 °C, of a lubricating oil composition in an internal combustion engine, the method comprising: supplying a lubricating oil composition to the internal combustion engine, where the lubricating oil composition comprises an antioxidant composition comprising:
 - a) fluid diphenylamine antioxidant comprising: 1) di(C₈-alkyl substituted phenyl) amine and 2) less than 15 mass% of mono-C₈-alkyl substituted diphenylamine (based upon the weight of mono- C₈-alkyl substituted phenylamines, di- C₈-alkyl substituted phenylamines, and any tri- C₈-alkyl substituted phenylamines present in the antioxidant composition)
 wherein the lubricating oil composition has an HFRR average Friction Coefficient at 140 °C of at least five percent 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) than the HFRR average Friction Coefficient at 140 °C of the same lubricating oil composition except that the fluid diphenylamine antioxidant has been replaced with the same amount of diphenylamine antioxidant having:
 - 1) about 68 mass% di-C₉-alkyl substituted diphenylamine,
 - 2) about 29 mass% of mono-C₉-alkyl substituted diphenylamine, and
 - 3) about 3 mass% of tri-C₉-alkyl substituted diphenylamine, based upon the weight of 1), 2) and 3), as determined by UPLC.

48. A method of reducing wear, as determined by MTM-R Wear Scar Volume, μm^3 , of a lubricating oil composition in an internal combustion engine, the method comprising: supplying a lubricating oil composition to the internal combustion engine, where the lubricating oil composition comprises an antioxidant composition comprising:
- fluid diphenylamine antioxidant comprising: 1) di(C_8 -alkyl substituted phenyl) amine and 2) less than 15 mass% of mono- C_8 -alkyl substituted diphenylamine (based upon the weight of mono- C_8 -alkyl substituted phenylamines, di- C_8 -alkyl substituted phenylamines, and any tri- C_8 -alkyl substituted phenylamines present in the antioxidant composition)

wherein the lubricating oil composition has an at least a 15% reduction (such as at least a 25% reduction, such as at least a 35% reduction, such as at least a 45 % reduction, such as at least a 55% reduction, such as at least a 65 % reduction, such as at least a 75% reduction, such as at least an 85% reduction) in wear scar volume, μm^3 , as compared to the same lubricating oil composition except that the fluid diphenylamine antioxidant has been replaced with the same amount of diphenylamine antioxidant having:

- 1) about 68 mass% di- C_9 -alkyl substituted diphenylamine,
- 2) about 29 mass% of mono- C_9 -alkyl substituted diphenylamine, and
- 3) about 3 mass% of tri- C_9 -alkyl substituted diphenylamine, based upon the weight of 1), 2) and 3), as determined by UPLC; and or

wherein the lubricating oil composition has an at least a 15% reduction (such as at least a 25% reduction, such as at least a 35% reduction, such as at least a 45 % reduction, such as at least a 55% reduction, such as at least a 65 % reduction, such as at least a 75% reduction, such as at least an 85% reduction, such as at least a 95% reduction, such as at least a 99% reduction, such as at least a 99.4% reduction) in wear scar volume, μm^3 , as compared to the same lubricating oil composition except that the fluid diphenylamine antioxidant has been replaced with a 1:1 blend of solid diphenylamine antioxidant and C_8 - C_{10} tri-methylol propane ester providing the same amount of diphenylamine antioxidant to the lubricating oil composition.

49. A method of reducing piston deposits, as determined by MHT4 TEOST, mg, of a lubricating oil composition in an internal combustion engine, the method comprising: supplying a lubricating oil composition to the internal combustion engine, where the lubricating oil composition comprises an antioxidant composition comprising:
- fluid diphenylamine antioxidant comprising: 1) di(C_8 -alkyl substituted phenyl) amine and 2) less than 15 mass% of mono- C_8 -alkyl substituted diphenylamine (based upon the weight of mono- C_8 -alkyl substituted phenylamines, di- C_8 -alkyl substituted phenylamines, and any tri- C_8 -alkyl substituted phenylamines present in the antioxidant composition) , and
 - one or more polar diluents, octadecenylsuccinic anhydride-tetraethylenepentamine, one or more triazole corrosion inhibitors, and or one or more dialkyl fumarate/vinyl acetate copolymers,

wherein the lubricating oil composition has an at least a 15% reduction (such as at least a 25% reduction, such as at least a 35% reduction, such as at least a 45 % reduction, such as at least a 55% reduction, such as at least a 65 % reduction, such as at least a 70% reduction) in deposits, mg, as compared to the same lubricating oil composition except that the fluid diphenylamine antioxidant has been replaced with the same amount of diphenylamine antioxidant having:

- 1) about 68 mass% di-C₉-alkyl substituted diphenylamine,
- 2) about 29 mass% of mono-C₉-alkyl substituted diphenylamine, and
- 3) about 3 mass% of tri-C₉-alkyl substituted diphenylamine, based upon the weight of 1), 2) and 3), as determined by UPLC.

50. A method of reducing piston deposits, as determined by MHT4 TEOST, mg, of a lubricating oil composition in an internal combustion engine, the method comprising: supplying a lubricating oil composition to the internal combustion engine, where the lubricating oil composition comprises an antioxidant composition comprising:

- a) diphenylamine antioxidant comprising: 1) di(C₈-alkyl substituted phenyl) amine and 2) less than 15 mass% of mono-C₈-alkyl substituted diphenylamine (based upon the weight of mono- C₈-alkyl substituted phenylamines, di- C₈-alkyl substituted phenylamines, and any tri- C₈-alkyl substituted phenylamines present in the antioxidant composition)

wherein the lubricating oil composition has an at least a 15% reduction (such as at least a 25% reduction, such as at least a 35% reduction, such as at least a 45 % reduction, such as at least a 55% reduction, such as at least a 65 % reduction) in wear scar volume, μm^3 , as compared to the same lubricating oil composition except that the fluid diphenylamine antioxidant has been replaced with a 1:1 blend of solid diphenylamine antioxidant and C₈-C₁₀ tri-methylol propane ester providing the same amount of diphenylamine antioxidant to the lubricating oil composition.

51. A lubricating oil composition comprising fluid diphenylamine antioxidant comprising: 1) di(C₈-alkyl substituted phenyl) amine and 2) less than 15 mass% of mono-C₈-alkyl substituted diphenylamine (based upon the weight of mono- C₈-alkyl substituted phenylamines, di- C₈-alkyl substituted phenylamines, and any tri- C₈-alkyl substituted phenylamines present in the antioxidant composition).

52. A lubricating oil composition comprising base oil and molten diphenylamine antioxidant comprising: 1) di(C₈-alkyl substituted phenyl) amine and 2) less than 15 mass% of mono-C₈-alkyl substituted diphenylamine (based upon the weight of mono- C₈-alkyl substituted phenylamines, di- C₈-alkyl substituted phenylamines, and any tri- C₈-alkyl substituted phenylamines present in the antioxidant composition).

53. A lubricating oil composition comprising molten diphenylamine antioxidant comprising: 1) di(C₈-alkyl substituted phenyl) amine and 2) less than 15 mass% of mono-C₈-alkyl substituted diphenylamine (based upon the weight of mono- C₈-alkyl substituted phenylamines, di- C₈-alkyl substituted phenylamines, and any tri- C₈-alkyl substituted phenylamines present in the antioxidant composition).
54. A method to prepare a lubricating oil composition comprising combining one or more components with base oil and thereafter combining the base oil and one or more components with molten diphenylamine antioxidant comprising: 1) di(C₈-alkyl substituted phenyl) amine and 2) less than 15 mass% of mono-C₈-alkyl substituted diphenylamine (based upon the weight of mono- C₈-alkyl substituted phenylamines, di- C₈-alkyl substituted phenylamines, and any tri- C₈-alkyl substituted phenylamines present in the antioxidant composition), where the components optionally comprise one or more of:
- B) one or more detergents;
 - D) one or more friction modifiers;
 - E) one or more antioxidants, other than the antioxidants of 1) above;
 - F) one or more pour point depressants;
 - G) one or more anti-foaming agents;
 - H) one or more viscosity modifiers;
 - I) one or more dispersants;
 - J) one or more inhibitors and/or antirust agents; and/or
 - K) one or more anti-wear agents.
55. A method to prepare a lubricating oil composition comprising combining a concentrate with base oil and thereafter combining the base oil and concentrate with molten diphenylamine antioxidant comprising: 1) di(C₈-alkyl substituted phenyl) amine and 2) less than 15 mass% of mono-C₈-alkyl substituted diphenylamine (based upon the weight of mono- C₈-alkyl substituted phenylamines, di- C₈-alkyl substituted phenylamines, and any tri- C₈-alkyl substituted phenylamines present in the antioxidant composition), where the concentrate optionally comprises one or more of:
- B) one or more detergents;
 - D) one or more friction modifiers;
 - E) one or more antioxidants, other than the antioxidants of 1) above;
 - F) one or more pour point depressants;
 - G) one or more anti-foaming agents;
 - H) one or more viscosity modifiers;
 - I) one or more dispersants;
 - J) one or more inhibitors and/or antirust agents; and/or
 - K) one or more anti-wear agents.

56. A method to prepare a lubricating oil composition comprising combining base oil with molten diphenylamine antioxidant comprising: 1) di(C₈-alkyl substituted phenyl) amine and 2) less than 15 mass% of mono-C₈-alkyl substituted diphenylamine (based upon the weight of mono- C₈-alkyl substituted phenylamines, di- C₈-alkyl substituted phenylamines, and any tri- C₈-alkyl substituted phenylamines present in the antioxidant composition) and thereafter combining the base oil and molten diphenylamine with a concentrate, optionally thereafter combining the base oil, molten diphenylamine and concentrate with and at least one additional component, such as one or more of:
- B) one or more detergents;
 - D) one or more friction modifiers;
 - E) one or more antioxidants, other than the antioxidants of 1) above;
 - F) one or more pour point depressants;
 - G) one or more anti-foaming agents;
 - H) one or more viscosity modifiers;
 - I) one or more dispersants;
 - J) one or more inhibitors and/or antirust agents; and/or
 - K) one or more anti-wear agents.
57. A booster package comprising molten diphenylamine antioxidant comprising: 1) di(C₈-alkyl substituted phenyl) amine and 2) less than 15 mass% of mono-C₈-alkyl substituted diphenylamine (based upon the weight of mono- C₈-alkyl substituted phenylamines, di- C₈-alkyl substituted phenylamines, and any tri- C₈-alkyl substituted phenylamines present in the antioxidant composition), and at least one other component, such as one or more of:
- B) one or more detergents;
 - D) one or more friction modifiers;
 - E) one or more antioxidants, other than the antioxidants of 1) above;
 - F) one or more pour point depressants;
 - G) one or more anti-foaming agents;
 - H) one or more viscosity modifiers;
 - I) one or more dispersants;
 - J) one or more inhibitors and/or antirust agents; and/or
 - K) one or more anti-wear agents.