

Lubricant Compositions Containing Aralkyl Substituted Diphenylamine Antioxidants

[0001] This application claims priority to and the benefit of European Patent Office Patent Application No. EP23218550, filed December 20, 2023, the contents of which are incorporated by reference.

FIELD OF THE INVENTION

[0002] This disclosure relates to the use of di(aralkyl 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.

BACKGROUND OF THE INVENTION

[0003] The present invention relates to lubricating oil compositions which exhibit improved oxidation characteristics and/or improved viscometric properties. 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.

[0004] 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.

[0005] 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.

[0006] 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.).

[0007] C₉ alkyl substituted diphenylamine antioxidants are commonly used in engine oil formulations, however there is a desire to replace C₉ alkyl substituted diphenylamine antioxidant. Other diphenylamine antioxidants are available for use but have known issues in lubricating oil compositions such as poor blending into engine oils and/or poor stability in engine oils at treat rates commonly used in modern lubricating oils.

[0008] 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 substantially 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 substantially 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 aralkyl substituted diphenylamine-based 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.

[0009] 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.

[0010] Aralkyl substituted diphenylamines are often solids that are difficult to combine directly into lubricating oil compositions and even if they are combined into an oil formulation, the aralkyl substituted diphenylamine antioxidant materials can contribute to instability of the oil or additive package. Thus, there is a desire to improve the stability and/or the viscosity

impact of organic fluids such as engine oils, gear oils, hydraulic fluids, compressor oils, turbine oils, and grease.

[0011] GB 1,112,784 discloses substituted diphenylamines for use as anti-oxidants for acetal copolymer, EPDM copolymer rubber, synthetic lubricant di(2-ethylhexyl)sebacate), polyethylene, polypropylene, and, in combination with dialkyl 3,3'-thiodipropionates, for polyethylene, polypropylene, acrylonitrile-butadiene-styrene copolymer, and natural rubber.

[0012] 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.

[0013] US 2023/0250353 discloses the use of diester materials to increase oxidation resistance of lubricating oil compositions.

[0014] It has now surprisingly been found by the present inventors that compositions comprising certain aralkyl substituted diphenylamines 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.

SUMMARY OF THE INVENTION

[0015] This disclosure relates to lubricating oil additives that maintain or improve oxidation performance and/or improve kinematic viscosity growth in lubricating oils. More particularly, the present disclosure relates to a stable antioxidant composition, comprising a homogeneous diphenylamine antioxidant fluid comprising di-aralkyl substituted diphenylamine and at least 45 mass% mono-aralkyl substituted diphenylamine, based upon the weight of the mono- and di-substituted diphenylamines, wherein the diphenylamine antioxidant fluid is clear after 90 days at 20 °C in a clear glass container without agitation. The aralkyl group of the aralkyl substituted diphenylamine is preferably represented by the formula (I) hereinafter, where Ph is a substituted or unsubstituted phenyl group, preferably unsubstituted phenyl, R¹ is C₁ to C₂₀ hydrocarbyl group, R² is C₁ to C₂₀ hydrocarbyl group, R¹ and R² are independently methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, phenyl, naphthyl, alkyl substituted phenyl, or an isomer thereof, and R¹ and R² may be bound to each other.

[0016] The disclosure further relates to a stable antioxidant composition (that may optionally be homogeneous or heterogeneous (such as a solution, a dispersion, a slurry, a colloid and the like), comprising: diphenylamine antioxidant comprising: 1) di(aralkyl substituted

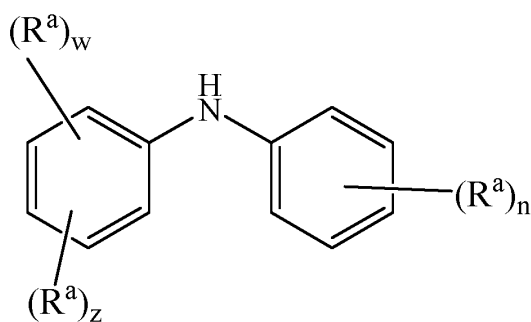
phenyl) amine, and 2) 45 mass % or more (such as 50 to 95 mass%, such as 60 to 90 mass%, such 70 to 85 mass%) of mono-aralkyl substituted diphenylamine (based upon the weight of mono-aralkyl substituted phenyl amines and di- aralkyl substituted phenyl amines present in the antioxidant composition). Suitably, said stable antioxidant composition is clear after 90 days at 20 °C in a clear glass container without agitation (such as a combination of 60 mass% of the mono-aralkyl substituted diphenylamine and 40 mass% of di(aralkyl substituted phenyl) amine is clear after 90 days at 20 °C).

[0017] The disclosure further relates to a stable antioxidant composition (that may optionally be homogeneous or heterogeneous (such as a solution, a dispersion, a slurry, a colloid and the like), comprising diphenylamine antioxidant comprising:

a) from 45 to 95 mass% (such as 45 mass% to 90 mass%, such as 50 mass% to 85 mass%, such as 55 mass% to 80 mass%, such as 60 mass% to 80 mass%, such as 65 mass% to 75 mass%,) mono-aralkyl substituted diphenylamine represented by the Formula (III) where n is 1, w is 0, and z is 0; and

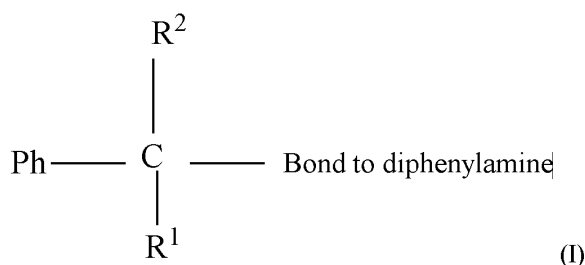
b) 5 to 55 mass% (such as 5 to 10 mass% , such as 15 to 50 mass%, such as 45 to 20 mass%, such as 20 to 40 mass%, such as 25 to 35 mass%) of di-aralkyl substituted diphenylamine represented by Formula (III), where n is 1, w is 0, and z is 1,

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



Formula (III)

where n is 1 or 0, z is 0 or 1, and w is 0 or 1; and each R^a is independently represented by the formula (I):



where Ph is a substituted or unsubstituted phenyl group, R^1 is C_1 to C_{20} (such as C_1 to C_{12}) hydrocarbyl group, R^2 is C_1 to C_{20} (such as C_1 to C_{12}) hydrocarbyl group, and R^1 and R^2 may be bound to each other. Suitably, said stable antioxidant composition is clear after 90 days at 20 °C in a clear glass container without agitation (such as a combination of 60 mass% of the mono-aralkyl substituted diphenylamine and 40 mass% of di(aralkyl substituted phenyl) amine is clear after 90 days at 20 °C).

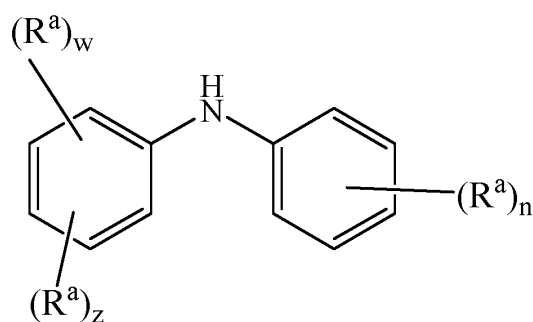
[0018] The disclosure further relates to stable antioxidant compositions comprising aralkyl-diphenylamine antioxidant comprising:

a) from 45 to 95 mass% (such as 45 mass% to 90 mass%, such as 50 mass% to 85 mass%, such as 55 mass% to 80 mass%, such as 60 mass% to 80 mass%, such as 65 mass% to 75 mass%,) mono-aralkyl substituted diphenylamine represented by the Formula (III) where n is 1, w is 0, and z is 0; and

b) 5 to 55 mass% (such as 5 to 10 mass%, such as 15 to 50 mass%, such as 45 to 20 mass%, such as 20 to 40 mass%, such as 25 to 35 mass%) of di-aralkyl substituted diphenylamine represented by Formula (III), where n is 1, w is 0, and z is 1, and

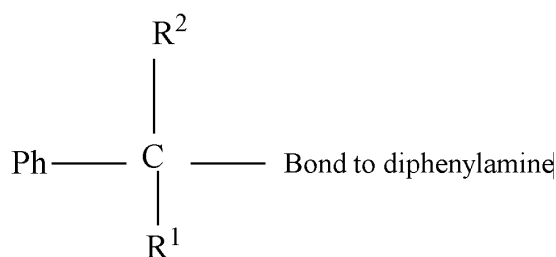
c) from 0 to less than 10 mass% (such 0.1 to 5 mass%, such as 0.05 to 5 mass%, such as a 5 mass% or less, such as 4 mass% or less, such as 3 mass% or less, such as 2 mass% or less, such as 1 mass% or less, such as 0.5 mass% or less, such as less than 0.3 mass%, such as less than 0.1 mass%, such as 0 mass%) tri-aralkyl 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 n is 1 or 0, z is 0 or 1, and w is 0 or 1; and each R^a is independently represented by the formula (I):



(I)

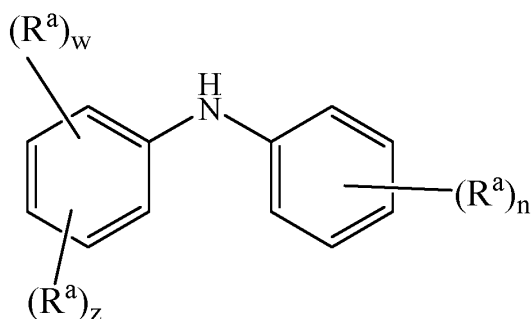
where Ph is a substituted or unsubstituted phenyl group, R^1 is C_1 to C_{20} (such as C_1 to C_{12}) hydrocarbyl group, R^2 is C_1 to C_{20} (such as C_1 to C_{12}) hydrocarbyl group, and R^1 and R^2 may be bound to each other. Suitably, said stable antioxidant composition is clear after 90 days at 20 °C in a clear glass container without agitation (such as a combination of 60 mass% of the mono-aralkyl substituted diphenylamine and 40 mass% of di(aralkyl substituted phenyl) amine is clear after 90 days at 20 °C)

[0019] In embodiments, Ph may be unsubstituted phenyl or Ph may be substituted phenyl, where the phenyl group is substituted with 1, 2, 3, 4, or 5 hydrocarbyl groups, such as C_1 to C_{20} alkyl groups (such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, and isomers thereof), and/or C_5 to C_{30} aryl groups (such as cyclopentylidene, phenyl, benzyl, and the like), and or C_5 to C_{30} aralkyl groups (such as tolyl), and oxygen containing groups such as alkoxy and/or benzoate.

[0020] In embodiments, R^1 and R^2 are independently methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, phenyl, naphthyl, alkyl substituted phenyl (such as tolyl), or an isomer thereof (such as isooctyl, methylheptyl, dimethylhexyl, ethylhexyl, trimethylpentyl, methylethylpentyl, dimethylethylbutyl, diethylbutyl, methylpropylbutyl, and the like).

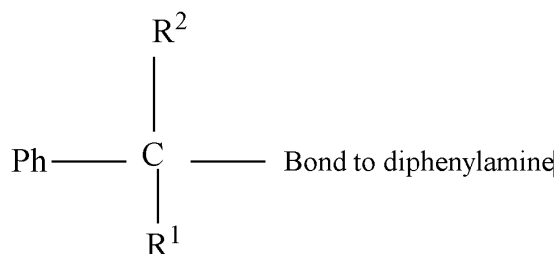
[0021] The disclosure further relates to an additive concentrate, such as a storage stable additive concentrate, for use in forming a lubricating oil composition, the additive concentrate consisting of from 1 to less than 50 mass % base oil, based on the total mass of the additive concentrate, and a plurality of lubricant composition additives contained therein, wherein the combined amount of all of said plurality of lubricant composition additives in the additive concentrate is greater than 50 mass % on an active ingredient basis, based on the total mass of the additive concentrate, wherein the plurality of said lubricant composition additives includes an antioxidant composition in the form of a fluid, as defined herein, which comprises: (a) a mono-aralkyl substituted diphenylamine, as defined herein; and (b) a di-aralkyl substituted diphenylamine, as defined herein, wherein the mono-aralkyl substituted diphenylamine is present in an amount of at least 45 mass %, based upon the total mass of said mono-aralkyl substituted diphenylamine and said di-aralkyl substituted diphenylamine in the antioxidant composition.

[0022] The disclosure further relates to an additive concentrate, such as a storage stable additive concentrate, for use in forming a lubricating oil composition, the additive concentrate consisting of from 1 to less than 50 mass % base oil, based on the total mass of the additive concentrate, and a plurality of lubricant composition additives contained therein, wherein the combined amount of all of said plurality of lubricant composition additives in the additive concentrate is greater than 50 mass % on an active ingredient basis, based on the total mass of the additive concentrate, wherein the plurality of said lubricant composition additives includes an antioxidant composition in the form of a fluid (e.g. liquid), as defined herein, which comprises: (a) a mono-aralkyl substituted diphenylamine represented by a compound of Formula III where n is 1, w is 0, and z is 0, and (b) a di-aralkyl substituted diphenylamine represented by a compound of Formula III, where n is 1, w is 0, and z is 1, where a compound of Formula III is:



Formula III

wherein each R^a in a compound of Formula III independently represents a substituent group of Formula I:



Formula I

wherein Ph is a substituted or unsubstituted phenyl group, R¹ is C₁ to C₂₀ hydrocarbyl group, R² is C₁ to C₂₀ hydrocarbyl group, and R¹ and R² may be bound to each other; and, wherein the mono-aralkyl substituted diphenylamine is present in an amount from 45 to 95 mass %, the di-aralkyl substituted diphenylamine is present in an amount of 5 to 55 mass %, based upon the total mass of said mono-aralkyl substituted diphenylamine and said di-aralkyl substituted diphenylamine in the antioxidant composition.

[0023] It will be understood that the mass to mass ratio of mono-aralkyl substituted diphenylamine to di-aralkyl substituted diphenylamine in the antioxidant composition is identical to the mass to mass ratio of mono-aralkyl substituted diphenylamine to di-aralkyl substituted diphenylamine in the additive concentrate and/or a lubricating oil composition formed therefrom.

[0024] In an embodiment, Ph in a substituent group of Formula I is an unsubstituted phenyl group.

[0025] In an embodiment, R¹ and R² in a substituent group of Formula I are independently a C₁ to C₂₀ alkyl group, such as a C₁ to C₁₂ alkyl group, such as a C₁ to C₄ alkyl group. In an embodiment, R¹ and R² in a substituent group of Formula I are independently selected from methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl or dodecyl.

[0026] In an embodiment, Ph in a substituent group of Formula I is an unsubstituted phenyl group, R¹ in a substituent group of Formula I is methyl, and R² in a substituent group of Formula I is methyl.

[0027] In an embodiment, the antioxidant composition, as defined herein, such as the (a) mono-aralkyl substituted diphenylamine antioxidant and the (b) di-aralkyl substituted diphenylamine antioxidant, as defined herein, are present in a combined total amount of from 0.01 to 40, such as from 0.020 to 30, such as from 0.025 to 20, such as from 0.05 to 15, such as

from 0.1 to 10, such as from 0.5 to 8 mass%, such as from 1 to 5, mass %, based on the total mass of the additive concentrate.

[0028] In an embodiment, the additive concentrate further includes one or more additives selected from dispersants, friction modifiers; antioxidants, other than the antioxidants of (a) and (b), pour point depressants, anti-foaming agents, viscosity modifiers, corrosion inhibitors, antirust agents, and/or anti-wear agents.

[0029] The disclosure further relates to a lubricating oil composition, such as a storage stable lubricating oil composition, comprising or resulting from the admixing of at least 50 mass% of one or more base oils, based upon the weight of the lubricating oil composition; and an antioxidant composition and/or additive concentrate described herein.

[0030] In an embodiment, the antioxidant composition, as defined herein, such as the (a) mono-aralkyl substituted diphenylamine antioxidant and the (b) di-aralkyl substituted diphenylamine antioxidant, as defined herein, are present in a combined total amount of from 0.01 to 20, such as from 0.05 to 15, such as from 0.1 to 10, such as from 0.5 to 8, such as from 0.6 to 8, such as from 0.7 to 8, such as from 1 to 5, mass%, based on the total mass of the lubricating oil composition.

[0031] In an embodiment, the base oil of the lubricating oil composition is selected from one or more of API Group I, II, III, IV base oils. In an embodiment, the base oil of the lubricating oil composition comprises at least 50 mass % Group II and or Group III base oil.

[0032] In an embodiment, the additive concentrate additive concentrate, as defined herein, and/or the lubricating oil composition, as defined herein, may further include a polar diluent as defined herein. Suitably, the polar diluent polar diluent is 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 tri-methylolpropane; and, iii) phthalates, terephthalates, isophthalates, trimellitates and pyromellitates. In an embodiment, the the polar diluent is one or more diluent(s) selected from the group consisting of (di-propylene glycol) dibenzoate, C₈-C₁₀ tri-methylol propane ester, trioctyl trimellitate, and dioctylterephthalate. In an embodiment, the polar diluent comprises (di-propylene glycol) dibenzoate.

[0033] When the polar diluent is present, the additive concentrate may comprise 0.01 to 40, such as from 0.02 to 30, such as from 0.025 to 20, such as from 0.05 to 15, such as 0.1 to 10, such as 0.5 to 8, such as 1 to 5, mass% of (iii) polar diluent, as defined herein, based upon the total weight of the additive concentrate.

[0034] When the polar diluent is present, the lubricating oil composition may comprise may comprise from 0.5 to 15, such as 0.5 to 10, 0.5 to 8, such as 0.6 to 15, such as 0.6 to 10, such as 0.6 to 8, such as 0.7 to 15, such as 0.7 to 10, such as 0.7 to 8, such as 1 to 15, such as 1 to 10, such as 1 to 8, mass% of (iii) polar diluent, as defined herein, based upon the total weight of the lubricating oil composition.

[0035] The disclosure further relates to the use of an antioxidant composition in the form of a liquid, as defined herein, comprising: (a) a mono-aralkyl substituted diphenylamine antioxidant, as defined herein, and (b) a di-aralkyl substituted diphenylamine antioxidant, as defined herein, as an additive in an additive concentrate to form a storage stable additive concentrate, as measured by the Storage Stability Test Method defined herein, wherein the additive concentrate consists of 1 to less than 50 mass % base oil, based on the total mass of the additive concentrate, and a plurality of lubricant composition additives contained therein, as defined herein, wherein the combined amount of all of said plurality of lubricant composition additives in the additive concentrate is greater than 50 mass % on an active ingredient basis, based on the total mass of the additive concentrate.

[0036] The disclosure further relates to the use, in the lubrication of a spark-ignited or compression-ignited internal combustion engine, of (a) a mono-aralkyl substituted diphenylamine antioxidant, as defined herein, and (b) a di-aralkyl substituted diphenylamine antioxidant, as defined herein, as a combination of additives in an amount in a lubricating oil composition to improve anti-oxidation characteristics and/or to mitigate or reduce viscosity increase, such as to mitigate or reduce K_v100 viscosity increase, in of the lubricating oil composition during operation of the internal combustion engine, wherein the mass to mass ratio of mono-aralkyl substituted diphenylamine antioxidant to di-aralkyl substituted diphenylamine antioxidant in the lubricating oil composition is from 45:55 to 95:5, and wherein the lubricating oil composition includes at least 50 mass % of one or more base oils, based upon the total mass of the lubricating oil composition.

[0037] According to another aspect, there is provided the use of the lubricating oil composition described herein for lubrication of an engine.

BRIEF DESCRIPTION OF THE DRAWINGS

[0038] Figure 1 (Fig. 1) shows typical aralkylated phenyl amine isomers produced using alpha methyl styrene.

DEFINITIONS

[0039] For purposes of this specification and all claims to this disclosure, the following words and expressions, if and when used, have the meanings ascribed below.

[0040] 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.).

[0041] 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.

[0042] The term “**LOC**” means lubricating oil composition.

[0043] 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.

[0044] The term “**minor amount**” means 50 mass% or less of a composition; such as less than 50 mass% 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.

[0045] 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 alternatively referred to as weight percent (“weight %”, “mass%”, or “% w/w”).

[0046] 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.

[0047] 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.

[0048] The terms “**group**” and “**radical**” are used interchangeably herein.

[0049] The term “**hydrocarbon**” means a compound of hydrogen and carbon atoms. A “heteroatom” is an atom other than carbon or hydrogen. When referred to as “hydrocarbons”, particularly as “refined hydrocarbons”, the hydrocarbons may also contain one or more heteroatoms or heteroatom-containing groups (such as halo, especially chloro and fluoro, amino, alkoxyl, mercapto, alkylmercapto, nitro, nitroso, sulfoxy, etc.) in minor amounts (*e.g.*, where the heteroatom(s) do not substantially alter the hydrocarbon properties of the hydrocarbon compound).

[0050] The term “**hydrocarbyl**” means a radical that contains hydrogen and carbon atoms. Suitably, the group consists essentially of, preferably consists only of, hydrogen and carbon atoms, unless specified otherwise. Suitably, the hydrocarbyl group comprises an aliphatic hydrocarbyl group. The term “hydrocarbyl” includes “alkyl”, “alkenyl”, “alkynyl”, and “aryl” as defined herein. Hydrocarbyl groups may contain one or more atoms/groups other than carbon and hydrogen provided they do not affect the essentially hydrocarbyl nature of the hydrocarbyl group. Those skilled in the art will be aware of such atoms/groups (*e.g.*, halo, especially chloro and fluoro, amino, alkoxyl, mercapto, alkylmercapto, nitro, nitroso, sulfoxy, etc.).

[0051] 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. Suitably, the alkyl group comprises a linear or branched acyclic alkyl group. Suitable alkyl groups comprise a linear or branched acyclic alkyl group, such as a linear or branched C₁ to C₁₂ acyclic alkyl group, such as a linear or branched C₁ to C₆ acyclic alkyl group, such as a linear or branched C₁ to C₄ acyclic alkyl group. Further suitable alkyl groups comprise a linear C₁ to C₁₂ acyclic alkyl group, such as a linear C₁ to C₆ acyclic alkyl group, such as a linear C₁ to C₄ 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.

[0052] 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 carbon to carbon 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.

[0053] The term “**alkylene**” means a C₁ to C₂₀, such as a C₁ to C₁₀, bivalent saturated aliphatic radical, which may be linear or branched, and which is derivable by removing 2 hydrogen atoms from the corresponding alkyl group. 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.

[0054] An “**olefin**”, alternatively referred to as “**alkene**”, is a linear, branched, or cyclic compound of carbon and hydrogen having at least one carbon to carbon 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.

[0055] 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.

[0056] The term “**aryl**” means a group containing at least one aromatic ring, such as phenyl, naphthyl, anthracenyl, and the like. Aryl groups are typically C₆ to C₄₀ (such as C₆ 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.

[0057] 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).

[0058] An alkaryl group is an aryl group that has been substituted with one or more alkyl groups (where the alkyl group may be a substituted or unsubstituted alkyl group).

[0059] An aralkyl is an alkyl group that has been substituted with one or more aryl groups (where the aryl group may be a substituted or unsubstituted aryl group). A substituent group derived from styrene can be an aralkyl group when the substituent is incorporated through the ethylene moiety of the styrene. Suitable aralkyl groups include a linear or branched acyclic alkyl group, such as a linear or branched C₁ to C₁₂ acyclic alkyl group, such as a linear or branched C₁ to C₆ acyclic alkyl group, such as a linear or branched C₁ to C₄ acyclic alkyl group, that has been substituted with one or more, such as substituted with a single, phenyl group(s), such as unsubstituted phenyl group(s).

[0060] The term “**antioxidant**” or equivalent term (e.g., “oxidation stabilizer” or “oxidation inhibitor”) refers to a composition, or a component, 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.

[0061] A “**hindered phenol**” is a phenol with one or more bulky substituent hydrocarbyl groups (i.e. hydrocarbyl 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.

[0062] The term “**halogen**” or “**halo**” means a group 17 atom or a radical of group 17 atom, such as fluoro, chloro, bromo, and iodo.

[0063] The term “**ashless**” in relation to an additive or composition means the additive or composition, respectively, does not include a metal.

[0064] The term “**ash-containing**” in relation to an additive or composition means the additive or composition, respectively, includes a metal.

[0065] The term “**effective amount**” in respect of an additive means an amount of such an additive in a composition, such as a lubricating oil composition or additive concentrate, so that the additive provides the desired technical effect.

[0066] 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.

[0067] The term “**effective major amount**” in respect of an additive means an amount of such an additive of more than 50 mass% of the lubricating oil composition so that the additive provides the desired technical effect.

[0068] The term “**ppm**” means parts per million by mass, based on the total mass of the lubricating oil composition, unless otherwise indicated.

[0069] 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.

[0070] The term “**stable**” or “**to stabilise**” in relation to a composition (including, but not limited to antioxidant compositions, concentrate packages, lubricating oil compositions) comprising one or more diphenylamine antioxidants, such as (a) a mono-aralkyl substituted diphenylamine and (b) a di-aralkyl substituted diphenylamine antioxidants, refers to the storage stability of the composition as evidenced by the formation of any haze and/or sediment and/or gelation of the composition during storage. Suitably, the stability of a composition is assessed at 60°C and atmospheric pressure over a 10 week period, using the Storage Stability Test Method as described herein. Suitably, a composition is deemed stable if there has been no haze formation (*i.e.* clear and/or bright) or a slight haze formation which is only visible under natural light under close inspection.

[0071] 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.

[0072] 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.

[0073] 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.

[0074] 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 M_w divided by M_n . Unless otherwise noted, all molecular weight units (*e.g.*, M_w , M_n , M_z) are reported in g/mol.

[0075] **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. “High TBN” is considered to be greater than or equal to 200 KOH/g, or greater than 300 mgKOH/g, or 300 to 500 mgKOH/g. “Low TBN” is considered less than 200 KOH/g, or less than 100 KOH/g.

[0076] **Total Acid Number** (“TAN”) is determined by ASTM D664.

[0077] **Aniline point** is determined according ASTM 611, Method A.

[0078] **Phosphorus, Boron, Calcium, Zinc, Molybdenum, Sodium, Silicon, and Magnesium** content are measured by ASTM D5185.

[0079] **Sulfur content in oil** formulations is measured by ASTM D5185.

[0080] **Sulfated ash** (“SASH”) content is measured by ASTM D874.

[0081] **Kinematic viscosity** (KV100, KV40, etc.) is determined pursuant to ASTM D445-19a and reported in units of cSt, unless otherwise specified.

[0082] **Viscosity index** is determined according to ASTM D2270.

[0083] **Saponification number** is determined by ASTM D94, and reported in units of mgKOH/g.

[0084] 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.

[0085] 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.

[0086] Further, it is understood that any upper and lower quantity, range and ratio limits set forth herein may be independently combined.

[0087] 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

[0088] 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.

[0089] The lubricating oil compositions, the anti-oxidant compositions, the concentrate compositions, and the booster pack compositions 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.

[0090] For purposes of this disclosure and the claims thereto “**mono-aralkyl substituted diphenylamine**”, also referred to as “(aralkyl 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 aralkyl group.

[0091] For purposes of this disclosure and the claims thereto “**di-aralkyl substituted diphenylamine**”, also referred to as “di(aralkyl substituted phenyl) amine”, means a nitrogen atom bound to: 1) hydrogen, and 2) two phenyl groups each independently substituted with one aralkyl group.

[0092] For purposes of this disclosure and the claims thereto “**tri-aralkyl substituted diphenylamine**”, also referred to as “di(aralkyl substituted phenyl) (aralkyl substituted phenyl) amine, means a nitrogen atom bound to 1) hydrogen, 2) a phenyl group independently substituted with two aralkyl groups, each of which is independently linear or branched, and 3) a phenyl group substituted with one aralkyl group.

[0093] For purposes of this disclosure 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 aralkyl groups.

[0094] For purposes of this disclosure and the claims thereto “**unsubstituted diphenylamine**”, means a nitrogen atom bound to 1) hydrogen, 2) two unsubstituted phenyl groups.

[0095] For purposes of this disclosure 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.

[0096] For purposes of this disclosure and the claims thereto “**di-C₉-alkyl substituted diphenylamine**”, also referred to as “di(C₉-alkyl substituted phenyl) amine”, 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.

[0097] For purposes of this disclosure and the claims thereto “**tri-C₉-alkyl substituted diphenylamine**”, also referred to as “(diC₉-alkyl substituted phenyl) (C₉-alkylphenyl)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.

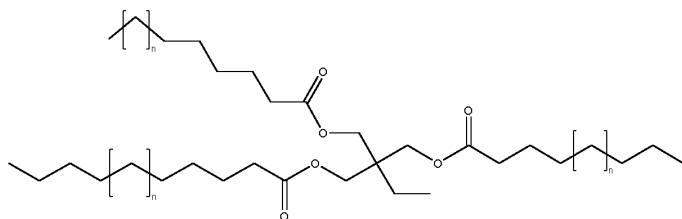
[0098] For purposes of this disclosure and the claims thereto, when a composition (including, but not limited to antioxidant compositions, concentrate packages, lubricating oil compositions) comprising one or more diphenylamine antioxidants (such as aralkyl substituted diphenylamine antioxidants) is described as “**clear and/or stable at 20°C and 60 °C for 600 hours**”, it means that the composition comprising the diphenylamine antioxidant(s) is observed to be clear (meaning having no crystallization, precipitation or cloudiness) or slight haze formation which is only visible under natural light under close inspection, after 600 hours of being held in a clear glass container, such as a centrifuge tube, at 20°C and 60 °C, respectively with no agitation.

[0099] For purposes of this disclosure and the claims thereto, when a composition (including, but not limited to antioxidant compositions, concentrate packages, lubricating oil compositions) comprising one or more diphenylamine antioxidants (such as aralkyl substituted 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 diphenylamine antioxidant(s) is observed to be clear (meaning having no crystallization, precipitation or cloudiness) or slight haze formation which is only visible under natural light under close inspection, after X hours of being held in a clear glass container, such as a centrifuge tube, at Y°C with no agitation.

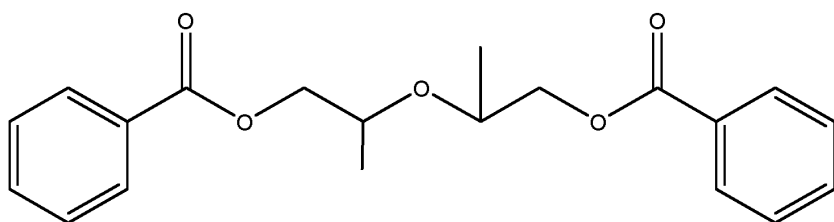
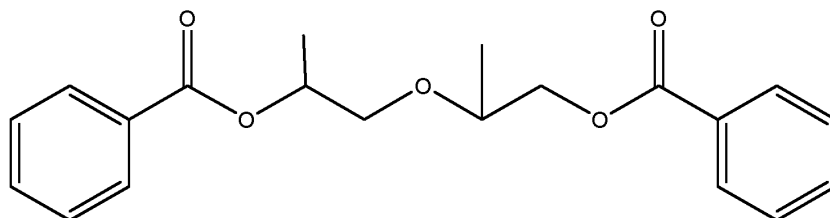
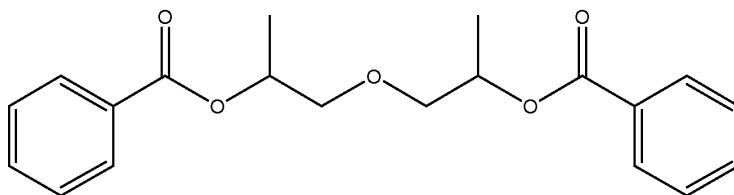
[0100] Aralkylated diphenylamines (such as Naugard™ 445, SI Group, Brussels, Belgium) are antioxidants that are commonly used in the lubricant, rubber and plastics industries. However, they are difficult to use in many lubricant applications as they are solid at typical mixing temperatures and do not blend well in a liquid or molten state. Thus the inventive composition herein utilizing aralkylated diphenylamines at certain mono-/di- substitution ratios and optionally in combination with certain polar diluents provides new compositions and methods of use for the Lubricants industry.

Polar Diluents

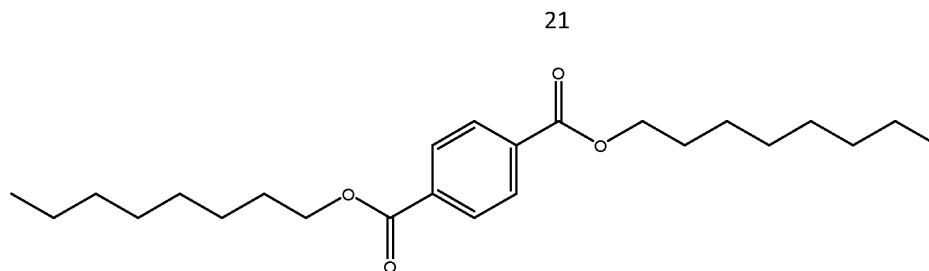
[0101] For purposes of this disclosure and claims thereto, when **hydrogen-bond acceptor groups** are described as being 2, 3, 4, 5, or 6 atoms (such as carbon atoms) apart, the hydrogen acceptor is not included in that count. For example, in the C₈-C₁₀ tri-methylol propane ester formula below (n is 0, 1 or 2), the ester groups are considered three atoms apart (specifically 3 carbon atoms apart).



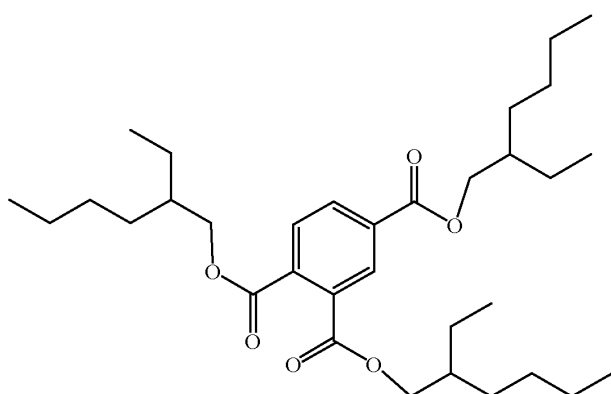
While in the (dipropylene glycol) dibenzoate formulas below, the ester groups are considered two atoms apart (specifically 2 carbon atoms apart) from the “-O-” ether group.



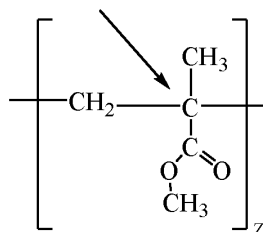
Likewise, in the dioctyl terephthalate formula below, the ester groups are considered four atoms apart (specifically 4 carbon atoms apart).



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).



[0102] 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 or ether-group) capable of participating in a hydrogen bond with the positively charged hydrogen atom from the amine functionality of the di(aralkyl substituted phenyl) amine. Sterically hindered groups (such as a sterically hindered oxygen containing group, such as a sterically hindered ester and or sterically hindered ether group) that are not capable of participating in a hydrogen bond with the positively charged hydrogen atom from the amine functionality of the di(aralkyl 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 sp^3 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 sp^3 carbon (identified by the arrow) and thus is considered sterically hindered.



[0103] In embodiments, the polar diluent has an aniline point of 0°C or less, such as about -5 °C or less, such as about -10 °C or less, such as about -15 °C or less, such as -20 °C or less.

[0104] In embodiments, the polar diluent has at 2, 3, 4 or 5 available hydrogen-bond acceptor groups (such as an oxygen containing group, such as one or more ester and or ether groups) that are 2, 3, 4, 5, or 6 carbon atoms (such as 2, 3, or 4 carbon atoms) apart.

[0105] In embodiments, the polar diluent(s) comprise one or more diluent(s) 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 C_{8-C10} tri-methylol propane ester), and iii) 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).

[0106] In embodiments, the polar diluent(s) comprise 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 tri-methylolpropane, and iii) phthalates, terephthalates, isophthalates, trimellitates and pyromellitates.

[0107] In embodiments, the polar diluent(s) comprise one or more diluent(s) selected from the group consisting of: i) di- and tri-esters derived from propylene glycol, ii) C_{8-C10} alkyl triesters derived from tri-methylol propane ester), and iii) C₆ to C₂₄ dialkyl terephthalates, C₆ to C₂₄ dialkyl isophthalates, and C₆ to C₂₄ dialkyl phthalates.

[0108] In embodiments, the polar diluent(s) comprise one or more diluent(s) selected from the group consisting of: (di-propylene glycol) dibenzoate, C_{8-C10} Tri-methylol propane ester, trioctyl trimellitate, and dioctylterephthalate.

[0109] Preferred polar diluents useful herein include dioctyl terephthalate, trioctyl trimellitate, (dipropylene glycol) dibenzoate, and C_{8-C10} Tri-methylol propane ester, (Priolube™ 3970).

[0110] In embodiments, the hydrogen-bond acceptor groups do not comprise sulfur, preferably are absent sulfur.

[0111] In embodiments, the diluent does not comprise one or more dialkyl 3,3'-thiodipropionates (such as di(ethylhexyl) 3,3'-thiodipropionate, and or didodecyl 3,3'-thiodipropionate).

[0112] In embodiments, the diluent is absent didodecyl 3,3'-thiodipropionate.

[0113] In embodiments, the diluent does not comprise Group V base stock, such as diester base stock.

[0114] In embodiments, the diluent does not comprise 90 mass% or more Group V base stock, such as the diluent does not comprise 92 to less than 100 mass% Group V base stock, such as the diluent does not comprise 95 to 99 mass % Group V base stock, such as the diluent does not comprise 98 to 99.9 mass% Group V base stock, based upon the weight of the group V basestock and the aralkyl substituted diphenylamine.

[0115] In embodiments, the diluent does not comprise di(alkyl)sebacate group V base oil, such as di(C₂ to C₂₄dialkyl)sebacate group V base oil, such as di(C₆ to C₁₈dialkyl)sebacate group V base oil.

[0116] In embodiments, the diluent is absent di(2-ethylhexyl)sebacate) group V base oil.

Stable Antioxidant Compositions

[0117] This disclosure further relates to a stable antioxidant composition (that may optionally be homogeneous or heterogeneous (such as a solution, a dispersion, a slurry, a colloid and the like), comprising diphenylamine antioxidant comprising:

1) di-aralkyl substituted diphenylamine and

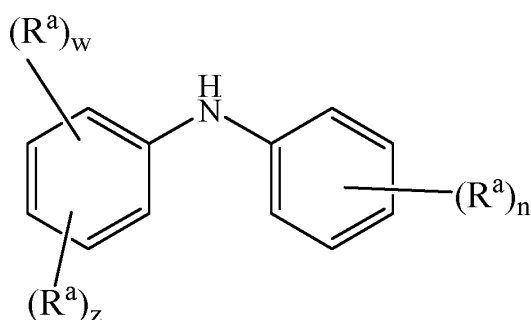
2) from 45 to 95 mass% (such as 45 mass% to 90 mass%, such as 50 mass% to 85 mass%, such as 55 mass% to 80 mass%, such as 60 mass% to 80 mass%, such as 65 mass% to 75 mass%,) of mono-aralkyl substituted diphenylamine (based upon the weight of mono-aralkyl substituted diphenylamines and di-aralkyl substituted diphenylamines present in the antioxidant composition), where optionally, said stable antioxidant composition is clear after 90 days at 20 °C in a clear glass container without agitation (such as a combination of 60 mass% of the mono-aralkyl substituted diphenylamine and 40 mass% of di(aralkyl substituted phenyl) amine is clear after 90 days at 20 °C in a clear glass container without agitation).

[0118] This disclosure further relates to stable antioxidant compositions comprising aralkyl-substituted diphenylamine antioxidant comprising:

a) from 45 to 95 mass% (such as 45 mass% to 90 mass%, such as 50 mass% to 85 mass%, such as 55 mass% to 80 mass%, such as 60 mass% to 80 mass%, such as 65 mass% to 75 mass%,) mono-aralkyl substituted diphenylamine represented by the Formula (III) where n is 1, w is 0, and z is 0; and

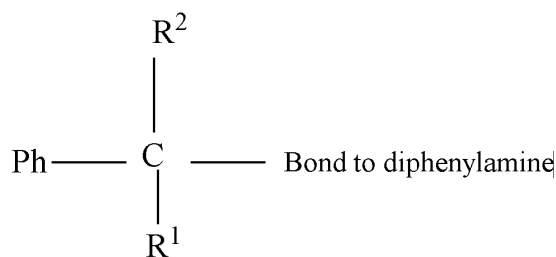
b) 5 to 55 mass% (such as 5 to 10 mass%, such as 15 to 50 mass%, such as 45 to 20 mass%, such as 20 to 40 mass%, such as 25 to 35 mass%) of di-aralkyl substituted diphenylamine represented by Formula (III), where n is 1, w is 0, and z is 1,

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



Formula (III)

where n is 1 or 0, z is 0 or 1, and w is 0 or 1; and each R^a is independently represented by the formula (I):



(I)

where Ph is a substituted or unsubstituted phenyl group, R¹ is C₁ to C₂₀ (such as C₁ to C₁₂) hydrocarbyl group, R² is C₁ to C₂₀ (such as C₁ to C₁₂) hydrocarbyl group, and R¹ and R² may be bound to each other; and optionally said stable antioxidant composition comprising a) and b) is clear after 90 days at 20 °C in a clear glass container without agitation (such as a combination of 60 mass% of the mono-aralkyl substituted diphenylamine and 40 mass% of di(aralkyl substituted phenyl) amine is clear after 90 days at 20 °C).

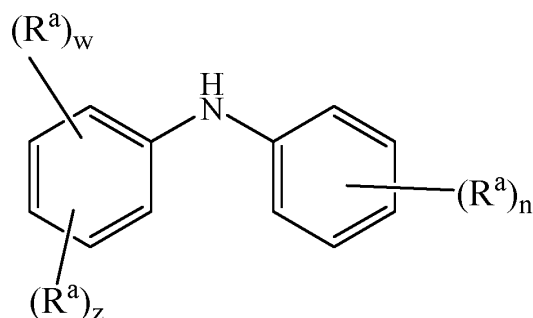
[0119] This disclosure further relates to stable antioxidant compositions comprising aralkyl-diphenylamine antioxidant comprising:

a) from 45 to 95 mass% (such as 45 mass% to 90 mass%, such as 50 mass% to 85 mass%, such as 55 mass% to 80 mass%, such as 60 mass% to 80 mass%, such as 65 mass% to 75 mass%,) mono-aralkyl substituted diphenylamine represented by the Formula (III) where n is 1, w is 0, and z is 0; and

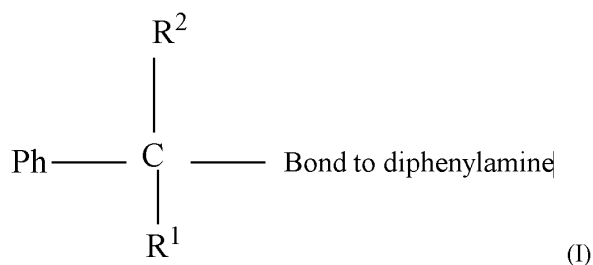
b) 5 to 55 mass% (such as 5 to 10 mass%, such as 15 to 50 mass%, such as 45 to 20 mass%, such as 20 to 40 mass%, such as 25 to 35 mass%) of di-aralkyl substituted diphenylamine represented by Formula (III), where n is 1, w is 0, and z is 1, and

c) from 0 to less than 10 mass% (such as 0.1 to 5 mass%, such as 0.05 to 3 mass%, such as a 5 mass% or less, such as 4 mass% or less, such as 3 mass% or less, such as 2 mass% or less, such as 1 mass% or less, such as 0.5 mass% or less, such as less than 0.3 mass%, such as less than 0.1 mass%, such as 0 mass%) tri-aralkyl 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:



where n is 1 or 0, z is 0 or 1, and w is 0 or 1; and each R^a is independently represented by the formula (I):



where Ph is a substituted or unsubstituted phenyl group, R^1 is C_1 to C_{20} (such as C_1 to C_{12}) hydrocarbyl group, R^2 is C_1 to C_{20} (such as C_1 to C_{12}) hydrocarbyl group, and R^1 and R^2 may be bound to each other, wherein, optionally, said stable antioxidant composition comprising a), b) and c) is clear after 90 days at 20 °C in a clear glass container without agitation (such as a combination of 69 mass% of the mono-aralkyl substituted diphenylamine, 40 mass% of di-aralkyl substituted diphenylamine and 1 mass% of tri-aralkyl substituted diphenylamine is clear after 90 days at 20 °C in a clear glass container without agitation).

[0120] In embodiments, Ph may be unsubstituted phenyl or Ph may be substituted phenyl, where the phenyl group is substituted with 1, 2, 3, 4, or 5 hydrocarbyl groups, such as C_1 to C_{20} alkyl groups (such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, and isomers thereof), and/or C_5 to C_{30} aryl groups (such as cyclopentadiene, phenyl, benzyl, and the like), and/or C_5 to C_{30} aralkyl groups (such as tolyl), and oxygen containing groups such as alkoxy and/or benzoate.

[0121] In embodiments, R^1 and R^2 are independently methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, phenyl, naphthyl, alkyl substituted phenyl (such as tolyl), or an isomer thereof (such as isooctyl, methylheptyl, dimethylhexyl, ethylhexyl, trimethylpentyl, methylethylpentyl, dimethylethylbutyl, diethylbutyl, methylpropylbutyl, and the like).

[0122] In embodiments, the antioxidant composition is a fluid (such as a liquid or molten mass) at a temperature of 20 °C or more, such as 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; such as 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, such as 90°C or more, such as 95°C or more, such as 100°C or more.

[0123] In embodiments, the antioxidant composition is obtained by combining the di-aralkyl substituted diphenylamine and mono-aralkyl substituted diphenylamine at a temperature that renders them liquid, such as a temperature near their melting point, such as at or above their melting point, to form a fluid (such as a liquid or molten mass). In embodiments, the antioxidant composition is obtained by combining the di-aralkyl substituted diphenylamine and mono-aralkyl substituted diphenylamine at a temperature of 20 °C or more, such as 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; such as 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, such as 90°C or more, such as 95°C or more, such as 100°C or more.

[0124] In embodiments, when solid di-aralkyl substituted diphenylamine and solid mono-aralkyl substituted diphenylamine are combined and rendered fluid (such as by melting together), the aralkyl substituted diphenylamine composition remains a fluid after being cooled below each of the melting points of the di-aralkyl substituted diphenylamine and mono-aralkyl substituted diphenylamine. Specifically, the liquid mono-aralkyl substituted diphenylamine/di-aralkyl substituted diphenylamine combination remains liquid after being cooled below 80°C, such as being cooled below 60°C, such as being cooled below 50°C, such as being cooled to a temperature from -20°C to 80°C, such as from 0 to 60 °C.

[0125] In embodiments, a fluid (such as a liquid or molten mass, such as a homogeneous fluid) stable antioxidant composition is obtained by combining an aralkylene (such as alpha methyl styrene) with diphenylamine and a catalyst (such as an acid catalyst) to form a reaction product as shown in Figure 1 comprising di-aralkyl substituted diphenylamine and mono-aralkyl substituted diphenylamine, optionally removing solvent, trisubstituted diphenylamine, and unreacted diphenylamine and aralkylene (such as alpha methyl styrene), and thereafter optionally cooling the combination to a temperature of 0 °C to more, 20 °C or more, such as 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; such as 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, where the combination remains a fluid, such as a homogeneous fluid, at temperatures of 0 °C or to 90 °C, such as at temperatures of 10 °C to 80 °C, such as at temperatures of 15 °C to 70°C, such as at temperatures of 20 °C to 65°C.

[0126] Aralkyl 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.

[0127] In embodiments, the stable antioxidant composition may comprise one or more polar diluents as described herein. Suitably, the polar diluent comprises 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 and or an ether group) capable of participating in a hydrogen bond with the positively charged hydrogen atom from the amine functionality of the di(aralkyl substituted phenyl) amine.

[0128] In embodiments, the polar diluent(s) are one or more diluents 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),

and

iii) C₆ to C₂₄ dialkyl terephthalates, such as C₈ to C₁₆ dialkyl terephthalates, such as dioctyl terephthalate.

[0129] The stable antioxidant compositions may also comprise detergent, such as carboxylate detergent, such as salicylate detergent, such as calcium and or magnesium salicylate detergent.

[0130] The stable antioxidant compositions may also comprise detergent, such as sulfonate detergent, such as calcium and or magnesium sulfonate detergent.

[0131] 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.

[0132] 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.

[0133] In embodiments, the stable antioxidant composition comprises:

- i) 1 to 99 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) 0 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) 1 to 99 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

[0134] 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 mass%, such as 1 to 5 mass%) base oil, and 2) lubricant composition additives (such as described herein) which are typically then further blended with additional base oil to form a lubricating oil product.

[0135] This disclosure 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-aralkyl substituted diphenylamine and
 - 2) 45 mass % or more (such as 45 to 95 mass%, such as 50 to 90 mass%, such as 55 to 85 mass%, such as 60 to 85 mass%, such as 65 to 85 mass%, such as 70 to 80 mass%) of mono-aralkyl substituted diphenylamine (based upon the weight of mono-aralkyl substituted diphenylamines and di-aralkyl substituted diphenylamines present in the antioxidant composition), where optionally, said stable antioxidant composition is clear after 90 days at 20 °C in a clear glass container without agitation (such as a combination of 60 mass% of the mono-aralkyl substituted diphenylamine and 40 mass% of di(aralkyl substituted phenyl) amine is clear after 90 days at 20 °C in a clear glass container without agitation);
 - b) optionally, polar diluent having an aniline point of 0°C or less, such as -5°C or less, and at least 2 available hydrogen-bond acceptor groups (such as ester and or ether 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),
(optionally, wherein the combination of the polar diluent b) combined with the diphenylamine antioxidant of a) is clear after 90 days at 20 °C in a clear glass container without agitation);
- 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.

[0136] In embodiments, 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; such as 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.

[0137] This disclosure further relates to concentrate compositions comprising or resulting from the admixing of:

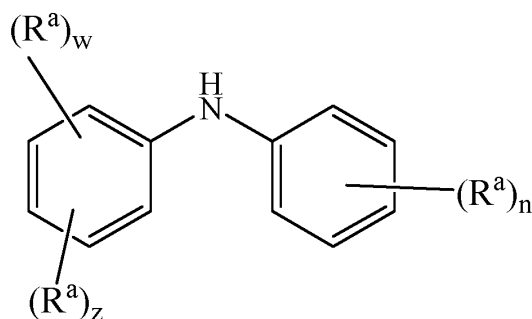
- (i) from 1 to less than 50 mass% (alternatively 5 to 45 mass%, alternatively 7 to 40 mass%, alternatively 10 to 35 mass%, alternatively 10 to 25 mass%), based upon the weight of the composition, of one or more **base oil(s)**;
- (ii) from 0.10 to 40 mass% (in particular 0.15 to 30 mass%, alternatively 0.20 mass% to 20 mass%, alternatively 0.25 to 10 mass%), based upon the weight of the composition, of one or more **detergent(s)**, such as carboxylate detergents, such as calcium salicylate detergent;
- (iii) from 0.10 to 60 mass% (in particular 0.15 to 50 mass%, alternatively 5 mass% to 40 mass%, alternatively 0.25 to 20 mass%), based upon the weight of the composition, of one or more **dispersant(s)** (such as PIBSA-PAM); and
- (iv) from 0.010 to 40 mass% (in particular 0.10 to 30 mass%, alternatively 0.10 to 20 mass%, alternatively 0.10 to 15 mass%, alternatively 0.15 to 10 mass%, alternatively 0.20 mass% to 5 mass%, alternatively 0.25 to 2 mass%), based upon the weight of the concentrate, of diphenylamine antioxidant comprising:

1) one or more **di-aralkyl substituted diphenylamine** represented by Formula (III), where n is 1, z is 1 and w is 0), and

2) from 45 mass % or more (such as 45 to 95 mass%, such as 50 to 90 mass%, such as 55 to 85 mass% , such as 60 to 85 mass%, such as 65 to 85 mass%, such 70 to 80 mass%) (based upon the weight of mono-aralkyl substituted diphenylamines and di-aralkyl substituted diphenylamines present in the antioxidant composition) of **mono-aralkyl substituted diphenylamine** represented by Formula (III), where n is 1, z is 0 and w is 0), and

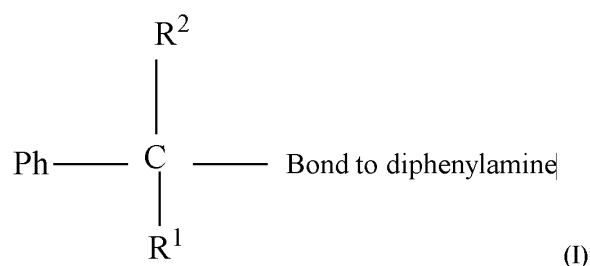
3) from 0 to 5 mass% (such as 0 to 1.5 mass%, such as 0 to 1 mass%, such as 0.001 to 0.5 mass%, such as 0.005 to less than 0.3 mass%, such as 0.001 to 0.1 mass%) of **tri-aralkyl**

substituted diphenylamine represented by Formula (III), where n is 1, z is 1 and w is 1), based upon the weight of the concentrate:



Formula (III)

where: n is 1 or 0, z is 0 or 1, and w is 0 or 1; and each R^a is independently represented by the formula (I):



where Ph is a substituted or unsubstituted phenyl group, R^1 is C_1 to C_{20} (such as C_1 to C_{12}) hydrocarbyl group, R^2 is C_1 to C_{20} (such as C_1 to C_{12}) hydrocarbyl group, and R^1 and R^2 may be bound to each other;

(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.

[0138] In embodiments, the concentrate composition may optionally be absent solvent (such as aliphatic or aromatic solvent) and/or absent functionalized base oil.

[0139] This disclosure also relates to concentrate compositions comprising or resulting from the admixing of:

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

- B) from 0.10 to 45 mass% (in particular, from 0.10 to 35 mass%, alternatively 0.010 to 30 mass%, alternatively 0.15 to 20 mass%, alternatively 0.20 mass% to 5 mass%, alternatively 0.25 to 4 mass%) of stable antioxidant composition as described herein, based upon the weight of the concentrate,
- C) from 0.1 to 40 mass% (in particular, 0.25 to 30 mass%, alternatively 0.4 to 20 mass%, alternatively 0.5 to 10 mass%, alternatively 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 10 mass% (in particular, 0.1 to 5 mass%, alternatively 0.1 to 4 mass%, alternatively 0.25 to 3 mass%, alternatively 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 mono-oleate);
- E) optionally, from 0.01 to 30 mass% (in particular, 0.01 to 20 mass%, alternatively 0.01 to 15 mass%, alternatively 0.1 to 10 mass%), based on total weight of the concentrate composition, of one or more **antioxidant(s)** (such as blends of antioxidants, such as , and hindered phenol antioxidants), other than B) above;
- F) optionally, from 0.01 to 5 mass% (in particular, 0.01 to 3 mass%, alternatively 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%, alternatively 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, in particular 0.15 to 50 mass%, from 0.1 to 40 mass%, alternatively 1 to 30 mass%, alternatively 5 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%, alternatively 1 to 5 mass% alternatively 0.25 to 0.75 mass%), based on total weight of the lubricating composition, of one or more **anti-wear agents** (such as blends of anti-wear agents, such as ZDDP).
- [0140] Concentrates may be present in the lubricating oil composition at from of 0.5 mass% to 40 mass%, such as 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.

[0141] Optionally, the concentrate may be absent functionalized oil.

[0142] In embodiments, the concentrate composition may optionally be absent solvent (such as aliphatic or aromatic solvent) and/or absent functionalized base oil.

[0143] Optionally, the concentrate may be absent phenolic antioxidant.

[0144] 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.

[0145] 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 to 1600 g/mol, such as 700 to 1200 g/mol.

[0146] 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) of block copolymer, such as block, star, random, and/or tapered block copolymer.

[0147] In embodiments, the concentrate may be substantially free of or absent block copolymer, such as block, star, random, and/or tapered block copolymer.

[0148] 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) of styrenic copolymer, such as block, star, random, and/or tapered styrenic block copolymer).

[0149] In embodiments, the concentrate may be substantially free of or absent styrenic copolymer, such as block, star, random, and/or tapered styrenic block copolymer).

[0150] 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.

[0151] In embodiments, the concentrate may substantially free of or absent functionalized diluent, such as functionalized oil.

[0152] 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

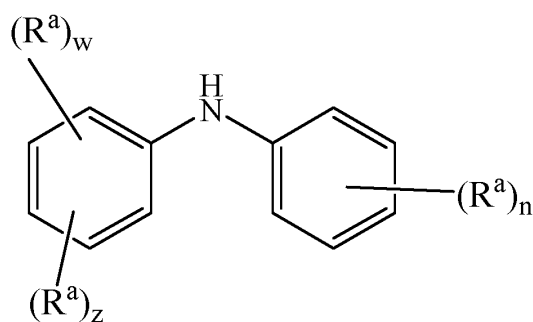
[0153] This disclosure further relates to stable lubricating oil compositions (also referred to as "LOC", "lubricant compositions", "lubricating compositions", or "lubricant oil compositions") comprising or resulting from the admixing of:

- (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 as described herein.

[0154] This disclosure relates to stable lubricating oil compositions comprising or resulting from the admixing of:

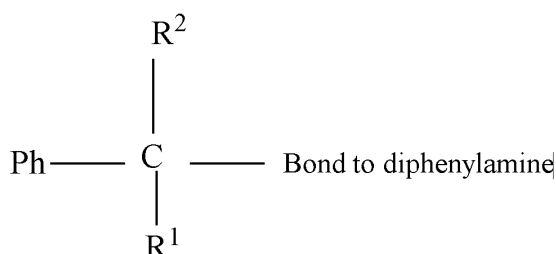
- (a) from 1 to 99 mass% (alternatively 30 to 95 mass%, alternatively 50 to 90 mass%, alternatively 60 to 95 mass%, alternatively 70 to 85 mass%) of one or more **base oils**, based upon the weight of the lubricating composition;
- (b) from 0.01 to 20 mass% (in particular 0.1 to 12 mass%, alternatively 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%, alternatively 0.20 mass% to 5 mass%, alternatively 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%, alternatively 0.15 to 10 mass%, alternatively 0.20 mass% to 5 mass%, alternatively 0.25 to 2 mass%, alternatively 0.5 to 1 mass%), based upon the weight of the lubricating oil composition, of antioxidant comprising one or more diphenylamine antioxidants comprising: a) from 45 to 95 mass% (such as 45 mass% to 90 mass%, such as 50 mass% to 85 mass%, such as 55 mass% to 80 mass%, such as 60 mass% to 80 mass%, such as 65 mass% to 75 mass%) of mono-aralkyl substituted diphenylamine represented by the Formula (III) where n is 1, w is 0, and z is 0; and b) 5 to 55 mass% (such as 55 to 10 mass%, such as 15 to 50 mass%, such as 45 to 20 mass%, such as 20 to 40 mass%, such as 25 to 35 mass%) of di-aralkyl substituted diphenylamine represented by Formula (III), where n is 1, w is 0, and z is 1,

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



Formula (III)

where n is 1 or 0, z is 0 or 1, and w is 0 or 1; and each R^a is independently represented by the formula:



where Ph is a substituted or unsubstituted phenyl group, R^1 is C_1 to C_{20} (such as C_1 to C_{12}) hydrocarbyl group, R^2 is C_1 to C_{20} (such as C_1 to C_{12}) hydrocarbyl group, and R^1 and R^2 may be bound to each other;

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 aralkyl substituted 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**.

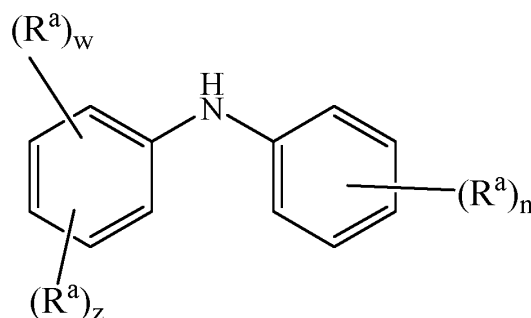
[0155] Note that **Comparative Formulation A** is **C₉-alkyl** diphenylamine not an **aralkyl** diphenylamine. **C₉-alkyl** diphenylamine was selected as the comparison as **C₉-alkyl** diphenylamine performance is generally considered superior to typical aralkyl diphenylamine performance. Hence **C₉-alkyl** diphenylamine is a more relevant comparison.

[0156] This disclosure also relates to lubricating oil compositions comprising or resulting from the admixing of:

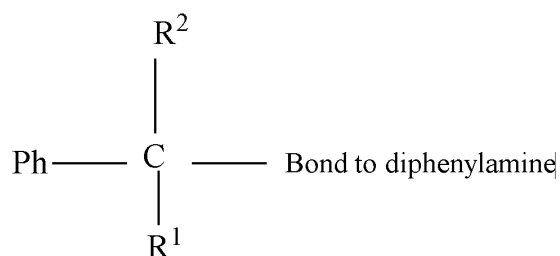
A) from 1 to 99 mass% (alternatively 30 to 95 mass%, alternatively 50 to 90 mass%, alternatively 60 to 95 mass%, alternatively 70 to 85 mass%) based upon the weight of the lubricating oil composition, of one or more **base oils**;

B) from 0.01 to 20 mass% (in particular 0.10 to 15 mass%, alternatively, 0.15 to 10 mass%, alternatively 0.20 mass% to 5 mass%, alternatively 0.25 to 2.5 mass%, alternatively 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-aralkyl substituted diphenylamine represented by Formula (III) below, where n is 1, w is 0, and z is 1, and
- ii) at least 45 mass%, based upon the weight of the lubricating oil composition, of mono-aralkyl 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-aralkyl 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 w is 0 or 1, n is 1 and z is 0 or 1, and each R^a is independently represented by the formula:



where Ph is a substituted or unsubstituted phenyl group, R¹ is C₁ to C₂₀ (such as C₁ to C₁₂, such as C₁) hydrocarbyl group, R² is C₁ to C₂₀ (such as C₁ to C₁₂, such as C₁) hydrocarbyl group, and R¹ and R² may be bound to each other;

C) from 0.10 to 20 mass% (in particular, 0.15 to 10 mass%, alternatively 0.20 mass% to 5 mass%, alternatively 0.25 to 2 mass%), based upon the weight of the lubricating oil composition, of one or more **detergents**, such as carboxylate detergents (such as blends of detergents);

D) optionally, from 0.01 to 5 mass% (in particular 0.1 to 4 mass%, alternatively 0.25 to 3 mass%, alternatively 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%, alternatively 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%, alternatively 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%, alternatively 0.01 to 5 mass%, alternatively 0.1 to 4 mass%, alternatively 0.1 to 2 mass%, alternatively 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%, alternatively 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%, alternatively 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%, alternatively 0.1 to 3 mass%, alternatively 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%, alternatively 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%, alternatively 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).

[0157] 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.

[0158] 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.

[0159] 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.

[0160] 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.

[0161] In embodiments, element K is present in addition to the base oil, detergent, and the one or more functionalized polymers described herein.

[0162] This disclosure further relates to a lubricating oil composition wherein di-aralkyl 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-aralkyl 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 0.5 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.

[0163] This disclosure further relates to a lubricating oil composition wherein di-aralkyl 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 20 mass% or less, such as 15 mass% or less, such

as 10 mass% or less, such as 8 mass% or less, such as 5 mass% or less, based upon the mass of the lubricating composition and mono-aralkyl 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 20 mass% or less, such as 15 mass% or less, such as 10 mass% or less, such as 8 mass% or less, such as 5 mass% or less, based upon the mass of the lubricating composition.

[0164] In embodiments, the lubricating oil composition may further comprising zinc dialkyldithiophosphate.

[0165] In embodiments, the lubricating oil composition may further comprises hindered phenolic antioxidant.

[0166] In embodiments, the lubricating oil composition may further comprises a molybdenum containing compound such as a dimeric and or trimeric molybdenum containing compound, optionally providing 50 to 1000 ppm Mo to the lubricating oil composition.

[0167] 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.

[0168] In embodiments, the lubricating oil composition may further comprise ethoxylated alcohol.

[0169] 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 of less than 100 mgKOH/g.

[0170] 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 having from 1 to 500 mmol soap, such as 5 to 400 mmol soap to the lubricating oil composition.

[0171] 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 detergent having a TBN over 100 mgKOH/g and a second detergent having a TBN less than 100 mgKOH/g) and 2) from 1 to 500 mmol soap, such as 5 to 400 mmol soap to the lubricating oil composition.

[0172] This disclosure 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 aralkyl substituted 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].

[0173] This disclosure 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**.

[0174] This disclosure 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%, such as within 8%, such as within 6%, such as within 5%, such as within 4%) of the oxidation of **Comparative Formulation A** [**Comparative Formulation A** is defined to be the same lubricating oil composition except that the aralkyl substituted 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].

[0175] This disclosure 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 such as at least 40% less, such as about 12 to about 35% less) than the percent viscosity increase of **Comparative Formulation A**.

[0176] This disclosure further relates to a lubricating oil composition where:

A) 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%, such as within 8%, such as within 6%, such as within 5%, such as within 4%) of the oxidation of **Comparative Formulation A**; and

B) 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 such as at least 40% less, such as about 12 to about 40% less) than the percent viscosity increase of **Comparative Formulation A**, [**Comparative Formulation A** is defined to be the same lubricating oil composition except that the aralkyl substituted 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].

[0177] 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.

[0178] 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.

[0179] The lubricating compositions of the present disclosure may contain low levels of phosphorus, namely not greater than 1600, such as not greater than 1200, such as 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.

[0180] Suitably, the lubricant composition may have a phosphorus level of 1200 ppm or less, alternatively 1000 ppm or less, alternatively 800ppm or less, as measured by ASTM D5185.

[0181] 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, such as at least 0.6, such as at least 0.65.

[0182] Typically, the lubricating compositions may contain low levels of sulfur. Suitably, the lubricating composition contains up to 0.4, such as up to 0.3, such as 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.

[0183] Typically, the lubricating compositions may contain low levels of sulfated ash, such as 1.2 % or less, such as 1.0 mass% or less, such as 0.9 mass or less %, such as 0.8 mass% or less, alternatively 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).

[0184] 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).

[0185] In embodiments, the kinematic viscosity at 100° C ("KV100") of the lubricating composition may range from 1 to 30 cSt, alternatively 3 to 20, alternatively 3 to 17 cSt, alternatively 3.5 to 16.3 cSt alternatively 9.3 to less than 12.5 cSt, alternatively 12.5 to less than 16.3 cSt, as determined according to ASTM D 445-19a).

[0186] 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. Suitably, 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. Alternatively, 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. Alternatively, 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).

[0187] Optionally, the lubricating oil composition containing diphenylamine antioxidants described herein may be absent phenolic antioxidant.

[0188] 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.

[0189] In embodiments, the lubricating oil composition may comprise less than 75 ppm boron, alternatively less than 60 ppm boron, alternatively from 1 to 70 ppm boron. Alternatively, the lubricating oil composition may be absent boron.

[0190] 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.

[0191] 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.

[0192] 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.

[0193] 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)

[0194] 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.

[0195] 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.

[0196] 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.)

[0197] In embodiments, the lubricating compositions of the present disclosure may be a passenger car motor oil.

[0198] In embodiments, the lubricating compositions of the present disclosure may be a passenger car diesel oil.

[0199] 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%.

[0200] 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.

[0201] 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.

[0202] The lubricating composition disclosed herein may have a SAE viscosity grade of 0W-Y, wherein Y may be 12, 16, or 20. In one embodiment, the lubricating composition has an SAE viscosity grade of 0W-12.

[0203] The internal combustion engines that may be lubricated with the compositions described herein may be engines designed for moving vehicles (such as automobiles, trucks, generators, marine engines etc.), stationary engines, such as heavy duty internal combustion engines or standing generators comprising internal combustion engines.

[0204] The internal combustion engines that may be lubricated with the compositions described herein may be passenger car engines, diesel engines, hydrogen engines, ammonia engines, natural gas engines, gasoline engines, marine engines, and or motorcycle engines.

[0205] In embodiments, the lubricating compositions disclosed herein may be used in heavy-duty engines (*e.g.*, heavy-duty vehicles having a gross vehicle weight rating of 10,000 pounds or more).

[0206] In embodiments, the lubricating compositions disclosed herein may be used in light-duty engines (*e.g.*, light-duty vehicles having a gross vehicle weight rating of less than 10,000 pounds).

[0207] In embodiments, the lubricating compositions disclosed herein may be used as passenger car motor oils.

A. Base Oil

[0208] 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.

[0209] 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.

[0210] 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%, from 5 mass% to 50 mass%, or from 5 mass% to less than 50 mass% of active ingredient, based upon the weight of the concentrate.

[0211] Common oils useful as base oils include animal and vegetable oils (*e.g.*, castor and lard oil), liquid petroleum oils, and hydrotreated 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.

[0212] 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, 19th edition, January 2021, 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.

[0213] In another embodiment, the base oil may comprise polyalphaolefins comprising oligomers of linear olefins having 6 to 14 carbon atoms, such as 8 to 12 carbon atoms, such as 10 carbon atoms having a Kinematic viscosity at 100° C of 10 cSt or more (as measured by ASTM D445); and may have a viscosity index ("VI"), as determined by ASTM D2270, of 100 or more, such as 110 or more, such as 120 or more, such as 130 or more, such as 140 or more; and/or having a pour point of -5° C or less (as determined by ASTM D97), such as -10° C or less, such as -20° C or less.

[0214] In another embodiment polyalphaolefin oligomers useful in the present disclosure may comprise C₂₀ to C₁₅₀₀ paraffins, such as C₄₀ to C₁₀₀₀ paraffins, such as C₅₀ to C₇₅₀ paraffins, such as 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 alternatively 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).

[0215] 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.

[0216] 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.

[0217] Another suitable class of synthetic lubricating oils useful as base oils comprises the esters of dicarboxylic acids (*e.g.*, phthalic acid, succinic acid, alkyl succinic acids and alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, 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.

[0218] Esters useful as synthetic 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.

[0219] Desirable ester base oils are commercially available as Esterex™ Esters (ExxonMobil Chemical Company, Houston, Texas).

[0220] 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.

[0221] 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.

[0222] 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 typically substantially free from materials introduced through manufacturing, contamination, or previous use.

[0223] 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).

[0224] In particular, oils from renewable sources, *i.e.*, based in part on carbon and energy captured from the environment, such as biological sources, are useful herein.

[0225] The various base oils are often categorized as Group I, II, III, IV, or V according to the API EOLCS 1509 definition (American Petroleum Institute Publication 1509, see section E.1.3, 19th edition, January 2021, www.API.org). Generally speaking, Group I base stocks have a viscosity index of between about 80 to 120 and contain greater than about 0.03 % sulfur

and/or less than about 90 % saturates. Group II base stocks have a viscosity index of between about 80 to 120 and contain less than or equal to about 0.03 % sulfur and greater than or equal to about 90 % saturates. Group III base stocks have a viscosity index greater than about 120 and contain less than or equal to about 0.03 % sulfur and greater than about 90 % saturates. Group IV base stocks include polyalphaolefins (PAO). Group V base stocks include base stocks not included in Groups I-IV. (Viscosity index measured by ASTM D 2270, saturates is measured by ASTM D2007, and sulfur is measured by ASTM D5185, D2622, ASTM D4294, ASTM D4927, and ASTM D3120).

[0226] 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, such as 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.

[0227] The base oil useful herein may be selected from any of the synthetic, natural, or re-refined oils (such as those typically used as crankcase lubricating oils for spark-ignited and compression-ignited engines). Mixtures of synthetic and/or natural and/or re-refined base oils may be used if desired. Multi-modal mixtures (such as bi- or tri-modal mixtures) of Group I, II, III, IV, and/or V base stocks may be used if desired.

[0228] 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, alternatively of 3 to 30 cSt, alternatively 4 to 20 cSt at 100° C, alternatively 5 to 10 cSt, alternatively 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 such as of about 2.5 cSt to about 9 cSt.

[0229] The base oil or base oil blend typically has a saturate content of at least 65 mass%, such as at least 75 mass%, such as at least 85 mass%, such as at least 90 mass% as determined by ASTM D2007.

[0230] Suiatbaly, the base oil or base oil blend may have a sulfur content of less than 1 mass%, such as less than 0.6 mass%, such as 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.

[0231] 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.

[0232] In embodiments, the viscosity index (VI) of the base oil is at least 95, such as at least 110, such as at least 120, even such as at least 125, such as from about 130 to 240, in particular from about 105 to 140 (as determined by ASTM D2270).

[0233] 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.

[0234] 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.

[0235] 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%, such as from about 70 to about 95 mass%, and such as from about 80 to about 95 mass%, based on the total weight of the composition.

[0236] Typically, one or more base oils are present in the lubricating composition in an amount of 32 mass% or more, alternatively 55 mass% or more, alternatively 60 mass% or more,

alternatively 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, such as 95 mass% or less, even such as 90 mass% or less. Alternatively, one or more base oils are present in the lubricating composition at from 1 to 99 mass%, alternatively 50 to 97 mass%, alternatively to 60 to 95 mass%, alternatively 70 to 95 mass%, based upon the weight of the lubricating composition.

[0237] The base oils and blends thereof described above are also useful for making concentrates as well as for making lubricants therefrom.

[0238] 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.

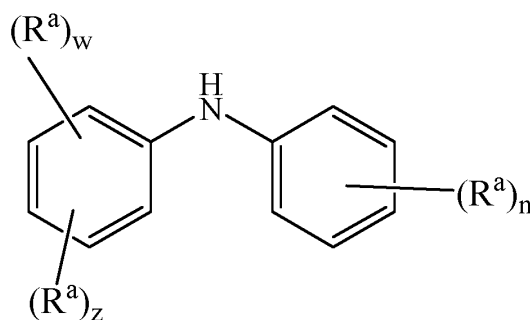
[0239] Typically, one or more base oils are present in the concentrate composition in an amount of 50 mass% or less, alternatively 40 mass% or less, alternatively 30 mass% or less, alternatively 20 mass% or less, based on the total weight of the concentrate composition. Typically, one or more base oils are present in the concentrate composition at an amount of 0.1 to 49 mass%, alternatively 5 to 40 mass%, alternatively to 10 to 30 mass%, alternatively 15 to 25 mass%, based upon the weight of the concentrate composition.

B. Antioxidants

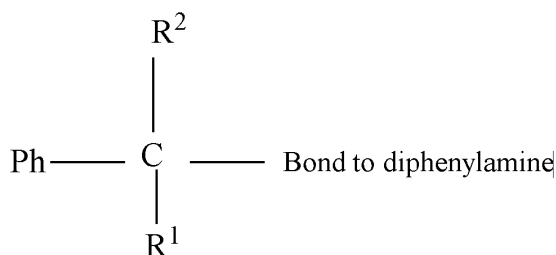
[0240] The present disclosure relates to antioxidants that disrupt oxidation and increase the useful life of lubricating oils. More particularly, the present disclosure may describe antioxidant compositions comprising a plurality of antioxidative lubricant additives. In embodiments, the antioxidant comprises **diphenylamine antioxidant** and optionally one or more additional antioxidants and/or optionally one or more carboxylate detergents, where **mono-aralkyl substituted diphenylamines** are absent or present at 45 mass% or more (such as 50 to 95 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 disclosure in lubricating oil compositions. Primary antioxidants, optional additional antioxidants and detergents compatible with the present disclosure are described herein.

[0241] The antioxidant composition useful herein typically comprises a primary antioxidant and one or more optional additional antioxidants. Preferred primary antioxidants of the present disclosure typically comprise **diphenylamine anti-oxidants** comprising 5 to 55 mass% (such as 55 to 10 mass%, such as 15 to 50 mass%, such as 45 to 20 mass%, such as 20 to 40 mass%, such as, 25 to 35 mass%) of **di-aralkyl substituted diphenylamine**, and from 45 to 95 mass% (such as 45 mass% to 90 mass%, such as 50 mass% to 85 mass%, such as 55 mass% to 80 mass%, such as 60 mass% to 80 mass%, such as 65 mass% to 75 mass%,) of **mono-aralkyl substituted diphenylamine**, based upon the weight of the mono- and di- aralkyl substituted diphenylamines.

[0242] The primary antioxidants employed in the lubricating oil of the present disclosure are typically represented by Formula (III):



where n is 1, z is 0 or 1, and w is 0 or 1, and each R^a is independently represented by the formula:



where Ph is a substituted or unsubstituted phenyl group, R^1 is C_1 to C_{20} (such as C_1 to C_{12} , such as C_1) hydrocarbyl group, R^2 is C_1 to C_{20} (such as C_1 to C_{12} , such as C_1) hydrocarbyl group, and R^1 and R^2 may be bound to each other, where preferably the at least 45% of the primary antioxidant has n is 1, z is 0 and w is 0, based upon the weight of compounds represented by Formula (III). Preferably Ph is phenyl, and R^1 and R^2 are methyl.

[0243] In embodiments, the primary antioxidants employed in the lubricating oil of the present disclosure comprise more than a) 45 mass% mono(4-(2-phenylpropan-2-yl)phenyl)amine, b) less than 55 mass% of bis(4-(2-phenylpropan-2-yl)phenyl)amine, and c) less than 10 mass% of tri(4-(2-phenylpropan-2-yl)phenyl)amine, based upon the weight of a), b) and c).

[0244] In embodiments, the diphenylamine antioxidant composition may comprise less than 55 mass%, or 50 mass% or less, or 45 mass% or less, or 40 mass% or less, or 30 mass% or less, or 20 mass% or less, 15 mass% and more than 5 mass %, such as more than 10 mass% of di-aralkyl substituted diphenylamines represented by Formula (III), where w is 0, n is 1 and z is 1), based upon the weight of the diphenylamine antioxidant composition.

[0245] In embodiments, the diphenylamine antioxidant composition may comprise more than 45 mass%, or 50 mass% or more, or 55 mass% or more, or 60 mass% or more, or 70 mass% or more, or 80 mass% or more, or 90 mass% or more, or 92 mass% or more, or 93 mass% or more, or 94 mass% or more, or 45 to 95 mass% and not less than 45 mass% of mono-aralkyl substituted diphenylamines represented by Formula (III), where n is 1, w is 0, and z is 0, based upon the weight of the diphenylamine antioxidant composition.

[0246] This disclosure further relates to an antioxidant composition comprising an antioxidant composition comprising or made by admixing:

1) phenylamine antioxidant comprising one or more di-aralkyl substituted diphenylamine as represented by Formula (III) where n is 1, z is 1 and w is 0 and one or more mono-aralkyl substituted diphenylamine as represented by Formula (III) where n is 1, z is 0 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, mono-alkyl substituted diphenylamine(s) is represented by Formula (III) where n is 0, w is 0 and z is 1, are present at more than 45 mass%, such as from 45 mass% to 95 mass%, based upon the weight of **diphenylamine antioxidant** composition.

[0247] In embodiments, the di-aralkyl 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 a 100%) of the R^a groups in the para position (i.e., para to the bond to the phenylamine);

(ii) optionally less than 10%, such 5% or less, such as 0%, of the R^a 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 R^a groups in a meta position (i.e., meta to the bond to the phenylamine),
based upon the weight of the di-aralkyl substituted diphenylamine.

[0248] This disclosure further relates to diphenylamine antioxidant comprising:

- 1) di(aralkyl substituted phenyl) amine, and
- 2) from 50 to 95 mass% mono-aralkyl substituted diphenylamine, based upon the weight of the mono- and di-phenyl amines present.

[0249] This disclosure further relates to diphenylamine antioxidant comprising:

- 1) 5 to 55 mass% of di(C₉-aralkyl substituted phenyl) amines,
- 2) from 45 to 95 mass% of mono-C₉-aralkyl substituted diphenylamine, and
- 3) from 0 to less than 5 mass% of tri-C₉-aralkyl substituted diphenylamine, based upon the weight of 1), 2) and 3).

[0250] This disclosure further relates to diphenylamine antioxidant composition comprising:

- a) from 45 to 95 mass% mono-aralkyl substituted diphenylamine represented by the Formula (III) where n is 1, w is 0, and z is 0,
- b) 5 to 55 mass% of di(aralkyl substituted phenyl) amines represented by Formula (III), where n is 1, w is 0, and z is 1,
- c) from 0 to less than 5 mass% (such as from 0 to less than 3 mass%) tri-aralkyl 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).

[0251] This disclosure further relates to diphenylamine antioxidant composition comprising:

- a) from 45 to 95 mass% mono-aralkyl (such as mono-C₉-aralkyl) substituted diphenylamines represented by the Formula (III) where n is 1, w is 0, and z is 0,
- b) 5 to 55 mass% of di-aralkyl (such as di-C₉-aralkyl) substituted diphenylamines represented by Formula (III), where w is 0, n is 1 and z is 1,
- c) 5 mass% or less of tri-aralkyl (such as tri-C₉-aralkyl) substituted diphenylamines represented by Formula (III), where w + n + z = 3,
- d) 1 mass% or less of unsubstituted diphenylamines represented by Formula (I) where n 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.

[0252] This disclosure further relates to diphenylamine antioxidant composition comprising:

- a) from 55 to 90 mass% mono-aralkyl substituted diphenylamines represented by the Formula (III) where w is 0, n is 1 and z is 0,
- b) 10 to 45 mass% or more of di-aralkyl substituted diphenylamines represented by Formula (III), where w is 0, n is 1 and z is 1,
- c) 5 mass% or less of tri-aralkyl substituted diphenylamines represented by Formula (I), 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).

[0253] In embodiments, the di-aralkyl substituted diphenylamines represented by Formula (III) comprise di(4-(2-phenylpropan-2-yl)phenyl)amine.

[0254] 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 content of mono-, di-, and tri-aralkyl substituted diphenylamines may be determined by ultra-performance liquid chromatography as described in the Experimental Section.

[0255] The di-aralkyl substituted diphenylamines described herein are typically synthesized by reaction of alpha-methyl styrene with diphenylamine in the presence of Lewis acid catalyst. Further, di-aralkyl substituted diphenylamines may also be synthesized by a reaction of 4-(2-phenylpropan-2-yl)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).

[0256] 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%.

[0257] 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

[0258] The present disclosure may employ one or more additional antioxidants in combination with the primary antioxidants. Examples of suitable additional antioxidants are copper-containing antioxidants, sulfur-containing antioxidants, aromatic amine-containing antioxidants, hindered phenolic antioxidants, dithiophosphates derivatives, molybdenum succinimides, and metal thiocarbamates (such Zn or Mo-dialkyldithiocarbamates). In an embodiment, an antioxidant, such as an aromatic amine-containing antioxidant, and/or hindered phenolic antioxidants is present.

[0259] The additional antioxidant(s) may be present, in a total amount of, 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%.

[0260] When present in a concentrate, the additional antioxidant may be present, in a total amount of, 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%.

[0261] Examples of additional phenolic anti-oxidants 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.

[0262] Particularly useful hindered phenol antioxidants 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).

[0263] 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. The general types of amine additional 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.

[0264] Sulfur-containing antioxidants are also useful herein, for example, sulfurized alkyl phenols and alkali or alkaline earth metal salts thereof.

[0265] An additional antioxidant employed in the lubricating oil of the present disclosure may be a molybdenum succinimide.

[0266] Suitable dithiocarbamates antioxidants 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(dibutyldithiocarbamate), ethylenebis(dibutylthiocarbamate) and isobutyl disulfide-2, 2'-bis(dibutyldithiocarbamate).

[0267] The additional antioxidant employed in the lubricating oil of the present disclosure may be a sterically hindered phenol described in US 9,512,380, such as those shown at columns 82 to 100.

[0268] Additional antioxidant additives may be used in an amount of about 0.01 to 10 (alternatively 0.01 to 5, alternatively 0.01 to 3) mass%, alternatively about 0.03 to 5 mass%, alternatively 0.05 to less than 3 mass%, based upon the weight of the lubricating composition.

[0269] 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.

[0270] 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

[0271] 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 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.

[0272] 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.

[0273] Suitable detergent additive(s) useful in the present disclosure comprises calcium and/or magnesium metal salts. The detergent may be a calcium and/or magnesium carboxylate (*e.g.*, salicylates), sulfonate, or phenate detergent. Suitably, 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.

[0274] 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. 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, such as 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% (such as at least 125 mass%) of that stoichiometrically required.

[0275] Metal salts of phenols and sulfurized phenols may be 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.

[0276] 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 hydroxybenzoic 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. are typically prepared by carboxylation, for example by the Kolbe-Schmitt process, of phenoxides. Processes for overbasing the salicylic acid(s) and forming the detergents are known to those skilled in the art.

[0277] Preferred substituents in oil-soluble salicylic acids are alkyl substituents. In alkyl-substituted salicylic acids, the alkyl groups advantageously contain 5 to 100, such as 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 may be at least 9 to ensure adequate oil solubility.

[0278] 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.

[0279] In an embodiment, the compositions of the disclosure include an overbased alkaline earth metal detergent, as defined herein, such as an overbased calcium or magnesium detergent, such as an overbased calcium or magnesium salicylate detergent and/or an overbased calcium or magnesium sulfonate detergent.

[0280] 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 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.

[0281] 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.

[0282] Alternatively, the detergent additive(s) may comprise a magnesium salicylate, such as 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 alternatively of 150 mgKOH/g or less, such as 100 mgKOH/g or less.

[0283] Alternatively, the detergent additive(s) may comprise a combination of magnesium salicylate and magnesium sulfonate.

[0284] The magnesium detergent, when present, may provide the lubricating composition thereof with from 200-4000 ppm of magnesium atoms, suitably from 200-2000 ppm, from 300 to 1500 or from 450-1200 ppm of magnesium atoms (ASTM D5185).

[0285] The detergent composition may comprise (or consist of) a combination of one or more magnesium sulfonate detergents and one or more calcium salicylate detergents.

[0286] The combination of one or more magnesium sulfonate detergents and one or more calcium salicylate detergents may provide 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, such as at

least 750 ppm, such as at least 900 ppm of atomic calcium, such as from 500-4000 ppm, such as from 750-3000 ppm, such as from 900-2000 ppm atomic calcium (ASTM D5185).

[0287] 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.

[0288] Suitably the calcium detergent, such as a calcium salicylate, calcium sulfonate, or calcium phenate, 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 alternatively 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.

[0289] Calcium detergent, when present, is suitably present in amount sufficient to provide from 500-4000 ppm, such as from 750-3000 ppm such as from 900-2000 ppm atomic calcium to the lubricating oil composition (ASTM D5185).

[0290] Suitably the total atomic amount of metal from detergent in the lubrication composition according to all aspects of the disclosure is suitably from 500 to 5000 ppm, such as from 500 to 3000 ppm and such as from 500 to 2000 ppm (ASTM D5185).

[0291] In preferred embodiments, the composition of the present disclosure 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 %. The carboxylate detergents may be overbased (as measured by ASTM D2896) or low overbased (TBN from 15 to 30). One or more overbased carboxylate detergents (*e.g.*, low overbased and medium overbased) may be used.

[0292] 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.

[0293] 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 may be used in amounts in the range of 0.05 to 20.0 mass%, such as from 1.0 to 10.0 mass% and such as in the range of from 2.0 to 5.0 mass%, based on the total weight of the lubricating composition).

[0294] The total sulfated ash content of the lubricating composition herein is typically not greater than 2.0 mass%, alternatively at a level of not greater than 1.0 mass% and alternatively at a level of not greater than 0.8 mass%, based on the total weight of the lubricating composition as determined by ASTM D874.

[0295] 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, alternatively in the range of from 100 to 650, alternatively in the range of from 10 to 500 mgKOH/g, alternatively in the range of from 30 to 350 mgKOH/g, and alternatively in the range of from 50 to 300 mgKOH/g, as measured by ASTM D2896.

[0296] 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.

[0297] 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.

[0298] 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.

[0299] 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.

[0300] Typically, lubricating compositions formulated for use in heavy-duty diesel engines comprise detergents at from about 0.1 to about 10 mass%, alternatively from about 0.5 to about 7.5 mass%, alternatively from about 1 to about 6.5 mass%, based on the lubricating composition.

[0301] Typically, lubricating compositions formulated for use in a passenger-car engines comprise detergents at from about 0.1 to about 10 mass%, alternatively from about 0.5 to about 7.5 mass%, alternatively from about 1 to about 6.5 mass%, based on the lubricating composition.

[0302] Typically, lubricating compositions formulated for use in a drive train (e.g., transmissions) comprise detergents at from about 0.1 to about 10 mass%, alternatively from about 0.5 to about 7.5 mass%, alternatively from about 2 to about 6.5 mass%, based on the lubricating composition.

D. Friction Modifiers

[0303] 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 that lower the coefficient of friction are particularly advantageous in combination with the base oils and lubricating compositions of this disclosure.

[0304] Illustrative friction modifiers may include, for example, organometallic compounds or materials, or mixtures thereof, such as, 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 1998/26030, sulfides of molybdenum and molybdenum dithiophosphate, and US Patent No. 10,829,712

[0305] Lubricating oil compositions useful in all aspects of the present disclosure may contain from 10 to 1000, such as 30 to 750, such as 0 to 500, such as 50-200 ppm of molybdenum (measured as atoms of molybdenum).

[0306] Ashless friction modifiers may be present in the lubricating oil compositions of the present disclosure and are known generally and include esters formed by reacting carboxylic acids and anhydrides with alkanols and amine-based friction modifiers. Illustrative ashless friction modifiers useful in the lubricating compositions described herein include, for example, alkoxylated fatty acid esters (e.g. polyoxypropylene stearate, polyoxybutylene stearate, polyoxyethylene isostearate, polyoxypropylene isostearate, polyoxyethylene palmitate), alkanolamides (e.g. , lauric acid diethylalkanolamide, palmitic acid diethylalkanolamide), polyol fatty acid esters (e.g. glycerol monooleate, glycerol monostearate) , borated glycerol fatty acid esters (e.g. borated glycerol monooleate), fatty alcohol ethers (e.g. stearyl ether, myristyl ether), and mixtures thereof

[0307] 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%.

F. Pour Point Depressants

[0308] These materials, otherwise known as lube oil flow improvers, lower the minimum temperature at which the fluid will flow or can be poured. Such additives are well known. Typical examples are C₈ to C₁₈ dialkyl fumarate/vinyl acetate copolymers, polyalkyl methacrylates and the like. Such additives may be used in an amount of about 0.01 to 5 mass%, such as about 0.01 to 1.5 mass%, based upon the weight of the lubricating composition.

G. Anti-Foam Agents

[0309] Anti-foam agents may advantageously be added to lubricant compositions and/or concentrates described herein to prevent or retard the formation of foams. Suitable anti-foam agents include: silicones and fluoro-silicones, for example, polysiloxanes, such as silicon oil or polydimethyl siloxane and phenyl-methyl polysiloxane, and siloxane polyether copolymers.

[0310] Anti-foam agents are commercially available (e.g. from Dow Corning Corporation, Union Carbide Corporation, and OSI Specialties, Inc) 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, based on the weight of the lubricating oil composition.

H. Viscosity Modifiers

[0311] Viscosity modifiers function to impart high and low temperature operability to a lubricating oil. The VM used may have that sole function, or it may be multifunctional. Multifunctional viscosity modifiers that also function as dispersants are also known. Suitable viscosity modifiers are polyisobutylene, copolymers of ethylene and propylene and higher alpha-olefins, polymethacrylates, polyalkylmethacrylates, methacrylate copolymers, copolymers of an unsaturated dicarboxylic acid and a vinyl compound, inter-polymers of styrene and acrylic esters, and partially hydrogenated copolymers of styrene/ isoprene, styrene/butadiene, and isoprene/butadiene, as well as the partially hydrogenated homopolymers of butadiene and isoprene and isoprene/divinylbenzene.

[0312] 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.

[0313] 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

[0314] 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. Suitably, the dispersant is ashless.

[0315] Suitable ashless dispersants comprise amine, alcohol, amide, or ester polar moieties attached to a polymer backbone often via a bridging group. Examples include oil-soluble salts, esters, amino-esters, amides, imides, and oxazolines of long chain hydrocarbon substituted mono and dicarboxylic acids or their anhydrides; thiocarboxylate derivatives of long chain hydrocarbons; long chain aliphatic hydrocarbons having a polyamine attached directly thereto; and Mannich condensation products formed by condensing a long chain substituted phenol with formaldehyde and a polyalkylene polyamine. As is known in the art, ashless dispersants may be borated or non-borated.

Dispersants of (Poly)alkenylsuccinic derivatives

[0316] 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.

[0317] 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), pentaethylenehexamine (PEHA), and N-phenyl-p-phenylenediamine (ADPA).

[0318] The dispersant may comprise one or more PIBSA-PAMs, where the PIB is derived from polyisobutylene having an Mn of from 600 to 5000, such as from 700 to 4000, such as from 800 to 3000, such as from 900 to 2500 g/mol and the polyamine is derived from hydrocarbyl-substituted polyamines, such as tetraethylene pentamine, pentaethylene hexamine, tetraethylenepentamine (TEPA), pentaethylenehexamine (PEHA), N-phenyl-p-phenylenediamine (ADPA).

[0319] 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.

[0320] The above dispersants, such as the (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.

[0321] 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.

[0322] 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.

[0323] The dispersant may comprise one or more borated and one or more non-borated PIBSA-PAM's.

J. Corrosion Inhibitors/Anti-rust Agents

[0324] Corrosion inhibitors may be used to reduce the corrosion of metals. Suitable corrosion inhibitors comprise thiadiazole polysulfides containing from 5 to 50 carbon atoms, their derivatives and polymers thereof. Derivatives of 1, 3, 4 thiadiazoles such as those described in U.S. Patent Nos. 2,719,125; 2,719,126; and 3,087,932; are typical. Other examples include thio- and polythio-sulfenamides of thiadiazoles such as those described in UK Patent Specification No. 1,560,830. Benzotriazoles derivatives also fall within this class of additives.

[0325] Corrosion inhibitors can be used in any effective amount of 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%. Alternatively, such additives may be used in an amount of about 0.01 to 5 mass%, such as about 0.01 to 1.5 mass%, based upon the weight of the lubricating composition.

[0326] Suitable rust inhibitors comprise nonionic polyoxyalkylene polyols and esters thereof, polyoxyalkylene phenols, and anionic alkyl sulfonic acids. A rust inhibitor may be used in any effective amount of 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%.

K. Anti-wear Agents

[0327] The lubricating oil composition of the present disclosure can contain one or more anti-wear agents that can reduce friction and reduce wear. 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.

[0328] In embodiments, the anti-wear agent is or comprises a dihydrocarbyl dithiophosphate metal salt, such as zinc dialkyl dithiophosphate (ZDDP) 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.

[0329] 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 (ZDDPs).

[0330] A metal alkylthiophosphate and more particularly a metal dialkyl dithio phosphate in which the metal constituent is zinc, or zinc dialkyl dithio phosphate (ZDDP) can be a useful component of the lubricating compositions of this disclosure. ZDDP can be derived from primary alcohols, secondary alcohols or mixtures thereof. ZDDP compounds generally are of the formula $Zn[SP(S)(OR_1)(OR_2)]_2$ where R_1 and R_2 are C_1 - C_{18} alkyl groups, preferably C_2 - C_{12} alkyl groups. These alkyl groups may be straight chain or branched. Alcohols used in the ZDDP can be 2-propanol, butanol, secondary butanol, pentanols, hexanols such as 4-methyl-2-pentanol, n-hexanol, n-octanol, 2-ethyl hexanol, alkylated phenols, and the like. Mixtures of secondary alcohols or of primary and secondary alcohol can be used. Alkyl aryl groups may also be used. Useful zinc dithiophosphates include secondary zinc dithiophosphates such as those available from The Lubrizol Corporation under the trade designations "LZ™ 677A", "LZ™ 1095" and "L™Z 1371", from Chevron Oronite under the trade designation "OLOA™ 262" and from Afton Chemical under the trade designation "HiTEC™ 7169".

[0331] In embodiments, the zinc compound can be a zinc dithiocarbamate complex, such as a zinc dithiocarbamate.

[0332] 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%, such as from about 0.5 mass% to about 1.0 mass%, and such as from about 0.6 mass% to about 0.8 mass%, based on the total weight of the lubricating composition.

[0333] The anti-wear additives, such as ZDDP and/or the zinc carbamates, are typically used in amounts of from about 2 mass% to about 20 mass%, such as from about 3 mass% to about 15 mass%, based on the total weight of the additive concentrate.

[0334] Suitably, the anti-wear additive is ZDDP, such as 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.

L. Demulsifiers

[0335] 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%, such as about 0.01 to 2 mass%.

M. Seal Compatibility Agents

[0336] Seal compatibility agents include 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%, such as 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

[0337] Extreme pressure agents can prevent sliding metal surfaces from seizing under conditions of extreme pressure. Non-limiting examples of suitable extreme pressure agents include sulfurized animal or vegetable fats or oils, sulfurized animal or vegetable fatty acid esters and sulfurized olefins. 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

[0338] 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. 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%, alternatively 0.1 to 1.5 mass%), based on total weight of the lubricating oil composition.

[0339] 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.

[0340] 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
aralkyl substituted diphenylamine	0.01 - 20	0.1 - 8	1 to 5
Additional Antioxidant that is not di-aralkyl substituted diphenylamine	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
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
Basestock	Balance (such as 50 to 95 %)	Balance	Balance

[0341] 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
aralkyl substituted diphenylamine	0.1 - 15	0.5 - 5	1 to 5
Amine (other than aralkyl substituted diphenylamine) and or phenol based Antioxidant	0.01 - 7	0.10 - 5	1 to 5
Molybdenum containing compound	0.01-10	0.1 to 7	0.1 to 5
Antifoaming Agent	0.001 - 5	0.001 - 0.2	0.001-0.1
Friction Modifier	0 - 5	0 - 1.5	0.1 to 5
Viscosity Modifier	0.01 - 25	1 - 20	5-15
Optional additional additives	0 -20	0.1-10	0.1- 5
Basestock (50 to 99 mass%)	Balance	Balance	Balance

[0342] 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
aralkyl substituted diphenylamine	0.1 - 15	0.5 - 5	0.5 to 3
Amine (other than aralkyl substituted diphenylamine) and or phenol (preferably amine) based antioxidant	0.01 - 7	0.10 - 5	1 to 5
Sulfurized antioxidant	0.01 - 20	0.1 to 10	0.5 - 5
Molybdenum containing compound	0.01-10	0.1 to 7	0.1 to 5
Antifoaming Agent	0.001 - 5	0.001 - 0.2	0.001-0.1
Friction Modifier	0 - 5	0 - 1.5	0.1 to 5
Viscosity Modifier	0.01 - 25	1 - 20	5-15
ZDDP	0 -20	0.1-10	0.1- 10
Optional additional additives	0 -20	0.1-10	0.1- 10
Basestock (50 to 99 mass%)	Balance	Balance	Balance

[0343] 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

[0344] 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.

[0345] This disclosure also relates to a method of lubricating an internal combustion engine during operation of the engine comprising:

- (i) Providing the lubricating composition as 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).

[0346] 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, alternatively from 1 to 75 mass% renewable fuel, alternatively 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.

[0347] The renewable fuel component is typically produced from vegetable oil (such as palm oil, rapeseed oil, soybean oil, jatropha oil), microbial oil (such as algae oil), animal fats (such as cooking oil, animal fat, and/or fish fat) and/or biogas. Renewable fuel refers to biofuel produced from biological resources formed through contemporary biological processes. In an embodiment, the renewable fuel component is produced by means of a hydrotreatment process. Hydrotreatment involves various reactions where molecular hydrogen reacts with other

components, or the components undergo molecular conversions in the presence of molecular hydrogen and a solid catalyst. The reactions include, but are not limited to, hydrogenation, hydrodeoxygenation, hydrodesulfurization, hydrodenitrification, hydrodemetallization, hydrocracking, and isomerization. The renewable fuel component may have different distillation ranges, which provide the desired properties to the component, depending on the intended use.

Uses

[0348] 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.

[0349] 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 or a light duty diesel engine.

[0350] 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.

[0351] In embodiments, the lubricating oils of this disclosure are used in spark-assisted high compression internal combustion engines.

[0352] 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.)

[0353] In embodiments, the lubricating compositions of the present disclosure are suitably used in the lubrication of the crankcase of a passenger car diesel engine.

[0354] 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.

[0355] 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:

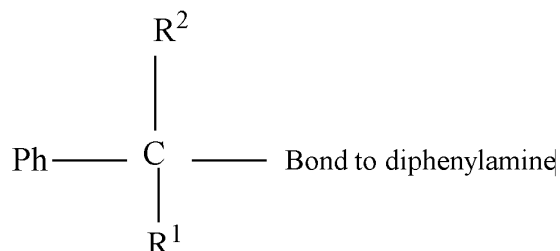
(i) providing a lubricating composition described herein to the internal combustion engine;

- (ii) providing a hydrocarbon fuel and or biofuel to the internal combustion engine; and
- (iii) combusting the fuel in the internal combustion engine.

[0356] 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.

[0357] This disclosure further relates to:

1. A stable antioxidant composition, comprising a homogeneous diphenylamine antioxidant fluid comprising di-aralkyl substituted diphenylamine and at least 45 mass% mono-aralkyl substituted diphenylamine, based upon the weight of the mono-and di- substituted diphenylamines, wherein the diphenylamine antioxidant fluid is clear after 90 days at 20 °C in a clear glass container without agitation.
2. The stable antioxidant composition of paragraph 1, wherein the aralkyl group of the aralkyl substituted diphenylamines is independently represented by the formula:



where Ph is a substituted or unsubstituted phenyl group, R¹ is C₁ to C₂₀ hydrocarbyl group, R² is C₁ to C₂₀ hydrocarbyl group, and R¹ and R² may be bound to each other.

3. The stable antioxidant composition of paragraph 2, wherein Ph is unsubstituted phenyl and R¹ and R² are independently methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, phenyl, naphthyl, alkyl substituted phenyl, or an isomer thereof.
4. The stable antioxidant composition of paragraph 2, wherein Ph is unsubstituted phenyl, R² is methyl, and R¹ is methyl.
5. The stable antioxidant composition of paragraph 1, further comprising polar diluent having an aniline point of 0°C or less, and at least 2 available hydrogen-bond acceptor groups

(such oxygen containing groups, such as ester and or ether groups) that are 2, 3, 4, 5, or 6 atoms apart, optionally wherein the hydrogen-bond acceptor groups do not comprise sulfur.

6. The stable antioxidant composition of paragraph 5, 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 tri-methylolpropane, and
- iii) phthalates, terephthalates, isophthalates, trimellitates and pyromellitates.

7. The stable antioxidant composition of paragraph 1, wherein mono and di are combined to form a homogeneous fluid 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 antioxidant composition of paragraph 5, wherein the polar diluent(s) are one or more diluent(s) selected from the group consisting of: (di-propylene glycol) dibenzoate, C₈-C₁₀ Tri-methylol propane ester, trioctyl trimellitate, and dioctylterephthalate.

9. The stable antioxidant composition of paragraph 1, further comprising detergent, such as carboxylate (such as salicylate) and or sulfonate detergent.

10. 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.

11. The stable antioxidant composition of paragraph 1, further comprising one or more base oils, dispersants, friction modifiers; pour point depressants, anti-foaming agents, viscosity modifiers, corrosion inhibitors, antirust agents, and/or anti-wear agents.

12. The stable antioxidant composition of paragraph 1, where the stable antioxidant composition comprises:

- i) 1 to 99 mass% of the aralkyl substituted diphenylamine antioxidant;
 - ii) optionally 1 to 99 mass% of polar diluent,
 - iii) optionally, 1 to 98 mass% of detergent,
- based upon the weight of the stable antioxidant composition, and
- iv) 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).

13. The stable antioxidant composition of paragraph 1, further comprising salicylate detergent and or sulfonate detergent, such as calcium salicylate detergent and/or magnesium sulfonate detergent.

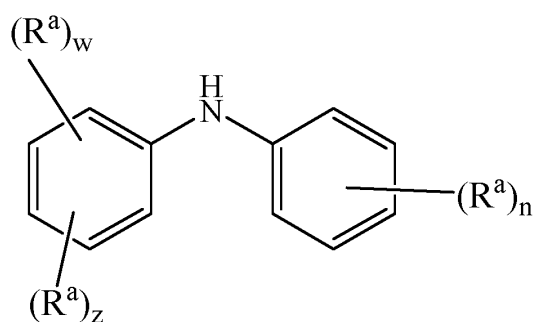
14. The stable antioxidant composition of paragraph 1, wherein the composition comprises:

a) 45 to 95 mass% mono-aralkyl substituted diphenylamine represented by the Formula (III) where n is 1, w is 0, and z is 0,

b) 5 to 55 mass% of di-aralkyl substituted diphenylamine represented by Formula (III), where n is 1, w is 0, and z is 1,

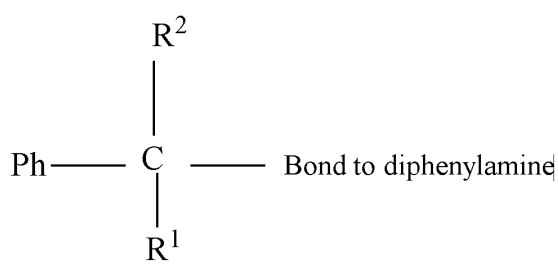
c) from 0 to less than 10 mass% (such as from 0 to less than 5 mass%) tri-aralkyl substituted diphenylamine represented by Formula (III), where n is 1, w is 1 and z is 1,

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 n is 1 or 0, z is 0 or 1, and w is 0 or 1; and each R^a is independently represented by the formula (I):



(I)

where Ph is a substituted or unsubstituted phenyl group, R^1 is C_1 to C_{20} hydrocarbyl group, R^2 is C_1 to C_{20} hydrocarbyl group, and R^1 and R^2 may be bound to each other.

15. The stable antioxidant composition of any of paragraphs 1 to 14 wherein the composition is obtained by combining an aralkylene (such as alpha methyl styrene) and

diphenylamine with a catalyst to obtain a combination comprising mono-aralkyl substituted diphenylamine and di-aralkyl substituted diphenylamine.

16. A stable concentrate composition comprising:
 - i) the stable antioxidant composition of any of paragraphs 1 to 15;
 - ii) optional 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) above, pour point depressants, anti-foaming agents, viscosity modifiers, corrosion inhibitors, antirust agents, and/or anti-wear agents.
17. The stable concentrate composition of paragraph 16, 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.
18. The stable concentrate composition of paragraph 16, wherein the wherein the stable concentrate composition is clear after 90 days at 20 °C in a clear glass container without agitation.
19. The concentrate composition of any of paragraphs 16 to 18, wherein the concentrate comprises:
 - 1) aralkyl substituted diphenylamine antioxidant comprising:
 - a) di-aralkyl substituted diphenylamine and b) from 45 to 95 mass% of mono-aralkyl substituted diphenylamine, based upon the weight of the mono- and di-aralkyl substituted phenyl amines present in the concentrate and b) one or more polar diluents having an aniline point of 0°C or less and at least 2 available hydrogen-bond acceptor groups (such as ester and /or ether 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.
20. A booster pack comprising:
 - 1) 1 to 99 mass % of aralkyl substituted diphenylamine antioxidant composition comprising:

a) 5 to 65 mass% of di-aralkyl substituted diphenylamine and b) from 45 to 95 mass% of mono-aralkyl substituted diphenylamine, based upon the weight of the mono- and di-aralkyl substituted phenyl amines present in the concentrate;

b) optionally 1 to 99 mass% of polar diluent having an aniline point of 0°C or less, and at least 2 available hydrogen-bond acceptor groups (ester and/or ether 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 150 hours at 20 °C in a clear glass container without agitation; and

2) optionally, 1 to 99 mass % of detergent.

21. The booster pack of paragraph 20, further comprising one or more molybdenum containing compounds.

22. The booster pack of paragraph 20, further comprising one or more of the following components.

i) optionally, one or more friction modifiers;

ii) optionally, one or more antioxidants, other than the antioxidants represented by

Formula (I);

iii) optionally, one or more pour point depressants;

iv) optionally, one or more anti-foaming agents;

v) optionally, one or more viscosity modifiers;

vi) optionally, one or more base oils;

vii) optionally, one or more inhibitors and/or antirust agents; and/or

viii) optionally, one or more anti-wear agents.

23. 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 antioxidant composition, booster pack, and or stable concentrate composition of any paragraphs 1 to 22.

24. A stable lubricating oil composition comprising or made by admixing:

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

(ii) one or more dispersants;

(iii) one or more detergents having from 1 to 500 mmol/kg soap (based upon the weight of the detergent);

(iv) antioxidant composition, comprising:

a) aralkyl substituted diphenylamine antioxidant comprising: 1) di(aralkyl substituted phenyl) amine and 2) more than 45 mass% of mono-aralkyl substituted diphenylamine (based upon the weight of mono-aralkyl substituted phenyl amines, diaralkyl substituted phenyl amines, and any tri-aralkyl substituted phenyl amines present in the antioxidant composition); and

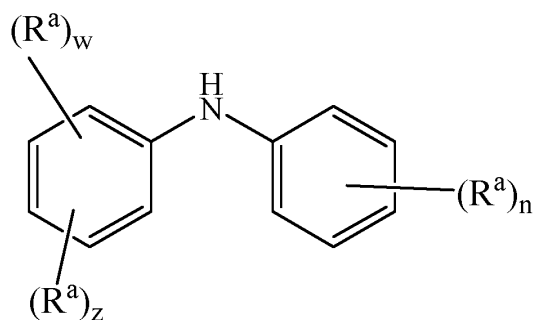
b) optionally, polar diluent having an aniline point of 0°C or less, and at least 2 available hydrogen-bond acceptor groups (such as ester and /or ether groups) that are 2, 3, 4, 5, or 6 atoms apart;

(v) optionally one or more Mo containing compounds;

(vi) optionally one or more fatty acid esters, such as sulfated fatty acid methyl esters; and

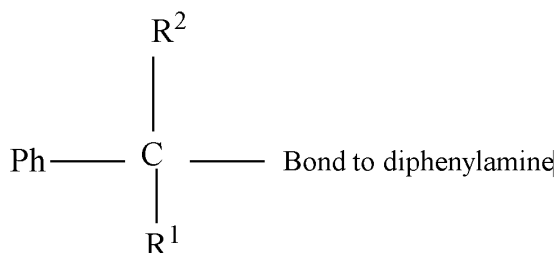
(vii) optionally, one or more antioxidants not represented by Formula III,

where Formula (III) is:



Formula (III)

where n is 1 or 0, z is 0 or 1, and w is 0 or 1; and each R^a is independently represented by the formula:



where Ph is a substituted or unsubstituted phenyl group, R¹ is C₁ to C₂₀ hydrocarbyl group, R² is C₁ to C₂₀ hydrocarbyl group, and R¹ and R² may be bound to each other.

25. The stable lubricating oil composition of paragraph 23 or 24, wherein the stable lubricating oil composition is clear after 90 days at 20 °C in a clear glass container without agitation.

26. The lubricating oil composition of paragraphs 23, 24 or 25, 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 aralkyl substituted 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 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 aralkyl substituted 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.

27. The lubricating oil composition of any of paragraphs 23 to 26, further comprising zinc dialkyldithiophosphate, hindered phenolic antioxidant, and or molybdenum containing compound.

28. The lubricating oil composition of any of paragraphs 23 to 27, 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.

29. The lubricating oil composition any of paragraphs 23 to 28, 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 (I);

- F) optionally, one or more pour point depressants;
 - G) optionally, one or more anti-foaming agents;
 - H) optionally, one or more viscosity modifiers;
 - J) optionally, one or more inhibitors and/or antirust agents; and/or
 - K) optionally, one or more anti-wear agents.
30. The lubricating oil composition of paragraph 29, 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.
31. The lubricating oil composition of paragraphs 19 to 26 where lubrication oil composition is a lubricating oil for an internal combustion engine.
32. The lubricating oil composition of paragraph 31 wherein the engine is a passenger car engine, a diesel engine, a hydrogen engine, an ammonia engine, a natural gas engine, a gasoline engine, a marine engine, and or a motorcycle engine.
33. The lubricating oil composition of paragraph 31 wherein the engine is a heavy duty diesel engine or a light duty diesel engine.
34. The lubricating oil composition of paragraph 31 wherein the engine is a two or four stroke engine.
35. The lubricating oil composition of any of paragraphs 23 to 34 wherein the base oil is selected from one or more of API Group I, II, III, IV, and V base oils.
36. The lubricating oil composition of any of paragraphs 23 to 35 wherein the base oil comprises one or more API Group V base oils (optionally the Group V base oil is present at 20 mass% or less, such as 10 mass% or less, 5 mass% or less in the lubricating oil composition).
37. The lubricating oil composition of any of paragraphs 23 to 36 wherein the base oil comprises gas to liquid and or coal to liquid base oil, such as group II and or group III gas to liquid and or coal to liquid base oil.
38. The lubricating oil composition of any of paragraphs 23 to 37 wherein the base oil comprises at least 50 mass % Group II and or Group III base oil.

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

- (i) providing to an internal combustion engine the lubricating oil composition of any of paragraphs 23 to 38;
- (ii) providing a fuel in the internal combustion engine; and
- (iii) combusting the fuel in the internal combustion engine.

40. The use of lubricating oil composition of any of paragraphs 23 to 39 in an internal combustion engine, where the oil sump temperature is greater than 100 °C or greater than 120 °C.

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

- 1) heating an antioxidant composition to a fluid 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-aralkyl substituted diphenylamine and b) from 45 to 95 mass% of mono-aralkyl substituted diphenylamine, based upon the weight of the mono- and di-aralkyl substituted phenyl amines present in the concentrate, wherein the combination of mono-aralkyl substituted diphenylamine of b) combined with the di-aralkyl substituted diphenylamine of a) is a clear fluid after 150 hours at 20 °C in a clear glass container without agitation.
42. A method of improving viscometric growth 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) di-aralkyl substituted diphenylamine and b) from 45 to 95 mass% of mono-aralkyl substituted diphenylamine, based upon the weight of the mono- and di-aralkyl substituted phenyl amines present in the concentrate, wherein the combination of mono-aralkyl substituted diphenylamine of b) combined with the di-aralkyl substituted

diphenylamine of a) is a clear fluid after150 hours at 20 °C in a clear glass container without agitation.

[0358] The following non-limiting examples are provided to illustrate the disclosure.

Experimental

[0359] All molecular weights are number average molecular weights (Mn) reported in g/mol, as determined by gel permeation chromatography using polystyrene standards, unless otherwise noted. "A.I.", "a.i.", and "ai" are mass% active ingredient, unless otherwise indicated.

Testing Procedures

[0360] **KV100** is Kinematic viscosity measured at 100° C according to ASTM D445-19a.

[0361] **L109 Oxidation** 216 hr (reported in units of absorbance per centimeter, A/cm) was determined using the CEC-L-109-14 Oxidation Test for Engine Oils Operating in the Presence of Biodiesel Fuel over 216 hours.

[0362] **Analytical Method 1:** Ultra-Performance Liquid Chromatography (UPLC) with UV and mass spectrometer detectors using the conditions detailed in Table A. The mass spectrometer chromatograms were used to confirm identity of the mono-, di and tri-aralkyl substituted diphenylamines. The UV chromatograms were used to establish the relative % of each aralkyl substituted diphenylamine by comparing the area under the curve for each constituent.

Table A. UPLC method to analyse substituted diphenylamines.

Ultra-performance liquid chromatograph	Agilent Infinite II 1260
Sample concentration	0.4 mg/mL in acetonitrile
Injection volume	1 mL (microliter)
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 (microns)
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% phane 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

[0363] Analytical Method 2: High-Performance Liquid Chromatography (HPLC) with diode array detector using the conditions detailed in Table B were used to analyse Intermediate 1 and Product 1.

Table B. HPLC method to analyse Intermediate 1 and Product 1.

High-performance liquid chromatograph	Agilent 1100 HPLC
Sample concentration	0.5 mg/mL in acetonitrile
Injection volume	3 mL (microliters)
Flow rate	0.67 mL/min
Column description	Kinetex EVO C18 Core-Shell: Dimensions – 100 x 3 mm, Particle size 2.6 mm (microns)
Column Temperature	30 °C
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: 98-5% phase A, 2-95% phase B over 15.3 mins Stage 2: 5% phase A, 95% phase B for 5.1 mins Stage 3: 5-98% phase A, 95-2% phase B over 0.1 mins Stage 4: 98% phase A, 2% phase B over 5.0 mins
UV detector	Agilent G1315B DAD detector
Detection wave length	190-400 nm

[0364] Storage Stability Test Method: 100 ml of the sample to be tested is poured into a centrifuge tube and the tube is supported near-vertically in an oven and heated at the desired temperature, such as at 60°C or 20°C, without agitation. The initial condition of all samples was observed and then observed at specific time points (e.g. every 96 hours), over a period of time, such as 10 weeks, for evidence of crystallization, precipitation or cloudiness. The centrifuge tube was visually observed under natural light for sediment. The outside of the centrifuge tube was cleaned with solvent, if required, to ensure a clear view. The following observations were made:

[0365] Evidence of Sediment - Sediment is hard, solid particles which have collected at the very bottom of the tube. If sediment is present, often there is some light sediment or emulsion with a distinguishable top surface of interface just above the hard sediment. This is referred to as the “Haze Layer” (cuff). The % volume of sediment and % volume of light sediment or emulsion, if present, is recorded. During the inspection of the samples, if the sample showed sediment volume over 0.05 mass %, the sample was deemed to have failed at that point

[0366] Visual Inspection - Where no distinguishable hard sediment is present, the sample is assessed visually. The sample is rated in the following categories: (a) no haze, sample is

clear and bright; (b) slight haze only visible under natural light under close inspection; (c) haze visible under natural light without close inspection; (d) opaque; (e) phase separation. If a sample is clear and bright (a) and there is no phase separation or if there is a slight haze only visible under natural light under close inspection (b) then the sample is deemed to have passed. If a sample falls within anyone of categories (c) to (e) then the sample is deemed to have failed..

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 in oil derived from PIB having an Mn of 2000 g/mol or more
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
Ca Salicylate	Calcium Salicylate Detergent (50 to 400 TBN) in oil
Ca sulfonate	Calcium sulfonate detergent in oil
Mg sulfonate	Magnesium sulfonate detergent in oil
ZDDP	ZDDP (derived from primary and or secondary alcohols) in oil
Phenol antioxidant	Hindered phenol antioxidant, Irganox™ L135
Mo-friction modifier	Trimeric MoDTC antioxidant/friction modifier
Corrosion Inhibitor	Triazole corrosion inhibitor
Organic Friction Modifier	glycerol mono-oleate
PIBSA	Polyisobutylene succinic anhydride in oil
PIB	polyisobutylene
Anti-foamant	PDMS silicone anti-foamant
LOFI- lube oil flow improver	C8-18 dialkylfumarate/vinyl acetate copolymer in oil
Star H-SD block copol	Hydrogenated styrene-diene block star viscosity modifier in oil
PAO	based PAO VI 120-140, KV100 4-6 cSt
diluent	Group I base oil

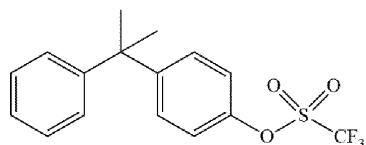
[0367] **Bis(4-(2-phenylpropan-2-yl)phenyl)amine** was sourced from SI Group (Brussels, Belgium) as Naugard™ 445, containing mono-(2-phenylpropan-2-yl)diphenylamine, tri-(2-phenylpropan-2-yl) diphenylamine and di-(2-phenylpropan-2-yl)diphenylamine isomers as shown in the table below.

	Bis(4-(2-phenylpropan-2-yl) phenyl)amine (mass%*)
Mono- Substituted	1.6
Di- Substituted	96.7

Tri- Substituted	1.7
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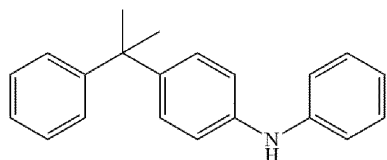
*based upon the weight of the mono, di and tri aralkyl substituted diphenylamines.

[0368] Intermediate 1: Synthesis of 4-(2-Phenylpropan-2-yl)phenyl trifluoromethanesulfonate



[0369] To a stirred solution of 4-cumylphenol (500 g, 2.36 mol) in dichloromethane (10 L) at -5°C was added pyridine (865 g, 10.9 mol). The mixture was warmed to 0°C, triflic anhydride (1044 g, 3.70 mol) was added dropwise to the solution over 2 hours and the reaction mixture was stirred for a further 30 minutes. The reaction was warmed to 20°C over 3 hours, then poured in a mixture of ice (5 kg) and water (10 L). The dichloromethane phase was collected and the aqueous phase washed three times with dichloromethane (7.5 L). The organic extracts were combined, then washed sequentially with 5% HCl_(aq) (7.5 L) then 5 wt% Na₂CO_{3(aq)} (7.5 L) and finally saturated brine (7.5 L). The organic phase was dried (Na₂SO₄) and the dichloromethane was removed under vacuum (40°C) to give 4-(2-Phenylpropan-2-yl)phenyl trifluoromethanesulfonate as a red liquid (808 g, 100 % yield), 99.7% pure 4-(2-Phenylpropan-2-yl)phenyl trifluoromethanesulfonate by HPLC (Analytical Method 2).

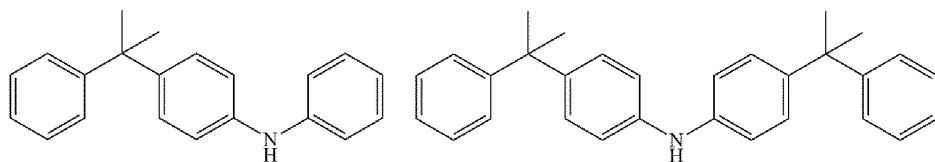
[0370] Product 1: Synthesis of *N*-phenyl-4-(2-phenylpropan-2-yl)aniline



[0371] A mixture of 4-(2-phenylpropan-2-yl)phenyl trifluoromethanesulfonate (Intermediate 1) (500 g, 1.45 mol), aniline (270 g, 2.99 mol), caesium carbonate (945 g, 2.90 mol) and X-Phos™ (70 g, 0.147 mol) in *tert*-butyl alcohol and 1,4-dioxane (9.6 L, 1:5) was stirred vigorously under nitrogen at 20°C. Palladium acetate (8 g, 0.036 mol) was added to the mixture, and the reaction was then heated to 100°C and stirred for 16 hours. The mixture was cooled to less than 60°C, diluted with ethyl acetate (8 L), filtered through celite and the solvent was removed under vacuum (70°C). The resulting residue was diluted with ethyl acetate (6 L), washed twice with saturated brine (8 L) and dried over Na₂SO_{4(s)} for 16 hours. The mixture

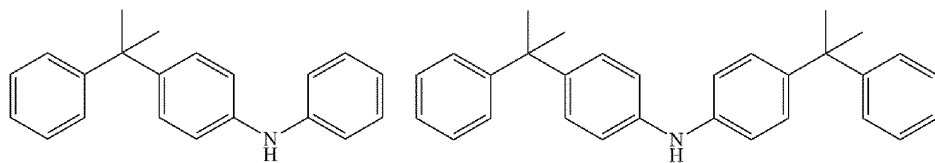
was filtered, and the solvent was removed from the filtrate under vacuum (70°C) to give a brown oil. The brown oil was purified via silica gel (2 x 5.5 kg) column chromatography (2.5% ethyl acetate/hexane). Fractions containing product were concentrated in under vacuum (70°C) to give pure N-phenyl-4-(2-phenylpropan-2-yl)aniline (366 g) as a yellow semi-solid which was dissolved in hot ethyl acetate (4 L), filtered and the solvent was removed under vacuum (70°C). The solid residue was mixed with hexane (6.2 L), stirred for 16 hours and the product was collected by filtration and dried in a vacuum oven to give Product 1 (N-phenyl-4-(2-phenylpropan-2-yl)aniline, 1300 g) as a colourless crystalline solid. HPLC (Analytical Method 2) Retention time 13.7 mins; Purity 99.7%; 69% yield.

[0372] Product 2: Synthesis of 65 mass% N-phenyl-4-(2-phenylpropan-2-yl)aniline and 35 mass% bis(4-(2-phenylpropan-2-yl)phenyl)amine



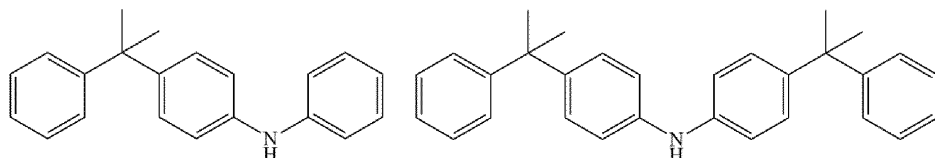
[0373] Mixture of diphenylamine (30.8 g, 0.182 mol) and clay catalyst (Fulcat™-22 D) (3.08 g) in xylene (50 mL) was refluxed at 160°C to dry the catalyst by removing water as an azeotrope with xylene for 1 hour. The mixture was cooled to 140°C, alpha-methylstyrene was added dropwise over 10 mins and the reaction was stirred at 140°C for 2 hours. HPLC analysis (Analytical Method 1) showed that 30% of the diphenylamine remained unreacted. The xylene and unreacted diphenylamine were removed by vacuum distillation to give the component which was used in stability studies without further purification. The ratio of mono- to di-substituted alpha-methyl styrenated diphenylamine was 65:35 (based upon the mass of the mono- and di-substituted DPA's). No tri-substituted alpha-methyl styrenated diphenylamine was observed. UPLC/MS analysis (Analytical Method 1): N-phenyl-4-(2-phenylpropan-2-yl)aniline had a retention time of 5.74 min and [M+H] 288.1; and bis(4-(2-phenylpropan-2-yl)phenyl)amine had a retention time of 6.86 min and [M+H] 406.1.

[0374] Comparative Component 1: Preblend of 40 mass% N-phenyl-4-(2-phenylpropan-2-yl)aniline (Product 1) and 60 mass% bis(4-(2-phenylpropan-2-yl)phenyl)amine



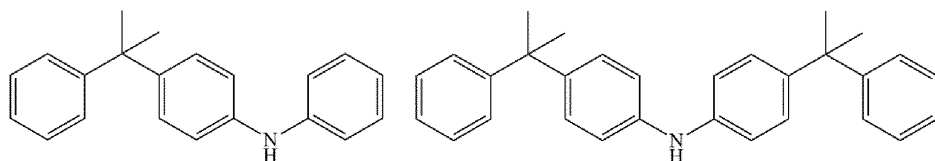
[0375] Bis(4-(2-phenylpropan-2-yl)phenyl)amine (1.80 g, 4.44 mmol) and N-phenyl-4-(2-phenylpropan-2-yl)aniline (1.20 g, 4.18 mmol) were heated together to 100°C. On melting the mixture was stirred for 30 mins, then cooled to 20°C to give a colourless viscous liquid.

[0376] **Component 2: Preblend of 70 mass% N-phenyl-4-(2-phenylpropan-2-yl)aniline (Product 1) and 30 mass% bis(4-(2-phenylpropan-2-yl)phenyl)amine**



[0377] Bis(4-(2-phenylpropan-2-yl)phenyl)amine (0.90 g, 2.22 mmol) and N-phenyl-4-(2-phenylpropan-2-yl)aniline (2.10 g, 7.32 mmol) were heated together to 100°C. On melting the mixture was stirred for 30 mins, then cooled to 20°C to give a colourless liquid.

[0378] **Component 3: Synthesis of 60 mass% N-phenyl-4-(2-phenylpropan-2-yl)aniline and 40 mass% bis(4-(2-phenylpropan-2-yl)phenyl)amine (Product 1)**



[0379] Bis(4-(2-phenylpropan-2-yl)phenyl)amine (80 g, 0.197 mol) and N-phenyl-4-(2-phenylpropan-2-yl)aniline (120 g, 0.418 mol) were heated together to 100°C. On melting the mixture was stirred for 30 mins, then cooled to 20°C to give a yellow liquid.

[0380] **Comparative Component 4** 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 (Analytical Method 1).

Component Stability Studies

[0381] Components 1 to 3 were blended using the conditions stated above, then cooled to 20°C and stored in clear centrifuge tubes with no agitation. The time were observed at 24 hours and 3 months and recorded, the results are given in the table below.

	Comparative Component 1 (40:60 / mono:di)	Component 2 (70:30 / mono:di)	Component 3 (60:40 / mono:di)
Colour	Yellow	Yellow	Yellow
State at 24 hrs	Liquid	Liquid	Liquid
State at 3 months	Crystallization observed/Crystals present	Hazy liquid	Hazy liquid
Conclusion	not stable	stable	stable

[0382] At 40 mass% and 30 mass% of bis(4-(1-phenylpropyl)phenyl)amine the component mixtures were stable for more than 3 months.

Concentrated Additive Package and Finished Oil Stability Test

[0383] Oil A and Comparative Oil B were blended at equal mass% with Component 3 and Comparative Component 4 respectively using the method below and with the additives detailed in Table 1.

[0384] **Blend Method:** Component 3 or Comparative Component 4 was first blended into a concentrated additive package. The component to be tested was added at 60°C with PIBSA, PIBSA-PAM and borated PIBSA-PAM into the remaining additive package components, which had already been blended together at 60°C for 15 minutes.

[0385] Into Group III basestock was added LOFI and star H-SD block copolymer viscosity modifier at 60°C and the mixture was stirred for 30 mins. Whilst still at 60°C, the concentrated additive package was added and the mixture was stirred for a further 30 minutes, to give Oil A (Component 3) and Comparative Oil B (Comparative Component 4).

[0386] The finished oils and concentrated additive packages were stored in clear centrifuge tubes at 20°C and 60°C, without agitation. The stability on storage by visual appearance was recorded and results are shown in Table 1.

Table 1.

Components* (Mass%)	Oil A	Comparative Oil B
Ca Salicylate-225 TBN	2.1	2.1
Ca Salicylate-65 TBN	0.5	0.5
ZDDP	1.0	1.0
Comparative Component 4		0.8
Component 3 (60:40 / mono:di)	0.8	

Group III base oil, 4-6 cSt	71	71
Results from Blending studies		
Concentrated Additive Package Stability: Oil appearance at 12 weeks at 20 °C.	Slight haze	Clear and bright
Concentrated Additive Package Stability: Oil appearance at 12 weeks at 60 °C.	Slight haze	Slight haze
Finished Oil Stability: Oil appearance at 10 weeks at 20 °C.	Clear and bright	Clear and bright
Finished Oil Stability: Oil appearance at 10 weeks at 60 °C.	Clear and bright	Clear and bright

*each concentrated additive package had the same amount of PIBSA-PAM, borated PIBSA-PAM, PIBSA, anti-foamant LOFI, star H-SD block copolymer VM and Group I diluent oil.

[0387] Both Oil A and Comparative Oil B are stable up to 10 weeks. The concentrated additive package for Oil A had a slight haze on storage at both 20°C and 60°C. This was considered as a good result, especially considering the concentrated additive package for Comparative Oil B also had a slight haze on storage at 60°C.

Finished Oil Blending Methods for Performance Testing

[0388] The Oils in Examples 1-3 were blended by combining Component 3 or Comparative Component 4 with LOFI and viscosity modifier in base stock at 80°C, then a concentrated additive package and organic friction modifier (Example 2) were added at 60°C. The additive package contained the remaining components of the engine oil. The concentrated additive package was blended at 60°C by first blending the phenolic antioxidant (Examples 1 and 2), antifoamant, Mo-friction modifier (Examples 3), salicylate detergent and ZDDP with diluent oil, followed by PIBSA-PAM, borated PIBSA-PAM, PIBSA-Ester Dispersant (Example 3) and PIBSA. The formulated oils are shown in Tables 2, 4, and 6 below.

Example 1

[0389] Component 3 and Comparative Component 4 were each blended at equal mass% (0.8 mass%) into the formulation described in Table 2 to form Oil C and Comparative Oil D, respectively.

Table 2.

Components** (Mass %)	Oil C	Comparative Oil D
Calcium salicylate	1.9	1.9

ZDDP	0.8	0.8
Phenolic Antioxidant	0.4	0.4
Component 3 (60:40 / mono:di)	0.8	
Comparative Component 4		0.8
PAO	20.0	20.0
Group III Basestock	51.4	51.4
Ash (mass %)	0.84	0.84
Elemental Analysis ICP		
B ppm	500	500
Ca (mass %)	0.18	0.18
Mg (mass %)	0.001	0.001
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 VM.

[0390] Oil C and Comparative Oil D were tested for oxidation stability and viscosity control using the test conditions detailed in CEC-L-109-14, with a test run time of 216 hours. The data are reported in Table 3.

Table 3.

Component (Mass %)		Oil C	Comparative Oil D
Comparative Component 4			0.8
Component 3 (60:40 / mono:di)		0.8	
CEC-L-109-14 test results	Oxidation FTIR (A/cm)	34.8	39
	% Change in K _v 100	57.4	69.7

[0391] In Table 3, the data show that at the end of the tests, Oil C (containing Component 3) maintained good oxidation control, while obtaining excellent reduced viscosity increase (12.3% difference in % change in K_v100) at end of the test compared to Comparative Oil D (containing Comparative Component 4).

Example 2

[0392] Components 2 and 3 and Comparative Component 4 were each blended at equal mass% (1.5 mass%) into the formulation described in Table 4 to form Oils E and F and Comparative Oil G respectively.

Table 4.

Components*** (Mass %)	Oil E	Oil F	Comparative Oil G
Magnesium salicylate	0.6	0.6	0.6
Calcium salicylate	1.4	1.4	1.4
ZDDP	1.0	1.0	1.0
Phenolic antioxidant	0.2	0.2	0.2
Component 2 (70:30 / mono:di)	1.5		
Component 3 (60:40 / mono:di)		1.5	
Comparative Component 4			1.5
PAO	21.0	21.0	21.0
Group III Basestock	58.3	58.3	58.3
Ash (mass %)	0.77	0.77	0.77
Elemental Analysis ICP			
B ppm	72	72	72
Ca (mass %)	0.13	0.13	0.13
Mg (mass %)	0.05	0.05	0.05
N (mass %)	0.12	0.12	0.11
P (mass %)	0.08	0.08	0.08
S (mass %)	0.18	0.18	0.18
Si ppm	6.2	6.2	6.2

***each oil had the same amount of PIBSA-PAM, borated PIBSA-PAM, organic friction modifier, PIBSA, anti-foamant, Group I diluent oil, PAO diluent, LOFI, and Star H-SD block copol VM-2.

[0393] Oils E and F and Comparative Oil G, were tested for oxidation stability and viscosity control using the test conditions detailed in CEC-L-109-14, with a test run time of 216 hours. The data are reported in Table 5.

Table 5.

Component Mass %		Oil E	Oil F	Comparative Oil G
Component 2(70:30 / mono:di)		1.5		
Component 3(60:40 / mono:di)			1.5	
Comparative Component 4				1.5
CEC-L-109-14 test results	Oxidation FTIR (A/cm)	27.9	29.3	33.9
	% Change in Kv100	37.7	39.2	62.6

[0394] In Table 5, the data show that at the end of the tests, Oils E and F maintained good oxidation control, while obtaining excellent reduced viscosity increase at end of the test compared to Comparative Oil H, 24.9% and 23.4% difference respectively.

Example 4

[0395] Component 3 and Comparative Component 4 were each blended into the formulations described in Table 6 to form Oils H, I, J, K and L and Comparative Oils C-M, C-N, C-O, C-P, and C-Q, respectively.

Table 6. formulations.

Components **** Mass %	H	I	J	K	L	C-M	C-N	C-O	C-P	C-Q
Magnesium salicylate	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Calcium salicylate	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4
ZDDP	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Component 3 (60:40 / mono:di)	0.3	0.5	0.75	1.0	1.25					
Comparative Component 4						0.3	0.5	0.75	1.0	1.25
Group III base oil	79.1	79.0	78.7	78.5	78.2	79.1	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	0.76	0.76
Elemental Analysis ICP										
B ppm	101	101	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	0.11	0.11
Mg (mass %)	0.06	0.06	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	83	83
N (mass %)	0.10	0.10	0.11	0.12	0.14	0.10	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	0.08	0.08
S (mass %)	0.19	0.19	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	13	13

**** each oil had the same amount of PIBSA-PAM, borated PIBSA-PAM, Mo Friction modifier, PIBSA, PIBSA-Ester Dispersant, anti-foamant, Group I diluent oil, LOFI, and Star H-SD block copol VM-2.

[0396] Oils H, I, J, K and L and Comparative Oils C-M, C-N, C-O, C-P, and C-Q were tested for oxidation stability and viscosity control according to CEC-L-109-14 test with a test run time of 216 hours. The data are reported in Table 7.

Table 7.

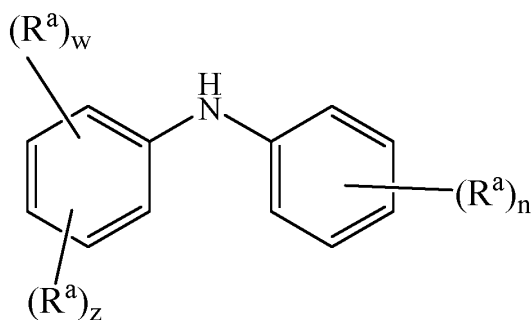
Component (Mass %)		H	I	J	K	L	C-M	C-N	C-O	C-P	C-Q
Component 4							0.3	0.5	0.75	1.0	1.25
Component 3 (60:40 / mono:di)		0.3	0.5	0.75	1.0	1.25					
CEC-L-109-14 test results	Oxidation FTIR (A/cm)	95.8	59.3	39.5	29.9	28.5	91.6	63.4	43.9	35.9	30.2
	% Change in K _v 100	137.7	60.2	47.1	37.2	12.9	121.1	72.9	60.3	52.7	48.2

[0397] At all treat rates the oils containing Component 3 maintained oxidation control that was comparable to or better than the comparative oils. At the four higher treat rates (0.5, 0.75, 1.0 and 1.25 mass %) Oils I, J, K and L containing Component 3 had a 12.7, 13.2, 15.5 and 35.3% lower relative viscosity increase (% Change in K_v100) versus oils C-N, C-O, C-P, and C-Q containing Comparative Component 4, respectively.

[0398] 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 disclosure have been illustrated and described, various modifications can be made without departing from the spirit and scope of the disclosure. Accordingly, it is not intended that the disclosure be limited thereby. The term "comprising" is considered synonymous with the term "including." Likewise, whenever a composition, an element, or a group of elements is preceded with the transitional phrase "comprising", it is understood that we also contemplate the same composition or group of elements with transitional phrases "consisting essentially of", "consisting of", "selected from the group of consisting of", or "is" preceding the recitation of the composition, element, or elements and vice versa.

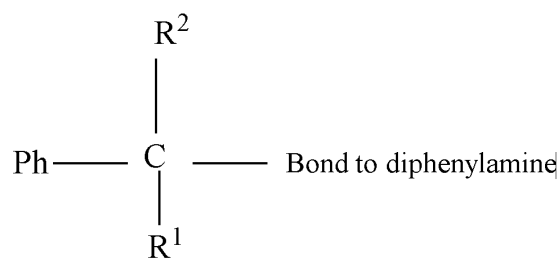
Claims

1. An additive concentrate for use in forming a lubricating oil composition, the additive concentrate consisting of from 1 to less than 50 mass % base oil, based on the total mass of the additive concentrate, and a plurality of lubricant composition additives contained therein, wherein the combined amount of all of said plurality of lubricant composition additives in the additive concentrate is greater than 50 mass % on an active ingredient basis, based on the total mass of the additive concentrate, wherein the plurality of said lubricant composition additives includes an antioxidant composition in the form of a fluid which comprises: (a) a mono-aralkyl substituted diphenylamine; and (b) a di-aralkyl substituted diphenylamine, wherein the mono-aralkyl substituted diphenylamine is present in an amount of at least 45 mass %, based upon the total mass of said mono-aralkyl substituted diphenylamine and said di-aralkyl substituted diphenylamine in the antioxidant composition.
2. An additive concentrate as claimed in claim 1, wherein: (a) the mono-aralkyl substituted diphenylamine of the antioxidant composition is represented by a compound of Formula III where n is 1, w is 0, and z is 0, and (b) the di-aralkyl substituted diphenylamine of the antioxidant composition is represented by a compound of Formula III, where n is 1, w is 0, and z is 1, where a compound of Formula III is:



Formula III

wherein each R^a in a compound of Formula III independently represents a substituent group of Formula I:



Formula I

wherein Ph is a substituted or unsubstituted phenyl group, R¹ is C₁ to C₂₀ hydrocarbyl group, R² is C₁ to C₂₀ hydrocarbyl group, and R¹ and R² may be bound to each other; and,

wherein the mono-aralkyl substituted diphenylamine is present in an amount from 45 to 95 mass %, the di-aralkyl substituted diphenylamine is present in an amount of 5 to 55 mass %, based upon the total mass of said mono-aralkyl substituted diphenylamine and said di-aralkyl substituted diphenylamine in the antioxidant composition.

3. An additive concentrate as claimed in claim 2, wherein Ph in a substituent group of Formula I is an unsubstituted phenyl group.
4. An additive concentrate as claimed in claim 2 or 3, wherein R¹ and R² in a substituent group of Formula I are independently selected from methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl or dodecyl.
5. An additive concentrate as claimed in claim 2, wherein Ph in a substituent group of Formula I is an unsubstituted phenyl group, R¹ in a substituent group of Formula I is methyl, and R² in a substituent group of Formula I is methyl.
6. An additive concentrate as claimed in any one of the preceding claims, wherein the (a) mono-aralkyl substituted diphenylamine antioxidant and the (b) di-aralkyl substituted diphenylamine antioxidant are present in a combined total amount of from 0.01 to 40 mass %, based on the total mass of the additive concentrate.
7. An additive concentrate as claimed in any one of the preceding claims, wherein the additive concentrate further includes a detergent.

8. An additive concentrate as claimed in claim 7, wherein the detergent comprises a salicylate detergent which is a calcium or magnesium salicylate detergent and/or the detergent comprises a sulfonate detergent which is a calcium or magnesium sulfonate detergent.
9. An additive concentrate as claimed in anyone of the preceding claims, wherein the additive concentrate further includes one or more additives selected from dispersants, friction modifiers; antioxidants, other than the antioxidants of (a) and (b), pour point depressants, anti-foaming agents, viscosity modifiers, corrosion inhibitors, antirust agents, and/or anti-wear agents.
10. An additive concentrate as claimed in any one of the proceeding claims, wherein the additive concentrate further comprises one or more polar diluents selected from the group consisting of:
 - (i) di-esters derived from propylene glycol,
 - (ii) C₈₋₁₆ alkyl tri-esters derived from tri-methylolpropane, and
 - (iii) phthalates, terephthalates, isophthalates, trimellitates and pyromellitates, preferably one or more polar diluents selected from the group consisting of: (di-propylene glycol) dibenzoate, C₈-C₁₀ tri-methylol propane ester, trioctyl trimellitate, and dioctyl terephthalate.
11. A lubricating oil composition, comprising or formed by admixing:
 - (i) at least 50 mass % of one or more base oils, based upon the total mass of the lubricating oil composition; and,
 - (ii) an additive concentrate as claimed in any one of claims 1 to 10.
12. A lubricating oil composition as claimed in claim 11, wherein the lubricating oil composition comprises zinc dialkyldithiophosphate, hindered phenolic antioxidant, and/or a molybdenum containing compound.
13. A lubricating oil composition as claimed in claim 11 or 12, wherein the base oil is selected from one or more of API Group I, II, III, IV base oils.

14. The use of an antioxidant composition in the form of a liquid, as defined in any one of claims 1 to 10, comprising: (a) a mono-aralkyl substituted diphenylamine antioxidant, as defined in any one of claims 1 to 10, and (b) a di-aralkyl substituted diphenylamine antioxidant, as defined in any one of claims 1 to 10, as an additive in an additive concentrate to form a storage stable additive concentrate, as measured by the Storage Stability Test Method defined in the description, wherein the additive concentrate consists of 1 to less than 50 mass % base oil, based on the total mass of the additive concentrate, and a plurality of lubricant composition additives contained therein, wherein the combined amount of all of said plurality of lubricant composition additives in the additive concentrate is greater than 50 mass % on an active ingredient basis, based on the total mass of the additive concentrate.
15. The use, in the lubrication of a spark-ignited or compression-ignited internal combustion engine, of (a) a mono-aralkyl substituted diphenylamine antioxidant, as defined in any one of claims 1 to 10, and (b) a di-aralkyl substituted diphenylamine antioxidant, as defined in any one of claims 1 to 10, as a combination of additives in an amount in a lubricating oil composition to improve anti-oxidation characteristics and/or to mitigate or reduce viscosity increase of the lubricating oil composition during operation of the internal combustion engine, wherein the mass to mass ratio of mono-aralkyl substituted diphenylamine antioxidant to di-aralkyl substituted diphenylamine antioxidant in the lubricating oil composition is from 45:55 to 95:5, and wherein the lubricating oil composition includes at least 50 mass % of one or more base oils, based upon the total mass of the lubricating oil composition.
16. A lubricating oil composition as claimed in any one of claims 11 to 13 or a use as claimed in claim 15, wherein the (a) mono-aralkyl substituted diphenylamine antioxidant and the (b) a di-aralkyl substituted diphenylamine antioxidant are present in a combined total amount of from 0.5 to 8 mass %, based on the total mass of the lubricating oil composition.