

LUBRICANT COMPONENT SELECTIONS FOR REDUCED ENGINE SLUDGE

TECHNICAL FIELD

[0001] The present disclosure relates to additive packages for lubricating compositions and, in particular, component selections for additive packages to achieve improved performance in passenger car motor oil lubricating compositions.

BACKGROUND

[0002] Lubricants intended for use as motor oils (also commonly referred to as engine oils, crankcase oils, lubricating compositions, or lubricating oil compositions) in gasoline or diesel automobile engines commonly include a base oil or a blend of base oils of lubricating viscosity and one or more additives to meet certain performance requirements for the intended application. Modern automotive industry standards are placing increasingly stringent requirements in terms of composition and/or performance of such oils, which often leaves little room for lubricant formulation flexibility. As lubricant manufacturers strive to meet the various automotive industry standards, it becomes a challenge to cost effectively achieve all the needed performance and industry standards at the same time.

[0003] The American Petroleum Institute (API) classifies base oil for lubricants into five groups with API Groups I, II, and III defining mineral oils categorized by saturates, sulfur, and viscosity index. API Group IV relates to polyalphaolefin base oils, and API Group V includes all other base oils. In the context of mineral oils, it is generally appreciated that the performance a mineral oil provides to a lubricant improves from Group I to Group III with the API Group III mineral oils being the most preferred in terms of performance quality and with the Group I and the Group II mineral oils tending to provide one or more performance debits under modern automotive industry standards. As such, the trend in the automotive lubricant industry has been to use higher amounts of the API Group III mineral oils when formulating lubricants to meet the strict demands of today's industry and automotive standards.

[0004] One area of recent focus in the automotive industry is an evaluation of the lubricant's role in sludge formation in cylinder head, oil sump, valve covers, and/or timing covers of engines during extended operation. Newer and more stringent engine tests, such as the M271 EVO fired engine test (CEC L-107-19), place heightened demands on lubricants to not only minimize

sludge formation, but also adequately suspend sludge in solution to minimize fluid viscosity increases and the associated oil pressure increases at the same time. The M271 EVO fired engine test is a demanding test to achieve passing performance and, in many instances, OEMs require higher than passing performance; thus, API Group III mineral oils have been the mainstay base oil for achieving performance in this test.

SUMMARY

[0005] The present disclosure relates to a passenger car motor oil lubricating composition and methods of lubricating a combustion engine suitable for improving at least one of deposits, sludge, oxidization, and wear. In one approach or embodiment, the passenger car motor oil lubricating composition and methods using the composition includes a blend of base oils of lubricating viscosity including a majority of API Group II base oils. In one embodiment, the method of lubricating a combustion engine for passing (as defined herein) the M271 EVO fired engine test of CEC L-107-19 includes the following: lubricating a combustion engine with a lubricating oil composition; wherein the lubricating oil composition includes: a base oil of lubricating viscosity having about 50 weight percent or more of a hydrotreated mineral oil with more than about 90 weight percent saturates, less than about 0.03 weight percent of sulfur, and a viscosity index (ASTM D2270) of about 120 or less; a detergent system having (i) less than about 5 weight percent of metal from non-sulfonate detergents and (ii) a total base number (TBN) thereof less than about 10 mg KOH/gram and that contributes about 60 to about 85 percent of the total lubricating oil composition TBN as measured pursuant to ASTM D2896; an antiwear system including one or more zinc dihydrocarbyl dithiophosphate compounds having alkyl groups derived from primary alcohols, secondary alcohols, or combination thereof and providing about 200 to about 1000 ppm phosphorus; an antioxidant system including one or more phenolic antioxidant compounds, one or more aminic antioxidant compounds, or combinations thereof; and wherein the lubricating oil composition includes one or more of the following to achieve an elevated passing average engine sludge rating of 9.0 +/- 0.3 merits or higher under CEC L-107-19: (a) the detergent system includes a majority of one or more overbased sulfonate detergents (preferably overbased magnesium sulfonate detergents); (b) the antiwear system includes a majority of zinc dihydrocarbyl dithiophosphate compounds having an

average of 8 or more carbon atoms per phosphorus atom; and/or (c) the antioxidant system includes a majority of phenolic antioxidant compounds.

[0006] In yet other embodiments, the method of the previous paragraph may include one or more other steps, features, or embodiments in any combination. These other steps, features, or embodiments include one or more of the following: wherein the lubricating oil composition includes (a) the detergent system having the majority of one or more overbased sulfonate detergents and, preferably, overbased magnesium sulfonate detergents and, in some approaches, further including a weight ratio of magnesium-to-calcium of about 600:1 or greater and providing about 70 to about 85 percent of the total lubricating oil composition TBN as measured pursuant to ASTM D2896; and/or wherein the lubricating oil composition further includes a majority of the phosphorus from the zinc dihydrocarbyl dithiophosphate compounds of the antiwear system provided by one or more zinc dihydrocarbyl dithiophosphate compounds having an average of 6 or fewer carbon atoms per phosphorus atom; and/or wherein the lubricating oil composition further includes one or more phenolic antioxidant compounds and one or more aminic antioxidant compounds in the antioxidant system and further includes a weight ratio of oxygen in ppm from the phenolic compounds to nitrogen in ppm from the aminic compounds (e.g., ratio of O/N) of about 4:1 to about 6:1; and/or wherein the lubricating oil composition includes (b) the majority of phosphorus from the zinc dihydrocarbyl dithiophosphate compounds of the antiwear system provided by a zinc dihydrocarbyl dithiophosphate compounds having an average of 8 or more carbon atoms per phosphorus atom; and/or wherein about 90 to about 100 weight percent of the phosphorus from the zinc dihydrocarbyl dithiophosphate compounds of the antiwear system is provided by the zinc dihydrocarbyl dithiophosphate compounds having an average of 8 or more carbon atoms per phosphorus atom; and/or wherein the lubricating oil composition further includes both calcium and magnesium provided by the detergent system and with a weight ratio of calcium-to-magnesium of about 0.8:1 to about 1.5; and/or wherein the lubricating oil composition further includes one or more phenolic antioxidant compounds and one or more aminic antioxidant compounds in the antioxidant system and with a weight ratio of oxygen in ppm contributed from the one or more phenolic antioxidant compounds to nitrogen in ppm contributed from the one or more aminic antioxidants compounds (e.g., a weight ratio of O/N) of about 4:1 to about 6:1; and/or wherein the lubricating oil composition includes (c) the

antioxidant system having a majority of phenolic antioxidant compounds and further having a weight ratio of oxygen in ppm contributed from the phenolic antioxidant compounds to nitrogen in ppm from the aminic antioxidant compounds (O/N) of greater than about 100:1; and/or wherein the lubricating oil composition further includes both calcium and magnesium provided by the detergent system and with a weight ratio of detergent calcium to detergent magnesium of at least about 0.8:1 to about 1.5:1; and/or wherein the lubricating oil composition further includes a majority of the phosphorus from the zinc dihydrocarbyl dithiophosphate compounds of the antiwear system is provided by zinc dihydrocarbyl dithiophosphate compounds having an average of 6 or fewer carbon atoms per phosphorus atom; and/or wherein the base oil of lubricating viscosity is about 75 to about 90 weight percent of the hydrotreated mineral oil having more than about 90 weight percent saturates, less than about 0.03 weight percent of sulfur, and a viscosity index (ASTM D2270) of about 120 or less; and/or wherein the detergent system TBN is about 5 to less than 10 mg KOH/gram; and/or wherein the TBN of the lubricating oil composition is about 7 to about 12 mg KOH/gram as measured pursuant to ASTM D2896; and/or wherein the detergent system is substantially free of phenate detergents; and/or wherein the detergent system consists essentially of sulfonate detergents providing calcium, magnesium, or combinations thereof; and/or wherein the antioxidant system is substantially free of mono-alkyl phenolic amine antioxidants; and/or wherein the lubricating oil composition includes no more than about 1.3 weight percent of one or more dispersant olefin copolymer viscosity index improvers; and/or wherein the lubricating oil composition is substantially free of dispersant olefin copolymer viscosity index improvers; and/or wherein the lubricating oil composition has at least about 1000 ppm of total nitrogen; and/or wherein the lubricating oil composition includes one or more nitrogen-containing dispersant additives providing about 600 ppm or more dispersant nitrogen to the lubricating oil composition; and/or wherein the lubricating oil composition includes less than about 200 ppm molybdenum; and/or wherein the lubricating oil composition includes less than about 150 ppm of boron; and/or wherein the lubricating oil composition is substantially free of API Group III base oils.

[0007] In yet other embodiments, the present disclosure includes lubricating compositions including any embodiment as described in this summary.

[0008] In yet further embodiments, the present disclosure includes the use of any embodiment of the methods and/or any embodiment of the lubricating composition as described in this summary to achieve an elevated passing average engine sludge rating of 9.0 +/- 0.3 merits or higher under CEC L-107-19.

DETAILED DESCRIPTION

[0009] The present disclosure relates to passenger car motor oils and methods of lubricating a combustion engine using the passenger car motor oil to achieve passing, and in some instances, elevated passing performance in the M271 EVO fired engine test of CEC L-107-19, and in particular, methods of achieving passing (and preferably elevated) performance in this fired engine test when the passenger car motor oils include increased amounts of the less-desired API Group II base oils. Surprisingly, it was discovered that performance debits when using the less-desired API Group II base oils could be overcome with select componentry of the lubricant's additive system carefully controlled and when combined with increased amounts of the less-desired API Group II base oil.

[0010] In particular, the methods and the passenger car motor oil lubricating compositions herein include a base oil of lubricating viscosity or a blend of base oils of lubricating viscosity including at least about 50 weight percent or more (preferably, about 60 weight percent or more, about 70 weight percent or more, about 80 weight percent or more, or about 85 weight percent or more) of a base oil derived from a hydrotreated mineral oil with more than 90 weight percent saturates, less than 0.03 weight percent of sulfur, and a viscosity index (ASTM D2270) of 120 or less (e.g., a majority of an API Group II base oil) and still achieve passing (and preferably elevated) performance as defined herein in the M271 EVO fired engine testing of CEC L-107-19 (that is, average engine sludge rating (AES) or 9.0 +/- 0.3 merits or higher).

[0011] It was surprisingly discovered that even with higher levels of the less-desired API Group II base oil, any performance debit from this lower quality base oil in the M271 fired engine test could be overcome if the passenger car motor oil lubricating composition included select additive componentry that achieves a performance synergy. Such select additive componentry includes at least (1) a detergent system having (1)(i) less than about 5 weight percent of metal from non-sulfonate detergents (e.g., wherein non-sulfonate detergents include

metal-containing phenate, salicylate, calixyrate, and/or other non-sulfonate detergents) and, preferably, less than 2 weight percent, more preferably, less than 1 weight percent, and most preferably, no functional amounts of metal from non-sulfonate detergents and (1)(ii) a detergent total base number (TBN) thereof less than 10 mg KOH/gram and that contributes about 60 to about 85 percent of the total lubricating oil composition TBN as measured pursuant to ASTM D2896 and (2) an additive system selected to achieve an average engine sludge rating of 9.0 +/- 0.3 merits or higher pursuant to CEC L-107-19 when used in combination with the detergent system and, in particular, wherein the additive system includes at least one or more of the following: (2)(a) the detergent system includes a majority of one or more overbased sulfonate detergents (preferably overbased magnesium sulfonate detergents); (2)(b) the antiwear system includes a majority of zinc dihydrocarbyl dithiophosphate compounds having an average of 8 or more carbon atoms per phosphorus atom; and/or (2)(c) the antioxidant system includes a majority of phenolic antioxidant compounds. The methods of lubricating a combustion engine using such passenger car motor oil lubricating compositions including high amounts of API Group II base oils surprisingly exhibits an average engine sludge (AES) rating of at least about 9.0 merits (+/- 0.3 merits) under CEC L-107-19.

[0012] Base Oil or Base Oil Blend:

[0013] As discussed in the background, API Group II base oils are becoming less desired when formulating passenger car motor oils due to the many performance debits when performing required industry tests. The API Group II base oils are generally less pure and less refined than the preferred API Group III. For instance, API Group II base oils typically include hydrotreated mineral oils having more than 90 weight percent saturates, less than 0.03 weight percent of sulfur, and a viscosity index (ASTM D2270) of 120 or less. In terms of mineral oil base oils, this is less refined than the more-preferred API Group III base oils that have higher viscosity index, are more severely hydrocracked, and generally more refined than the Group II base oils. In some embodiments, the base oils or base oil blends herein may be substantially free of API Group III base oils and, in such context, may have less than about 10 weight percent, less than about 5 weight percent, less than about 2 weight percent, less than about 1 weight percent, less than

about 0.5 weight percent, less than about 0.1 weight percent, or no functional amounts of API Group III base oils. Base oils are generally described in Table 1 below.

[0014] Table 1

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

[0015] In one approach or embodiment, the methods and the lubricating oil compositions herein include a base oil of lubricating viscosity or a blend of base oils of lubricating viscosity including a majority of or at least about 50 weight percent or more (preferably, about 60 weight percent or more, about 70 weight percent or more, about 80 weight percent or more, or about 85 weight percent or more) of an API Group II base oil or a base oil derived from a hydrotreated mineral oil having more than 90 weight percent saturates, less than 0.03 weight percent of sulfur, and a viscosity index (ASTM D2270) of 120 or less. In other approaches or embodiments, the methods and the lubricant oil compositions herein include a base oil or base oil blend that is at least about 50 weight percent of the API Group II base oil, or in other embodiments, about 50 to about 100 weight percent of the composition (about 75 to about 90 weight, about 80 to about 90 weight percent, or about 85 to about 90 weight percent) of the API Group II base oil or a base oil derived from a hydrotreated mineral oil having more than 90 weight percent saturates, less than 0.03 weight percent of sulfur, and a viscosity index (ASTM D2270) of 120 or less. The remainder of the base oil in any blend herein is one of an API Group I or III mineral base oil, an API Group IV base oil, an API Group V base oil, or any mixtures thereof. In some embodiments, the base oil or base oil blends herein may have a KV100 of about 2 to about 20 cSt, in other approaches, about 5 to about 15 cSt, about 8 to about 15 cSt, in yet other approaches, about 10 to about 15 cSt.

[0016] As appreciated by those of ordinary skill, mineral oils may include oils obtained by drilling or from plants and animals or any mixtures thereof. For example, such oils may include, but are not limited to, castor oil, lard oil, olive oil, peanut oil, corn oil, soybean oil, and linseed oil, as well as mineral lubricating oils, such as liquid petroleum oils and solvent-treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic or mixed paraffinic-naphthenic

types. Such oils may be partially or fully hydrogenated, if desired. Oils derived from coal or shale may also be useful.

[0017] Useful synthetic lubricating oils may include hydrocarbon oils such as polymerized, oligomerized, or interpolymerized olefins (e.g., polybutylenes, polypropylenes, propyleneisobutylene copolymers); poly(1-hexenes), poly(1-octenes), trimers or oligomers of 1-decene, e.g., poly(1-decenes), such materials being often referred to as α -olefins, and mixtures thereof; alkyl-benzenes (e.g. dodecylbenzenes, tetradecylbenzenes, dinonyl-benzenes, di-(2-ethylhexyl)-benzenes); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenyls); diphenyl alkanes, alkylated diphenyl alkanes, alkylated diphenyl ethers and alkylated diphenyl sulfides and the derivatives, analogs and homologs thereof or mixtures thereof. Polyalphaolefins are typically hydrogenated materials.

[0018] Other synthetic lubricating oils include polyol esters, diesters, liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, and the diethyl ester of decane phosphonic acid), or polymeric tetrahydrofurans. Synthetic oils may be produced by Fischer-Tropsch reactions and typically may be hydroisomerized Fischer-Tropsch hydrocarbons or waxes. In one embodiment oils may be prepared by a Fischer-Tropsch gas-to-liquid synthetic procedure as well as other gas-to-liquid oils.

[0019] The amount of the oil of lubricating viscosity present may be the balance remaining after subtracting from 100 wt% the sum of the amount of the performance additives inclusive of viscosity index improver(s) and/or pour point depressant(s) and/or other top treat additives. For example, the oil of lubricating viscosity that may be present in a finished fluid may be a major amount, such as greater than about 50 wt%, greater than about 60 wt%, greater than about 70 wt%, greater than about 80 wt%, greater than about 85 wt%, or greater than about 90 wt%.

[0020] As generally used herein, the terms "oil composition," "lubrication composition," "lubricating oil composition," "lubricating oil," "lubricant composition," "lubricant," and "lubricating" are considered synonymous, fully interchangeable terminology referring to a passenger car motor oil lubrication product comprising a major amount of a base oil component having the blend amounts noted above plus minor amounts of an additive system and/or other optional components that is preferably capable against one or more industry or OEM specification standards.

[0021] The Detergent System

[0022] The lubricating oil compositions herein include a detergent system with little to no metal provided from non-sulfonate detergent (e.g., little to no metal from metal-containing phenate detergents, salicylate detergents, calixyrate detergents, and other non-sulfonate detergents) and otherwise a select detergent composition that provides a specific contribution to the total base number (TBN) of the overall lubricating oil composition. In one embodiment, for instance, the methods and lubricating oil compositions herein may have (i) less than about 5 weight percent of metal from non-sulfonate detergent (preferably, less than about 2 weight percent metal from non-sulfonate detergent, more preferably less than 1 weight percent metal from a non-sulfonate detergent, and most preferably no metals contributed from non-sulfonate detergent) and (ii) a detergent composition that provides a detergent total base number (TBN) of less than about 10 mg KOH/gram and that contributes about 60 to about 85 percent of the total lubricating oil composition TBN as measured pursuant to ASTM D2896.

[0023] In one approach or embodiment, the detergent systems herein include one or more detergent additives that preferably include a calcium-containing detergent additive, and more preferably a sulfonate-based, calcium-providing detergent. In another embodiment, the one or more detergent additives may also include a magnesium-containing detergent additive, and more preferably, a sulfonate-based, magnesium detergent additive. In yet other embodiments, the detergent systems may be blends of calcium detergents and magnesium detergents, and preferably sulfonate-based calcium and magnesium detergents. These select detergent additives provide a detergent total base number (TBN) to the lubricant of at least about 4 mg KOH/g, at least about 5 mg KOH/g, at least about 6 mg KOH/g, or at least about 7 mg KOH/g as measured pursuant to ASTM D2896, and in other approaches or embodiments, the detergent additives herein provide a detergent TBN of about 10 mg KOH/g or less to the lubricants (e.g., about 4 to about 10 mg KOH/g, about 5 to about 10 mg KOH/g, about 6 to about 10 mg KOH/g, or about 7 to about 10 mg KOH/g). Such detergent additives provide about 60 to about 85 percent of the total lubricating oil composition TBN as measured pursuant to ASTM D2896 (in other approaches, about 65 to about 85 percent, about 70 to about 85 percent, or about 75 to about 85 percent). That is, the total lubricating oil compositions herein may have a finished fluid TBN of

about 7 to about 12 mg KOH/gram as measured pursuant to ASTM D2896 and the detergent systems herein may contribute about 60 to about 85 percent of the total fluid TBN (in other approaches, about 65 to about 85 percent, about 70 to about 85 percent, or about 75 to about 85 percent).

[0024] Suitable detergents and their methods of preparation are described in greater detail in numerous patent publications, including US 7,732,390 and references cited therein, which are incorporated herein by reference. The passenger car motor oil lubricating compositions herein may include about 0.1 to about 5 weight percent of individual and/or total detergent additives, and in other approaches, about 0.15 to about 3 weight percent, and in yet other approaches, about 0.15 to 2.6 weight percent of individual and/or total detergent additives so long as the detergent additives meet the calcium, magnesium, and/or TBN levels noted herein.

[0025] Generally, suitable detergents in the lubricants herein (subject to the noted requirements of metals, detergent types, calcium, magnesium, and/or TBN herein) may include linear or branched alkali or alkaline earth metal salts, such as calcium, sodium, or magnesium, of petroleum sulfonic acids and long chain mono- or di-alkylaryl sulfonic acids with the aryl group being benzyl, tolyl, and xylyl and/or various phenates or derivatives of phenates. Examples of suitable detergents include, subject the required amounts of sulfonate soap noted above, low-based/neutral and overbased variations of the following detergents: calcium phenates, calcium sulfur containing phenates, calcium sulfonates, calcium calixarates, calcium salixarates, calcium salicylates, calcium carboxylic acids, calcium phosphorus acids, calcium mono- and/or di-thiophosphoric acids, calcium alkyl phenols, calcium sulfur coupled alkyl phenol compounds, calcium methylene bridged phenols, magnesium phenates, magnesium sulfur containing phenates, magnesium sulfonates, magnesium calixarates, magnesium salixarates, magnesium salicylates, magnesium carboxylic acids, magnesium phosphorus acids, magnesium mono- and/or di-thiophosphoric acids, magnesium alkyl phenols, magnesium sulfur coupled alkyl phenol compounds, magnesium methylene bridged phenols, sodium phenates, sodium sulfur containing phenates, sodium sulfonates, sodium calixarates, sodium salixarates, sodium salicylates, sodium carboxylic acids, sodium phosphorus acids, sodium mono- and/or di-thiophosphoric acids, sodium alkyl phenols, sodium sulfur coupled alkyl phenol compounds, or sodium methylene bridged phenols.

[0026] The detergents herein may be overbased, and as understood, overbased detergent additives are well-known in the art and may be alkali or alkaline earth metal overbased detergent additives. Such detergent additives may be prepared by reacting a metal oxide or metal hydroxide with a substrate and carbon dioxide gas. The substrate is typically an acid, for example, an acid such as an aliphatic substituted sulfonic acid, an aliphatic substituted carboxylic acid, or an aliphatic substituted phenol. The term “overbased” relates to metal salts, such as metal salts of sulfonates, carboxylates, salicylates and/or phenates, wherein the amount of metal present exceeds the stoichiometric amount. Such salts may have a conversion level in excess of 100% (i.e., they may comprise more than 100% of the theoretical amount of metal needed to convert the acid to its “normal,” “neutral” salt). The expression “metal ratio,” often abbreviated as MR, is used to designate the ratio of total chemical equivalents of metal in the overbased salt to chemical equivalents of the metal in a neutral salt according to known chemical reactivity and stoichiometry. In a normal or neutral salt, the MR is one and in an overbased salt, MR, is greater than one. They are commonly referred to as overbased, hyperbased, or superbased salts and may be salts of organic sulfur acids, carboxylic acids, or phenols.

[0027] As used herein, the term “TBN” is used to denote the Total Base Number in mg KOH/g as measured by the method of ASTM D2896. The detergents herein may be neutral or overbased. For example, a low-base or neutral detergent herein may have a total base number (TBN) less than about 250 mg KOH/gram (e.g., about 0 to less than about 250). Overbased detergents herein may have a total base number (TBN) of about 250 mg KOH/gram or greater, or about 300 mg KOH/gram or greater, or about 350 mg KOH/gram or greater, or about 375 mg KOH/gram or greater, or about 400 mg KOH/gram or greater. The overbased detergent may have a metal to substrate ratio of from 1.1:1 or less, or from 2:1 or less, or from 4:1 or less, or from 5:1 or less, or from 7:1 or less, or from 10:1 or less, or from 12:1 or less, or from 15:1 or less, or from 20:1 or less.

[0028] Examples of suitable overbased detergents include (subject to the noted requirements of non-sulfonate metals contributions, calcium, magnesium, and/or TBN herein), but are not limited to, overbased calcium phenates, overbased calcium sulfur containing phenates, overbased calcium sulfonates, overbased calcium calixarates, overbased calcium salixarates, overbased calcium salicylates, overbased calcium carboxylic acids, overbased calcium phosphorus acids,

overbased calcium mono- and/or di-thiophosphoric acids, overbased calcium alkyl phenols, overbased calcium sulfur coupled alkyl phenol compounds, overbased calcium methylene bridged phenols, overbased magnesium phenates, overbased magnesium sulfur containing phenates, overbased magnesium sulfonates, overbased magnesium calixarates, overbased magnesium salixarates, overbased magnesium salicylates, overbased magnesium carboxylic acids, overbased magnesium phosphorus acids, overbased magnesium mono- and/or di-thiophosphoric acids, overbased magnesium alkyl phenols, overbased magnesium sulfur coupled alkyl phenol compounds, or overbased magnesium methylene bridged phenols. Preferably, the detergents are magnesium sulfonate and/or calcium sulfonate and, as mentioned above, substantially free of non-sulfonate detergents (e.g., preferably substantially free of phenate detergents). More preferably, the detergents herein are overbased magnesium sulfonate and/or overbased calcium sulfonate detergents as noted in the various embodiments.

[0029] In other embodiments, the TBN of the detergents herein may reflect a neat or non-diluted version of the detergent component. For example, the fluids herein may include overbased calcium sulfonate and/or an overbased magnesium sulfonate, as a neat additive, having a TBN of about 300 to about 450, and in other approaches, about 380 to about 420.

[0030] In one embodiment, the detergent systems herein contribute predominately magnesium metal (and preferably substantially all or all magnesium metal). In such embodiments, the detergent systems herein are predominately magnesium sulfonate (e.g., greater than 80 weight percent magnesium sulfonate, greater than 90 weight percent magnesium sulfonate, greater than 95 weight percent magnesium sulfonate, greater than 98 weight percent magnesium sulfonate, or in some approaches, 100 weight percent magnesium sulfonate (or any ranges therebetween)). In yet other embodiments, detergent system with predominately magnesium metal may also have an optional weight ratio of detergent magnesium-to-detergent calcium of about 600:1 or greater (and in other approaches, 620:1 or greater; 650:1 or greater; or about 600:1 to about 1000:1). In embodiments, such detergent systems herein may also provide about 70 to about 85 weight percent of the total lubricating oil composition TBN as measured pursuant to ASTM D2896. As also discussed more below, such detergent systems herein may be coupled, in yet other embodiments, with an additive system that is (1) substantially free of dispersant olefin copolymer viscosity index improvers in order to achieve M271 EVO

performance, (2) an antiwear system having metal dihydrocarbyl dithiophosphate compounds derived from secondary alcohols and having, on average, 6 or less carbon atoms per phosphorus (and in some embodiments, 200 to 800 ppm of phosphorus from such antiwear compounds); and/or (3) a mixed antioxidant system providing a weight ratio of antioxidant oxygen to antioxidant nitrogen (e.g., a weight ratio of O/N) of 4:1 to 10:1. As used herein, substantially free (in any embodiment of this disclosure unless noted otherwise) refers to a composition having less than 1 weight percent, less than about 0.5 weight percent, less than about 0.2 weight percent, less than about 0.1 weight percent, or no functional amounts of the noted additive.

[0031] In yet further approaches, the detergent system contributes both calcium and magnesium metals (preferably, calcium and magnesium sulfonate detergents) and with a selected ratio of detergent calcium-to-detergent magnesium of about 0.8:1 to about 1.5:1 (in other approaches, about 0.8:1 to about 1.2:1 or about 0.8:1 to about 1.0:1). As discussed more below, such detergent system may be coupled, in yet other embodiments, (1) with select antiwear systems and/or (2) select antioxidant systems in order to achieve M271 EVO performance. For instance, such detergent systems may be coupled with an additive system that includes a metal containing antiwear system with phosphorus provided from zinc dihydrocarbyl dithiophosphate compounds derived from primary alcohols and having, on average, 8 or more carbon atoms per phosphorus; and at the same time, the additive system may be substantially free of dispersant olefin copolymer viscosity index improvers. In yet further embodiments, such detergent system of this embodiment may also be coupled with an additive system that includes one or more antioxidant additives that includes a majority of phenolic antioxidant additives (and preferably, substantially all phenolic antioxidant additives) and, in some embodiments, with the weight ratio of oxygen in ppm contributed from phenolic antioxidant compounds to nitrogen in ppm from aminic antioxidant compounds (that is, a weight ratio of O/N) greater than 100:1 (greater than 150:1, greater than 175:1, greater than 200:1), and in yet other embodiments, the additive system may also be substantially free of dispersant olefin copolymer viscosity index improvers.

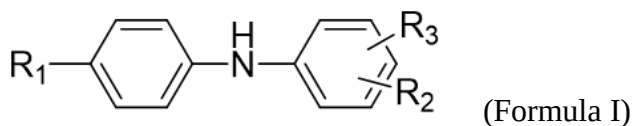
[0032] Optional Viscosity Index Improver

[0033] The methods and the lubricating oil compositions herein may, in some embodiments, also contain an additive system with one or more optional viscosity index improvers coupled

with the detergent systems described above and, if included, the optional viscosity index improver may preferably be a dispersant olefin copolymer viscosity index improver (and in this context, the lubricating oil compositions may include up to about 1.5 weight percent or up to about 1.3 weight percent of the viscosity index improver). In other embodiments as noted above, the lubricating oil compositions herein are substantially free of dispersant olefin copolymer viscosity index improvers (and in this context, substantially free of dispersant olefin copolymer viscosity improvers means less than about 1.0 weight percent, about 0.5 weight percent or less, about 0.2 weight percent or less, about 0.1 weight percent or less, or no functional amounts of dispersant olefin copolymer viscosity improvers). If included, suitable viscosity index improvers may include polyolefins, olefin copolymers, ethylene/propylene copolymers, polyisobutenes, hydrogenated styrene-isoprene polymers, styrene/maleic ester copolymers, hydrogenated styrene/butadiene copolymers, hydrogenated isoprene polymers, alpha-olefin maleic anhydride copolymers, polymethacrylates, polyacrylates, polyalkyl styrenes, hydrogenated alkenyl aryl conjugated diene copolymers, or mixtures thereof.

[0034] In one approach, suitable dispersant olefin copolymer viscosity index improvers may include a highly grafted, multi-functional olefin copolymer that is the reaction product of (1) an acylated olefin copolymer, where the acylated copolymer includes a copolymer, copolymers, or terpolymers of ethylene and one or more C₃ to C₂₀ alpha-olefins and optionally a non-conjugated diene or triene on which has been grafted ethylenically unsaturated carboxylic reactants to a level of 0.3 to 0.75 carboxylic groups per 1000 number average molecular weight units (Mn), and (2) a polyamine compound. Suitable dispersant olefin copolymer viscosity index improves are described in US 6,107,257, which is incorporated herein by reference.

[0035] In one approach or embodiment, the polyamine compound of the dispersant olefin copolymer viscosity index improver is preferably an N-arylphenylene diamine represented by Formula I:



wherein R₁ is hydrogen, -NH-aryl, -NH-arylalkyl, -NH-alkyl, or a branched or straight chain radical having from 4 to 24 carbon atoms that can be alkyl, alkenyl, alkoxyl, aralkyl, alkaryl,

hydroxyalkyl or aminoalkyl; R_2 is $-NH_2$, $-CH_2-(CH_2)_n-NH_2$, or $-CH_2$ -aryl- NH_2 , in which n is an integer of 1 to 10; and R_3 is hydrogen, alkyl, alkenyl, alkoxyl, aralkyl, or alkaryl wherein any moiety thereof may have 4 to 24 carbon atoms.

[0036] The olefin copolymer substrate may include, in some embodiments, about 15 to about 80 mol percent ethylene and about 85 to about 20 mole percent of one or more C_3 to C_{23} alpha-olefins with a preferred mol ratio of about 35 to about 75 mole percent ethylene and about 65 to about 25 mole percent of one or more C_3 to C_{20} alpha-olefins, a more preferred mol ratio being about 50 to about 70 mol percent ethylene and about 50 to about 30 mole percent of one or more C_3 to C_{20} alpha-olefins, and a most preferred mol ratio being about 55 to about 65 mole percent ethylene and about 45 to about 35 mole percent of one or more C_3 to C_{20} alpha-olefin. The polymer substrate, that is the ethylene copolymer or terpolymer, is an oil-soluble, linear or branched polymer or copolymer having a number average molecular weight from about 20,000 to about 150,000 as determined by gel permeation chromatography, with a preferred number average molecular weight range of about 30,000 to about 110,000.

[0037] An ethylenically unsaturated carboxylic acid material is next grafted onto the polymer backbone to form an acylated ethylene copolymer. These carboxylic reactants which are suitable for grafting onto the ethylene copolymer contain at least one ethylenic bond and at least one, preferably two, carboxylic acid or its anhydride groups or a polar group which is convertible into said carboxyl groups by oxidation or hydrolysis. Preferably, the carboxylic reactants are selected from the group consisting of acrylic, methacrylic, cinnamic, crotonic, maleic, fumaric and itaconic reactants. More preferably, the carboxylic reactants are selected from the group consisting of maleic acid, fumaric acid, maleic anhydride, or a mixture of two or more of these. Maleic anhydride or a derivative thereof is generally most preferred due to its commercial availability and ease of reaction. In the case of unsaturated ethylene copolymers or terpolymers, itaconic acid or its anhydride is preferred due to its reduced tendency to form a cross-linked structure during the free-radical grafting process.

[0038] The ethylenically unsaturated carboxylic acid materials typically can provide one or two carboxylic groups per mole of reactant to the grafted polymer. That is, maleic anhydride can provide two carboxylic groups per molecule to the grafted polymer. The carboxylic reactant is grafted onto the prescribed polymer backbone in an amount to provide 0.3 to 0.75 carboxylic

groups per 1000 number average molecular weight units of the polymer backbone, preferably 0.3 to 0.5 carboxylic groups per 1000 number average molecular weight. For example, a copolymer substrate with Mn of 20,000 is grafted with 6 to 15 carboxylic groups per polymer chain or 3 to 7.5 moles of maleic anhydride per mole of polymer. A copolymer with Mn of 100,000 is grafted with 30 to 75 carboxylic groups per polymer chain or 15 to 37.5 moles of maleic anhydride per polymer chain.

[0039] In the embodiments including the dispersant olefin copolymer viscosity index improver, the lubricating oil compositions herein may include up to about 1.5 weight percent, up to about 1.3 weight percent, up to about 1.25 weight percent, or up to about 1 weight percent of the dispersant olefin copolymer viscosity index improver. In other embodiments, and if included, the lubricating oil compositions herein may include about 0.8 weight percent to about 1.5 weight percent, about 0.8 to about 1.3 weight percent, or about 0.9 to about 1.2 weight percent of the dispersant olefin copolymer viscosity index improver (or any other ranges within such endpoints). As noted above, such amounts of the dispersant olefin copolymer viscosity index improver may be coupled with or combined with, in some embodiments, selected features of the detergent system (e.g., a detergent system that contributes both calcium and magnesium metals and with a ratio of detergent calcium to detergent magnesium of at least 2:1) in order to achieve M271 EVO performance.

[0040] Metal Dihydrocarbyl Dithiophosphate Compounds

[0041] The methods and the lubricating compositions herein may, in some embodiments, also include an antiwear system of one or more metal dihydrocarbyl dithiophosphate compounds, such as but not limited to, a zinc dihydrocarbyl dithiophosphate compound (ZDDP). If used, the one or more metal dihydrocarbyl dithiophosphate compounds may provide up to about 1,000 ppm phosphorus to the lubricant, up to about 900 ppm phosphorus, or up to about 800 ppm phosphorus to the lubricating oil compositions or provide at least about 200 ppm of phosphorus, at least about 400 ppm of phosphorus, at least about 600 ppm phosphorus, or about 700 ppm of phosphorus. When used in the lubricants herein, the hydrocarbyl groups of the one or more metal dihydrocarbyl dithiophosphate compounds may be derived from primary alcohols,

secondary alcohols, or a mixture of secondary alcohols and primary alcohols as described more herein.

[0042] In one approach, the metal dihydrocarbyl dithiophosphate compounds herein may be derived from primary alcohols and the average number of carbon atoms in the hydrocarbyl groups of the metal dihydrocarbyl dithiophosphate compounds may be, on average, 8 or more carbon atoms per phosphorus (e.g., 8 to 16, 8 to 12, or 8 to 10 carbons on average per phosphorus). In this approach, the metal dihydrocarbyl dithiophosphate compound may provide about 1,000 ppm phosphorus to the lubricant, up to about 900 ppm phosphorus, or up to about 800 phosphorus to the lubricating oil compositions or provide at least about 200 ppm of phosphorus, at least about 400 ppm of phosphorus, at least about 600 ppm phosphorus, or about 700 ppm of phosphorus. In this embodiment, such metal dihydrocarbyl dithiophosphate compounds may provide substantially all or all of the antiwear phosphorus (e.g., about 80 weight percent or more of the antiwear phosphorus, about 90 weight percent or more of the antiwear phosphorus, about 95 weight percent or more of the antiwear phosphorus, about 98 weight percent or more or more of the antiwear phosphorus, about 99 weigh percent or more of the antiwear phosphorus, or about 100 weight percent of the antiwear phosphorus). Such ZDDP may be particularly suitable in embodiments of the methods and lubricating compositions including the mixed calcium and magnesium detergents and the mixed aminic and phenolic antioxidants as described herein.

[0043] In another approach, the metal dihydrocarbyl dithiophosphate compounds herein may be derived from secondary alcohols and the average number of carbon atoms in the hydrocarbyl groups may be, on average, 6 or fewer carbon atoms per phosphorus (e.g., 2 to 6, 3 to 6, or 4 to 6 carbons on average per phosphorus). In this alternative approach, such metal dihydrocarbyl dithiophosphate compound may provide about 1,000 ppm phosphorus to the lubricant, up to about 900 ppm phosphorus, or up to about 800 phosphorus to the lubricating oil compositions or provide at least about 200 ppm of phosphorus, at least about 400 ppm of phosphorus, at least about 600 ppm phosphorus, or about 700 ppm of phosphorus. In this embodiment, such metal dihydrocarbyl dithiophosphate compounds may provide substantially all or all of the antiwear phosphorus (e.g., about 80 weight percent or more of the antiwear phosphorus, about 90 weight percent or more of the antiwear phosphorus, about 95 weight percent or more of the antiwear

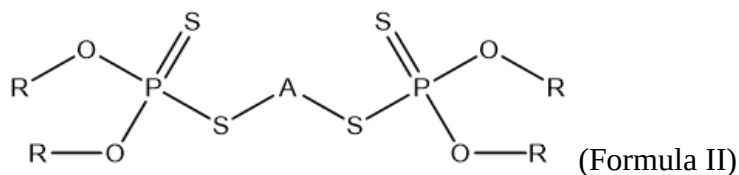
phosphorus, about 98 weight percent or more of the antiwear phosphorus, about 99 weight percent or more of the antiwear phosphorus, or about 100 weight percent of the antiwear phosphorus). This alternative ZDDP may be particularly suitable in embodiments of the methods and lubricating compositions including the mixed calcium and magnesium detergents combined with an antioxidant system with only phenolic antioxidants as described herein, or such ZDDP may also be suitable for embodiments of the methods and compositions herein including the magnesium only detergent system.

[0044] In various embodiments, suitable metal dihydrocarbyl dithiophosphates compounds may include between 5 to about 10 weight percent metal (such as, about 6 to about 9 weight percent metal such as zinc), about 8 to about 18 weight percent sulfur (such as about 12 to about 18 weight percent sulfur, or about 8 to about 15 weight percent sulfur), and about 4 and 20 weight percent phosphorus (such as, about 4 to about 15 weight percent phosphorus, or about 4 to about 9 weight percent phosphorus). Suitable metal dihydrocarbyl dithiophosphate compounds may comprise dihydrocarbyl dithiophosphate metal salts wherein the metal may be an alkali metal, alkaline earth metal, aluminum, lead, tin, molybdenum, manganese, nickel, copper, titanium, zirconium, zinc, or combinations thereof. Preferably, the metal is zinc.

[0045] The alkyl groups on the metal dihydrocarbyl dithiophosphate compounds when used in the passenger car motor oil herein may be derived from primary alcohols, secondary alcohols, phenols, or mixtures thereof as the case may be and as needed for each embodiment described herein. For example, the hydrocarbyl groups may be derived from 2-ethyl hexanol, methyl isobutyl carbinol (MIBC), isobutanol, and isopropanol, and the like. In one approach, about 60 mol percent or more of the alkyl groups may be derived from primary alcohols (such as, but not limited to, 2-ethyl hexanol and/or isobutyl alcohol) and about 40 mol percent or less of alkyl groups may be derived from secondary alcohols (such as, but not limited to, isopropyl alcohol, methyl isobutyl carbinol, and the like, and/or combinations thereof). In another approach, all of the alkyl groups on the metal dihydrocarbyl dithiophosphate compounds may be derived from a primary alcohol, such as 2-ethyl hexanol or others noted herein. In other approaches, all of the alkyl groups on the metal dihydrocarbyl dithiophosphate compounds may be derived from a secondary alcohol, such as, but not limited to isopropyl alcohol, or methyl isobutyl carbinol, and the like alcohols.

[0046] In general, subject to the limitations noted above, the metal dihydrocarbyl dithiophosphate compounds of the passenger car motor oil may be derived from, but not limited to, alcohols selected from 2-ethylhexanol, propanol, methyl pentanol, methyl heptanol, heptanol, octanol, nonanol, decanol, dodecanol, and/or iso-variants thereof. Examples of suitable metal dihydrocarbyl dithiophosphate compounds include, but are not limited, to: zinc O,O-di(C₃₋₁₄-alkyl)dithiophosphate; zinc O,O-bis(2-ethylhexyl) dithiophosphate; zinc O,O-diisooctyl dithiophosphate; zinc O,O-bis(dodecylphenyl) dithiophosphate; zinc O,O-diisodecyl dithiophosphate; zinc O,O-bis(6-methylheptyl) dithiophosphate; zinc O,O-dioctyl dithiophosphate; zinc O,O-dipentyl dithiophosphate; zinc O-(2-methylbutyl)-O-(2-methylpropyl)dithiophosphate; and zinc O-(3-methylbutyl)-O-(2-methylpropyl) dithiophosphate, or combinations thereof.

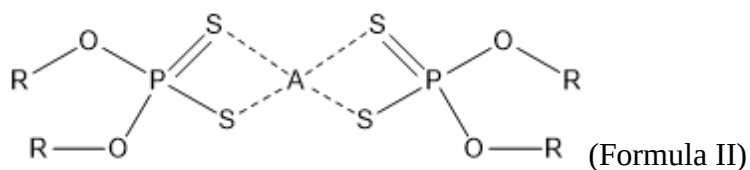
[0047] In approaches or embodiments, the metal dihydrocarbyl dithiophosphate compound suitable for the passenger car motor oils herein may have a structure of Formula II:



wherein each R in Formula I independently contains from 3 to 18 carbon atoms, or 3 to 12 carbon atoms, or about 3 to 10 carbon atoms so long as each phosphorus atom has, on average, at least 8 or more total carbons (such on average 8 to 16 carbons) in one embodiment (and preferably derived from primary alcohols), and in another embodiment, each phosphorus atom has an average of 6 or less carbons (such as on average 2 to 6 carbons) per phosphorus atom (and preferably derived from secondary alcohols). Again, mixtures of such compounds may also be used. For example, each R may independently be ethyl, n-propyl, i-propyl, n-butyl, i-butyl, sec-butyl, amyl, n-hexyl, i-hexyl, n-octyl, decyl, dodecyl, octadecyl, ethylhexyl, 2-ethylhexyl, phenyl, butylphenyl, cyclohexyl, methylcyclopentyl, propenyl, butenyl, and the like groups. The number of carbon atoms in each R group in the formula above will generally be 3 or greater, 4 or greater, 6 or greater, 8 or greater, or 10 or greater. In one embodiment, each phosphorus atom may have R groups with an average of 3 to 6 carbons per phosphorus atom (derived from isopropyl and methylpentyl groups) and, in another embodiment, each phosphorus atom may have R groups with an average of 8 or more carbons (such as an average of 10 to 16

carbons) per phosphorus atom (derived from ethylhexyl or isobutyl groups). Mixtures of such compounds may also be used herein. Preferably, each R may be linear or branched C8 or 2-ethylhexyl groups, C3 or isopropyl groups, C4 or isobutyl groups, and/or C8 or methylpentyl groups. In Formula I, A is a metal, such as aluminum, lead, tin, molybdenum, manganese, nickel, copper, titanium, zirconium, zinc, or combinations thereof and, preferably, A is zinc. When the metal dihydrocarbyl dithiophosphate compound has the structure shown in Formula I and with A being zinc, the compound may have about 4 to about 9 weight percent phosphorus and about 6 to about 9 weight percent zinc and a zinc to phosphorus ratio of about 1.0 to about 1.5.

[0048] In some approaches or embodiments, it is understood in the art that a more accurate representation of the sulfur-zinc coordination arrangement may be represented by the symmetrical arrangement shown below with the chemical structure of Formula II that may be used herein as interchangeable with Formula I shown above. It is also understood that the structures shown in Formulas I and II may be present as monomer, dimer, trimer, or oligomer (such as a tetramer).



[0049] Dihydrocarbyl dithiophosphate metal salts may be prepared in accordance with known techniques by first forming a dihydrocarbyl dithiophosphoric acid (DDPA), usually by reaction of one or more alcohols or phenols with P_2S_5 and then neutralizing the formed DDPA with a metal compound, such as zinc oxide. For example, DDPA may be made by reacting mixtures of alcohols including the suitable amounts of primary alcohols (and if needed, suitable blends of primary and secondary alcohols) with P_2S_5 . In this case, the DDPA includes alkyl groups predominately derived from primary alcohols or both primary and secondary alcohols as needed to meet the required primary alcohol content in the final product. Alternatively, multiple DDPA's can be prepared where the alkyl groups on one DDPA are derived entirely from secondary alcohols and the alkyl groups on another DDPA are derived entirely from primary alcohols. The DDPA's are then blended together to form a mixture of DDPA's having alkyl groups meeting the noted primary alcohol content.

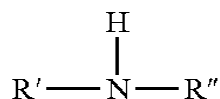
[0050] As mentioned, the passenger car motor oil may include blends of metal dihydrocarbyl dithiophosphate compounds derived from primary alcohols and/or secondary alcohols. In one approach, the finished lubricants herein may include about 1 to about 5 weight percent of any of the noted metal dihydrocarbyl dithiophosphate compounds individually or blends thereof.

[0051] Antioxidant System

[0052] The methods and the lubricating compositions herein may, in some embodiments, also include an additive system having select antioxidant compounds (or blends thereof) including one or more phenolic antioxidant compounds, one or more aminic antioxidant compounds, or combinations thereof. In some embodiments, for instance, the methods and lubricating compositions herein include both one or more phenolic antioxidant compounds and one or more aminic antioxidant compounds and, in some embodiments, also has a select weight ratio of oxygen in ppm contributed from the one or more phenolic antioxidant compounds to nitrogen in ppm from the one or more aminic antioxidant compounds (e.g., a weight ratio of O/N) of about 300:1 or less, and in other approaches or embodiments, the weight ratio of oxygen in ppm contributed from the one or more phenolic antioxidant compounds to nitrogen in ppm from the one or more aminic antioxidant compounds (e.g., the weight ratio of O/N) is about 300:1 to about 4:1, or about 300:1 to about 100:1, or about 200:1 to about 300:1 or about 4:1 to about 50:1 or about 4:1 to about 20:1 or preferably, about 4:1 to about 10:1.

[0053] In one approach or embodiment, the aminic antioxidants may include, but are not limited to, antioxidants selected from aromatic amines, alkylated diphenylamines, phenyl- α -naphthylamines, alkylated phenyl- α -naphthylamines, hindered non-aromatic amines, and the like, or combinations thereof. The total amount of the aminic antioxidant in the methods and lubricating compositions herein is in an amount to deliver up to about 200 ppm of antioxidant nitrogen and, in some approaches, about 100 ppm to about 200 ppm antioxidant nitrogen, in other approaches, about 125 to about 190 ppm of antioxidant nitrogen, or in yet further approaches, about up to about 150 ppm to about 180 ppm of antioxidant nitrogen. In other approaches, the methods and lubricating compositions herein may include up to about 1 weight percent of the aminic antioxidant, or about 0.5 to about 1 weight percent of the aminic antioxidant.

[0054] In some approaches, the aminic antioxidant may be one or more aromatic amine antioxidants and may include, but are not limited to, diarylamines having the formula:



wherein R' and R'' each independently represents a substituted or unsubstituted aryl group having from 6 to 30 carbon atoms. If substituted, suitable substituents for the aryl group of R' and R'' include aliphatic hydrocarbon groups such as alkyl having from 1 to 30 carbon atoms, hydroxy groups, halogen radicals, carboxylic acid or ester groups, or nitro groups. The aryl group may be substituted or unsubstituted phenyl or naphthyl, particularly wherein one or both of the aryl groups are substituted with at least one alkyl having from 4 to 30 carbon atoms, preferably from 4 to 18 carbon atoms, most preferably from 4 to 9 carbon atoms. In approaches, one or both aryl groups may be substituted, e.g. mono-alkylated diphenylamine, di-alkylated diphenylamine, C9 alkylated diphenyl amines, or mixtures of mono- and di-alkylated diphenylamines.

[0055] Examples of diarylamine antioxidants that may be used include, but are not limited to: diphenylamine; various alkylated diphenylamines, 3-hydroxydiphenylamine, N-phenyl-1,2-phenylenediamine, N-phenyl-1,4-phenylenediamine, monobutyldiphenyl-amine, dibutyl-diphenylamine, monooctyldiphenylamine, dioctyldiphenylamine, monononyl-diphenylamine, dinonyldiphenylamine, monotetradecyldiphenylamine, ditetradecyl-diphenylamine, phenyl-alpha-naphthylamine, monooctyl phenyl-alpha-naphthylamine, phenyl-beta-naphthylamine, monoheptyldiphenylamine, diheptyl-diphenylamine, p-oriented styrenated diphenylamine, mixed butyloctyldiphenylamine, and mixed octylstyryl-diphenylamine.

[0056] Suitable phenolic or hindered phenolic antioxidants may contain a secondary butyl and/or a tertiary butyl group as a sterically hindering group. The phenol group may be further substituted with a hydrocarbyl group and/or a bridging group linking to a second aromatic group. Examples of suitable phenolic or hindered phenol antioxidants include 2,6-di-tert-butylphenol, 4-methyl-2,6-di-tert-butylphenol, 4-ethyl-2,6-di-tert-butylphenol, 4-propyl-2,6-di-tert-butylphenol or 4-butyl-2,6-di-tert-butylphenol, or 4-dodecyl-2,6-di-tert-butylphenol. In one embodiment the hindered phenol antioxidant may be an ester and may include, for instance, Irganox™ L-135 available from BASF or an addition product derived from 2,6-di-tert-butylphenol and an alkyl

acrylate, wherein the alkyl group may contain about 1 to about 18, or about 2 to about 12, or about 2 to about 8, or about 2 to about 6, or about 4 carbon atoms. Another commercially available hindered phenol antioxidant may be an ester and may include EthanoxTM 4716 available from Albemarle Corporation. In embodiments, phenolic antioxidants of the methods and compositions herein contribute up to about 800 ppm of phenolic antioxidant oxygen, and in other approaches, about 500 to about 800 ppm of phenolic antioxidant oxygen, or about 600 to about 800 ppm of phenolic antioxidant oxygen. In some embodiments, the methods and lubricating compositions herein may also include about 0.5 to about 1.5 weight percent of the phenolic or hindered phenol antioxidants, and in other embodiments, about 0.6 to about 1.2 weight percent of phenolic or hindered phenol antioxidants. In one embodiment, the antioxidant system only includes phenolic antioxidants.

[0057] As noted above, when the methods and lubricating compositions include both one or more of the aminic antioxidants and one or more of the phenolic or hindered phenol antioxidant, and in such embodiments, then the methods and compositions also have a weight ratio of oxygen in ppm contributed from the one or more phenolic antioxidant compounds to nitrogen in ppm from the one or more aminic antioxidant compounds (e.g., a ratio of O/N) of about 300:1 or less, and in other approaches or embodiments, the weight ratio of oxygen in ppm contributed from the one or more phenolic antioxidant compounds to nitrogen in ppm from the one or more aminic antioxidant compounds (O/N) is about 300:1 to about 4:1, or about 300:1 to about 100:1, or about 200:1 to about 300:1, or about 4:1 to about 50:1, or about 4:1 to about 20:1, or about 4:1 to about 10:1. In other approaches, the methods and compositions herein may include substantially all phenolic antioxidant compounds (e.g., at least about 700 ppm of antioxidant oxygen (about 900 to about 1500 ppm antioxidant oxygen, or about 1000 to about 1500 ppm antioxidant oxygen) and little to no antioxidant nitrogen (e.g., less than 10 ppm of antioxidant nitrogen, less than 5 ppm of antioxidant nitrogen, less than 2 ppm of antioxidant nitrogen, or no functional amounts of antioxidant nitrogen).

[0058] Lubricating a Combustion Engine to Achieve Low Engine Sludge

[0059] The present disclosure relates to various methods of lubricating a combustion engine for passing (or achieving elevated passing performance) of the M271 EVO fired engine test of

CEC L-107-19 (wherein passing is defined herein as elevated passing performance with an average engine sludge (AES) rating of 9.0 +/- 0.3 merits) when using a majority of the less-desired API Group II base oils. As shown by the Example below, the methods include lubricating a combustion engine with a lubricating oil composition including a base oil of lubricating viscosity having about 50 weight percent or more of a hydrotreated mineral oil with more than 90 weight percent saturates, less than 0.03 weight percent of sulfur, and a viscosity index (ASTM D2270) of 120 or less (e.g., a majority of less-desired API Group II base oil) combined with selected additive componentry to overcome the performance debits of the lower quality API Group II base oil.

[0060] In one embodiment, the selected additive componentry includes at least a detergent system having (i) little to no non-sulfonate detergents or, preferably, less than about 5 weight percent of metal from non-sulfonate detergents and (ii) a total base number (TBN) thereof less than 10 mg KOH/gram and that contributes about 60 to about 85 percent of the total lubricating oil composition TBN as measured pursuant to ASTM D2896. However, in some cases, the detergent system by itself cannot achieve high average engine sludge (e.g., M271 merits of 9.0 +/- 0.3 or higher) when using high amounts of the less-desired API Group II base oil, and therefore, other specifically selected componentry is combined with the detergent system to achieve performance.

[0061] In other embodiments, therefore, the additive systems herein also include one or more specifically selected other components surprisingly discovered to have synergy with the detergent system to achieve the elevated average engine sludge rating of 9.0 +/- 0.3 merits or higher pursuant to CEC L-107-19 even with the API Group II base oils and little to no phenate detergents. Such componentry of the additive system is described more specifically above and includes, in various embodiments, at least one or more of (a) an antiwear system including one or more zinc dihydrocarbyl dithiophosphate compounds having alkyl groups derived from primary alcohols, secondary alcohols, or combination thereof and providing about 200 to about 1000 ppm phosphorus; (b) an antioxidant system including one or more phenolic antioxidant compounds, one or more aminic antioxidant compounds, or combinations thereof; and one or more of the following to achieve the elevated passing average engine sludge rating of 9.0 +/- 0.3 merits or higher pursuant to CEC L-107-19 (c) the detergent system includes a majority of one or more

overbased magnesium sulfonate detergents; (d) the antiwear system includes a majority of zinc dihydrocarbyl dithiophosphate compounds having an average of 8 or more carbon atoms per phosphorus atom; and/or (e) the antioxidant system includes a majority of phenolic antioxidant compounds. In some embodiments, the additive systems may also include select amounts of the one or more dispersant olefin copolymer viscosity index improvers as described above. As shown in the Examples, selecting the detergent system and the correct additive system components overcomes any performance debits in the M271 EVO fired engine test when using a majority of API Group II base oils and little to no phenate detergents when it was previously thought necessary to include phenate detergents and high amounts of API Group III base oils to achieve low engine sludge (e.g., high merits) in this fired engine test.

[0062] Optional Components:

[0063] The methods and lubricating oil compositions herein may also include a number of optional components combined with the detergent systems and other additive system componentry discussed above and as needed to meet performance standards. Those optional components are described in the following paragraphs. In some embodiments, the methods and lubricant oil compositions herein may include at least about 1000 ppm of total nitrogen that includes at least about 600 ppm of dispersant nitrogen. In other embodiments, the methods and lubricating oil compositions herein may also include additives that provide molybdenum but less than about 200 ppm of molybdenum (in other approaches, about 150 ppm or less, about 100 ppm or less, about 80 ppm or less, or about 50 ppm or less) and yet other additives that provide boron but less than about 150 ppm of boron.

[0064] Dispersants: The methods and lubricating oil compositions may optionally include one or more other dispersants or mixtures thereof. Dispersants are often known as ashless-type dispersants because, prior to mixing in a lubricating oil composition, they do not contain ash-forming metals and do not contribute ash when added to a lubricant. Ashless type dispersants are characterized by a polar group attached to a relatively high molecular weight hydrocarbon chain. Typical ashless dispersants include N-substituted long chain alkenyl succinimides. Examples of N-substituted long chain alkenyl succinimides include polyisobutylene succinimide with the number average molecular weight of the polyisobutylene substituent being in the range about

350 to about 50,000, or to about 5,000, or to about 3,000, as measured by GPC. Succinimide dispersants and their preparation are disclosed, for instance in U.S. Pat. No. 7,897,696 or U.S. Pat. No. 4,234,435. The alkenyl substituent may be prepared from polymerizable monomers containing about 2 to about 16, or about 2 to about 8, or about 2 to about 6 carbon atoms. Succinimide dispersants are typically the imide formed from a polyamine, typically a poly(ethyleneamine). In embodiments, the dispersants may provide about 600 to about 1000 ppm of dispersant nitrogen.

[0065] Preferred amines are selected from polyamines and hydroxylamines. Examples of polyamines that may be used include, but are not limited to, diethylene triamine (DETA), triethylene tetramine (TETA), tetraethylene pentamine (TEPA), and higher homologues such as pentaethylene hexamine (PEHA), and the like.

[0066] A suitable heavy polyamine is a mixture of polyalkylene-polyamines comprising small amounts of lower polyamine oligomers such as TEPA and PEHA (pentaethylene hexamine) but primarily oligomers with 6 or more nitrogen atoms, 2 or more primary amines per molecule, and more extensive branching than conventional polyamine mixtures. A heavy polyamine preferably includes polyamine oligomers containing 7 or more nitrogen atoms per molecule and with 2 or more primary amines per molecule. The heavy polyamine comprises more than 28 wt. % (e.g. >32 wt. %) total nitrogen and an equivalent weight of primary amine groups of 120-160 grams per equivalent.

[0067] In some approaches, suitable polyamines are commonly known as PAM and contain a mixture of ethylene amines where TEPA and pentaethylene hexamine (PEHA) are the major part of the polyamine, usually less than about 80%.

[0068] Typically, PAM has 8.7-8.9 milliequivalents of primary amine per gram (an equivalent weight of 115 to 112 grams per equivalent of primary amine) and a total nitrogen content of about 33-34 wt. %. Heavier cuts of PAM oligomers with practically no TEPA and only very small amounts of PEHA but containing primarily oligomers with more than 6 nitrogen atoms and more extensive branching, may produce dispersants with improved dispersancy.

[0069] In an embodiment the present disclosure further comprises at least one polyisobutylene succinimide dispersant derived from polyisobutylene with a number average molecular weight in the range about 350 to about 50,000, or to about 5000, or to about 3000, as

determined by GPC. The polyisobutylene succinimide may be used alone or in combination with other dispersants.

[0070] In some embodiments, polyisobutylene, when included, may have greater than 50 mol%, greater than 60 mol%, greater than 70 mol%, greater than 80 mol%, or greater than 90 mol% content of terminal double bonds. Such PIB is also referred to as highly reactive PIB (“HR-PIB”). HR-PIB having a number average molecular weight ranging from about 800 to about 5000, as determined by GPC, is suitable for use in embodiments of the present disclosure. Conventional PIB typically has less than 50 mol%, less than 40 mol%, less than 30 mol%, less than 20 mol%, or less than 10 mol% content of terminal double bonds.

[0071] An HR-PIB having a number average molecular weight ranging from about 900 to about 3000 may be suitable, as determined by GPC. Such HR-PIB is commercially available, or can be synthesized by the polymerization of isobutene in the presence of a non-chlorinated catalyst such as boron trifluoride, as described in US Patent No. 4,152,499 to Boerzel, et al. and U.S. Patent No. 5,739,355 to Gateau, et al. When used in the aforementioned thermal ene reaction, HR-PIB may lead to higher conversion rates in the reaction, as well as lower amounts of sediment formation, due to increased reactivity. A suitable method is described in U.S. Patent No. 7,897,696.

[0072] In one embodiment, the present disclosure further comprises at least one dispersant derived from polyisobutylene succinic anhydride (“PIBSA”). The PIBSA may have an average of between about 1.0 and about 2.0 succinic acid moieties per polymer.

[0073] The % actives of the alkenyl or alkyl succinic anhydride can be determined using a chromatographic technique. This method is described in column 5 and 6 in U.S. Pat. No. 5,334,321.

[0074] The percent conversion of the polyolefin is calculated from the % actives using the equation in column 5 and 6 in U.S. Pat. No. 5,334,321.

[0075] Unless stated otherwise, all percentages are in weight percent and all molecular weights are number average molecular weights determined by gel permeation chromatography (GPC) using commercially available polystyrene standards (with a number average molecular weight of 180 to about 18,000 as the calibration reference).

[0076] In one embodiment, the dispersant may be derived from a polyalphaolefin (PAO) succinic anhydride. In one embodiment, the dispersant may be derived from olefin maleic anhydride copolymer. As an example, the dispersant may be described as a poly-PIBSA. In an embodiment, the dispersant may be derived from an anhydride which is grafted to an ethylene-propylene copolymer.

[0077] A suitable class of nitrogen-containing dispersants may be derived from olefin copolymers (OCP), more specifically, ethylene-propylene dispersants which may be grafted with maleic anhydride. A more complete list of nitrogen-containing compounds that can be reacted with the functionalized OCP are described in U.S. Patent Nos. 7,485,603; 7,786,057; 7,253,231; 6,107,257; and 5,075,383; and/or are commercially available.

[0078] One class of suitable dispersants may also be Mannich bases. Mannich bases are materials that are formed by the condensation of a higher molecular weight, alkyl substituted phenol, a polyalkylene polyamine, and an aldehyde such as formaldehyde. Mannich bases are described in more detail in U.S. Patent No. 3,634,515.

[0079] A suitable class of dispersants may also be high molecular weight esters or half ester amides. A suitable dispersant may also be post-treated by conventional methods by a reaction with any of a variety of agents. Among these are boron, urea, thiourea, dimercaptothiadiazoles, carbon disulfide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, maleic anhydride, nitriles, epoxides, carbonates, cyclic carbonates, hindered phenolic esters, and phosphorus compounds. US 7,645,726; US 7,214,649; and US 8,048,831 are incorporated herein by reference in their entireties.

[0080] In addition to the carbonate and boric acids post-treatments both the compounds may be post-treated, or further post-treatment, with a variety of post-treatments designed to improve or impart different properties. Such post-treatments include those summarized in columns 27-29 of U.S. Pat. No. 5,241,003, hereby incorporated by reference. Such treatments include, treatment with: Inorganic phosphorous acids or anhydrides (e.g., U.S. Pat. Nos. 3,403,102 and 4,648,980); Organic phosphorous compounds (e.g., U.S. Pat. No. 3,502,677); Phosphorous pentasulfides; Boron compounds as already noted above (e.g., U.S. Pat. Nos. 3,178,663 and 4,652,387); Carboxylic acid, polycarboxylic acids, anhydrides and/or acid halides (e.g., U.S. Pat. Nos. 3,708,522 and 4,948,386); Epoxides polyepoxiates or thioepoxides (e.g., U.S. Pat. Nos.

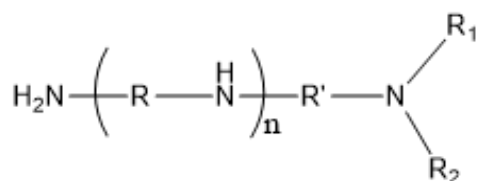
3,859,318 and 5,026,495); Aldehyde or ketone (e.g., U.S. Pat. No. 3,458,530); Carbon disulfide (e.g., U.S. Pat. No. 3,256,185); Glycidol (e.g., U.S. Pat. No. 4,617,137); Urea, thiourea or guanidine (e.g., U.S. Pat. Nos. 3,312,619; 3,865,813; and British Patent GB 1,065,595); Organic sulfonic acid (e.g., U.S. Pat. No. 3,189,544 and British Patent GB 2,140,811); Alkenyl cyanide (e.g., U.S. Pat. Nos. 3,278,550 and 3,366,569); Diketene (e.g., U.S. Pat. No. 3,546,243); A diisocyanate (e.g., U.S. Pat. No. 3,573,205); Alkane sultone (e.g., U.S. Pat. No. 3,749,695); 1,3-Dicarbonyl Compound (e.g., U.S. Pat. No. 4,579,675); Sulfate of alkoxylated alcohol or phenol (e.g., U.S. Pat. No. 3,954,639); Cyclic lactone (e.g., U.S. Pat. Nos. 4,617,138; 4,645,515; 4,668,246; 4,963,275; and 4,971,711); Cyclic carbonate or thiocarbonate linear monocarbonate or polycarbonate, or chloroformate (e.g., U.S. Pat. Nos. 4,612,132; 4,647,390; 4,648,886; 4,670,170); Nitrogen-containing carboxylic acid (e.g., U.S. Pat. 4,971,598 and British Patent GB 2,140,811); Hydroxy-protected chlorodicarbonyloxy compound (e.g., U.S. Pat. No. 4,614,522); Lactam, thiolactam, thiolactone or dithiolactone (e.g., U.S. Pat. Nos. 4,614,603 and 4,666,460); Cyclic carbonate or thiocarbonate, linear monocarbonate or polycarbonate, or chloroformate (e.g., U.S. Pat. Nos. 4,612,132; 4,647,390; 4,646,860; and 4,670,170); Nitrogen-containing carboxylic acid (e.g., U.S. Pat. No. 4,971,598 and British Patent GB 2,440,811); Hydroxy-protected chlorodicarbonyloxy compound (e.g., U.S. Pat. No. 4,614,522); Lactam, thiolactam, thiolactone or dithiolactone (e.g., U.S. Pat. Nos. 4,614,603, and 4,666,460); Cyclic carbamate, cyclic thiocarbamate or cyclic dithiocarbamate (e.g., U.S. Pat. Nos. 4,663,062 and 4,666,459); Hydroxyaliphatic carboxylic acid (e.g., U.S. Pat. Nos. 4,482,464; 4,521,318; 4,713,189); Oxidizing agent (e.g., U.S. Pat. No. 4,379,064); Combination of phosphorus pentasulfide and a polyalkylene polyamine (e.g., U.S. Pat. No. 3,185,647); Combination of carboxylic acid or an aldehyde or ketone and sulfur or sulfur chloride (e.g., U.S. Pat. Nos. 3,390,086; 3,470,098); Combination of a hydrazine and carbon disulfide (e.g. U.S. Pat. No. 3,519,564); Combination of an aldehyde and a phenol (e.g., U.S. Pat. Nos. 3,649,229; 5,030,249; 5,039,307); Combination of an aldehyde and an O-diester of dithiophosphoric acid (e.g., U.S. Pat. No. 3,865,740); Combination of a hydroxyaliphatic carboxylic acid and a boric acid (e.g., U.S. Pat. No. 4,554,086); Combination of a hydroxyaliphatic carboxylic acid, then formaldehyde and a phenol (e.g., U.S. Pat. No. 4,636,322); Combination of a hydroxyaliphatic carboxylic acid and then an aliphatic dicarboxylic acid (e.g., U.S. Pat. No. 4,663,064); Combination of formaldehyde and a

phenol and then glycolic acid (e.g., U.S. Pat. No. 4,699,724); Combination of a hydroxyaliphatic carboxylic acid or oxalic acid and then a diisocyanate (e.g. U.S. Pat. No.4,713,191); Combination of inorganic acid or anhydride of phosphorus or a partial or total sulfur analog thereof and a boron compound (e.g., U.S. Pat. No. 4,857,214); Combination of an organic diacid then an unsaturated fatty acid and then a nitrosoaromatic amine optionally followed by a boron compound and then a glycolating agent (e.g., U.S. Pat. No. 4,973,412); Combination of an aldehyde and a triazole (e.g., U.S. Pat. No. 4,963,278); Combination of an aldehyde and a triazole then a boron compound (e.g., U.S. Pat. No. 4,981,492); Combination of cyclic lactone and a boron compound (e.g., U.S. Pat. No. 4,963,275 and 4,971,711). The above-mentioned patents are herein incorporated in their entireties.

[0081] The TBN of a suitable dispersant may be from about 10 to about 65 mg KOH/g dispersant, on an oil-free basis, which is comparable to about 5 to about 30 TBN if measured on a dispersant sample containing about 50% diluent oil. TBN is measured by the method of ASTM D2896.

[0082] In yet other embodiments, the optional dispersant additive may be a hydrocarbyl substituted succinamide or succinimide dispersant. In approaches, the hydrocarbyl substituted succinamide or succinimide dispersant may be derived from a hydrocarbyl substituted acylating agent reacted with a polyalkylene polyamine and wherein the hydrocarbyl substituent of the succinamide or the succinimide dispersant is a linear or branched hydrocarbyl group having a number average molecular weight of about 250 to about 5,000 as measured by GPC using polystyrene as a calibration reference.

[0083] In some approaches, the polyalkylene polyamine used to form the dispersant has the Formula



wherein each R and R', independently, is a divalent C1 to C6 alkylene linker, each R₁ and R₂, independently, is hydrogen, a C1 to C6 alkyl group, or together with the nitrogen atom to which they are attached form a 5- or 6-membered ring optionally fused with one or more aromatic or

non-aromatic rings, and n is an integer from 0 to 8. In other approaches, the polyalkylene polyamine is selected from the group consisting of a mixture of polyethylene polyamines having an average of 5 to 7 nitrogen atoms, triethylenetetramine, tetraethylenepentamine, and combinations thereof.

[0084] The dispersant, if present, can be used in an amount sufficient to provide up to about 20 wt%, based upon the final weight of the lubricating oil composition. Another amount of the dispersant that can be used may be about 0.1 wt% to about 15 wt%, or about 0.1 wt% to about 10 wt%, about 0.1 to 8 wt%, or about 1 wt% to about 10 wt%, or about 1 wt% to about 8 wt%, or about 1 wt% to about 6 wt%, based upon the final weight of the lubricating oil composition. In some embodiments, the lubricating oil composition utilizes a mixed dispersant system. A single type or a mixture of two or more types of dispersants in any desired ratio may be used.

[0085] Other Antioxidants: The lubricating oil compositions herein also may optionally contain one or more additional antioxidants. Antioxidant compounds are known and include for example, phenates, phenate sulfides, sulfurized olefins, phosphosulfurized terpenes, sulfurized esters, aromatic amines, alkylated diphenylamines (e.g., nonyl diphenylamine, di-nonyl diphenylamine, octyl diphenylamine, di-octyl diphenylamine), phenyl-alpha-naphthylamines, alkylated phenyl-alpha-naphthylamines, hindered non-aromatic amines, phenols, hindered phenols, oil-soluble molybdenum compounds, macromolecular antioxidants, or mixtures thereof. Antioxidant compounds may be used alone or in combination.

[0086] Examples of suitable olefins that may be sulfurized to form a sulfurized olefin include propylene, butylene, isobutylene, polyisobutylene, pentene, hexene, heptene, octene, nonene, decene, undecene, dodecene, tridecene, tetradecene, pentadecene, hexadecene, heptadecene, octadecene, nonadecene, eicosene or mixtures thereof. In one embodiment, hexadecene, heptadecene, octadecene, nonadecene, eicosene or mixtures thereof and their dimers, trimers and tetramers are especially useful olefins. Alternatively, the olefin may be a Diels-Alder adduct of a diene such as 1,3-butadiene and an unsaturated ester, such as, butylacrylate.

[0087] Another class of sulfurized olefin includes sulfurized fatty acids and their esters. The fatty acids are often obtained from vegetable oil or animal oil and typically contain about 4 to about 22 carbon atoms. Examples of suitable fatty acids and their esters include triglycerides, oleic acid, linoleic acid, palmitoleic acid or mixtures thereof. Often, the fatty acids are obtained

from lard oil, tall oil, peanut oil, soybean oil, cottonseed oil, sunflower seed oil or mixtures thereof. Fatty acids and/or ester may be mixed with olefins, such as α -olefins.

[0088] In another alternative embodiment the antioxidant composition also contains a molybdenum-containing antioxidant in addition to the phenolic and/or aminic antioxidants discussed above. When a combination of these three antioxidants is used, preferably the ratio of phenolic to aminic to molybdenum-containing component treat rates is (0 to 3) : (0 to 3) : (0 to 3).

[0089] The one or more antioxidant(s) may be present in ranges about 0 wt% to about 20 wt%, or about 0.1 wt% to about 10 wt%, or about 1 wt% to about 5 wt%, of the lubricating oil composition.

[0090] Antiwear Agents: The methods and lubricating oil compositions herein also may optionally contain one or more other antiwear agents. Examples of suitable additional antiwear agents include, but are not limited to, a metal thiophosphate; a metal dialkyldithiophosphate; a phosphoric acid ester or salt thereof; a phosphate ester(s); a phosphite; a phosphorus-containing carboxylic ester, ether, or amide; a sulfurized olefin; thiocarbamate-containing compounds including, thiocarbamate esters, alkylene-coupled thiocarbamates, and bis(S-alkyldithiocarbamyl)disulfides; and mixtures thereof. A suitable antiwear agent may be a molybdenum dithiocarbamate. The phosphorus containing antiwear agents are more fully described in European Patent 612 839. The metal in the dialkyl dithio phosphate salts may be an alkali metal, alkaline earth metal, aluminum, lead, tin, molybdenum, manganese, nickel, copper, titanium, or zinc. A useful antiwear agent may be zinc dialkyldithiophosphate.

[0091] Further examples of suitable antiwear agents include titanium compounds, tartrates, tartrimides, oil soluble amine salts of phosphorus compounds, sulfurized olefins, phosphites (such as dibutyl phosphite), phosphonates, thiocarbamate-containing compounds, such as thiocarbamate esters, thiocarbamate amides, thiocarbamic ethers, alkylene-coupled thiocarbamates, and bis(S-alkyldithiocarbamyl) disulfides. The tartrate or tartrimide may contain alkyl-ester groups, where the sum of carbon atoms on the alkyl groups may be at least 8. The antiwear agent may in one embodiment include a citrate.

[0092] The antiwear agent may be present in ranges including about 0 wt% to about 15 wt%, or about 0.01 wt% to about 10 wt%, or about 0.05 wt% to about 5 wt%, or about 0.1 wt% to about 3 wt% of the lubricating oil composition.

[0093] Boron-Containing Compounds: The methods and lubricating oil compositions herein may optionally contain one or more boron-containing compounds. Examples of boron-containing compounds include borate esters, borated fatty amines, borated epoxides, borated detergents, and borated dispersants, such as borated succinimide dispersants, as disclosed in U.S. Patent No. 5,883,057. The boron-containing compound, if present, can be used in an amount sufficient to provide up to about 8 wt%, about 0.01 wt% to about 7 wt%, about 0.05 wt% to about 5 wt%, or about 0.1 wt% to about 3 wt% of the lubricating oil composition.

[0094] Extreme Pressure Agents: The methods and lubricating oil compositions herein also may optionally contain one or more extreme pressure agents. Extreme Pressure (EP) agents that are soluble in the oil include sulfur- and chlorosulfur-containing EP agents, chlorinated hydrocarbon EP agents and phosphorus EP agents. Examples of such EP agents include chlorinated wax; organic sulfides and polysulfides such as dibenzyl disulfide, bis(chlorobenzyl) disulfide, dibutyl tetrasulfide, sulfurized methyl ester of oleic acid, sulfurized alkyl phenol, sulfurized dipentene, sulfurized terpene, and sulfurized Diels-Alder adducts; phosphosulfurized hydrocarbons such as the reaction product of phosphorus sulfide with turpentine or methyl oleate; phosphorus esters such as the dihydrocarbyl and trihydrocarbyl phosphites, e.g., dibutyl phosphite, diheptyl phosphite, dicyclohexyl phosphite, pentylphenyl phosphite; dipentylphenyl phosphite, tridecyl phosphite, distearyl phosphite and polypropylene substituted phenyl phosphite; metal thiocarbamates such as zinc dioctyldithiocarbamate and barium heptylphenol diacid; amine salts of alkyl and dialkylphosphoric acids, including, for example, the amine salt of the reaction product of a dialkyldithiophosphoric acid with propylene oxide; and mixtures thereof.

[0095] Friction Modifiers: The methods and lubricating oil compositions herein also may optionally contain one or more friction modifiers. Suitable friction modifiers may comprise metal containing and metal-free friction modifiers and may include, but are not limited to, imidazolines, amides, amines, succinimides, alkoxylated amines, alkoxylated ether amines, amine oxides, amidoamines, nitriles, betaines, quaternary amines, imines, amine salts, amino

guanadine, alkanolamides, phosphonates, metal-containing compounds, glycerol esters, sulfurized fatty compounds and olefins, sunflower oil other naturally occurring plant or animal oils, dicarboxylic acid esters, esters or partial esters of a polyol and one or more aliphatic or aromatic carboxylic acids, and the like.

[0096] Suitable friction modifiers may contain hydrocarbyl groups that are selected from straight chain, branched chain, or aromatic hydrocarbyl groups or mixtures thereof, and may be saturated or unsaturated. The hydrocarbyl groups may be composed of carbon and hydrogen or hetero atoms such as sulfur or oxygen. The hydrocarbyl groups may range from about 12 to about 25 carbon atoms. In some embodiments the friction modifier may be a long chain fatty acid ester. In another embodiment the long chain fatty acid ester may be a mono-ester, or a di-ester, or a (tri)glyceride. The friction modifier may be a long chain fatty amide, a long chain fatty ester, a long chain fatty epoxide derivatives, or a long chain imidazoline.

[0097] Other suitable friction modifiers may include organic, ashless (metal-free), nitrogen-free organic friction modifiers. Such friction modifiers may include esters formed by reacting carboxylic acids and anhydrides with alkanols and generally include a polar terminal group (e.g. carboxyl or hydroxyl) covalently bonded to an oleophilic hydrocarbon chain. An example of an organic ashless nitrogen-free friction modifier is known generally as glycerol monooleate (GMO) which may contain mono-, di-, and tri-esters of oleic acid. Other suitable friction modifiers are described in U.S. Pat. No. 6,723,685, herein incorporated by reference in its entirety.

[0098] Aminic friction modifiers may include amines or polyamines. Such compounds can have hydrocarbyl groups that are linear, either saturated or unsaturated, or a mixture thereof and may contain from about 12 to about 25 carbon atoms. Further examples of suitable friction modifiers include alkoxylated amines and alkoxylated ether amines. Such compounds may have hydrocarbyl groups that are linear, either saturated, unsaturated, or a mixture thereof. They may contain from about 12 to about 25 carbon atoms. Examples include ethoxylated amines and ethoxylated ether amines.

[0099] The amines and amides may be used as such or in the form of an adduct or reaction product with a boron compound such as a boric oxide, boron halide, metaborate, boric acid or a

mono-, di- or tri-alkyl borate. Other suitable friction modifiers are described in U.S. Pat. No. 6,300,291, herein incorporated by reference in its entirety.

[00100] A friction modifier may optionally be present in ranges such as about 0 wt% to about 10 wt%, or about 0.01 wt% to about 8 wt%, or about 0.1 wt% to about 4 wt%.

[00101] Molybdenum-containing component: The methods and lubricating oil compositions herein also may optionally contain one or more molybdenum-containing compounds. An oil-soluble molybdenum compound may have the functional performance of an antiwear agent, an antioxidant, a friction modifier, or mixtures thereof. An oil-soluble molybdenum compound may include molybdenum dithiocarbamates, molybdenum dialkyldithiophosphates, molybdenum dithiophosphinates, amine salts of molybdenum compounds, molybdenum xanthates, molybdenum thioxanthates, molybdenum sulfides, molybdenum carboxylates, molybdenum alkoxides, a trinuclear organo-molybdenum compound, and/or mixtures thereof. The molybdenum sulfides include molybdenum disulfide. The molybdenum disulfide may be in the form of a stable dispersion. In one embodiment the oil-soluble molybdenum compound may be selected from the group consisting of molybdenum dithiocarbamates, molybdenum dialkyldithiophosphates, amine salts of molybdenum compounds, and mixtures thereof. In one embodiment the oil-soluble molybdenum compound may be a molybdenum dithiocarbamate.

[00102] Suitable examples of molybdenum compounds which may be used include commercial materials sold under the trade names such as Molyvan® 822, Molyvan® A, Molyvan® 2000, Molyvan® 855, Molyvan® 1055, and Molyvan® 3000 from R. T. Vanderbilt Co., Ltd., and Adeka Sakura-Lube® S-165, S-200, S-300, S-310G, S-525, S-600, S-700, and S-710 available from Adeka Corporation, and mixtures thereof. Suitable molybdenum components are described in US 5,650,381; US RE 37,363 E1; US RE 38,929 E1; and US RE 40,595 E1, incorporated herein by reference in their entireties.

[00103] Additionally, the molybdenum compound may be an acidic molybdenum compound. Included are molybdic acid, ammonium molybdate, sodium molybdate, potassium molybdate, and other alkaline metal molybdates and other molybdenum salts, e.g., hydrogen sodium molybdate, MoOCl_4 , MoO_2Br_2 , $\text{Mo}_2\text{O}_3\text{Cl}_6$, molybdenum trioxide or similar acidic molybdenum compounds. Alternatively, the compositions can be provided with molybdenum by molybdenum/sulfur complexes of basic nitrogen compounds as described, for example, in U.S.

Pat. Nos. 4,263,152; 4,285,822; 4,283,295; 4,272,387; 4,265,773; 4,261,843; 4,259,195 and 4,259,194; and WO 94/06897, incorporated herein by reference in their entireties.

[00104] Another class of suitable organo-molybdenum compounds are trinuclear molybdenum compounds, such as those of the formula $\text{Mo}_3\text{S}_k\text{L}_n\text{Q}_z$ and mixtures thereof, wherein S represents sulfur, L represents independently selected ligands having organo groups with a sufficient number of carbon atoms to render the compound soluble or dispersible in the oil, n is from 1 to 4, k varies from 4 through 7, Q is selected from the group of neutral electron donating compounds such as water, amines, alcohols, phosphines, and ethers, and z ranges from 0 to 5 and includes non-stoichiometric values. At least 21 total carbon atoms may be present among all the ligands' organo groups, such as at least 25, at least 30, or at least 35 carbon atoms. Additional suitable molybdenum compounds are described in U.S. Pat. No. 6,723,685, herein incorporated by reference in its entirety.

[00105] The oil-soluble molybdenum compound may be present in an amount sufficient to provide about 0.5 ppm to about 2000 ppm, about 1 ppm to about 700 ppm, about 1 ppm to about 550 ppm, about 5 ppm to about 300 ppm, or about 20 ppm to about 250 ppm of molybdenum.

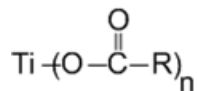
[00106] Transition Metal-containing compounds: In another embodiment, the oil-soluble compound may be a transition metal containing compound or a metalloid. The transition metals may include, but are not limited to, titanium, vanadium, copper, zinc, zirconium, molybdenum, tantalum, tungsten, and the like. Suitable metalloids include, but are not limited to, boron, silicon, antimony, tellurium, and the like.

[00107] In an embodiment, an oil-soluble transition metal-containing compound may function as antiwear agents, friction modifiers, antioxidants, deposit control additives, or more than one of these functions. In an embodiment the oil-soluble transition metal-containing compound may be an oil-soluble titanium compound, such as a titanium (IV) alkoxide. Among the titanium containing compounds that may be used in, or which may be used for preparation of the oil-soluble materials of, the disclosed technology are various Ti (IV) compounds such as titanium (IV) oxide; titanium (IV) sulfide; titanium (IV) nitrate; titanium (IV) alkoxides such as titanium methoxide, titanium ethoxide, titanium propoxide, titanium isopropoxide, titanium butoxide, titanium 2-ethylhexoxide; and other titanium compounds or complexes including but not limited to titanium phenates; titanium carboxylates such as titanium (IV) 2-ethyl-1-3-hexanedioate or

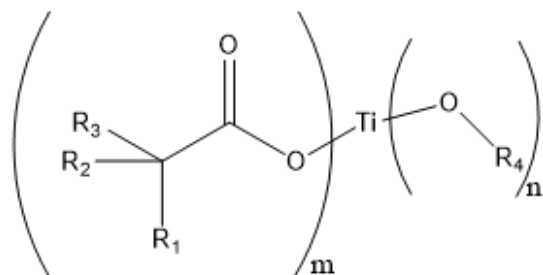
titanium citrate or titanium oleate; and titanium (IV) (triethanolaminate)isopropoxide. Other forms of titanium encompassed within the disclosed technology include titanium phosphates such as titanium dithiophosphates (e.g., dialkyldithiophosphates) and titanium sulfonates (e.g., alkylbenzenesulfonates), or, generally, the reaction product of titanium compounds with various acid materials to form salts, such as oil-soluble salts. Titanium compounds can thus be derived from, among others, organic acids, alcohols, and glycols. Ti compounds may also exist in dimeric or oligomeric form, containing Ti--O--Ti structures. Such titanium materials are commercially available or can be readily prepared by appropriate synthesis techniques which will be apparent to the person skilled in the art. They may exist at room temperature as a solid or a liquid, depending on the particular compound. They may also be provided in a solution form in an appropriate inert solvent.

[00108] In one embodiment, the titanium can be supplied as a Ti-modified dispersant, such as a succinimide dispersant. Such materials may be prepared by forming a titanium mixed anhydride between a titanium alkoxide and a hydrocarbyl-substituted succinic anhydride, such as an alkenyl- (or alkyl) succinic anhydride. The resulting titanate-succinate intermediate may be used directly or it may be reacted with any of a number of materials, such as (a) a polyamine-based succinimide/amide dispersant having free, condensable --NH functionality; (b) the components of a polyamine-based succinimide/amide dispersant, i.e., an alkenyl- (or alkyl-) succinic anhydride and a polyamine, (c) a hydroxy-containing polyester dispersant prepared by the reaction of a substituted succinic anhydride with a polyol, aminoalcohol, polyamine, or mixtures thereof. Alternatively, the titanate-succinate intermediate may be reacted with other agents such as alcohols, aminoalcohols, ether alcohols, polyether alcohols or polyols, or fatty acids, and the product thereof either used directly to impart Ti to a lubricant, or else further reacted with the succinic dispersants as described above. As an example, 1 part (by mole) of tetraisopropyl titanate may be reacted with about 2 parts (by mole) of a polyisobutene-substituted succinic anhydride at 140-150° C for 5 to 6 hours to provide a titanium modified dispersant or intermediate. The resulting material (30 g) may be further reacted with a succinimide dispersant from polyisobutene-substituted succinic anhydride and a polyethylenepolyamine mixture (127 grams + diluent oil) at 150° C for 1.5 hours, to produce a titanium-modified succinimide dispersant.

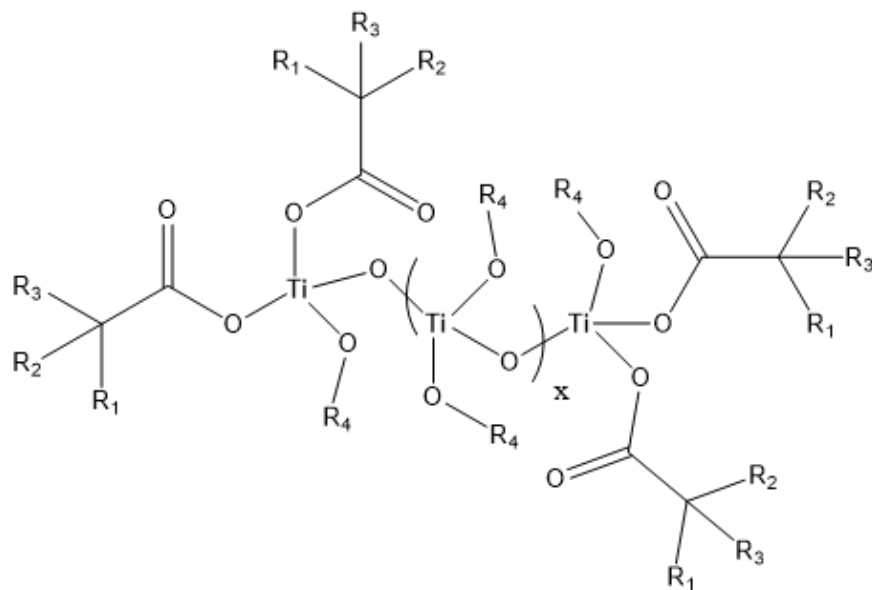
[00109] Another titanium containing compound may be a reaction product of titanium alkoxide and C₆ to C₂₅ carboxylic acid. The reaction product may be represented by the following formula:



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



wherein m + n = 4 and n ranges from 1 to 3, R₄ is an alkyl moiety with carbon atoms ranging from 1-8, R₁ is selected from a hydrocarbyl group containing from about 6 to 25 carbon atoms, and R₂ and R₃ are the same or different and are selected from a hydrocarbyl group containing from about 1 to 6 carbon atoms, or the titanium compound may be represented by the formula:



wherein x ranges from 0 to 3, R₁ is selected from a hydrocarbyl group containing from about 6 to 25 carbon atoms, R₂, and R₃ are the same or different and are selected from a hydrocarbyl group

containing from about 1 to 6 carbon atoms, and R₄ is selected from a group consisting of either H, or C₆ to C₂₅ carboxylic acid moiety.

[00110] Suitable carboxylic acids may include, but are not limited to caproic acid, caprylic acid, lauric acid, myristic acid, palmitic acid, stearic acid, arachidic acid, oleic acid, erucic acid, linoleic acid, linolenic acid, cyclohexanecarboxylic acid, phenylacetic acid, benzoic acid, neodecanoic acid, and the like.

[00111] In an embodiment the oil soluble titanium compound may be present in the lubricating oil composition in an amount to provide from 0 to 3000 ppm titanium by weight or 25 to about 1500 ppm titanium by weight or about 35 ppm to 500 ppm titanium by weight or about 50 ppm to about 300 ppm.

[00112] Viscosity Index Improvers: The lubricating oil compositions herein also may optionally contain one or more other viscosity index improvers. Suitable viscosity index improvers may include polyolefins, olefin copolymers, ethylene/propylene copolymers, polyisobutenes, hydrogenated styrene-isoprene polymers, styrene/maleic ester copolymers, hydrogenated styrene/butadiene copolymers, hydrogenated isoprene polymers, alpha-olefin maleic anhydride copolymers, polymethacrylates, polyacrylates, polyalkyl styrenes, hydrogenated alkenyl aryl conjugated diene copolymers, or mixtures thereof. Viscosity index improvers may include star polymers and suitable examples are described in US Publication No. 20120101017A1.

[00113] The lubricating oil compositions herein also may optionally contain one or more dispersant viscosity index improvers in addition to a viscosity index improver or in lieu of a viscosity index improver. Suitable viscosity index improvers may include functionalized polyolefins, for example, ethylene-propylene copolymers that have been functionalized with the reaction product of an acylating agent (such as maleic anhydride) and an amine; polymethacrylates functionalized with an amine, or esterified maleic anhydride-styrene copolymers reacted with an amine.

[00114] The total amount of viscosity index improver and/or dispersant viscosity index improver may be about 0 wt% to about 20 wt%, about 0.1 wt% to about 15 wt%, about 0.1 wt% to about 12 wt%, or about 0.5 wt% to about 10 wt%, of the lubricating oil composition.

[00115] Other Optional Additives: Other additives may be selected to perform one or more functions required of a lubricating fluid. Further, one or more of the mentioned additives may be multi-functional and provide functions in addition to or other than the function prescribed herein. A lubricating oil composition according to the present disclosure may optionally comprise other performance additives. The other performance additives may be in addition to specified additives of the present disclosure and/or may comprise one or more of metal deactivators, viscosity index improvers, detergents, ashless TBN boosters, friction modifiers, antiwear agents, corrosion inhibitors, rust inhibitors, dispersants, dispersant viscosity index improvers, extreme pressure agents, antioxidants, foam inhibitors, demulsifiers, emulsifiers, pour point depressants, seal swelling agents and mixtures thereof. Typically, fully-formulated lubricating oil will contain one or more of these performance additives.

[00116] Suitable metal deactivators may include derivatives of benzotriazoles (typically tolyltriazole), dimercaptothiadiazone derivatives, 1,2,4-triazoles, benzimidazoles, 2-alkyldithiobenzimidazoles, or 2-alkyldithiobenzothiazoles; foam inhibitors including copolymers of ethyl acrylate and 2-ethylhexylacrylate and optionally vinyl acetate; demulsifiers including trialkyl phosphates, polyethylene glycols, polyethylene oxides, polypropylene oxides and (ethylene oxide-propylene oxide) polymers; pour point depressants including esters of maleic anhydride-styrene, polymethacrylates, polyacrylates or polyacrylamides.

[00117] Suitable foam inhibitors include silicon-based compounds, such as siloxane.

[00118] Suitable pour point depressants may include polymethylmethacrylates or mixtures thereof. Pour point depressants may be present in an amount sufficient to provide from about 0 wt% to about 1 wt%, about 0.01 wt% to about 0.5 wt%, or about 0.02 wt% to about 0.04 wt% based upon the final weight of the lubricating oil composition.

[00119] Suitable rust inhibitors may be a single compound or a mixture of compounds having the property of inhibiting corrosion of ferrous metal surfaces. Non-limiting examples of rust inhibitors useful herein include oil-soluble high molecular weight organic acids, such as 2-ethylhexanoic acid, lauric acid, myristic acid, palmitic acid, oleic acid, linoleic acid, linolenic acid, behenic acid, and cerotic acid, as well as oil-soluble polycarboxylic acids including dimer and trimer acids, such as those produced from tall oil fatty acids, oleic acid, and linoleic acid. Other suitable corrosion inhibitors include long-chain alpha, omega-dicarboxylic acids in the

molecular weight range of about 600 to about 3000 and alkenylsuccinic acids in which the alkenyl group contains about 10 or more carbon atoms such as, tetrapropenylsuccinic acid, tetradecenylsuccinic acid, and hexadecenylsuccinic acid. Another useful type of acidic corrosion inhibitors are the half esters of alkenyl succinic acids having about 8 to about 24 carbon atoms in the alkenyl group with alcohols such as the polyglycols. The corresponding half amides of such alkenyl succinic acids are also useful. A useful rust inhibitor is a high molecular weight organic acid.

[00120] The rust inhibitor, if present, can be used in an amount sufficient to provide about 0 wt% to about 5 wt%, about 0.01 wt% to about 3 wt%, about 0.1 wt% to about 2 wt%, based upon the final weight of the lubricating oil composition.

[00121] In general terms, a suitable lubricant including the detergent metals herein may include additive components in the ranges listed in the following table.

[00122] Table 2: Suitable Lubricating Compositions

Component	Wt. % (Suitable Embodiments)	Wt. % (Suitable Embodiments)
Detergent Systems	0.02 - 5.0	0.2 - 2.5
Dispersant Systems	0 - 10.0	1 - 7.0
Antioxidant(s)	0.1 - 5.0	0.01 - 3.0
Ashless TBN booster(s)	0.0 - 1.0	0.01 - 0.5
Corrosion inhibitor(s)	0.0 - 5.0	0.0 - 2.0
Metal dihydrocarbyl dithiophosphate(s)	0.0 - 6.0	0.1 - 4.0
Ash-free phosphorus compound(s)	0.0 - 6.0	0.0 - 4.0
Antifoaming agent(s)	0.0 - 5.0	0.001 - 0.15
Antiwear agent(s)	0.0 - 1.0	0.0 - 0.8
Pour point depressant(s)	0.0 - 5.0	0.01 - 1.5
Viscosity index improver(s)	0.0 - 25.0	0 - 15.0
Dispersant viscosity index improver(s)	0.0 - 10.0	0.0 - 5.0
Friction modifier(s)	0.0 - 5.0	0.01 - 2.0
Base oil	<u>Balance</u>	<u>Balance</u>
Total	100	100

[00123] The percentages of each component above represent the weight percent of each component, based upon the weight of the final lubricating oil composition. The remainder of the lubricating oil composition consists of one or more base oils. Additives used in formulating the

compositions described herein may be blended into the base oil individually or in various sub-combinations. However, it may be suitable to blend all of the components concurrently using an additive concentrate (i.e., additives plus a diluent, such as a hydrocarbon solvent). Fully formulated lubricants conventionally contain an additive package, referred to herein as a dispersant/inhibitor package or DI package, that will supply the characteristics that are required in the formulation.

DEFINITIONS

[00124] For purposes of this disclosure, the chemical elements are identified in accordance with the Periodic Table of the Elements, CAS version, Handbook of Chemistry and Physics, 75th Ed. Additionally, general principles of organic chemistry are described in "Organic Chemistry", Thomas Sorrell, University Science Books, Sausalito: 1999, and "March's Advanced Organic Chemistry", 5th Ed., Ed.: Smith, M.B. and March, J., John Wiley & Sons, New York: 2001, the entire contents of which are hereby incorporated by reference.

[00125] As described herein, compounds may optionally be substituted with one or more substituents, such as are illustrated generally above, or as exemplified by particular classes, subclasses, and species of the disclosure.

[00126] Unless otherwise apparent from the context, the term "majority" or "major amount" is understood to mean an amount greater than or equal to 50 weight percent, greater than about 60 weight percent, greater than about 70 weight percent, or for example, from 50 to about 98 weight percent, about 60 to about 98 weight percent, about 70 to about 98 weight percent, or about 80 to about 98 weight percent relative to the total weight of the composition or about 50 to about 90 weight percent (or other ranges between any such endpoints). As also used herein, the term "minor amount" is understood to mean an amount less than 50 weight percent relative to the total weight of the composition.

[00127] As used herein, the term "hydrocarbyl group" or "hydrocarbyl" is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group having a carbon atom directly attached to the remainder of a molecule and having a predominantly hydrocarbon character. Examples of hydrocarbyl groups include: (1) hydrocarbon substituents, that is, aliphatic (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl, cycloalkenyl) substituents, and aromatic-, aliphatic-, and alicyclic-substituted aromatic substituents, as well as cyclic

substituents wherein the ring is completed through another portion of the molecule (e.g., two substituents together form an alicyclic radical); (2) substituted hydrocarbon substituents, that is, substituents containing non-hydrocarbon groups which, in the context of the description herein, do not alter the predominantly hydrocarbon substituent (e.g., halo (especially chloro and fluoro), hydroxy, alkoxy, mercapto, alkylmercapto, nitro, nitroso, amino, alkylamino, and sulfoxy); (3) hetero-substituents, that is, substituents which, while having a predominantly hydrocarbon character, in the context of this description, contain other than carbon in a ring or chain otherwise composed of carbon atoms. Hetero-atoms include sulfur, oxygen, nitrogen, and encompass substituents such as pyridyl, furyl, thienyl, and imidazolyl. In general, no more than two, or as a further example, no more than one, non-hydrocarbon substituent will be present for every ten carbon atoms in the hydrocarbonyl group; in some embodiments, there will be no non-hydrocarbon substituent in the hydrocarbonyl group.

[00128] As used herein the term "aliphatic" encompasses the terms alkyl, alkenyl, alkynyl, each of which being optionally substituted as set forth below.

[00129] As used herein, an "alkyl" group refers to a saturated aliphatic hydrocarbon group containing 1-12 (e.g., 1-8, 1-6, or 1-4) carbon atoms. An alkyl group can be straight or branched. Examples of alkyl groups include, but are not limited to, methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl, n-pentyl, n-heptyl, or 2-ethylhexyl. An alkyl group can be substituted (i.e., optionally substituted) with one or more substituents such as halo, phospho, cycloaliphatic [e.g., cycloalkyl or cycloalkenyl], heterocycloaliphatic [e.g., heterocycloalkyl or heterocycloalkenyl], aryl, heteroaryl, alkoxy, aroyl, heteroaroyl, acyl [e.g., (aliphatic)carbonyl, (cycloaliphatic)carbonyl, or (heterocycloaliphatic)carbonyl], nitro, cyano, amido [e.g., (cycloalkylalkyl)carbonylamino, arylcarbonylamino, aralkyl carbonylamino, (heterocycloalkyl) carbonylamino, (heterocycloalkylalkyl) carbonylamino, heteroarylcarbonylamino, heteroaralkyl carbonylamino alkylaminocarbonyl, cycloalkyl aminocarbonyl, heterocycloalkylaminocarbonyl, arylaminocarbonyl, or heteroaryl aminocarbonyl], amino [e.g., aliphaticamino, cycloaliphatic amino, or heterocyclo aliphaticamino], sulfonyl [e.g., aliphatic-SO₂-], sulfinyl, sulfanyl, sulfoxy, urea, thiourea, sulfamoyl, sulfamide, oxo, carboxy, carbamoyl, cycloaliphaticoxy, heterocyclo aliphaticoxy, aryloxy, heteroaryloxy, aralkyloxy, heteroarylalkoxy, alkoxycarbonyl, alkyl carbonyloxy, or hydroxy. Without limitation, some examples of substituted alkyls include

carboxyalkyl (such as HOOC-alkyl, alkoxycarbonylalkyl, and alkylcarbonyloxyalkyl), cyanoalkyl, hydroxyalkyl, alkoxyalkyl, acylalkyl, aralkyl, (alkoxyaryl)alkyl, (sulfonylamino)alkyl (such as (alkyl-SO₂-amino)alkyl), aminoalkyl, amidoalkyl, (cycloaliphatic)alkyl, or haloalkyl.

[00130] As used herein, an "alkenyl" group refers to an aliphatic carbon group that contains 2-8 (e.g., 2-12, 2-6, or 2-4) carbon atoms and at least one double bond. Like an alkyl group, an alkenyl group can be straight or branched. Examples of an alkenyl group include, but are not limited to allyl, isoprenyl, 2-butenyl, and 2-hexenyl. An alkenyl group can be optionally substituted with one or more substituents such as halo, phospho, cycloaliphatic [e.g., cycloalkyl or cycloalkenyl], heterocycloaliphatic [e.g., heterocycloalkyl or hetero cycloalkenyl], aryl, heteroaryl, alkoxy, aroyl, heteroaroyl, acyl [e.g., (aliphatic) carbonyl, (cycloaliphatic)carbonyl, or (heterocycloaliphatic)carbonyl], nitro, cyano, amido [e.g., (cycloalkylalkyl)carbonylamino, arylcarbonylamino, aralkylcarbonylamino, (hetero cycloalkyl) carbonylamino, (heterocycloalkylalkyl) carbonylamino, heteroarylcarbonylamino, heteroaralkylcarbonylamino alkylamino carbonyl, cycloalkylaminocarbonyl, hetero cyclo alkylaminocarbonyl, arylaminocarbonyl, or heteroarylaminocarbonyl], amino [e.g., aliphaticamino, cycloaliphaticamino, heterocycloaliphaticamino, or aliphaticsulfonylamino], sulfonyl [e.g., alkyl-SO₂- , cycloaliphatic-SO₂-, or aryl-SO₂-], sulfinyl, sulfanyl, sulfoxy, urea, thiourea, sulfamoyl, sulfamide, oxo, carboxy, carbamoyl, cycloaliphaticoxy, heterocycloaliphaticoxy, aryloxy, heteroaryloxy, aralkyloxy, heteroaralkoxy, alkoxycarbonyl, alkylcarbonyloxy, or hydroxy. Without limitation, some examples of substituted alkenyls include cyanoalkenyl, alkoxyalkenyl, acylalkenyl, hydroxyl alkenyl, aralkenyl, (alkoxyaryl) alkenyl, (sulfonylamino)alkenyl (such as (alkyl-SO₂-amino)alkenyl), aminoalkenyl, amidoalkenyl, (cycloaliphatic)alkenyl, or haloalkenyl.

[00131] As used herein, an "alkynyl" group refers to an aliphatic carbon group that contains 2-8 (e.g., 2-12, 2-6, or 2-4) carbon atoms and has at least one triple bond. An alkynyl group can be straight or branched. Examples of an alkynyl group include, but are not limited to, propargyl and butynyl. An alkynyl group can be optionally substituted with one or more substituents such as aroyl, heteroaroyl, alkoxy, cycloalkyloxy, heterocycloalkyloxy, aryloxy, heteroaryloxy, aralkyloxy, nitro, carboxy, cyano, halo, hydroxy, sulfo, mercapto, sulfanyl [e.g., aliphatic sulfanyl or cycloaliphatic sulfanyl], sulfinyl [e.g., aliphatic sulfinyl or cycloaliphatic sulfinyl], sulfonyl [e.g.,

aliphatic-SO₂-, aliphaticamino-SO₂-, or cycloaliphatic-SO₂-], amido [e.g., aminocarbonyl, alkylaminocarbonyl, alkylcarbonylamino, cyclo alkylaminocarbonyl, heterocycloalkylaminocarbonyl, cycloalkylcarbonylamino, arylamino carbonyl, arylcarbonylamino, aralkylcarbonylamino, (heterocycloalkyl) carbonylamino, (cycloalkylalkyl) carbonylamino, heteroaralkylcarbonylamino, heteroaryl carbonylamino or heteroaryl amino carbonyl], urea, thiourea, sulfamoyl, sulfamide, alkoxycarbonyl, alkyl carbonyloxy, cyclo aliphatic, heterocycloaliphatic, aryl, heteroaryl, acyl [e.g., (cycloaliphatic) carbonyl or (hetero cyclo aliphatic)carbonyl], amino [e.g., aliphaticamino], sulfoxy, oxo, carboxy, carbamoyl, (cycloaliphatic)oxy, (heterocyclo aliphatic) oxy, or (heteroaryl)alkoxy.

[00132] As used herein, an "amino" group refers to -NR^XR^Y wherein each of R^X and R^Y is independently hydrogen, alkyl, cycloalkyl, (cycloalkyl)alkyl, aryl, aralkyl, heterocycloalkyl, (heterocycloalkyl)alkyl, heteroaryl, carboxy, sulfanyl, sulfinyl, sulfonyl, (alkyl)carbonyl, (cycloalkyl)carbonyl, ((cycloalkyl)alkyl)carbonyl, arylcarbonyl, (aralkyl)carbonyl, (heterocyclo alkyl) carbonyl, ((heterocycloalkyl)alkyl)carbonyl, (heteroaryl)carbonyl, or (heteroaralkyl) carbonyl, each of which being defined herein and being optionally substituted. Examples of amino groups include alkylamino, dialkylamino, or arylamino. When the term "amino" is not the terminal group (e.g., alkylcarbonylamino), it is represented by -NR^X-. R^X has the same meaning as defined above.

[00133] As used herein, a "cycloalkyl" group refers to a saturated carbocyclic mono- or bicyclic (fused or bridged) ring of 3-10 (e.g., 5-10) carbon atoms. Examples of cycloalkyl groups include cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, adamantyl, norbornyl, cubyl, octahydro-indenyl, decahydro-naphthyl, bicyclo[3.2.1]octyl, bicyclo[2.2.2]octyl, bicyclo[3.3.1]nonyl, bicyclo[3.3.2.]decyl, bicyclo[2.2.2]octyl, adamantyl, or ((aminocarbonyl)cycloalkyl)cycloalkyl.

[00134] As used herein, a "heterocycloalkyl" group refers to a 3-10 membered mono- or bicyclic (fused or bridged) (e.g., 5- to 10-membered mono- or bicyclic) saturated ring structure, in which one or more of the ring atoms is a heteroatom (e.g., N, O, S, or combinations thereof). Examples of a heterocycloalkyl group include piperidyl, piperazyl, tetrahydropyranyl, tetrahydrofuryl, 1,4-dioxolanyl, 1,4-dithianyl, 1,3-dioxolanyl, oxazolidyl, isoxazolidyl, morpholinyl, thiomorpholyl, octahydrobenzofuryl, octahydrochromenyl, octahydrothio

chromenyl, octahydroindolyl, octahydropyrindinyl, decahydroquinolyl, octahydrobenzo[*b*]thiophenyl, 2-oxa-bicyclo[2.2.2]octyl, 1-aza-bicyclo[2.2.2]octyl, 3-aza-bicyclo[3.2.1]octyl, and 2,6-dioxa-tricyclo[3.3.1.0]nonyl. A monocyclic heterocycloalkyl group can be fused with a phenyl moiety to form structures, such as tetrahydroisoquinoline, which would be categorized as heteroaryls.

[00135] A "heteroaryl" group, as used herein, refers to a monocyclic, bicyclic, or tricyclic ring system having 4 to 15 ring atoms wherein one or more of the ring atoms is a heteroatom (e.g., N, O, S, or combinations thereof) and in which the monocyclic ring system is aromatic or at least one of the rings in the bicyclic or tricyclic ring systems is aromatic. A heteroaryl group includes a benzofused ring system having 2 to 3 rings. For example, a benzofused group includes benzo fused with one or two 4 to 8 membered heterocycloaliphatic moieties (e.g., indolizyl, indolyl, isoindolyl, 3H-indolyl, indolinyl, benzo[*b*]furyl, benzo[*b*]thiophenyl, quinolinyl, or isoquinolinyl). Some examples of heteroaryl are pyridyl, 1H-indazolyl, furyl, pyrrolyl, thienyl, thiazolyl, oxazolyl, imidazolyl, tetrazolyl, benzofuryl, isoquinolinyl, benzthiazolyl, xanthene, thioxanthene, phenothiazine, dihydroindole, benzo[1,3]dioxole, benzo[*b*]furyl, benzo[*b*]thiophenyl, indazolyl, benzimidazolyl, benzthiazolyl, puryl, cinnolyl, quinolyl, quinazolyl, cinnolyl, phthalazyl, quinazolyl, quinoxalyl, isoquinolyl, 4H-quinolizyl, benzo-1,2,5-thiadiazolyl, or 1,8-naphthyridyl.

[00136] Without limitation, monocyclic heteroaryls include furyl, thiophenyl, 2H-pyrrolyl, pyrrolyl, oxazolyl, thazolyl, imidazolyl, pyrazolyl, isoxazolyl, isothiazolyl, 1,3,4-thiadiazolyl, 2H-pyranyl, 4-H-pranyl, pyridyl, pyridazyl, pyrimidyl, pyrazolyl, pyrazyl, or 1,3,5-triazyl. Monocyclic heteroaryls are numbered according to standard chemical nomenclature.

[00137] Without limitation, bicyclic heteroaryls include indolizyl, indolyl, isoindolyl, 3H-indolyl, indolinyl, benzo[*b*]furyl, benzo[*b*]thiophenyl, quinolinyl, isoquinolinyl, indoliziny, isoindolyl, indolyl, benzo[*b*]furyl, benzo[*b*]thiophenyl, indazolyl, benzimidazolyl, benzthiazolyl, purinyl, 4H-quinolizyl, quinolyl, isoquinolyl, cinnolyl, phthalazyl, quinazolyl, quinoxalyl, 1,8-naphthyridyl, or pteridyl. Bicyclic heteroaryls are numbered according to standard chemical nomenclature.

[00138] As used herein, the term "treat rate" refers to the weight percent of a component in the finished lubricant or the passenger car motor oil.

[00139] The weight average molecular weight (Mw) and the number average molecular weight (Mn) may be determined with a gel permeation chromatography (GPC) instrument obtained from Waters or the like instrument and the data processed with Waters Empower Software or the like software. The GPC instrument may be equipped with a Waters Separations Module and Waters Refractive Index detector (or the like optional equipment). The GPC operating conditions may include a guard column, 4 Agilent PLgel columns (length of 300×7.5 mm; particle size of 5 μ, and pore size ranging from 100-10000 Å) with the column temperature at about 40°C. Un-stabilized HPLC grade tetrahydrofuran (THF) may be used as solvent, at a flow rate of 1.0 mL/min. The GPC instrument may be calibrated with commercially available poly(methyl methacrylate) (PMMA) standards having a narrow molecular weight distribution ranging from 960 – 1,568,000 g/mol. The calibration curve can be extrapolated for samples having a mass less than 500 g/mol. Samples and PMMA standards can be dissolved in THF and prepared at concentration of 0.1 to 0.5 wt. % and used without filtration. GPC measurements are also described in US 5,266,223, which is incorporated herein by reference. The GPC method additionally provides molecular weight distribution information; *see, for example*, W. W. Yau, J. J. Kirkland and D. D. Bly, “Modern Size Exclusion Liquid Chromatography”, John Wiley and Sons, New York, 1979, also incorporated herein by reference.

EXAMPLES

[00140] A better understanding of the present disclosure and its many advantages may be clarified with the following examples. The following examples are illustrative and not limiting thereof in either scope or spirit. Those skilled in the art will readily understand that variations of the components, methods, steps, and devices described in these examples can be used. Unless noted otherwise or apparent from the context of discussion in the Examples below and throughout this disclosure, all percentages, ratios, and parts noted in this disclosure are by weight. Reference to any standardized test method, unless apparent from the context of its use herein, refers to the version publicly available at the time of this disclosure.

[00141] Inventive and Comparative additive packages of Comparative Example 1 and Example 1 below were prepared including the following detergents, metal-containing antiwear additives, and/or antioxidants as set forth in each Example:

- Overbased magnesium sulfonate detergent having a TBN of about 410.
- Overbased calcium sulfonate detergent having a TBN of about 300.
- Overbased calcium phenate detergent having a TBN of 250.
- Neutral calcium sulfonate detergent having a TBN of 50 or less.
- ZDDP-Secondary was a zinc dialkyldithiophosphate and included alkyl groups derived from one or more secondary alcohols and having an average of 6 or fewer carbon atoms per phosphorus atom.
- ZDDP – Primary was a zinc dialkyldithiophosphate and included alkyl groups derived from one or more primary alcohols and having an average of 8 or more carbon atoms per each phosphorus atoms.
- Aminic Antioxidant – nonylated diphenyl amine.
- Phenolic Antioxidant – hindered phenolic ester.

[00142] COMPARATIVE EXAMPLE 1

[00143] The lubricants of these Comparative Examples included various detergents and base oils as set forth the Tables below. In addition to the components as listed in the Tables below, the Comparative additive packages of this Example also included other common additives suitable for passenger car motor oils and were the same for each of the lubricants of Comparative 1 and 2. The only variations in the additive packages of this Example were the below noted components of Table 3.

[00144] Table 3: Lubricating Oil Composition

		Comp 1	Comp 2
Detergent System			
OB Ca Sulfonate	Ca ppm	1690	2933
Neutral Ca Sulfonate	Ca ppm	-	140
OB Ca Phenate	Ca ppm	1118	-
OB Mg Sulfonate	Mg ppm	-	-
Base Oils			
API Group III	wt%	77.4	76.9

[00145] Table 4: Engine Sludge Merits (CEC L-107-19)

		Comp 1	Comp 2
Engine Sludge, Average (AES)	Merits	9.0	8.1

[00146] As shown in Tables 3 and 4, methods of lubricating in Comparative 1 included a lubricant with calcium phenate detergent and API Group III base oil was able to achieve a passing AES pursuant to CEC L-107-19 of 9.0 merits. However, when removing the calcium phenate detergent from the fluid to create the lubricant used in the methods of Comparative 2, the AES dropped to an unacceptable 8.1 merit rating even when still using API Group III base oils.

[00147] EXAMPLE 1

[00148] In this Example, Inventive and Comparative additive packages for lubricants were prepared by varying detergent systems, antiwear systems, and antioxidant systems in lubricating oil compositions that included a majority of API Group II base oils. In addition to the components as listed in the Tables below, the Comparative and Inventive additive packages of this Example also included other common additives suitable for passenger car motor oils and were the same for each evaluated additive package. The only variations in the additive packages of this Example were the above noted components to derive the fluid relationships of Table 5 below.

[00149] Table 5: Lubricating Oil Compositions

		Comp 3	Inv 1	Inv 2	Inv 3
Detergent System					
OB Ca Sulfonate	Ca ppm	1098	0	1098	1098
OB Ca Phenate	Ca ppm	0	0	0	0
OB Mg Sulfonate	Mg ppm	1247	1901	1247	1247
Antiwear System					
ZDDP – Secondary <C6	P ppm	779	779	0	779
ZDDP – Primary >C8	P ppm	0	0	779	0
Antioxidant System					
Aminic Antioxidant	N ppm	175	175	175	0
Phenolic Antioxidant	O ppm	737	737	737	1352
Base Oil					
API Group II	wt%	70.0	70.0	70.0	70.0
API Group IV	wt %	10.0	10.0	10.0	10.0

[00150] Table 6: Fluid Relationships

		Comp 3	Inv 1	Inv 2	Inv 3
KV100° C (D445)	cSt	12.6	12.6	12.6	12.6
B	ppm	52	52	52	52
Ca	ppm	1098	0	1098	1098
Mg	ppm	1247	1901	1247	1247
Mo	ppm	40	40	40	40
P	ppm	779	779	779	779
Zn	ppm	855	855	862	855
TOTAL Nitrogen	ppm	1095	1091	1095	920
S	ppm	1842	1697	1839	1842
Finished Fluid total TBN (D2896)	mg KOH/g	10.4	10.4	10.4	9.6
Calculated detergent TBN (D2896)	Mg KOH/g	8.1	8.1	8.1	8.1
% Detergent contribution to total TBN	%	79.4	78.6	81.0	84.4
Ca/Mg weight ratio	-	0.9	0	0.9	0.9
Mg/Ca weight ratio	-	1.1	-	1.1	1.1
Dispersant Nitrogen	ppm	894	894	894	894
O/N Antioxidant Weight Ratio	-	4.2	4.2	4.2	-

[00151] Table 7: Engine Sludge Merits (CEC L-107-19)

		Comp 3	Inv 1	Inv 2	Inv3
Engine Sludge, Average (AES)	Merits	8.6	8.9	9.1	9.1

[00152] As shown in Tables 5, 6, and 7, when methods of lubricating a combustion engine using the lubricating oil composition of Comparative 3 having a majority of API Group II base oil, the lubrication failed to achieve an AES rating of 9.0 or higher. Comparative 3 did not have the correct combinations of a detergent system, antiwear system, and/or antioxidant system to overcome the performance debits of such high amounts of the lower quality API Group II base oils. However, in the methods of Inventive 1, when the detergent system included a majority of magnesium sulfonate detergents, the methods of lubricating using such lubricating oil composition was able to achieve an improved AES. In the methods of Inventive 2, when the antiwear system included a majority of zinc dihydrocarbyl dithiophosphate compounds having an average of 8 or more carbon atoms per phosphorus atom, the methods of lubricating using such lubricating oil composition was also able to achieve a passing AES. Lastly, in the methods of Inventive 3, when the antioxidant system included a majority of phenolic antioxidants, the methods of lubricating using such lubricating oil composition was also able to achieve a passing AES. Inventive methods 1-3 all included a majority of API Group II base oils (e.g., a base oil

having more than about 90 weight percent saturates, less than about 0.03 weight percent of sulfur, and a viscosity index (ASTM D2270) of about 120 or less) and were able to achieve improved AES by selecting the appropriate detergent system, antiwear system, and/or antioxidant system as shown in Tables 5, 6, and 7.

[00153] It is noted that, as used in this specification and the appended claims, the singular forms “a,” “an,” and “the,” include plural referents unless expressly and unequivocally limited to one referent. Thus, for example, reference to “an antioxidant” includes two or more different antioxidants. As used herein, the term “include” and its grammatical variants are intended to be non-limiting, such that recitation of items in a list is not to the exclusion of other like items that can be substituted or added to the listed items

[00154] For the purposes of this specification and appended claims, unless otherwise indicated, all numbers expressing quantities, percentages or proportions, and other numerical values used in the specification and claims, are to be understood as being modified in all instances by the term “about.” Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that can vary depending upon the desired properties sought to be obtained by the present disclosure. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

[00155] It is to be understood that each component, compound, substituent or parameter disclosed herein is to be interpreted as being disclosed for use alone or in combination with one or more of each and every other component, compound, substituent or parameter disclosed herein.

[00156] It is further understood that each range disclosed herein is to be interpreted as a disclosure of each specific value within the disclosed range that has the same number of significant digits. Thus, for example, a range from 1 to 4 is to be interpreted as an express disclosure of the values 1, 2, 3 and 4 as well as any range of such values.

[00157] It is further understood that each lower limit of each range disclosed herein is to be interpreted as disclosed in combination with each upper limit of each range and each specific value within each range disclosed herein for the same component, compounds, substituent or

parameter. Thus, this disclosure to be interpreted as a disclosure of all ranges derived by combining each lower limit of each range with each upper limit of each range or with each specific value within each range, or by combining each upper limit of each range with each specific value within each range. That is, it is also further understood that any range between the endpoint values within the broad range is also discussed herein. Thus, a range from 1 to 4 also means a range from 1 to 3, 1 to 2, 2 to 4, 2 to 3, and so forth.

[00158] Furthermore, specific amounts/values of a component, compound, substituent or parameter disclosed in the description or an example is to be interpreted as a disclosure of either a lower or an upper limit of a range and thus can be combined with any other lower or upper limit of a range or specific amount/value for the same component, compound, substituent or parameter disclosed elsewhere in the application to form a range for that component, compound, substituent or parameter.

[00159] While particular embodiments have been described, alternatives, modifications, variations, improvements, and substantial equivalents that are or can be presently unforeseen can arise to applicants or others skilled in the art. Accordingly, the appended claims as filed and as they can be amended are intended to embrace all such alternatives, modifications variations, improvements, and substantial equivalents.

CLAIMS

What is claimed is:

1. A method of lubricating a combustion engine for passing the M271 EVO fired engine test of CEC L-107-19, the method comprising:
 - lubricating a combustion engine with a lubricating oil composition;
 - wherein the lubricating oil composition includes:
 - a base oil of lubricating viscosity having about 50 weight percent or more of a hydrotreated mineral oil with more than about 90 weight percent saturates, less than about 0.03 weight percent of sulfur, and a viscosity index (ASTM D2270) of about 120 or less;
 - a detergent system having (i) less than about 5 weight percent of metal from non-sulfonate detergents and (ii) a total base number (TBN) thereof less than 10 mg KOH/gram and that contributes about 60 to about 85 percent of the total lubricating oil composition TBN as measured pursuant to ASTM D2896;
 - an antiwear system including one or more zinc dihydrocarbyl dithiophosphate compounds having alkyl groups derived from primary alcohols, secondary alcohols, or combination thereof and providing about 200 to about 1000 ppm phosphorus;
 - an antioxidant system including one or more phenolic antioxidant compounds, one or more aminic antioxidant compounds, or combinations thereof; and
 - wherein the lubricating oil composition includes one or more of the following to achieve a passing average engine sludge rating of 9.0 +/- 0.3 merits or higher pursuant to CEC L-107-19:
 - (a) the detergent system includes a majority of one or more overbased sulfonate detergents;
 - (b) the antiwear system includes a majority of zinc dihydrocarbyl dithiophosphate compounds having an average of 8 or more carbon atoms per phosphorus atom; and/or
 - (c) the antioxidant system includes a majority of phenolic antioxidant compounds.
2. The method of claim 1, wherein the lubricating oil composition includes (a) the detergent system having the majority of one or more overbased magnesium sulfonate detergents and further including a ratio magnesium to calcium of about 600:1 or greater and providing

about 70 to about 85 percent of the total lubricating oil composition TBN as measured pursuant to ASTM D2896.

3. The method of claim 2, wherein the lubricating oil composition further includes a majority of the phosphorus from the zinc dihydrocarbyl dithiophosphate compounds of the antiwear system provided by one or more zinc dihydrocarbyl dithiophosphate compounds having an average of 6 or fewer carbon atoms per phosphorus atom.

4. The method of claim 3, wherein the lubricating oil composition further includes one or more phenolic antioxidant compounds and one or more aminic antioxidant compounds in the antioxidant system and further includes a ratio of oxygen in ppm from the phenolic compounds to nitrogen in ppm from the aminic compounds (O/N) of about 4:1 to about 6:1.

5. The method of claim 1, wherein the lubricating oil composition includes (b) the majority of phosphorus from the zinc dihydrocarbyl dithiophosphate compounds of the antiwear system provided by a zinc dihydrocarbyl dithiophosphate compounds having an average of 8 or more carbon atoms per phosphorus atom.

6. The method of claim 5, wherein about 90 to about 100 weight percent of the phosphorus from the zinc dihydrocarbyl dithiophosphate compounds of the antiwear system is provided by the zinc dihydrocarbyl dithiophosphate compounds having an average of 8 or more carbon atoms per phosphorus atom.

7. The method of claim 6, wherein the lubricating oil composition further includes both calcium and magnesium provided by the detergent system and with a ratio of calcium-to-magnesium of about 0.8:1 to about 1.5:1.

8. The method of claim 7, wherein the lubricating oil composition further includes one or more phenolic antioxidant compounds and one or more aminic antioxidant compounds in the antioxidant system and with a weight ratio of oxygen in ppm contributed from the one or

more phenolic antioxidant compounds to nitrogen in ppm contributed from the one or more aminic antioxidant compounds (O/N) of about 4:1 to about 6:1.

9. The method of claim 1, wherein the lubricating oil composition includes (c) the antioxidant system having a majority of phenolic antioxidant compounds and further having a weight ratio of oxygen in ppm contributed from the phenolic antioxidant compounds to nitrogen in ppm from the aminic antioxidant compounds (O/N) of greater than about 100:1; and/or wherein the lubricating oil composition further includes both calcium and magnesium provided by the detergent system and with a ratio of detergent calcium to detergent magnesium of at least about 0.8:1 to about 1.5:1; and/or wherein the lubricating oil composition further includes a majority of the phosphorus from the zinc dihydrocarbyl dithiophosphate compounds of the antiwear system is provided by zinc dihydrocarbyl dithiophosphate compounds having an average of 6 or fewer carbon atoms per phosphorus atom.

10. The method of claim 1, wherein the base oil of lubricating viscosity is about 75 to about 90 weight percent of the hydrotreated mineral oil having more than about 90 weight percent saturates, less than about 0.03 weight percent of sulfur, and a viscosity index (ASTM D2270) of about 120 or less; and/or wherein the antioxidant system is substantially free of mono-alkyl phenolic amine antioxidants.

11. The method of claim 1, wherein the detergent system TBN is about 5 to less than about 10 mg KOH/gram; and/or wherein the TBN of the lubricating oil composition is about 7 to about 12 mg KOH/gram as measured pursuant to ASTM D2896; and/or wherein the detergent system is substantially free of phenate detergents; and/or wherein the detergent system consists essentially of sulfonate detergents providing calcium, magnesium, or combinations thereof.

12. The method of claim 1, wherein the lubricating oil composition includes no more than about 1.3 weight percent of one or more dispersant olefin copolymer viscosity index

improvers; and/or wherein the lubricating oil composition is substantially free of dispersant olefin copolymer viscosity index improvers.

13. The method of claim 1, wherein the lubricating oil composition has at least about 1000 ppm of total nitrogen; and/or wherein the lubricating oil composition includes one or more nitrogen-containing dispersant additives providing about 600 ppm or more dispersant nitrogen to the lubricating oil composition.

14. The method of claim 1, wherein the lubricating oil composition includes less than about 200 ppm molybdenum; and/or wherein the lubricating oil composition includes less than about 150 ppm of boron.

15. The method of claim 1, wherein the lubricating oil composition is substantially free of API Group III base oils.