

ALKYLPHENOL DETERGENTS

TECHNICAL FIELD

[0001] The disclosed technology relates to hydrocarbyl- (e.g. alkyl-) phenol detergents and their salts. In particular, the disclosed technology includes a hydroxy-aromatic carboxylic acid.

5 Such compounds and their salts are useful as lubricant additives.

BACKGROUND OF THE INVENTION

[0002] Phenol-based detergents are known. Among these are phenates based on phenolic monomers, linked with sulfur bridges or alkylene bridges such as methylene linkages derived from formaldehyde. The phenolic monomers themselves are typically substituted with an aliphatic hydrocarbyl group to provide a measure of oil solubility. The hydrocarbyl groups may be alkyl groups, and, historically, dodecylphenol (or propylene tetramer-substituted phenol) has been widely used. An early reference to basic sulfurized polyvalent metal phenates is U.S. Patent 2,680,96, Walker et al., June 1, 1954; see also U.S. Patent 3,372, 1 16, Meinhardt, March 6, 1968.

[0003] Recently, however, certain alkylphenols and products prepared from them have come under increased scrutiny due to their association as potential endocrine disruptive materials. In particular, alkylphenol detergents which are based on phenols alkylated with oligomers of propylene, specifically propylene tetramer (or tetrapropenyl), may contain residual alkyl phenol species. There is interest, therefore, in developing alkyl-substituted phenol detergents, for uses in lubricants, fuels, and as industrial additives, which contain a reduced or eliminated amount of dodecylphenol component and other substituted phenols having propylene oligomer substituents of 10 to 15 carbon atoms. Nevertheless, it is desirable that the products should have similar oil-solubility parameters as phenates prepared from C10-15 propylene oligomers.

[0004] There have been several efforts to prepare phenate detergents that do not contain alkyl phenols derived from oligomers of propylene. U.S. Patent 7,435,709, Stonebraker et al., October 14, 2008, discloses a linear alkylphenol derived detergent substantially free of endocrine disruptive chemicals. It comprises a salt of a reaction product of (1) an olefin having at least 10 carbon atoms, where greater than 90 mole % of the olefin is a linear C20-C30 n-alpha olefin, and wherein less than 10 mole % of the olefin is a linear olefin of less than 20 carbon atoms, and less than 5 mole % of the olefin a branched chain olefin of 18 carbons or less, and (2) a hydroxyaromatic compound.

[0005] U.S. Application 201 1/0190185, Sinquin et al, August 4, 2011, discloses an overbased salt of an oligomerized alkylhydroxyaromatic compound. The alkyl group is derived from an olefin mixture comprising propylene oligomers having an initial boiling point of at least about 195 °C and a final boiling point of greater than 325 °C. The propylene oligomers may contain a distribution of carbon atoms that comprise at least about 50 weight percent of C14 to C20 carbon atoms.

[0006] U.S. Application 201 1/0124539, Sinquin et al, May 26, 2011, discloses an overbased, sulfurized salt of an alkylated hydroxyaromatic compound. The alkyl substituent is a residue of at least one isomerized olefin having from 15 to about 99 wt. % branching. The hydroxyaromatic compound may be phenol, cresols, xlenols, or mixtures thereof.

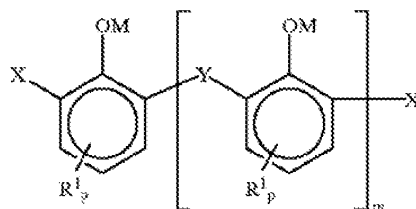
[0007] U.S. Application 201 1/01 18160, Campbell et al., May 19, 2011, discloses an alkylated hydroxyaromatic compound substantially free of endocrine disruptive chemicals. An alkylated hydroxyaromatic compound is prepared by reacting a hydroxyaromatic compound with at least one branched olefinic propylene oligomer having from about 20 to about 80 carbon atoms. Suitable hydroxyaromatic compounds include phenol, catechol, resorcinol, hydroquinone, pyrogallol, cresol, and the like.

[0008] U.S. Application 2010/0029529, Campbell et al., February 4, 2010, discloses an overbased salt of an oligomerized alkylhydroxyaromatic compound. The alkyl group is derived from an olefin mixture comprising propylene oligomers having an initial boiling point of at least about 195 °C and a final boiling point of no more than about 325 °C. Suitable hydroxyaromatic compounds include phenol, catechol, resorcinol, hydroquinone, pyrogallol, cresol, and the like.

[0009] U.S. Application 2008/0269351, Campbell et al., October 30, 2008, discloses an alkylated hydroxyaromatic compound substantially free of endocrine disruptive chemicals, prepared by reacting a hydroxyaromatic compound with a branched olefinic oligomer having from about 20 to about 80 carbon atoms.

[0010] WO/PCT application 2013/059173, Cook et al., discloses an overbased salt of an oligomerized alkylhydroxyaromatic compound. The alkyl group is a combination of very short hydrocarbyl group (i.e. 1 to 8 carbon atoms) and a long hydrocarbyl group (at least about 25 carbon atoms). Suitable compounds include those made from a mixture of para-cresol and polyisobutylene-substituted phenol.

[0011] Other general technology includes that of U.S. Patent 6,310,009, Carrick et al., October 30, 2001, which discloses salts of the general structure



where R may be an alkyl group of 1 to 60 carbon atoms, e.g., 9 to 18 carbon atoms. It is understood
 5 that R¹ will normally comprise a mixture of various chain lengths, so that the foregoing numbers will normally represent an average number of carbon atoms in the R¹ groups (number average).

SUMMARY OF THE INVENTION

[0012] The present invention provides an alkyl-phenol detergent composition having appropriate oil solubility which may also provide one or more other benefits to a lubricating
 10 composition including anti-wear performance, oxidation performance, and/or viscosity performance. In one embodiment the disclosed technology may provide a solution to potential problems posed by detergents containing C12 alkyl phenol moieties i.e., the disclosed invention may be free from or substantially free from C12 alkyl phenol moieties typically formed from oligomerisation or polymerisation of propylene.

15 [0013] The present invention provides an alkylphenol containing detergent comprising a polyolefin-substituted hydroxy-aromatic carboxylic acid or salt thereof, wherein the polyolefin is derived from a branched alkene having at least 4 carbon atoms and wherein the polyolefin has a number average molecular weight of 150 to 800 and wherein the detergent is a neutral or overbased salt of a carboxylic acid. In certain embodiments, the alkylphenol detergent of the present
 20 invention is substantially free of (or entirely free of, or contains less than 5 percent or 3 percent or 1 percent or 0.3 percent or 0.1 percent by mole of) oligomer units containing propylene. In certain embodiments, the alkylphenol detergent of the present invention is substantially free from or substantially free from C12 alkyl phenol moieties.

[0014] In one embodiment, the alkylphenol-containing detergent may be a polyolefin-
 25 substituted hydroxy-aromatic carboxylic acid or salt thereof, such as a salicylate. Detergents of

this type are ionic detergents, i.e. they generally comprise a salt of the detergent substrate (the phenol-containing material) and a suitable cationic counterion. Detergents of the disclosed technology may be metal-containing salts, amine or ammonium containing salts, or mixtures thereof. In one embodiment, the detergent comprises one or more alkali metals, one or more
5 alkaline earth metals, or mixtures thereof.

[0015] The present invention also includes a process to prepare an alkylphenol-containing detergent compound comprising (i) forming a polyolefin-substituted hydroxy-aromatic carboxylic acid wherein the polyolefin is derived from a branched alkene having at least 4 carbon atoms and wherein the polyolefin has a number average molecular weight of 150 to 800 to form a substrate
10 and (ii) reacting the substrate with a metal base (such as an alkali metal or alkaline earth metal oxide or hydroxide) in the presence of carbon dioxide to form an alkylphenol containing detergent. The reaction conditions for the process are known in the art and include alkylation of phenol in the presence of known catalysts including BF_3 , AlCl_3 , or HF . The reaction of the substrate with a metal base), in the presence of carbon dioxide are well known processes in the art of preparing
15 detergents.

[0016] The disclosed technology also provides a lubricant comprising an oil of lubricating viscosity and said alkylphenol detergent, as well as a method of lubricating a mechanical device with said lubricant.

[0017] The disclosed technology also provides a method of lubricating a mechanical device comprising supplying to the mechanical device a lubricating composition disclosed herein.
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[0018] The disclosed technology also provides for the use of the alkylphenol detergent in a lubricating composition to provide detergency, deposit control, and/or oxidative stability to the lubricant.

DETAILED DESCRIPTION OF THE INVENTION

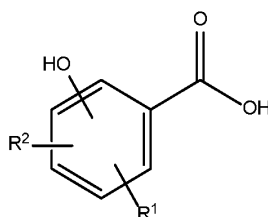
[0019] The disclosed technology provides an alkylphenol detergent, a lubricating composition, a method for lubricating a mechanical device, such as an internal combustion engine, and a use as disclosed herein.
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[0020] The alkylphenol detergent of the present invention comprises a polyolefin-substituted hydroxy-aromatic carboxylic acid wherein the polyolefin is derived from a branched alkene having

at least 4 carbon atoms and wherein the polyolefin has a number average molecular weight of 150 to 800.

[0021] The alkylphenol-containing detergent of the present invention is a polyolefin-substituted hydroxy-aromatic carboxylic acid. Such a detergent may be represented by the formula

5 (I):



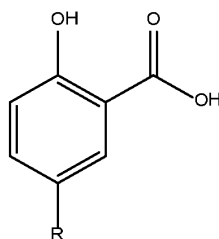
(I)

wherein R¹ is an alkyl group is derived from a branched polyolefin compound having at least 4 carbon atoms, for example, 8 to 50 carbon atoms, or at least 10 carbon atoms, or at least 12 carbon atoms, or at least 14 carbon atoms, or at least 16 carbon atoms, or at least 18 carbon atoms, or at least 20 carbon atoms, or at least 24 carbon atoms, or up to 40 carbon atoms, or up to 35 carbon atoms, or up to 30 carbon atoms. The polyolefin group may have a number-average molecular weight Mn of at least 150, or at least 200, or at least 300, or up to 800, or up to 600, or up to 500, or up to 400, or up to 360. R² may be a hydrogen or a hydrocarbyl group of at least one 1 up to about 40 carbon atoms. In one embodiment, R² may also be an alkyl group is derived from a branched polyolefin compound having at least 4 carbon atoms, for example, 8 to 50 carbon atoms, or at least 10 carbon atoms, or at least 12 carbon atoms, or at least 14 carbon atoms, or at least 16 carbon atoms, or at least 18 carbon atoms, or at least 20 carbon atoms, or at least 24 carbon atoms, or up to 40 carbon atoms, or up to 35 carbon atoms, or up to 30 carbon atoms. The polyolefin group may have a number-average molecular weight Mn of at least 150, or at least 200, or at least 300, or up to 800, or up to 600, or up to 500, or up to 400, or up to 360.

[0022] The polyolefin-substituted hydroxy-aromatic carboxylic acid may be selected from any known carboxylic acid in the art for such applications. The polyolefin-substituted hydroxy-aromatic carboxylic acid may be a neutral or overbased metal salt of a carboxylic acid. 4-hydroxybenzoic acid, 2-hydroxybenzoic acid (aka salicylic acid), 3-hydroxybenzoic acid, 1-hydroxy-2-naphthoic acid, 3-hydroxy-2-naphthoic acid, and 6-hydroxy-2-naphthoic acid.

[0023] The preparation of detergents from carboxylic acids is generally known to those skilled in the art. For example, methods of forming such detergents are disclosed in U.S. Patents 4,719,023 and 3,372,116. The present invention may be prepared by any methods now known or hereafter developed.

- 5 **[0024]** In one embodiment, the polyolefin-substituted hydroxy-aromatic carboxylic acid may be an alkylsalicylate or salicylate detergent. A salicylate detergent may be a neutral or overbased metal salt of alkylsalicylic acid. Alkylsalicylic acid may be represented by the formula (II)



(II)

- 10 **[0025]** In the polyolefin-substituted hydroxy-aromatic carboxylic acids shown in Formulas (I) and (II) above, R or R¹ represent the alkyl group of the alkylphenol. In the present invention, the alkyl group is derived from a branched polyolefin compound having at least 4 carbon atoms, for example, 8 to 50 carbon atoms, or at least 10 carbon atoms, or at least 12 carbon atoms, or at least 14 carbon atoms, or at least 16 carbon atoms, or at least 18 carbon atoms, or at least 20 carbon
15 atoms, or at least 24 carbon atoms, or up to 40 carbon atoms, or up to 35 carbon atoms, or up to 30 carbon atoms. The polyolefin group may have a number-average molecular weight Mn of at least 150, or at least 200, or at least 300, or up to 800, or up to 600, or up to 500, or up to 400, or up to 360. A polyolefin group with Mn of less than 500, e.g., up to about 400, for example about 300 to 400 is particularly suitable as it allows the compound to provide good detergent properties
20 for deposit control and cleanliness without resulting in viscosity creep or undesirable thickening of the oil.

- [0026]** Examples of branched polyolefin groups suitable for use as the R or R¹ group include polyolefin groups which are derived from a branched alkene having at least 4 carbon atoms, or up to 12 carbon atoms, or up to 8 carbon atoms, or up to 6 carbon atoms, such as a C4-C6 branched
25 alkene. Suitable branched alkenes include isobutylene (2-methylpropene), 2-methylbutene, 2-ethyl-1-butene, 2-methyl-1-pentene, 3-methyl-1-pentene, 4-methyl-1-pentene, 2-methyl, 3-

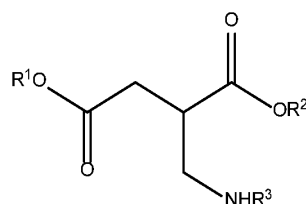
methy1-1-pentene, 2-ethyl-1-pentene, 3-ethyl-1-pentene, 2-methyl-1-hexene, 3-methyl-1-hexene, 2-ethyl-1-hexene, 3-ethyl-1-hexene, 4-ethyl-1-hexene, 2-methyl-1-heptene, 3-methyl-1-heptene, 2-methyl-1-octene, 2-methyl-1-nonene, 2-methyl-1-decene, 2-methyl-1-undecene, and mixtures thereof. Each polyolefin group is derived from at least two or at least three, or at least four, or up to twenty, or up to eighteen, or up to twelve branched alkene monomer units to form a chain with at least two or at least three, or at least four branches from the main chain. In one embodiment, the polyolefin includes a chain derived from at least four, or at least five, or up to eighteen, or up to eight, or up to seven, or up to six branched alkene units. The branched alkene may be branched at the alpha or beta position, or further along the longest chain. In one embodiment, R is derived from a branched alkene which is solely or at least partially isobutylene.

[0027] In one embodiment, the compound is free of C8 and higher unbranched alkyl groups.

[0028] In one embodiment, R, R¹, and R² are composed solely of carbon and hydrogen.

[0029] The polyolefin-substituted hydroxy-aromatic carboxylic acid, such as an alkylsalicylate, may be a neutral or nearly neutral salt of the carboxylic acid; by nearly neutral, it is meant that there is an excess of base of no more than 15 mol percent, i.e. if the salt is metal-containing, the metal ratio is 1.15 or less. In one embodiment the neutral salt of the polyolefin-substituted hydroxy-aromatic carboxylic acid, such as alkylsalicylic acid, may be an amine or ammonium salt, a metal salt, or mixtures thereof.

[0030] Amines suitable for use in the preparation of the neutral amine salted polyolefin-substituted hydroxy-aromatic carboxylic acid, such as an alkylsalicylate are not overly limited and may include any alkyl amine, though generally are fatty acid amines derived from fatty carboxylic acids. The alkyl group present in the amine may contain from 10 to 30 carbon atoms, or from 12 to 18 carbon atoms, and may be linear or branched. In some embodiments the alkyl group may be linear and unsaturated. Typical amines include pentadecylamine, octadecylamine, cetylamine, oleylamine, decylamine, dodecylamine, dimethyldodecylamine, tridecylamine, heptadecylamine, octadecylamine, stearylamine, and any combination thereof. In some embodiments the fatty acid derived amine salt of an alkylsalicylic acid may be a salt of oleylamine. In certain embodiments, the amine may be a gamma-aminoester compound; aminoesters of this type may be derived from Michael addition of a primary amine to an alkyl diester of itaconic acid represented by the formula



where R¹ and R² are hydrocarbyl groups containing 2 to 30 carbon atoms, and R³ is a hydrocarbyl group containing 4 to 50 carbon atoms. In some embodiments, R³ of the aminoester compound is an alkyl group that has at least one hydrocarbyl group substituted at the 1-, or 2-position of the
 5 alkyl group. In one embodiment, the aminoester is dibutyl 2-(((2-ethylhexyl)-amino)methyl)succinate.

[0031] In certain embodiments, the neutral salt of the polyolefin-substituted hydroxy-aromatic carboxylic acid, such as an alkylsalicylic acid may be a quaternary ammonium salt, also referred to as a quaternary nitrogen compound. Quaternary nitrogen compounds are characterized in that
 10 the nitrogen atom is four-coordinate; this results in a cationic species that is not protic, i.e. an acidic proton is not released under basic conditions. Quaternary nitrogen compounds may be characterized as falling into two large groups, four coordinate tetrahydrocarbylammonium compounds, for example tetrabutylammonium, and three coordinate aromatic compounds, for example N-hydrocarbylpyridinium.

[0032] In some embodiments the quaternary nitrogen salt may comprise the reaction product of (a) hydrocarbyl-substituted compound having a tertiary amino group and (b) a quaternizing agent suitable for converting the tertiary amino group of (a) to a quaternary nitrogen, wherein the quaternizing agent may be chosen from dialkyl sulfates, benzyl halides, hydrocarbyl substituted carbonates; hydrocarbyl epoxides in combination with an acid or mixtures thereof. In one
 20 embodiment, the quaternary nitrogen salt comprises the reaction product of (i) at least one compound chosen from: a polyalkene-substituted amine having at least one tertiary amino group and/or a Mannich reaction product having a tertiary amino group; and (ii) a quaternizing agent.

[0033] The polyolefin-substituted hydroxy-aromatic carboxylic acid detergents of the present invention may be metal-containing detergents. Metal-containing detergents may be neutral, or very
 25 nearly neutral, or overbased. An overbased detergent contains a stoichiometric excess of a metal base for the acidic organic substrate. This is also referred to as metal ratio. The term “metal ratio”

is the ratio of the total equivalents of the metal to the equivalents of the acidic organic compound. A neutral metal salt has a metal ratio of one. A salt having 4.5 times as much metal as present in a normal salt will have metal excess of 3.5 equivalents, or a ratio of 4.5. The term “metal ratio” is also explained in standard textbook entitled “Chemistry and Technology of Lubricants”, Third Edition, Edited by R. M. Mortier and S. T. Orszulik, Copyright 2010, page 219, sub-heading 7.25.

[0034] In one embodiment the overbased metal-containing polyolefin-substituted hydroxy-aromatic carboxylic acid may be calcium or magnesium overbased detergent. In one embodiment, the overbased detergent may comprise a calcium alkylphenol detergent with a metal ratio of at least 1.5, at least 3, at least 5, or at least 7. In certain embodiments, the overbased calcium alkylphenol detergent may have a metal ratio of 1.5 to 25, 2.5 to 20 or 5 to 16.

[0035] Alternatively, the polyolefin-substituted hydroxy-aromatic carboxylic acid detergent may be described as having TBN. Overbased carboxylic acid detergents, such as salicylates, typically have a total base number of 120 to 600 mg KOH/g, or 150 to 550 mg KOH/g, or 180 to 350 mg KOH/g. The amount of the alkylphenol-containing detergent present in a lubricant composition may be defined as the amount necessary to deliver an amount, or range of amounts, of TBN to the lubricant composition. In certain embodiments, the polyolefin-substituted hydroxy-aromatic carboxylic acid containing detergent may be present in a lubricant composition in amount to deliver 0.5 to 10 TBN to the composition, or 1 to 7 TBN, or 1.5 to 5 TBN to the composition.

[0036] Overbased detergents may also be defined as the ratio of the neutral detergent salt, also referred to as detergent soap, and the detergent ash. The overbased detergent may have a weight ratio of ash to soap of 3:1 to 1:8, or 1.5:1 to 1 to 4.1, or 1.3:1 to 1:3.4.

[0037] The polyolefin-substituted hydroxy-aromatic carboxylic acid detergent of the present invention may beneficially be used as an additive in a lubricant. The amount of the polyolefin-substituted hydroxy-aromatic carboxylic acid detergent in a lubricant may be 0.1 to 8 percent by weight, on an oil-free basis, but including the calcium carbonate and other salts present in an overbased composition. When present as an overbased detergent, the amount may typically be in the range of 0.1 to 25 weight percent, or 0.2 to 28, or 0.3 to 20, or 0.5 to 15 percent. The higher amounts are typical of marine diesel cylinder lubricants, e.g., 1 or 3 or 5 percent up to 25, 20, or 15 percent. Amounts used in gasoline or heavy-duty diesel engines (not marine) will typically be in lower ranges, such as 0.1 to 10 percent or 0.5 to 5 or 1 to 3 percent by weight. When used as a

substantially neutral or non-overbased salt, its amount may typically be correspondingly less for each of the engine types, e.g., 0.1 to 10 percent or 0.2 to 8 or 0.3 to 6 percent.

[0038] In certain embodiments, the amount of the polyolefin-substituted hydroxy-aromatic carboxylic acid detergent in a lubricant may be measured as the amount of alkylphenol-containing soap that is provided to the lubricant composition, irrespective of any overbasing. In one embodiment, the lubricant composition may contain 0.05 weight percent to 1.5 weight percent alkylphenol-containing soap, or 0.1 weight percent to 0.9 weight percent alkylphenol-containing soap. In one embodiment, the alkylphenol-containing soap provides 20 percent by weight to 100 percent by weight of the total detergent soap in the lubricating composition. In one embodiment the alkylphenol-containing soap provides 30 percent by weight to 80 percent by weight of the total detergent soap, or 40 percent by weight to 75 percent by weight of the total detergent soap of the lubricating composition.

[0039] A lubricant composition may contain alkylphenol-containing detergents different from that of the disclosed technology. In one embodiment, the lubricant composition of the disclosed technology comprises the polyolefin-substituted hydroxy-aromatic carboxylic acid or salt thereof detergent of the disclosed technology in an amount 0.1 to 25 weight percent, or 0.2 to 28, or 0.3 to 20, or 0.5 to 15 weight percent, and is free of or substantially free of an alkylphenol-containing detergent derived from alkylphenol which is derived from oligomers of propylene, especially tetrapropenyl. "Substantially free of" in this case means no more than 0.01 weight percent or an amount considered to arise through contamination or other unintentional means.

Oil of Lubricating Viscosity

[0040] The lubricating composition comprises of the present invention an oil of lubricating viscosity. Such oils include natural and synthetic oils, oil derived from hydrocracking, hydrogenation, and hydrofinishing, unrefined, refined, re-refined oils or mixtures thereof. A more detailed description of unrefined, refined and re-refined oils is provided in International Publication WO2008/147704, paragraphs [0054] to [0056] (a similar disclosure is provided in US Patent Application 2010/197536, see [0072] to [0073]). A more detailed description of natural and synthetic lubricating oils is described in paragraphs [0058] to [0059] respectively of WO2008/147704 (a similar disclosure is provided in US Patent Application 2010/197536, see [0075] to [0076]). Synthetic oils may also 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.

[0041] Oils of lubricating viscosity may also be defined as specified in April 2008 version of “Appendix E - API Base Oil Interchangeability Guidelines for Passenger Car Motor Oils and Diesel Engine Oils”, section 1.3 Sub-heading 1.3. “Base Stock Categories”. The API Guidelines are also summarized in US Patent US 7,285,516 (see column 11, line 64 to column 12, line 10).

[0042] In one embodiment the oil of lubricating viscosity may be an API Group I to III mineral oil, a Group IV synthetic oil, or a Group V naphthenic or ester synthetic oil, or mixtures thereof. In one embodiment the oil of lubricating viscosity may be an API Group II, Group III mineral oil, or a Group IV synthetic oil, or mixtures thereof.

[0043] The amount of the oil of lubricating viscosity present is typically the balance remaining after subtracting from 100 weight % the sum of the amount of the additives of the disclosed technology and the other performance additives.

[0044] The lubricating composition may be in the form of a concentrate and/or a fully formulated lubricant. If the lubricating composition of the disclosed technology (comprising the additives disclosed herein) is in the form of a concentrate which may be combined with additional oil to form, in whole or in part, a finished lubricant, the ratio of the of these additives to the oil of lubricating viscosity and/or to diluent oil include the ranges of 1:99 to 99:1 by weight, or 80:20 to 10:90 by weight. Typically the lubricating composition of the disclosed technology comprises at least 50 weight %, or at least 60 weight %, or at least 70 weight %, or at least 80 weight % of an oil of lubricating viscosity.

Engine Lubricating Compositions – Other Additives

[0045] Engine lubricating compositions in accordance with the present invention may also contain other additives that provide particular performance benefits to the engine lubricant. These additional additives may include detergents, antioxidants, dispersants, anti-wear agents, oil soluble titanium compounds, extreme pressure agents, foam inhibitors, viscosity modifiers, corrosion inhibitors, metal deactivators, pour point depressants, friction modifiers, demulsifiers, and seal swell agents. These additional components are described in more detail below.

[0046] The lubricating composition optionally further includes at least one detergent, other than the polyolefin-substituted hydroxy-aromatic carboxylic acid or salt thereof as described

herein. Exemplary optional detergents include overbased metal-containing detergents. The metal of the metal-containing detergent may be zinc, sodium, calcium, barium, or magnesium. An overbased metal-containing detergent may be chosen from sulfonates, non-sulfur containing phenates, sulfur containing phenates, salixarates, salicylates, and mixtures thereof, or borated equivalents thereof. The overbased detergent may be borated with a borating agent such as boric acid.

[0047] An overbased metal-containing detergent may also include “hybrid” detergents formed with mixed surfactant systems including phenate and/or sulfonate components, e.g., phenate/salicylates, sulfonate/phenates, sulfonate/salicylates, sulfonates/phenates/salicylates, as described, for example, in U.S. Pat. Nos. 6,429,178; 6,429,179; 6,153,565; and 6,281,179. Where a hybrid sulfonate/phenate detergent is employed, the hybrid detergent can be considered equivalent to amounts of distinct phenate and sulfonate detergents introducing like amounts of phenate and sulfonate soaps, respectively.

[0048] Example overbased metal-containing detergents include zinc, sodium, calcium and magnesium salts of sulfonates, phenates (including sulfur-containing and non-sulfur containing phenates), salixarates and salicylates. Such overbased sulfonates, salixarates, phenates and salicylates may have a total base number of 120 to 700, or 250 to 600, or 300 to 500 (on an oil free basis).

[0049] Overbased metal-containing detergents may be a zinc, sodium, calcium or magnesium salt of a sulfonate, a phenate, sulfur containing phenate, salixarate or salicylate. Overbased sulfonates, salixarates, phenates and salicylates typically have a total base number of 120 to 700 TBN. Overbased sulfonates typically have a total base number of 120 to 700, or 250 to 600, or 300 to 500 (on an oil free basis).

[0050] Example sulfonate detergents include linear and branched alkylbenzene sulfonate detergents, and mixtures thereof, which may have a metal ratio of at least 8, as described, for example, in U.S. Pub. No. 2005065045. Linear alkyl benzenes may have the benzene ring attached anywhere on the linear chain, usually at the 2, 3, or 4 position, or be mixtures thereof. Linear alkylbenzene sulfonate detergents may be particularly useful for assisting in improving fuel economy. In one embodiment, an alkylbenzene sulfonate detergent may be a branched alkylbenzene sulfonate, a linear alkylbenzene sulfonate, or mixtures thereof.

[0051] In one embodiment, the lubricating composition may be free of linear alkylbenzene sulfonate detergent. In one embodiment, a sulfonate detergent may be a metal salt of one or more oil-soluble alkyl toluene sulfonate compounds as disclosed in U.S. Pub. No. 20080119378.

[0052] The lubricating composition may include at least 0.01 wt. % or at least 0.1 wt. % of a detergent other than the polyolefin-substituted hydroxy-aromatic carboxylic acid or salt thereof, and in some embodiments, up to 2 wt. %, or up to 1 wt. % of another detergent.

[0053] The lubricating composition optionally further includes at least one antioxidant. Exemplary antioxidants useful herein include phenolic and aminic antioxidants, such as diarylamines, alkylated diarylamines, hindered phenols, and mixtures thereof. The diarylamine or alkylated diarylamine may be a phenyl- α -naphthylamine (PANA), an alkylated diphenylamine, an alkylated phenylnaphthylamine, or mixture thereof. Example alkylated diphenylamines include dinonyl diphenylamine, nonyl diphenylamine, octyl diphenylamine, dioctyl diphenylamine, didecyl diphenylamine, decyl diphenylamine, and mixtures thereof. Example alkylated diarylamines include octyl, dioctyl, nonyl, dinonyl, decyl and didecyl phenylnaphthylamines.

Hindered phenol antioxidants often contain a secondary butyl and/or a tertiary butyl group as a steric hindering group. The phenol group may be further substituted with a hydrocarbyl group (e.g., a linear or branched alkyl) and/or a bridging group linking to a second aromatic group. Examples of suitable hindered phenol antioxidants include 2,6-di-tert-butylphenol, 4-methyl-2,6-di-tert-butylphenol, 4-ethyl-2,6-di-tert-butylphenol, 4-propyl-2,6-di-tert-butylphenol, 4-butyl-2,6-di-tert-butylphenol, and 4-dodecyl-2,6-di-tert-butylphenol. In one embodiment, the hindered phenol antioxidant may be an ester, such as those described in U.S. Pat. No. 6,559,105. One such hindered phenol ester is sold as Irganox™ L-135, obtainable from Ciba.

[0054] When present, the lubricating composition may include at least 0.1 wt. % or at least 0.5 wt. %, or at least 1 wt. % antioxidant, and in some embodiments, up to 3 wt. %, or up to 2.75 wt. %, or up to 2.5 wt. % antioxidant.

[0055] The lubricating composition optionally further includes at least one dispersant. Exemplary dispersants include succinimide dispersants, Mannich dispersants, succinamide dispersants, and polyolefin succinic acid esters, amides, and ester-amides, and mixtures thereof. The succinimide dispersant, where present, may be as described above for the succinimides described as useful for cation M.

[0056] The succinimide dispersant may be derived from an aliphatic polyamine, or mixtures thereof. The aliphatic polyamine may be an ethylenepolyamine, a propylenepolyamine, a butylenepolyamine, or a mixture thereof. In one embodiment the aliphatic polyamine may be an ethylenepolyamine. In one embodiment the aliphatic polyamine may be chosen from
5 ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, polyamine still bottoms, and mixtures thereof.

[0057] In one embodiment, the dispersant may be a polyolefin succinic acid ester, amide, or ester-amide. A polyolefin succinic acid ester-amide may be a polyisobutylene succinic acid reacted with an alcohol (such as pentaerythritol) and a polyamine as described above. Example polyolefin
10 succinic acid esters include polyisobutylene succinic acid esters of pentaerythritol and mixture thereof.

[0058] The dispersant may be an N-substituted long chain alkenyl succinimide. An example of an N-substituted long chain alkenyl succinimide is polyisobutylene succinimide. Typically the polyisobutylene from which polyisobutylene succinic anhydride is derived has a number average
15 molecular weight of 350 to 5000, or 550 to 3000 or 750 to 2500. Succinimide dispersants and their preparation are disclosed, for example, in US Pat. Nos. 3,172,892, 3,219,666, 3,316,177, 3,340,281, 3,351,552, 3,381,022, 3,433,744, 3,444,170, 3,467,668, 3,501,405, 3,542,680, 3,576,743, 3,632,511, 4,234,435, Re 26,433, and 6,165,235, and 7,238,650 and EP Patent Application 0 355 895 A.

[0059] The succinimide dispersant may comprise a polyisobutylene succinimide, wherein the polyisobutylene from which polyisobutylene succinimide is derived has a number average
20 molecular weight of 350 to 5000, or 750 to 2500.

[0060] The exemplary dispersants may also be post-treated by conventional methods by a reaction with any of a variety of agents. Among these are boron compounds (such as boric acid),
25 urea, thiourea, dimercaptotriadiazoles, carbon disulfide, aldehydes, ketones, carboxylic acids, such as terephthalic acid, hydrocarbon-substituted succinic anhydrides, maleic anhydride, nitriles, epoxides, and phosphorus compounds. In one embodiment the post-treated dispersant is borated. In one embodiment the post-treated dispersant is reacted with dimercaptotriadiazoles. In one embodiment the post-treated dispersant is reacted with phosphoric or phosphorous acid. In one

embodiment the post-treated dispersant is reacted with terephthalic acid and boric acid (as described in U.S. Pub. No. 2009/0054278).

[0061] When present, the lubricating composition may include at least 0.01 wt. %, or at least 0.1 wt. %, or at least 0.5 wt. %, or at least 1 wt. % of other dispersant(s), and in some embodiments, up to 20 wt. %, or up to 15 wt. %, or up to 10 wt. %, or up to 6 wt. % or up to 3 wt. % dispersant.

[0062] The lubricating composition optionally further includes at least one antiwear agent. Examples of suitable antiwear agents suitable for use herein include titanium compounds, tartrates, tartrides, oil soluble amine salts of phosphorus compounds, sulfurized olefins, metal dihydrocarbyldithiophosphates (such as zinc dialkyldithiophosphates), 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 antiwear agent may in one embodiment include a tartrate, or tartride as described in U.S. Pub. Nos. 2006/0079413; 2006/0183647; and 2010/0081592. The tartrate or tartride may contain alkyl-ester groups, where the sum of carbon atoms on the alkyl groups is at least 8. The antiwear agent may, in one embodiment, include a citrate as is disclosed in US Pub. No. 20050198894.

[0063] The lubricating composition may in one embodiment further include a phosphorus-containing antiwear agent. Example phosphorus-containing antiwear agents include zinc dialkyldithiophosphates, phosphites, phosphates, phosphonates, and ammonium phosphate salts, and mixtures thereof.

[0064] When present, the lubricating composition may include at least 0.01 wt. %, or at least 0.1 wt. %, or at least 0.5 wt. % antiwear agent, and in some embodiments, up to 3 wt. %, or up to 1.5 wt. %, or up to 0.9 wt. antiwear agent.

[0065] The lubricating composition may include one or more oil-soluble titanium compounds, which may function as antiwear agents, friction modifiers, antioxidants, deposit control additives, or more than one of these functions. Example oil-soluble titanium compounds are disclosed in U.S. Pat. No. 7,727,943 and U.S. Pub. No. 2006/0014651. Example oil soluble titanium compounds include titanium (IV) alkoxides, such as titanium (IV) isopropoxide and titanium (IV) 2 ethylhexoxide. Such alkoxides may be formed from a monohydric alcohol, a vicinal 1,2-diol, a polyol, or mixture thereof. The monohydric alkoxides may have 2 to 16, or 3 to 10 carbon atoms.

In one embodiment, the titanium compound comprises the alkoxide of a vicinal 1,2-diol or polyol. 1,2-vicinal diols include fatty acid mono-esters of glycerol, where the fatty acid may be, for example, oleic acid. Other example oil soluble titanium compounds include titanium carboxylates, such as titanium neodecanoate.

5 **[0066]** When present in the lubricating composition, the amount of oil-soluble titanium compounds is included as part of the antiwear agent.

[0067] The lubricating composition may include an extreme pressure agent. Example extreme pressure agents that are soluble in the oil include sulfur- and chlorosulfur-containing EP agents, dimercaptothiadiazole or CS₂ derivatives of dispersants (typically succinimide dispersants),
10 derivative of chlorinated hydrocarbon EP agents and phosphorus EP agents. Examples of such EP agents include chlorinated wax; sulfurized olefins (such as sulfurized isobutylene), hydrocarbyl-substituted 2,5-dimercapto-1,3,4-thiadiazoles and oligomers thereof, organic sulfides and polysulfides, such as dibenzyl disulfide, bis-(chlorobenzyl) disulfide, dibutyl tetrasulfide, sulfurized methyl ester of oleic acid, sulfurized alkylphenol, sulfurized dipentene, sulfurized
15 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 dihydrocarbon and trihydrocarbon phosphites, e.g., dibutyl phosphite, diheptyl phosphite, dicyclohexyl phosphite, pentylphenyl phosphite; dipentylphenyl phosphite, tridecyl phosphite, distearyl phosphite and polypropylene substituted phenol phosphite; metal thiocarbamates, such
20 as zinc dioctyldithiocarbamate and barium heptylphenol diacid; amine salts of alkyl and dialkylphosphoric acids or derivatives including, for example, the amine salt of a reaction product of a dialkyldithiophosphoric acid with propylene oxide and subsequently followed by a further reaction with P₂O₅; and mixtures thereof. Some useful extreme pressure agents are described in US Pat. No. 3,197,405.

25 **[0068]** When present, the lubricating composition may include at least 0.01 wt. %, or at least 0.1 wt. %, or at least 0.5 wt. % extreme pressure agent, and in some embodiments, up to 3 wt. %, or up to 1.5 wt. %, or up to 0.9 wt. % of the extreme pressure agent.

[0069] The lubricating composition may include a foam inhibitor. Foam inhibitors that may be useful in the lubricant composition include polysiloxanes; copolymers of ethyl acrylate and 2-ethylhexylacrylate and optionally vinyl acetate; demulsifiers including fluorinated polysiloxanes,
30

trialkyl phosphates, polyethylene glycols, polyethylene oxides, polypropylene oxides and (ethylene oxide-propylene oxide) polymers.

[0070] The lubricating composition may include a viscosity modifier. Viscosity modifiers (also sometimes referred to as viscosity index improvers or viscosity improvers) useful in the lubricant composition are usually polymers, including polyisobutenes, polymethacrylates (PMA) and polymethacrylic acid esters, diene polymers, polyalkylstyrenes, esterified styrene-maleic anhydride copolymers, hydrogenated alkenylarene-conjugated diene copolymers and polyolefins also referred to as olefin copolymer or OCP. PMA's are prepared from mixtures of methacrylate monomers having different alkyl groups. The alkyl groups may be either straight chain or branched chain groups containing from 1 to 18 carbon atoms. Most PMA's are viscosity modifiers as well as pour point depressants. In one embodiment, the viscosity modifier is a polyolefin comprising ethylene and one or more higher olefin, such as propylene.

[0071] When present, the lubricating composition may include at least 0.01 wt. %, or at least 0.1 wt. %, or at least 0.3 wt. %, or at least 0.5 wt. % polymeric viscosity modifiers, and in some embodiments, up to 10 wt. %, or up to 5 wt. %, or up to 2.5 wt. % polymeric viscosity modifiers.

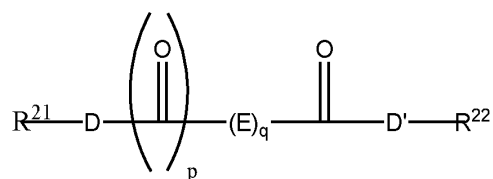
[0072] The lubricating composition may include a corrosion inhibitor. Corrosion inhibitors/metal deactivators that may be useful in the exemplary lubricating composition include fatty amines, octylamine octanoate, condensation products of dodecanyl succinic acid or anhydride, and a fatty acid such as oleic acid with a polyamine, derivatives of benzotriazoles (e.g., tolyltriazole), 1,2,4-triazoles, benzimidazoles, 2-alkyldithiobenzimidazoles and 2-alkyldithiobenzothiazoles.

[0073] The lubricating composition may include a pour point depressant. Pour point depressants that may be useful in the exemplary lubricating composition include polyalphaolefins, esters of maleic anhydride-styrene copolymers, polymethacrylates, polyacrylates, and polyacrylamides.

[0074] The lubricating composition may include a friction modifier. Friction modifiers that may be useful in the exemplary lubricating composition include fatty acid derivatives such as amines, esters, epoxides, fatty imidazolines, condensation products of carboxylic acids and polyalkylene-polyamines and amine salts of alkylphosphoric acids. The friction modifier may be an ash-free friction modifier. Such friction modifiers are those which typically not produce any

sulfated ash when subjected to the conditions of ASTM D 874. An additive is referred to as "non-metal containing" if it does not contribute metal content to the lubricant composition. As used herein the term "fatty alkyl" or "fatty" in relation to friction modifiers means a carbon chain having 8 to 30 carbon atoms, typically a straight carbon chain.

5 **[0075]** In one embodiment, the ash-free friction modifier may be represented by the formula:



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

[0076] In certain embodiments, the ash-free friction modifier is a fatty ester, amide, or imide of various hydroxy-carboxylic acids, such as tartaric acid, malic acid, lactic acid, glycolic acid, and mandelic acid. Examples of suitable materials include tartaric acid di(2-ethylhexyl) ester (i.e., di(2-ethylhexyl)tartrate), di(C₈-C₁₀)tartrate, di(C₁₂-C₁₅)tartrate, di-oleyltartrate, oleyltartramide, and oleyl maleimide.

[0077] In certain embodiments, the ash-free friction modifier may be chosen from long chain fatty acid derivatives of amines, fatty esters, or fatty epoxides; fatty imidazolines such as condensation products of carboxylic acids and polyalkylene-polyamines; amine salts of alkylphosphoric acids; fatty alkyl tartrates; fatty alkyl tartrimides; fatty alkyl tartramides; fatty

phosphonates; fatty phosphites; borated phospholipids, borated fatty epoxides; glycerol esters; borated glycerol esters; fatty amines; alkoxyated fatty amines; borated alkoxyated fatty amines; hydroxyl and polyhydroxy fatty amines including tertiary hydroxy fatty amines; hydroxy alkyl amides; metal salts of fatty acids; metal salts of alkyl salicylates; fatty oxazolines; fatty ethoxylated alcohols; condensation products of carboxylic acids and polyalkylene polyamines; or reaction products from fatty carboxylic acids with guanidine, aminoguanidine, urea, or thiourea and salts thereof.

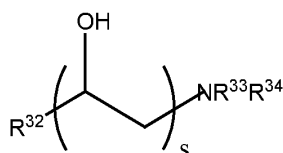
[0078] Friction modifiers may also encompass materials such as sulfurized fatty compounds and olefins, sunflower oil or soybean oil monoester of a polyol and an aliphatic carboxylic acid.

[0079] In another embodiment the friction modifier may be a long chain fatty acid ester. In another embodiment the long chain fatty acid ester may be a mono-ester and in another embodiment the long chain fatty acid ester may be a triglyceride.

[0080] The amount of the ash-free friction modifier in a lubricant may be 0.1 to 3 percent by weight (or 0.12 to 1.2 or 0.15 to 0.8 percent by weight). The material may also be present in a concentrate, alone or with other additives and with a lesser amount of oil. In a concentrate, the amount of material may be two to ten times the above concentration amounts.

[0081] Molybdenum compounds are also known as friction modifiers. The exemplary molybdenum compound does not contain dithiocarbamate moieties or ligands.

[0082] Nitrogen-containing molybdenum materials include molybdenum-amine compounds, as described in U.S. Pat. No. 6,329,327, and organomolybdenum compounds made from the reaction of a molybdenum source, fatty oil, and a diamine as described in U.S. Pat. No. 6,914,037. Other molybdenum compounds are disclosed in U.S. Pub. No. 20080280795. Molybdenum amine compounds may be obtained by reacting a compound containing a hexavalent molybdenum atom with a primary, secondary or tertiary amine represented by the formula $\text{NR}^{29}\text{R}^{30}\text{R}^{31}$, where each of R^{29} , R^{30} and R^{31} is independently hydrogen or a hydrocarbyl group of 1 to 32 carbon atoms and wherein at least one of R^{29} , R^{30} and R^{31} is a hydrocarbyl group of 4 or more carbon atoms or represented by the formula:



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

5 **[0083]** Specific examples of suitable amines include monoalkyl (or alkenyl) amines such as tetradecylamine, stearylamine, oleylamine, beef tallow alkylamine, hardened beef tallow alkylamine, and soybean oil alkylamine; dialkyl(or alkenyl)amines such as N-tetradecylmethylamine, N-pentadecylmethylamine, N-hexadecylmethylamine, N-stearylamine, N-oleylmethylamine, N-dococylmethylamine, N-beef tallow alkyl
10 methylamine, N-hardened beef tallow alkyl methylamine, N-soybean oil alkyl methylamine, ditetradecylamine, dipentadecylamine, dihexadecylamine, distearylamine, dioleylamine, didococylamine, bis(2-hexyldecyl)amine, bis(2-octyldodecyl)amine, bis(2-decyltetradecyl)amine, beef tallow dialkylamine, hardened beef tallow dialkylamine, and soybean oil dialkylamine; and trialk(en)ylamines such as tetradecyldimethylamine, hexadecyldimethylamine,
15 octadecyldimethylamine, beef tallow alkyldimethylamine, hardened beef tallow alkyldimethylamine, soybean oil alkyldimethylamine, dioleylmethylamine, tritetradecylamine, tristearylamine, and trioleylamine. Suitable secondary amines have two alkyl (or alkenyl) groups with 14 to 18 carbon atoms.

[0084] Examples of the compound containing the hexavalent molybdenum atom include
20 molybdenum trioxides or hydrates thereof ($MoO_3 \cdot nH_2O$), molybdenum acid (H_2MoO_4), alkali metal molybdates (Q_2MoO_4) wherein Q represents an alkali metal such as sodium and potassium, ammonium molybdates $\{(NH_4)_2MoO_4$ or heptamolybdate $(NH_4)_6[Mo_7O_{24}] \cdot 4H_2O\}$, $MoOCl_4$, MoO_2Cl_2 , MoO_2Br_2 , $Mo_2O_3Cl_6$ and the like. Molybdenum trioxides or hydrates thereof, molybdenum acid, alkali metal molybdates and ammonium molybdates are often suitable because
25 of their availability. In one embodiment, the lubricating composition comprises molybdenum amine compound.

[0085] Other organomolybdenum compounds of the invention may be the reaction products of fatty oils, mono-alkylated alkylene diamines and a molybdenum source. Materials of this sort are generally made in two steps, a first step involving the preparation of an aminoamide/glyceride
30 mixture at high temperature, and a second step involving incorporation of the molybdenum.

[0086] Examples of fatty oils that may be used include cottonseed oil, groundnut oil, coconut oil, linseed oil, palm kernel oil, olive oil, corn oil, palm oil, castor oil, rapeseed oil (low or high erucic acids), soyabean oil, sunflower oil, herring oil, sardine oil, and tallow. These fatty oils are generally known as glyceryl esters of fatty acids, triacylglycerols or triglycerides.

5 **[0087]** Examples of some mono-alkylated alkylene diamines that may be used include methylaminopropylamine, methylaminoethylamine, butylaminopropylamine, butylaminoethylamine, octylaminopropylamine, octylaminoethylamine, dodecylaminopropylamine, dodecylaminoethylamine, hexadecylaminopropylamine, hexadecylaminoethylamine, octadecylaminopropylamine, octadecylaminoethylamine, isopropoxypropyl-1,3-diaminopropane, and
10 octyloxypropyl-1,3-diaminopropane. Mono-alkylated alkylene diamines derived from fatty acids may also be used. Examples include N-coco alkyl-1,3-propanediamine (Duomeen[®]C), N-tall oil alkyl-1,3-propanediamine (Duomeen[®]T) and N-oleyl-1,3-propanediamine (Duomeen[®]O), all commercially available from Akzo Nobel.

[0088] Sources of molybdenum for incorporation into the fatty oil/diamine complex are
15 generally oxygen-containing molybdenum compounds include, similar to those above, ammonium molybdates, sodium molybdate, molybdenum oxides and mixtures thereof. One suitable molybdenum source comprises molybdenum trioxide (MoO₃).

[0089] Nitrogen-containing molybdenum compounds which are commercially available include, for example, Sakuralube[®] 710 available from Adeka which is a molybdenum amine
20 compound, and Molyvan[®] 855, available from R.T. Vanderbilt.

[0090] The nitrogen-containing molybdenum compound may be present in the lubricant composition at 0.005 to 2 wt. % of the composition, or 0.01 to 1.3 wt. %, or 0.02 to 1.0 wt. % of the composition. The molybdenum compound may provide the lubricant composition with 0 to 1000 ppm, or 5 to 1000 ppm, or 10 to 750 ppm 5 ppm to 300 ppm, or 20 ppm to 250 ppm of
25 molybdenum.

[0091] Demulsifiers useful herein include trialkyl phosphates, and various polymers and copolymers of ethylene glycol, ethylene oxide, propylene oxide, and mixtures thereof.

[0092] Seal swell agents useful herein include sulfolene derivatives such as Exxon Necton-37[™] (FN 1380) and Exxon Mineral Seal Oil[™] (FN 3200).

[0093] A lubricating composition may be prepared by adding the product of the process described herein to an oil of lubricating viscosity, optionally in the presence of other performance additives (as described herein below).

[0094] An engine lubricant in different embodiments may have a composition as illustrated in Table 1. All additives are expressed on an oil-free basis.

[0095] TABLE 1: Engine Lubricating Compositions

Additive	Embodiments (wt. %)		
	A	B	C
polyolefin-substituted hydroxy-aromatic carboxylic acid or salt thereof	0.1 to 20	0.5 to 10	1 to 5
Overbased Sulfonate Detergent	0 to 9	0.3 to 8	1 to 5
Phenol-based detergent	0 to 10	0.5 to 7	0.75 to 5
(Borated) Dispersant	0 to 12	0.5 to 8	1 to 5
Antioxidant	0 to 13	0.1 to 10	0.5 to 5
Antiwear Agent	0 to 15	0.1 to 10	0.3 to 5
Corrosion Inhibitor	0 to 2	0.1 to 1	0.2 to 0.5
Friction Modifier	0 to 6	0.05 to 4	0.1 to 2
Viscosity Modifier	0 to 10	0.5 to 8	1 to 6
Other Performance Additives	0 to 10	0 to 8	0 to 6
Oil of Lubricating Viscosity	Balance to 100 %		

[0096] Use of the Engine Lubricating Composition

[0097] The end use of the engine lubricating composition described herein includes use as a cylinder lubricant for an internal combustion engine, such as a 2-stroke marine diesel engine, but may also find use as an engine oil for a two or 4-stroke engine in a passenger car, heavy, medium and light duty diesel vehicles, small engines such as motorcycle and 2-stroke oil engines, as a driveline lubricant, including gear and automatic transmission oils, and for other industrial oils, such as hydraulic lubricants.

[0098] An exemplary method of lubricating a mechanical device, such as a cylinder of an internal combustion engine, includes supplying the exemplary lubricating composition to the device.

5 [0099] Generally, the lubricating composition is added to the lubricating system of an internal combustion engine, which then delivers the lubricating composition to the cylinder of the engine, during its operation, where it may be combusted with the fuel.

[0100] The internal combustion engine may be a diesel-fueled engine, such as a 2-stroke marine diesel engine, or a gasoline fueled engine, a natural gas fueled engine, a mixed gasoline/alcohol fueled engine, or a biodiesel fueled engine. The internal combustion engine may
10 be a 2-stroke or 4-stroke engine.

[0101] The lubricating composition may be suitable for use as a cylinder lubricant irrespective of the sulfur, phosphorus or sulfated ash (ASTM D-874) content of the fuel. The sulfur content of the lubricating composition, which is particularly suited to use as an engine oil lubricant, may be 1 wt. % or less, or 0.8 wt. % or less, or 0.5 wt. % or less, or 0.3 wt. % or less. In one embodiment,
15 the sulfur content may be in the range of 0.001 wt. % to 0.5 wt. %, or 0.01 wt. % to 0.3 wt. %. The phosphorus content may be 0.2 wt. % or less, or 0.12 wt. % or less, or 0.1 wt. % or less, or 0.085 wt. % or less, or 0.08 wt. % or less, or even 0.06 wt. % or less, 0.055 wt. % or less, or 0.05 wt. % or less. In one embodiment, the phosphorus content may be 100 ppm to 1000 ppm, or 200 ppm to 600 ppm. The total sulfated ash content may be 2 wt. % or less, or 1.5 wt. % or less, or 1.1 wt. %
20 or less, or 1 wt. % or less, or 0.8 wt. % or less, or 0.5 wt. % or less, or 0.4 wt. % or less. In one embodiment, the sulfated ash content may be 0.05 wt. % to 0.9 wt. %, or 0.1 wt. % to 0.2 wt. % or to 0.45 wt. %.

[0102] Other lubricating compositions may also be formulated using the polyolefin substituted hydroxy-aromatic carboxylic acid detergent of the present invention along with additional
25 additives. Exemplary other lubricating compositions are described below.

[0103] Driveline Lubricating Compositions

[0104] In one embodiment, the lubricating composition in accordance with the present invention is for use in a driveline device. Lubricating compositions for driveline devices may include the polyolefin-substituted hydroxy-aromatic carboxylic acid or salt thereof or salt thereof
30 as described herein in an oil of lubricating viscosity, optionally in the presence of other

performance additives, which may include dispersants, antiwear agents, dispersant viscosity modifiers, friction modifiers, viscosity modifiers, antioxidants, overbased detergents (other than the polyolefin-substituted hydroxy-aromatic carboxylic acid or salt thereof or salt thereof as described above), foam inhibitors, demulsifiers, or pour point depressants or mixtures thereof. In one embodiment the invention provides a lubricant composition comprising in addition to the polyolefin-substituted hydroxy-aromatic carboxylic acid or salt thereof, at least one of a polyisobutylene succinimide dispersant, an antiwear agent, a corrosion inhibitor, a dispersant viscosity modifier, a friction modifier, a viscosity modifier (typically a polymethacrylate having linear, comb or star architecture), an antioxidant (including phenolic and aminic antioxidants), an overbased detergent (including overbased sulphonates, phenates, and salicylates other than the polyolefin-substituted hydroxy-aromatic carboxylic acid or salt thereof or salt thereof described above), or mixtures thereof.

[0105] The amount of each other performance additive and chemistry of the other performance additive will depend on type of driveline device being lubricated. When present common additives across each driveline lubricant includes viscosity modifiers, dispersants, foam inhibitors, corrosion inhibitors, pour point depressants, demulsifiers, and seal swell agents.

[0106] Driveline lubricating compositions are described below. All additives are expressed on an oil-free basis.

[0107] Manual Transmission Lubricant

[0108] In one embodiment the invention provides a manual transmission lubricant composition comprising:

- an oil of lubricating viscosity,
- a thiadiazole (typically present at 0.05 to 1 wt %, or 0.07 to 0.7 wt %, or 0.1 to 0.3 wt %, or 0.15 to 0.25 wt %),
- a dispersant (typically present at 0.1 to 5 wt %, or 0.3 to 4 wt %, or 1 to 3 wt %, or 0.1 to 3 wt %),
- a phosphorus-containing antiwear agent chosen from (i) a non-ionic phosphorus compound, which may be a hydrocarbyl phosphite; or (ii) an amine salt of a phosphorus compound,

from about 0.1 to about 2 wt% of a detergent, typically present in an amount to deliver 110 to 700ppm, 130 to 600ppm, 150 to 500ppm or 160 to 400ppm calcium; and wherein from about 0.01 to about 2 wt%, or from about 0.1 to about 1.75 wt%, or about 0.2 to about 1.5 wt% of the detergent comprises the polyolefin-substituted hydroxy-aromatic carboxylic acid or salt thereof or salt thereof described herein.

[0109] The manual transmission may have synchromesh, or in another embodiment the manual transmission does not have a synchromesh. The synchromesh may be composed of aluminum, steel, bronze, molybdenum, brass (sintered or non-sintered), carbon in the form of fibers, graphitic material (optionally in combination with a cellulosic material), or a cellulosic material, or a phenolic resin.

[0110] In one embodiment the lubricant may comprise 0.03 to 1.0 wt %, or 0.1 to 0.6 wt %, or 0.2 to 0.5 wt % of calcium.

[0111] The lubricant may have 100 to 2000ppm, 150 to 1500ppm, 200 to 1000, or 250 to 800ppm, or 500 to 875 ppm of phosphorus delivered by an antiwear agent i.e., delivered by zinc dialkyl dithiophosphate or another phosphorus-containing antiwear agent.

[0112] In one embodiment the invention provides a method of lubricating a manual transmission comprising supplying to the manual transmission a lubricant composition comprising:

an oil of lubricating viscosity,

a thiadiazole (typically present at 0.05 to 1 wt %, or 0.07 to 0.7 wt %, or 0.1 to 0.3 wt %, or 0.15 to 0.25 wt %),

a dispersant (typically present at 0.1 to 5 wt %, or 0.3 to 4 wt %, or 1 to 3 wt %, or 0.1 to 3 wt %),

a phosphorus-containing antiwear agent chosen from (i) a non-ionic phosphorus compound, which may be a hydrocarbyl phosphite; or (ii) an amine salt of a phosphorus compound,

from about 0.1 to about 5 wt% of a detergent, typically present in an amount to deliver 110 to 700ppm, 130 to 600ppm, 150 to 500ppm or 160 to 400ppm calcium; and wherein from about 0.01 to about 2 wt%, or from about 0.1 to about 1.75 wt%, or about 0.2 to about 1.5 wt% of the

detergent comprises the polyolefin-substituted hydroxy-aromatic carboxylic acid or salt thereof described herein.

[0113] The thiadiazole compound may include mono- or di-hydrocarbyl substituted 2,5-dimercapto-1,3,4-thiadiazole compounds. Examples of a thiadiazole include 2,5-dimercapto-1,3,4-thiadiazole, or oligomers thereof, a hydrocarbyl-substituted 2,5-dimercapto-1,3,4-thiadiazole, a hydrocarbylthio-substituted 2,5-dimercapto-1,3,4-thiadiazole, or oligomers thereof. The oligomers of hydrocarbyl-substituted 2,5-dimercapto-1,3,4-thiadiazole typically form by forming a sulphur-sulphur bond between 2,5-dimercapto-1,3,4-thiadiazole units to form oligomers of two or more of said thiadiazole units. These thiadiazole compounds may also be used in the post treatment of dispersants as mentioned below in the formation of a dimercapthiadiazole derivative of a polyisobutylene succinimide.

[0114] Examples of a suitable thiadiazole compound include at least one of a dimercapthiadiazole, 2,5-dimercapto-[1,3,4]-thiadiazole, 3,5-dimercapto-[1,2,4]-thiadiazole, 3,4-dimercapto-[1,2,5]-thiadiazole, or 4,5-dimercapto-[1,2,3]-thiadiazole. Typically readily available materials such as 2,5-dimercapto-1,3,4-thiadiazole or a hydrocarbyl-substituted 2,5-dimercapto-1,3,4-thiadiazole or a hydrocarbylthio-substituted 2,5-dimercapto-1,3,4-thiadiazole are commonly utilised.

[0115] The other additives used in the manual transmission fluid may be selected from those described herein, or known to those skilled in the art, or those hereafter developed.

Automatic Transmission Lubricants

[0116] In one embodiment the invention provides an automatic transmission lubricant composition comprising:

an oil of lubricating viscosity,

a dispersant typically present at 0.01 to 5 wt %, or 0.05 to 3 wt %, or 0.1 to 3 wt %, or 0.1 to 2 wt %,

from about 0.1 to about 1, typically present in an amount to deliver 40 to 1000ppm, 50 to 700ppm, 60 to 600ppm or 70 to 250ppm calcium; and wherein from about 0.01 to about 0.8 wt%, or from about 0.1 to about 0.5 wt%, or about 0.2 to about 0.15 wt% of the detergent comprises the polyolefin-substituted hydroxy-aromatic carboxylic acid or salt thereof or salt thereof described herein, and

a friction modifier typically present at 0 to 4 wt %, or 0.1 to 4 wt %, 0.2 to 3 wt %, 0.3 to 3 wt %, 0.25 to 2.5 wt%. In one embodiment the friction modifier is present, and in an alternative embodiment the friction modifier is not present.

[0117] In one embodiment the invention provides a method of lubricating an automatic transmission comprising supplying to the automatic transmission a lubricant composition comprising:

an oil of lubricating viscosity,

a dispersant typically present at 0.5 to 3 wt %, or 1 to 2.5 wt %, or 1.5 to 4 wt %, or 1.5 to 3 wt %,

a phosphorus-containing antiwear agent chosen from (i) a non-ionic phosphorus compound, which may be a hydrocarbyl phosphite; or (ii) an amine salt of a phosphorus compound,

a thiadiazole, typically present at 0.1 to 0.5 wt %, or 0.2 to 0.4 wt %, or 0.25 to 0.35 wt %.

from about 0.1 to about 5 wt% of a detergent, typically present in an amount to deliver 40 to 700ppm, 50 to 600ppm, 60 to 500ppm or 70 to 250ppm calcium; and wherein from about 0.01 to about 2 wt%, or from about 0.1 to about 1.75 wt%, or about 0.2 to about 1.5 wt% of the detergent comprises the polyolefin-substituted hydroxy-aromatic carboxylic acid or salt thereof or salt thereof described herein, and

a friction modifier typically present at 0 to 4 wt %, or 0.1 to 4 wt %, 0.2 to 3 wt %, 0.3 to 3 wt %, 0.25 to 2.5 wt%. In one embodiment the friction modifier is present, and in an alternative embodiment the friction modifier is not present.

[0118] The automatic transmission includes continuously variable transmissions (CVT), infinitely variable transmissions (IVT), Toroidal transmissions, continuously slipping torque converted clutches (CSTCC), stepped automatic transmissions or dual clutch transmissions (DCT).

[0119] The other additives used in the automatic transmission fluid may be selected from those described herein, or known to those skilled in the art, or those hereafter developed.

[0120] The automatic transmission lubricant composition described herein may contain a calcium-containing detergent, other than the polyolefin-substituted hydroxy-aromatic carboxylic

acid of the present invention. The optional additional detergent may be an overbased detergent, a non-overbased detergent, or mixtures thereof. Typically the detergent may be overbased.

Off-Highway Vehicle

[0121] The polyolefin-substituted hydroxy-aromatic carboxylic acid or salt thereof or salt thereof described herein can be employed in lubricating compositions for off-highway vehicles, such as, for example, farm tractors and construction vehicles. Such vehicles often have a common sump that lubricates not only the transmission but also the gears, axles, and hydraulics in the vehicle. In one embodiment the invention includes a lubricant composition comprising:

an oil of lubricating viscosity,
a dispersant typically present at 0.1 to 3 wt %, or 0.1 to 2.5 wt %, or 0.2 to 2 wt %, from about 0.1 to about 5 wt% of a detergent, typically present in an amount to deliver 100 to 5000ppm, 500 to 4500ppm, 500 to 4250ppm, 650 to 4200ppm calcium; and wherein from about 0.01 to about 2 wt%, or from about 0.1 to about 1.75 wt%, or about 0.2 to about 1.5 wt% of the detergent comprises the polyolefin-substituted hydroxy-aromatic carboxylic acid or salt thereof or salt thereof described herein.

[0122] In one embodiment the invention includes a method of lubricating an off-highway vehicle comprising supplying to the vehicle a lubricant composition comprising:

an oil of lubricating viscosity,
a dispersant typically present at 0.1 to 3 wt %, or 0.1 to 2.5 wt %, or 0.2 to 2 wt %, a phosphorus-containing antiwear agent chosen from (i) a non-ionic phosphorus compound, which may be a hydrocarbyl phosphite, such as a zinc dialkyldithiophosphate; or (ii) an amine salt of a phosphorus compound,
from about 0.1 to about 5 wt% of a detergent, typically present in an amount to deliver 10 to 5000ppm, 500 to 4500ppm, 500 to 4250ppm, 650 to 4200ppm calcium; and wherein from about 0.01 to about 2 wt%, or from about 0.1 to about 1.75 wt%, or about 0.2 to about 1.5 wt% of the detergent comprises the polyolefin-substituted hydroxy-aromatic carboxylic acid or salt thereof or salt thereof described herein.

[0123] The off-highway vehicle lubricated typically has a wet-brake, a transmission, a hydraulic, a final drive, a power take-off system. These parts are typically lubricated by a single

lubricant supplied from a common sump. The transmission may be a manual transmission or an automatic transmission.

[0124] The other additives used in the off-highway vehicle may be selected from those described herein, or known to those skilled in the art, or those hereafter developed.

5 Hydraulics Oil, Turbine Oil or Circulating Oil

[0125] In one embodiment, the lubricating composition in accordance with the present invention is for use in a hydraulic system, turbine system or a circulating oil system. A hydraulic system is generally a device or apparatus in which a fluid, typically an oil-based fluid, transmits energy to different parts of the system by hydraulic force. A turbine lubricant is typically used to
10 lubricate the gears or other moving parts of a turbine (or turbine system), such as a steam turbine or a gas turbine. A circulating oil is typically used to distribute heat to or through a device or apparatus through which it is circulated.

[0126] In one embodiment the lubricant composition contains the polyolefin-substituted hydroxy-aromatic carboxylic acid or salt thereof or salt thereof as described herein in an amount
15 from 0.001 wt % or 0.005 wt % to 5 wt %, or 0.01 wt % or 0.05 wt % to 1.5 wt %, 0.05 wt % to 1 wt %, 0.01 wt % to 1 wt %, 0.01 wt % to 0.5 wt % of the overall composition.

[0127] The hydraulic, turbine, or circulating lubricant compositions may also contain one or more additional additives. In some embodiments the additional additives may include an antioxidant, an anti-wear agent, a corrosion inhibitor, a rust inhibitor, a foam inhibitor, a
20 dispersant, a demulsifier, a metal deactivator, a friction modifier, a detergent, other than the polyolefin-substituted hydroxy-aromatic carboxylic acid or salt thereof or metal salt thereof of the present invention, an emulsifier, an extreme pressure agent, a pour point depressant, a viscosity modifier, or any combination thereof.

[0128] The lubricant may thus comprise an antioxidant, or mixtures thereof. The anti-oxidant
25 may be present at 0 wt % to 4.0 wt %, or 0.02 wt % to 3.0 wt %, or 0.03 wt % to 1.5 wt % of the lubricant.

[0129] The lubricant compositions may also include a dispersant or mixtures thereof. Suitable dispersants include: (i) polyetheramines; (ii) borated succinimide dispersants; (iii) non-borated succinimide dispersants; (iv) Mannich reaction products of a dialkylamine, an aldehyde and a
30 hydrocarbyl substituted phenol; or any combination thereof. In some embodiments the dispersant

may be present at 0 wt % or 0.01 wt % to 2.0 wt%, 0.05 wt% to 1.5 wt %, or 0.005 wt % to 1 wt %, or 0.05 wt % to 0.5 wt % of the overall composition.

[0130] Anti-foam agents, also known as foam inhibitors, are known in the art and include organic silicones and non-silicon foam inhibitors. Examples of organic silicones include dimethyl
5 silicone and polysiloxanes. Examples of non-silicon foam inhibitors include copolymers of ethyl acrylate and 2-ethylhexylacrylate, terpolymers of ethyl acrylate, 2-ethylhexylacrylate and vinyl acetate, polyethers, polyacrylates and mixtures thereof. In some embodiments the anti-foam is a polyacrylate. Antifoams may be present in the composition from 0.001 wt % to 0.012 wt % or 0.004 wt % or even 0.001 wt % to 0.003 wt %.

10 **[0131]** Demulsifiers are known in the art and include derivatives of propylene oxide, ethylene oxide, polyoxyalkylene alcohols, alkyl amines, amino alcohols, diamines or polyamines reacted sequentially with ethylene oxide or substituted ethylene oxides or mixtures thereof. Examples of demulsifiers include polyethylene glycols, polyethylene oxides, polypropylene oxides, (ethylene oxide-propylene oxide) polymers and mixtures thereof. In some embodiments the demulsifiers is
15 a polyether. Demulsifiers may be present in the composition from 0.002 wt % to 0.012 wt %.

[0132] Pour point depressants are known in the art and include esters of maleic anhydride-styrene copolymers, polymethacrylates; polyacrylates; polyacrylamides; condensation products of
haloparaffin waxes and aromatic compounds; vinyl carboxylate polymers; and terpolymers of
20 dialkyl fumarates, vinyl esters of fatty acids, ethylene-vinyl acetate copolymers, alkyl phenol formaldehyde condensation resins, alkyl vinyl ethers and mixtures thereof.

[0133] The lubricant composition may also include a rust inhibitor. Suitable rust inhibitors include hydrocarbyl amine salts of alkylphosphoric acid, hydrocarbyl amine salts of dialkyldithiophosphoric acid, hydrocarbyl amine salts of hydrocarbyl aryl sulfonic acid fatty
25 carboxylic acids or esters thereof, an ester of a nitrogen-containing carboxylic acid, an ammonium sulfonate, an imidazoline, alkylated succinic acid derivatives reacted with alcohols or ethers, or any combination thereof; or mixtures thereof.

[0134] The rust inhibitors may be present in the range from 0 or 0.02 wt % to 0.2 wt %, from 0.03 wt % to 0.15 wt % , from 0.04 wt % to 0.12 wt %, or from 0.05 wt % to 0.1 wt % of the lubricating oil composition. The rust inhibitors may be used alone or in mixtures thereof.

[0135] The lubricant may contain a metal deactivator, or mixtures thereof. Metal deactivators may be chosen from a derivative of benzotriazole (typically tolyltriazole), 1,2,4-triazole, benzimidazole, 2-alkyldithiobenzimidazole or 2-alkyldithiobenzothiazole, 1-amino-2-propanol, a derivative of dimercaptothiadiazole, octylamine octanoate, condensation products of dodecenyl succinic acid or anhydride and/or a fatty acid such as oleic acid with a polyamine. The metal deactivators may also be described as corrosion inhibitors.

[0136] The metal deactivators may be present in the range from 0 or 0.001 wt % to 0.1 wt %, from 0.01 wt % to 0.04 wt % or from 0.015 wt % to 0.03 wt % of the lubricating oil composition. Metal deactivators may also be present in the composition from 0.002 wt % or 0.004 wt % to 0.02 wt %. The metal deactivator may be used alone or mixtures thereof.

[0137] In one embodiment the invention provides a lubricant composition further comprises a metal-containing detergent, other than the polyolefin-substituted hydroxy-aromatic carboxylic acid or salt thereof as described herein. The additional metal-containing detergent may be present at 0 wt % to 5 wt %, or 0.001 wt % to 1.5 wt %, or 0.005 wt % to 1 wt %, or 0.01 wt % to 0.5 wt % of the hydraulic composition.

[0138] The lubricant may comprise an extreme pressure agent. The extreme pressure agent may be a compound containing sulfur and/or phosphorus. Examples of extreme pressure agents include polysulfides, sulfurized olefins, thiadiazoles, or mixtures thereof.

[0139] The extreme pressure agent may be present at 0 wt % to 3 wt %, 0.005 wt % to 2 wt %, 0.01 wt % to 1.0 wt % of the hydraulics composition.

[0140] The lubricant may further comprise a viscosity modifier, or mixtures thereof. Viscosity modifiers (often referred to as viscosity index improvers) suitable for use in the invention include polymeric materials including a styrene-butadiene rubber, an olefin copolymer, a hydrogenated styrene-isoprene polymer, a hydrogenated radical isoprene polymer, a poly(meth)acrylic acid ester, a polyalkylstyrene, an hydrogenated alkenylaryl conjugated-diene copolymer, an ester of maleic anhydride-styrene copolymer or mixtures thereof. In some embodiments the viscosity modifier is a poly(meth)acrylic acid ester, an olefin copolymer or mixtures thereof. The viscosity modifiers may be present at 0 wt % to 10 wt %, 0.5 wt % to 8 wt %, 1 wt % to 6 wt % of the lubricant.

[0141] In one embodiment the lubricant disclosed herein may contain at least one friction modifier. The friction modifier may be present at 0 wt % to 3 wt %, or 0.02 wt % to 2 wt %, or 0.05 wt % to 1 wt %, of the lubricant composition.

[0142] In one embodiment the lubricant composition further includes an anti-wear agent. Typically the anti-wear agent may be a phosphorus anti-wear agent or mixtures thereof. The anti-wear agent may be present at 0 wt % to 5 wt %, 0.001 wt % to 2 wt %, 0.01 wt % to 1.0 wt % of the lubricant.

[0143] A hydraulic lubricant may thus comprise:
0.01 wt % to 2 wt % of the polyolefin-substituted hydroxy-aromatic carboxylic acid or
10 salt thereof or salt thereof as described herein,
0.0001 wt % to 0.15 wt % of a corrosion inhibitor chosen from 2,5-bis(tert-dodecyldithio)-1,3,4-thiadiazole, tolyltriazole, or mixtures thereof,
an oil of lubricating viscosity,
0.02 wt % to 3 wt % of antioxidant chosen from aminic or phenolic antioxidants, or
15 mixtures thereof,
0 wt % to 1.5 wt % of a dispersant such as a borated succinimide or a non-borated succinimide dispersant or a substantially nitrogen free dispersants as described herein,
0.001 wt % to 1.5 wt % of a neutral or slightly overbased calcium sulfonate and
0.001 wt % to 2 wt %, or 0.01 wt % to 1 wt % of an anti-wear agent chosen from zinc
20 dialkyldithiophosphate, zinc dialkylphosphate, amine salt of a phosphorus acid ester, or mixtures thereof.

[0144] A hydraulic lubricant may thus comprise:
0.01 wt % to 1.5 wt % of of the polyolefin-substituted hydroxy-aromatic carboxylic acid or salt thereof or salt thereof as described herein,
25 0.0001 wt % to 0.15 wt % of a corrosion inhibitor chosen from 2,5-bis(tert-dodecyldithio)-1,3,4-thiadiazole, tolyltriazole, or mixtures thereof,
an oil of lubricating viscosity,
0.02 wt % to 3 wt % of antioxidant chosen from aminic or phenolic antioxidants, or mixtures thereof,

0.005 wt % to 1.5 wt % of a dispersant, such as a borated succinimide or a non-borated succinimide dispersant or a substantially nitrogen free dispersant as described herein,

0.001 wt % to 1.5 wt % of a neutral or slightly overbased calcium sulfonate

0.001 wt % to 2 wt %, or 0.01 wt % to 1 wt % of an anti-wear agent chosen from zinc dialkyldithiophosphate, zinc dialkylphosphate, amine salt of a phosphorus acid ester, or mixtures thereof.

[0145] A hydraulic lubricant may also comprise a formulation defined in the following table:

TABLE 2: Hydraulic Lubricant Compositions

Hydraulic Lubricant compositions			
Additive	Embodiments (wt %)		
	A	B	C
Polyolefin-substituted hydroxy-aromatic carboxylic acid or salt thereof as described herein	0.01 to 2.0	0.01 to 1.5	0.01 to 1.0
Antioxidant	0 to 4.0	0.02 to 3.0	0.03 to 1.5
Dispersant	0 to 2.0	0.005 to 1.5	0.01 to 1.0
Detergent	0 to 5.0	0.001 to 1.5	0.005 to 1.0
Anti-wear Agent	0 to 5.0	0.001 to 2	0.1 to 1.0
Friction Modifier	0 to 3.0	0.02 to 2	0.05 to 1.0
Viscosity Modifier	0 to 10.0	0.5 to 8.0	1.0 to 6.0
Any Other Performance Additive (antifoam / demulsifier/pour point depressant)	0 to 1.3	0.00075 to 0.5	0.001 to 0.4
Metal Deactivator	0 to 0.1	0.01 to 0.04	0.015 to 0.03
Rust Inhibitor	0 to 0.2	0.03 to 0.15	0.04 to 0.12
Extreme Pressure Agent	0 to 3.0	0.005 to 2	0.01 to 1.0
Oil of Lubricating Viscosity	Balance to 100 %	Balance to 100 %	Balance to 100 %

[0146] Specific examples of a hydraulic lubricant include those summarized in the following table:

Table 3: Hydraulic Lubricant Compositions

Additive	Embodiments (wt %)		
	A	B	C
Polyolefin-substituted hydroxy-aromatic carboxylic acid or salt thereof as described herein	0.02	0.06	0.30
Antioxidant- aminic /phenolic	0.4	0.4	0.4
Calcium Sulfonate Detergent	0.02	0.1	0.2
Zinc dialkyl dithiophosphate	0.2	0.5	1.0
Any Other Performance Additive (antifoam /demulsifier/pour point depressant)	0.2	0.6	1.0
Triazole Metal Deactivator	0.005	0.0075	0.01
Oil of Lubricating Viscosity	Balance to 100 %	Balance to 100 %	Balance to 100 %

- 5 **[0147]** The other additives used in the hydraulic lubricant may be selected from those described herein, or known to those skilled in the art, or those hereafter developed.

EXAMPLES

[0148] A detergent in accordance with the present invention was prepared as follows:

- [0149]** A PIB phenol was prepared by reacting a high vinylidene 550 Mn polyisobutylene with
 10 phenol using BF₃ as a catalyst. The PIB phenol was then reacted with KOH to give potassium phenate, which was then heated to 150°C and vacuum stripped (25 mmHg/5 h) to remove water and the mixture was then exposed to CO₂ for 5 hrs. The final material was found to have a ratio of pib salicylate to pib phenol of 66% to 34% (determined by ¹³C NMR), %K = 3.31%, TBN = 56.41, 50% actives in dil oil. The potassium phenate/salicylate was then converted to an overbased
 15 calcium salicylate by treatment with 90 g CaCl₂ in MAOL (360 g) at 60 °C for 1 h. Hydrated lime (55 g), acetic acid (50% aq. solution) and a mixture and isobutyl and amyl alcohol (100 g) were

added and CO₂ was bubbled through the mixture at 60 °C for 40 minutes (0.6 cfh) to a DBN of 11. Volatile solvents were removed by vacuum distillation (150 °C, 25 mmHg, 30 minutes). The reaction mixture was then filtered and clear brown liquid was obtained. The final product was found to have 115 TBN by NN₂₉C, %K = 4.71 by D4951, SA = 15.665% by D874

5 **[0150]** The Total Base Number (TBN) may be determined using the methodology of ASTM D2896.

10 **[0151]** Lubricating compositions incorporating the polyolefin-substituted hydroxy-aromatic carboxylic acid of the present invention may be prepared as described herein and evaluated for cleanliness, i.e. the ability to prevent or reduce deposit formation; sludge handling; soot handling; antioxidancy; and wear reduction, anti-wear performance, deposit control, and oxidation control, among others.

15 **[0152]** Sludge handling performance of each lubricant may be evaluated in accordance with ASTM D4310-10 (Standard Test Method for Determination of Sludging and Corrosion Tendencies of Inhibited Mineral Oils). Performance is judged by measuring the total amount of sludge formed during the oxidation of lubricants and mineral oil based fluids in the presence of oxygen, water and copper and iron metals at elevated temperatures as well as the ability of these oils to corrode copper catalyst metals.

20 **[0153]** Anti-wear performance is measured in a programmed temperature high frequency reciprocating rig (HFRR) available from PCS Instruments. HFRR conditions for the evaluations are 200 g load, 75 minute duration, 1000 micrometer stroke, 20 hertz frequency, and temperature profile of 15 minutes at 40 °C followed by an increase in temperature to 160 °C at a rate of 2 °C per minute. Wear scar in micrometers and film formation as percent film thickness are then measured with lower wear scar values and higher film formation values indicating improved wear performance.

25 **[0154]** Deposit control is measured by the Komatsu Hot Tube (KHT) test, which employs heated glass tubes through which sample lubricant is pumped, approximately 5 mL total sample, typically at 0.31 mL/hour for an extended period of time, such as 16 hours, with an air flow of 10 mL/minute. The glass tube is rated at the end of test for deposits on a scale of 0 (very heavy varnish) to 10 (no varnish).

[0155] In the Panel Coker deposit test, the sample, at 105 °C., is splashed for 4 hours on an aluminum panel maintained at 325 °C. The aluminum plates are analyzed using image analysis techniques to obtain a universal rating. The rating score is based on “100” being a clean plate and “0” being a plate wholly covered in deposit.

5 [0156] Oxidation control is evaluated utilizing pressure differential scanning calorimetry (PDSC) which determines oxidation induction time (OIT) for lubricating compositions. This is a standard test procedure in the lubricating oil industry, based on CEC L-85 T-99. In this testing the lubricating composition is heated to an elevated temperature, typically about 25 °C below the average decomposition temperature for the sample being tested (in this case 215 °C at 690 kPa),
10 and the time to when the composition begins to decompose is measured. The longer the test time, reported in minutes, the better the oxidative stability of the composition and the additives present within it.

[0157] Driveline lubricating compositions, such as transmission fluids may be assessed for friction performance and durability using tests such as the variable speed friction test, friction
15 coefficient testing based on Falex LFW-1 or JASO M358, VT20 Durability test, JASO M349 anti-shudder durability test, or testing using an Automax® rig.

[0158] It is known that some of the materials described above may interact in the final formulation, so that the components of the final formulation may be different from those that are initially added. The products formed thereby, including the products formed upon employing
20 lubricant composition of the present invention in its intended use, may not be susceptible of easy description. Nevertheless, all such modifications and reaction products are included within the scope of the present invention; the present invention encompasses lubricant composition prepared by admixing the components described above.

[0159] Each of the documents referred to above is incorporated herein by reference. Except in
25 the Examples, or where otherwise explicitly indicated, all numerical quantities in this description specifying amounts of materials, reaction conditions, molecular weights, number of carbon atoms, and the like, are to be understood as modified by the word “about”. Unless otherwise indicated, each chemical or composition referred to herein should be interpreted as being a commercial grade material which may contain the isomers, by-products, derivatives, and other such materials which
30 are normally understood to be present in the commercial grade. However, the amount of each

chemical component is presented exclusive of any solvent or diluent oil, which may be customarily present in the commercial material, unless otherwise indicated. It is to be understood that the upper and lower amount, range, and ratio limits set forth herein may be independently combined. Similarly, the ranges and amounts for each element of the invention may be used together with
5 ranges or amounts for any of the other elements.

[0160] While the invention has been explained in relation to its preferred embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.