

LUBRICATING ENGINE OIL COMPOSITIONS CONTAINING DETERGENT COMPOUNDS

This application claims the benefit of and priority to U.S. Provisional Application Ser. No. 62/527,211, filed June 30, 2017.

BACKGROUND OF THE DISCLOSURE

[0001] Neutral and Overbased detergents are well described to provide lubricating properties. Often such detergent additives are proportioned with other lubricating additives to provide lubricating oil compositions that exhibit certain desired lubricating properties. Metal-containing detergents function both as detergents to control deposits, and as acid neutralizers or rust inhibitors, thereby reducing wear and corrosion and extending engine life. Detergents are utilized in lubricants for these benefits, but there are drawbacks to their use as well. Detergents are known to be detrimental to friction performance. Increased friction is associated with decreased fuel economy so this can be a drawback as fuel economy improvement is important for environmental and cost saving reasons.

[0002] A major challenge in engine oil formulation is developing lubricating oil compositions which simultaneously achieve wear control and inhibits corrosion, while also achieving improved fuel economy. Surprisingly, it has been found that lubricants formulated with alkylhydroxybenzoate detergents derived from isomerized normal alpha olefins show improvements in oxidation reduction, corrosion inhibition and friction performance.

SUMMARY OF THE DISCLOSURE

[0003] In accordance with one embodiment of the present disclosure, there is provided a lubricating oil composition which comprises:

- a. a major amount of an oil of lubricating viscosity, and
- b. an alkylhydroxybenzoate compound derived from C₁₀-C₄₀ isomerized normal alpha olefins, wherein the TBN of the alkylhydroxybenzoate detergents from 10 to 300 mgKOH/gm on an oil-free basis.

Also provided is a method of lubricating an engine comprising lubricating said engine with a lubricating oil composition comprising:

- a. a major amount of an oil of lubricating viscosity, and

- b. an alkylhydroxybenzoate compound derived from C₁₀-C₄₀ isomerized normal alfa olefins, wherein the TBN of the alkylhydroxybenzoate compound is 10 - 300 mgKOH/gm on an oil-free basis.

DETAILED DESCRIPTION OF THE DISLCOSURE

[0004] While the invention is susceptible to various modifications and alternative forms, specific embodiments thereof are herein described in detail. It should be understood, however, that the description herein of specific embodiments is not intended to limit the invention to the particular forms disclosed, but on the contrary, the intention is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the invention as defined by the appended claims.

[0005] To facilitate the understanding of the subject matter disclosed herein, a number of terms, abbreviations or other shorthand as used herein are defined below. Any term, abbreviation or shorthand not defined is understood to have the ordinary meaning used by a skilled artisan contemporaneous with the submission of this application.

DEFINITIONS

[0006] As used herein, the following terms have the following meanings, unless expressly stated to the contrary. In this specification, the following words and expressions, if and when used, have the meanings given below.

[0007] A "major amount" means in excess of 50 weight % of a composition.

[0008] A "minor amount" means less than 50 weight % of a composition, expressed in respect of the stated additive and in respect of the total mass of all the additives present in the composition, reckoned as active ingredient of the additive or additives.

[0009] "Active ingredients" or "actives" refers to additive material that is not diluent or solvent.

[0010] All percentages reported are weight % on an active ingredient basis (i.e., without regard to carrier or diluent oil) unless otherwise stated.

[0011] The abbreviation "ppm" means parts per million by weight, based on the total weight of the lubricating oil composition.

[0012] Total base number (TBN) was determined in accordance with ASTM D2896.

[0013] High temperature high shear (HTHS) viscosity at 150°C was determined in accordance with ASTM D4863.

[0014] Kinematic viscosity at 100°C (KV₁₀₀) was determined in accordance with ASTM D445.

[0015] Cold Cranking Simulator (CCS) viscosity at -35°C was determined in accordance with ASTM D5293.

[0016] Noack volatility was determined in accordance with ASTM D5800 Metal – The term “metal” refers to alkali metals, alkaline earth metals, or mixtures thereof.

[0017] Olefins – The term “olefins” refers to a class of unsaturated aliphatic hydrocarbons having one or more carbon-carbon double bonds, obtained by a number of processes. Those containing one double bond are called mono-alkenes, and those with two double bonds are called dienes, alkyldienes, or diolefins. Alpha olefins are particularly reactive because the double bond is between the first and second carbons. Examples are 1-octene and 1-octadecene, which are used as the starting point for medium-biodegradable surfactants. Linear and branched olefins are also included in the definition of olefins.

[0018] Normal Alpha Olefins – The term “Normal Alpha Olefins” “refers to olefins which are straight chain, non-branched hydrocarbons with carbon-carbon double bond present in the alpha or primary position of the hydrocarbon chain.

[0019] Isomerized Normal Alpha Olefin- The term “Isomerized Normal Alpha Olefin” as used herein refers to an alpha olefin that has been subjected to isomerization conditions which results in an alteration of the distribution of the olefin species present and/or the introduction of branching along the alkyl chain. The isomerized olefin product may be obtained by isomerizing a linear alpha olefin containing from about 10 to about 40 carbon atoms, preferably from about 20 to about 28 carbon atoms, and preferably from about 20 to about 24 carbon atoms.

[0020] All ASTM standards referred to herein are the most current versions as of the filing date of the present application.

[0021] In one aspect, the present disclosure is directed to a lubricating oil composition comprising:

- (a) a major amount of an oil of lubricating viscosity, and
- (b) a alkylhydroxybenzoate compound derived from C₁₀ - C₄₀ isomerized normal alpha olefins, wherein the alkylhydroxybenzoate compound has a TBN 10 - 300 mgKOH/gm on an oil-free basis.

[0022] In another aspect, the lubricating oil composition comprises a molybdenum compound.

[0023] In another aspect, provided is a method of lubricating an engine comprising lubricating said engine with lubricating oil composition comprising:

(a) a major amount of an oil of lubricating viscosity, and (b) an alkylhydroxybenzoate compound derived from C₁₀-C₄₀ isomerized normal alpha olefins, wherein the TBN of the alkylhydroxybenzoate compound is 10 - 300 mgKOH/gm on an oil-free basis.

[0024] In another aspect, the present disclosure generally relates to lubricating oil compositions which are suitable for automotive engines, motorcycle engines, natural gas engines, dual fuel engines, railroad locomotive engines, mobile natural gas engines, and as functional fluids for automotive and industrial applications.

[0025] Alkylhydroxybenzoate detergent derived from isomerized Normal Alpha Olefin (NAO)

[0026] In one aspect of the present disclosure, the alkylhydroxybenzoate detergent derived from C₁₀-C₄₀ isomerized NAO has a TBN of from 10 to 300, preferably from 50 to 300, more preferably from 100 to 300, even more preferably from 150 to 300, and most preferably from 175 to 250 mgKOH/gram on active basis.

[0027] In one aspect of the present disclosure, the alkylhydroxybenzoate detergent derived from C₁₀-C₄₀ isomerized NAO is a Ca alkylhydroxybenzoate detergent.

[0028] In one aspect of the present disclosure, the alkylhydroxybenzoate detergent derived from C₁₀-C₄₀ isomerized NAO can be an alkylated hydroxybenzoate detergent. In another embodiment, the detergent can be a salicylate detergent. In another embodiment, the detergent can be a carboxylate detergent.

[0029] In one aspect of the present disclosure, the alkylhydroxybenzoate derived from C₁₀-C₄₀ isomerized NAO having a TBN from 10 to 300 on an oil-free basis may be prepared as described in US Patent 8,893,499 which is herein incorporated in its entirety.

[0030] In one aspect of the present disclosure, the alkylhydroxybenzoate detergent having a TBN from 10 to 300 on an oil-free basis is made from an alkylphenol having an alkyl group derived from an isomerized alpha olefin having from about 14 to about 28 carbon atoms per molecule, preferably from about 20 to about 24 carbon, or preferably from about 20 to about 28 carbon atoms per molecule.

[0031] In one aspect of the present disclosure, the alkylhydroxybenzoate derived from C₁₀-C₄₀ isomerized NAO having a TBN from 10 to 300 on an active basis is made from an alkylphenol with an alkyl group derived from an isomerized NAO having an isomerization level (i) from about 0.10 to about 0.40, preferably from about 0.10 to about 0.35, preferably from about 0.10 to about 0.30, and more preferably from about 0.12 to about 0.30.

[0032] In one aspect of the present disclosure, the alkylhydroxybenzoate derived from C₁₀-C₄₀ isomerized NAO having a TBN from 10 to 300 on an active basis is made from one or more alkylphenols with an alkyl group derived from C₁₀-C₄₀ isomerized NAO and one or more alkylphenols with an alkyl group different from C₁₀-C₄₀ isomerized NAO.

[0033] In one aspect of the present disclosure, the isomerized NAO of the alkylhydroxybenzoate has an isomerization level of about 0.16, and has from about 20 to about 24 carbon atoms.

[0034] In one aspect of the present disclosure, the isomerized NAO of the alkylhydroxybenzoate has an isomerization level of about 0.26, and has from about 20 to about 24 carbon atoms.

[0035] In one aspect of the present disclosure, the lubricating oil composition comprises about 0.01 to 2.0 wt.% in terms of Ca content of the alkylhydroxybenzoate derived from C₁₀-C₄₀ isomerized NAO having a TBN from 10 to 300 on an active basis, preferably 0.1 to 1.0 wt. %, more preferably 0.05 to 0.5 wt. %, more preferably 0.1 to 0.5 wt.%.

[0036] In one aspect of the present disclosure, the lubricating oil composition comprising the alkylhydroxybenzoate derived from C₁₀-C₄₀ isomerized NAO having a TBN from 10 to 300 on an oil-free basis is an automotive engine oil composition, a gas engine oil composition, a dual fuel engine oil composition, a mobile gas engine oil composition, or a locomotive engine oil composition.

[0037] In one aspect of the present disclosure, the lubricating oil composition comprising the alkylhydroxybenzoate derived from C₁₀-C₄₀ isomerized NAO having a TBN from 10 to 300 on an oil-free basis is a functional fluid for automotive and industrial applications, such as transmission oil, hydraulic oil, tractor fluid, gear oil, and the like.

[0038] In one aspect of the present disclosure, the lubricating oil composition comprising the alkylhydroxybenzoate derived from C₁₀-C₄₀ isomerized NAO having a TBN from 10 to 300 on an oil-free basis is a multi-grade oil or mono-grade oil.

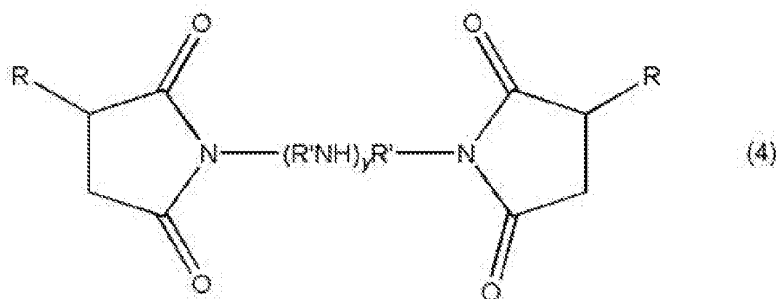
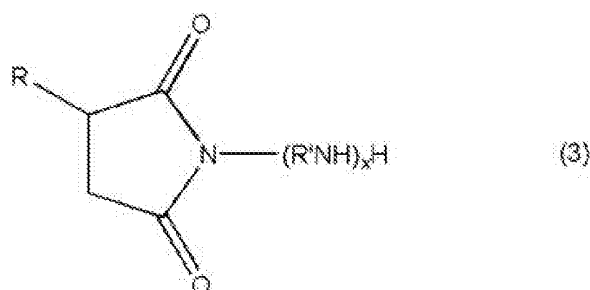
[0039] In one aspect of the present disclosure, the lubricating oil composition comprising the alkylhydroxybenzoate derived from C₁₀-C₄₀ isomerized NAO having a TBN from 10 to 300 on an oil-free basis lubricates crankcases, gears, as well as clutches.

Organomolybdenum compound

[0040] The organomolybdenum compound contains at least molybdenum, carbon and hydrogen atoms, but may also contain sulfur, phosphorus, nitrogen and/or oxygen atoms. Suitable organomolybdenum compounds include molybdenum dithiocarbamates,

molybdenum dithiophosphates, and various organic molybdenum complexes such as molybdenum carboxylates, molybdenum esters, molybdenum amines, molybdenum amides, which can be obtained by reacting molybdenum oxide or ammonium molybdates with fats, glycerides or fatty acids, or fatty acid derivatives (e.g., esters, amines, amides). The term “fatty” means a carbon chain having 10 to 22 carbon atoms, typically a straight carbon chain.

[0041] In one embodiment, the molybdenum amine is a molybdenum-succinimide complex. Suitable molybdenum-succinimide complexes are described, for example, in U.S. Patent No. 8,076,275. These complexes are prepared by a process comprising reacting an acidic molybdenum compound with an alkyl or alkenyl succinimide of a polyamine of structure (3) or (4) or mixtures thereof:



wherein R is a C₂₄ to C₃₅₀ (e.g., C₇₀ to C₁₂₈) alkyl or alkenyl group; R' is a straight or branched-chain alkylene group having 2 to 3 carbon atoms; x is 1 to 11; and y is 1 to 10.

[0042] The molybdenum compounds used to prepare the molybdenum-succinimide complex are acidic molybdenum compounds or salts of acidic molybdenum compounds. By “acidic” is meant that the molybdenum compounds will react with a basic nitrogen compound

as measured by ASTM D664 or D2896. Generally, the acidic molybdenum compounds are hexavalent. Representative examples of suitable molybdenum compounds include molybdenum trioxide, molybdic acid, ammonium molybdate, sodium molybdate, potassium molybdate and other alkaline metal molybdates and other molybdenum salts such as hydrogen salts, (e.g., hydrogen sodium molybdate), MoOCl_4 , MoO_2Br_2 , $\text{Mo}_2\text{O}_3\text{Cl}_6$, and the like.

[0043] The succinimides that can be used to prepare the molybdenum-succinimide complex are disclosed in numerous references and are well known in the art. Certain fundamental types of succinimides and the related materials encompassed by the term of art “succinimide” are taught in U.S. Patent Nos. 3,172,892; 3,219,666; and 3,272,746. The term “succinimide” is understood in the art to include many of the amide, imide, and amidine species which may also be formed. The predominant product however is a succinimide and this term has been generally accepted as meaning the product of a reaction of an alkyl or alkenyl substituted succinic acid or anhydride with a nitrogen-containing compound. Preferred succinimides are those prepared by reacting a polyisobutenyl succinic anhydride of about 70 to 128 carbon atoms with a polyalkylene polyamine selected from triethylenetetramine, tetraethylenepentamine, and mixtures thereof.

[0044] The molybdenum-succinimide complex may be post-treated with a sulfur source at a suitable pressure and a temperature not to exceed 120°C to provide a sulfurized molybdenum-succinimide complex. The sulfurization step may be carried out for a period of from about 0.5 to 5 hours (e.g., 0.5 to 2 hours). Suitable sources of sulfur include elemental sulfur, hydrogen sulfide, phosphorus pentasulfide, organic polysulfides of formula R_2S_x where R is hydrocarbyl (e.g., C_1 to C_{10} alkyl) and x is at least 3, C_1 to C_{10} mercaptans, inorganic sulfides and polysulfides, thioacetamide, and thiourea.

[0045] The molybdenum compounds are used in an amount that provides at least 50 ppm, at least 70 ppm, at least 90 ppm, at least 110 ppm, at least 130 ppm, at least 150 ppm, or at least 200 ppm (e.g., 50 to 1500 ppm, 70 to 1500 ppm, 90 to 1000 ppm, 110 to 1000 ppm, 130 to 1000 ppm, 150 to 1000 ppm, or 200 to 1000 ppm) by weight of molybdenum to the lubricating oil composition.

Friction Modifiers

[0046] The lubricating oil composition disclosed herein can comprise a friction modifier that can lower the friction between moving parts. Any friction modifier known by a person of ordinary skill in the art may be used in the lubricating oil composition. Non-limiting examples of suitable friction modifiers include fatty carboxylic acids; derivatives

(e.g., alcohol, esters, borated esters, amides, metal salts and the like) of fatty carboxylic acid; mono-, di- or tri-alkyl substituted phosphoric acids or phosphonic acids; derivatives (e.g., esters, amides, metal salts and the like) of mono-, di- or tri-alkyl substituted phosphoric acids or phosphonic acids; mono-, di- or tri-alkyl substituted amines; mono- or di-alkyl substituted amides and combinations thereof. In some embodiments, the friction modifier is selected from the group consisting of aliphatic amines, ethoxylated aliphatic amines, aliphatic carboxylic acid amides, ethoxylated aliphatic ether amines, aliphatic carboxylic acids, glycerol esters, aliphatic carboxylic ester-amides, fatty imidazolines, fatty tertiary amines, wherein the aliphatic or fatty group contains more than about eight carbon atoms so as to render the compound suitably oil soluble. In some embodiments, the friction modifier is a fatty acid derivative. In some embodiments, the fatty acid derivative is a fatty acid ester, a borated fatty acid ester, or an amide. In other embodiments, the friction modifier comprises an aliphatic substituted succinimide formed by reacting an aliphatic succinic acid or anhydride with ammonia or a primary amine. The amount of the friction modifier may vary from about 0.01 wt. % to about 10 wt. %, from about 0.05 wt. % to about 5 wt. %, or from about 0.1 wt. % to about 3 wt. %, based on the total weight of the lubricating oil composition.

Antiwear Agents

[0047] Antiwear agents reduce wear of metal parts. Suitable anti-wear agents include dihydrocarbyl dithiophosphate metal salts such as zinc dihydrocarbyl dithiophosphates (ZDDP) of formula (Formula 1):



wherein R^1 and R^2 may be the same or different hydrocarbyl radicals having from 1 to 18 (e.g., 2 to 12) carbon atoms and including radicals such as alkyl, alkenyl, aryl, arylalkyl, alkaryl and cycloaliphatic radicals. Particularly preferred as R^1 and R^2 groups are alkyl groups having from 2 to 8 carbon atoms (e.g., the alkyl radicals may be ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, *sec*-butyl, *n*-pentyl, isopentyl, *n*-hexyl, isohexyl, 2-ethylhexyl). In order to obtain oil solubility, the total number of carbon atoms (i.e., $\text{R}^1 + \text{R}^2$) will be at least 5. The zinc dihydrocarbyl dithiophosphate can therefore comprise zinc dialkyl dithiophosphates. The zinc dialkyl dithiophosphate is a primary, secondary zinc dialkyl dithiophosphate, or a combination thereof.

[0048] ZDDP may be present at 3 wt. % or less (e.g., 0.1 to 1.5 wt. %, or 0.5 to 1.0 wt %) of the lubricating oil composition.

[0049] In one embodiment, the lubricating oil composition containing the magnesium salicylate detergent described herein further comprises an antioxidant compound. In one

embodiment, the antioxidant is a diphenylamine antioxidant. In another embodiment, the antioxidant is a hindered phenol antioxidant. In yet another embodiment, the antioxidant is a combination of a diphenylamine antioxidant and a hindered phenol antioxidant.

Antioxidants

[0050] Antioxidants reduce the tendency of mineral oils during to deteriorate during service. Oxidative deterioration can be evidenced by sludge in the lubricant, varnish-like deposits on the metal surfaces, and by viscosity growth. Suitable antioxidants include hindered phenols, aromatic amines, and sulfurized alkylphenols and alkali and alkaline earth metals salts thereof.

[0051] The hindered phenol antioxidant often contains 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 (typically 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. Other useful hindered phenol antioxidants include 2,6-di-alkyl-phenolic propionic ester derivatives such as IRGANOX[®] L-135 from Ciba and bis-phenolic antioxidants such as 4,4'-bis(2,6-di-*tert*-butylphenol) and 4,4'-methylenbis(2,6-di-*tert*-butylphenol).

[0052] Typical aromatic amine antioxidants have at least two aromatic groups attached directly to one amine nitrogen. Typical aromatic amine antioxidants have alkyl substituent groups of at least 6 carbon atoms. Particular examples of aromatic amine antioxidants useful herein include 4,4'-dioctyldiphenylamine, 4,4'-dinonyldiphenylamine, *N*-phenyl-1-naphthylamine, *N*-(4-*tert*-octylphenyl)-1-naphthylamine, and *N*-(4-octylphenyl)-1-naphthylamine.

[0053] Antioxidants may be present at 0.01 to 5 wt. % (e.g., 0.1 to 2 wt. %) of the lubricating oil composition.

Dispersants

[0054] Dispersants maintain in suspension materials resulting from oxidation during engine operation that are insoluble in oil, thus preventing sludge flocculation and precipitation or deposition on metal parts. Dispersants useful herein include nitrogen-

containing, ashless (metal-free) dispersants known to be effective to reduce formation of deposits upon use in gasoline and diesel engines.

[0055] Suitable dispersants include hydrocarbyl succinimides, hydrocarbyl succinamides, mixed ester/amides of hydrocarbyl-substituted succinic acid, hydroxyesters of hydrocarbyl-substituted succinic acid, and Mannich condensation products of hydrocarbyl-substituted phenols, formaldehyde and polyamines. Also suitable are condensation products of polyamines and hydrocarbyl-substituted phenyl acids. Mixtures of these dispersants can also be used.

[0056] Basic nitrogen-containing ashless dispersants are well-known lubricating oil additives and methods for their preparation are extensively described in the patent literature. Preferred dispersants are the alkenyl succinimides and succinamides where the alkenyl-substituent is a long-chain of preferably greater than 40 carbon atoms. These materials are readily made by reacting a hydrocarbyl-substituted dicarboxylic acid material with a molecule containing amine functionality. Examples of suitable amines are polyamines such as polyalkylene polyamines, hydroxy-substituted polyamines and polyoxyalkylene polyamines.

[0057] Particularly preferred ashless dispersants are the polyisobutenyl succinimides formed from polyisobutenyl succinic anhydride and a polyalkylene polyamine such as a polyethylene polyamine of formula 2:



wherein z is 1 to 11. The polyisobutenyl group is derived from polyisobutene and preferably has a number average molecular weight (M_n) in a range of 700 to 3000 Daltons (e.g., 900 to 2500 Daltons). For example, the polyisobutenyl succinimide may be a bis-succinimide derived from a polyisobutenyl group having a M_n of 900 to 2500 Daltons.

[0058] As is known in the art, the dispersants may be post-treated (e.g., with a boronating agent or a cyclic carbonate).

[0059] Nitrogen-containing ashless (metal-free) dispersants are basic, and contribute to the TBN of a lubricating oil composition to which they are added, without introducing additional sulfated ash.

[0060] Dispersants may be present at 0.1 to 10 wt. % (e.g., 2 to 5 wt. %) of the lubricating oil composition.

Additional Detergents

[0061] The lubricating oil composition of the present invention can further contain one or more overbased detergents having a TBN of 10-800, 10-700, 30-690, 100-600, 150-600, 150-500, 200-450 mg KOH/g on an actives basis.

[0062] In some embodiments, the detergents that may be used include oil-soluble sulfonate, overbased sulfonate, non-sulfur containing phenate, sulfurized phenates, salixarate, salicylate, saligenin, complex detergents and naphthenate detergents and other oil-soluble alkylhydroxybenzoates of a metal, particularly the alkali or alkaline earth metals, e.g., barium, sodium, potassium, lithium, calcium, and magnesium. The most commonly used metals are calcium and magnesium, which may both be present in detergents used in a lubricant, and mixtures of calcium and/or magnesium with sodium.

[0063] Overbased metal detergents are generally produced by carbonating a mixture of hydrocarbons, detergent acid, for example: sulfonic acid, alkylhydroxybenzoate etc., metal oxide or hydroxides (for example calcium oxide or calcium hydroxide) and promoters such as xylene, methanol and water. For example, for preparing an overbased calcium sulfonate, in carbonation, the calcium oxide or hydroxide reacts with the gaseous carbon dioxide to form calcium carbonate. The sulfonic acid is neutralized with an excess of CaO or Ca(OH)₂, to form the sulfonate.

[0064] Overbased detergents may be low overbased, e.g., an overbased salt having a TBN below 100 on an actives basis. In one embodiment, the TBN of a low overbased salt may be from about 30 to about 100. In another embodiment, the TBN of a low overbased salt may be from about 30 to about 80. Overbased detergents may be medium overbased, e.g., an overbased salt having a TBN from about 100 to about 250. In one embodiment, the TBN of a medium overbased salt may be from about 100 to about 200. In another embodiment, the TBN of a medium overbased salt may be from about 125 to about 175. Overbased detergents may be high overbased, e.g., an overbased salt having a TBN above 250. In one embodiment, the TBN of a high overbased salt may be from about 250 to about 800 on an actives basis.

[0065] In one embodiment, the detergent can be one or more alkali or alkaline earth metal salts of an alkyl-substituted hydroxyaromatic carboxylic acid. Suitable hydroxyaromatic compounds include mononuclear monohydroxy and polyhydroxy aromatic hydrocarbons having 1 to 4, and preferably 1 to 3, hydroxyl groups. Suitable hydroxyaromatic compounds include phenol, catechol, resorcinol, hydroquinone, pyrogallol, cresol, and the like. The preferred hydroxyaromatic compound is phenol.

[0066] The alkyl substituted moiety of the alkali or alkaline earth metal salt of an alkyl-substituted hydroxyaromatic carboxylic acid is derived from an alpha olefin having from about 10 to about 80 carbon atoms. The olefins employed may be linear, isomerized linear, branched or partially branched linear. The olefin may be a mixture of linear olefins, a mixture of isomerized linear olefins, a mixture of branched olefins, a mixture of partially branched linear or a mixture of any of the foregoing.

[0067] In one embodiment, the mixture of linear olefins that may be used is a mixture of normal alpha olefins selected from olefins having from about 10 to about 40 carbon atoms per molecule. In one embodiment, the normal alpha olefins are isomerized using at least one of a solid or liquid catalyst.

[0068] In one embodiment, at least about 50 mole%, at least about 75 mole%, at least about 80 mole%, at least about 85 mole%, at least about 90 mole%, at least about 95 mole% of the alkyl groups contained within the alkali or alkaline earth metal salt of an alkyl-substituted hydroxyaromatic carboxylic acid such as the alkyl groups of an alkaline earth metal salt of an alkyl-substituted hydroxybenzoic acid detergent are a C₂₀ or higher. In another embodiment, the alkali or alkaline earth metal salt of an alkyl-substituted hydroxyaromatic carboxylic acid is an alkali or alkaline earth metal salt of an alkyl-substituted hydroxybenzoic acid that is derived from an alkyl-substituted hydroxybenzoic acid in which the alkyl groups are C₂₀ to about C₂₈ normal alpha-olefins. In another embodiment, the alkyl group is derived from at least two alkylated phenols. The alkyl group on at least one of the at least two alkyl phenols is derived from an isomerized alpha olefin. The alkyl group on the second alkyl phenol may be derived from branched or partially branched olefins, highly isomerized olefins or mixtures thereof.

[0069] In another embodiment, the alkali or alkaline earth metal salt of an alkyl-substituted hydroxyaromatic carboxylic acid is a salicylate derived from an alkyl group with 20-40 carbon atoms, preferably 20-28 carbon atoms, more preferably, isomerized 20-24 NAO.

[0070] Sulfonates may be prepared from sulfonic acids which are typically obtained by the sulfonation of alkyl substituted aromatic hydrocarbons such as those obtained from the fractionation of petroleum or by the alkylation of aromatic hydrocarbons. Examples included those obtained by alkylating benzene, toluene, xylene, naphthalene, diphenyl or their halogen derivatives. The alkylation may be carried out in the presence of a catalyst with alkylating agents having from about 3 to more than 70 carbon atoms. The alkaryl sulfonates usually contain from about 9 to about 80 or more carbon atoms, preferably from about 16 to about 60

carbon atoms, preferably about 16 to 30 carbon atoms, and more preferably 20-24 carbon atoms per alkyl substituted aromatic moiety.

[0071] Metal salts of phenols and sulfurized phenols, which are sulfurized phenate detergents, are prepared by reaction with an appropriate metal compound such as an oxide or hydroxide and neutral or overbased products may be obtained by methods well known in the art. Sulfurized phenols may be prepared by reacting a phenol with sulfur or a sulfur containing compound such as hydrogen sulfide, sulfur monohalide or sulfur dihalide, to form products which are generally mixtures of compounds in which 2 or more phenols are bridged by sulfur containing bridges.

[0072] Additional details regarding the general preparation of sulfurized phenates can be found in, for example, U.S. Pat. Nos. 2,680,096; 3,178,368, 3,801,507, and 8,580,717 the contents of which are incorporated herein by reference.

[0073] Considering now in detail, the reactants and reagents used in the present process, first all allotropic forms of sulfur can be used. The sulfur can be employed either as molten sulfur or as a solid (e.g., powder or particulate) or as a solid suspension in a compatible hydrocarbon liquid.

[0074] It is desirable to use calcium hydroxide as the calcium base because of its handling convenience versus, for example, calcium oxide, and also because it affords excellent results. Other calcium bases can also be used, for example, calcium alkoxides.

[0075] Suitable alkylphenols which can be used are those wherein the alkyl substituents contain a sufficient number of carbon atoms to render the resulting overbased sulfurized calcium alkylphenate composition oil-soluble. Oil solubility may be provided by a single long chain alkyl substitute or by a combination of alkyl substituents. Typically, the alkylphenol used will be a mixture of different alkylphenols, e.g., C₂₀ to C₂₄ alkylphenol.

[0076] In one embodiment, suitable alkyl phenolic compounds will be derived from isomerized alpha olefin alkyl groups having from about 10 to about 40 carbon atoms per molecule, having an isomerized level (I) of the alpha olefin between from about 0.1 to about 0.4. In one embodiment, suitable alkyl phenolic compounds will be derived from alkyl groups which are branched olefinic propylene oligomers or mixture thereof having from about 9 to about 80 carbon atoms. In one embodiment, the branched olefinic propylene oligomer or mixtures thereof have from about 9 to about 40 carbon atoms. In one embodiment, the branched olefinic propylene oligomer or mixtures thereof have from about 9 to about 18 carbon atoms. In one embodiment, the branched olefinic propylene oligomer or mixtures thereof have from about 9 to about 12 carbon atoms.

[0077] In one embodiment, suitable alkyl phenolic compounds comprise distilled cashew nut shell liquid (CNSL) or hydrogenated distilled cashew nut shell liquid. Distilled CNSL is a mixture of biodegradable meta-hydrocarbyl substituted phenols, where the hydrocarbyl group is linear and unsaturated, including cardanol. Catalytic hydrogenation of distilled CNSL gives rise to a mixture of meta-hydrocarbyl substituted phenols predominantly rich in 3-pentadecylphenol.

[0078] The alkylphenols can be para-alkylphenols, meta-alkylphenols or ortho alkylphenols. Since it is believed that p-alkylphenols facilitate the preparation of highly overbased calcium sulfurized alkylphenate where overbased products are desired, the alkylphenol is preferably predominantly a para alkylphenol with no more than about 45 mole percent of the alkylphenol being ortho alkylphenols; and more preferably no more than about 35 mole percent of the alkylphenol is ortho alkylphenol. Alkyl-hydroxy toluenes or xylenes, and other alkyl phenols having one or more alkyl substituents in addition to at least one long chained alkyl substituent can also be used. In the case of distilled cashew nut shell liquid, the catalytic hydrogenation of distilled CNSL gives rise to a mixture of meta-hydrocarbyl substituted phenols.

[0079] In one embodiment, the one or more overbased detergent can be a complex or hybrid detergent which is known in the art as comprising a surfactant system derived from at least two surfactants described above.

[0080] Generally, the amount of the detergent can be from about 0.001 wt. % to about 50 wt. %, or from about 0.05 wt. % to about 25 wt. %, or from about 0.1 wt. % to about 20 wt. %, or from about 0.01 to 15 wt. % based on the total weight of the lubricating oil composition.

Additional Co-Additives

[0081] The lubricating oil compositions of the present disclosure may also contain other conventional additives that can impart or improve any desirable property of the lubricating oil composition in which these additives are dispersed or dissolved. Any additive known to a person of ordinary skill in the art may be used in the lubricating oil compositions disclosed herein. Some suitable additives have been described in Mortier et al., "Chemistry and Technology of Lubricants", 2nd Edition, London, Springer, (1996); and Leslie R. Rudnick, "Lubricant Additives: Chemistry and Applications", New York, Marcel Dekker (2003), both of which are incorporated herein by reference. For example, the lubricating oil compositions can be blended with antioxidants, anti-wear agents, detergents such as metal

detergents, rust inhibitors, dehazing agents, demulsifying agents, metal deactivating agents, friction modifiers, pour point depressants, antifoaming agents, co-solvents, corrosion-inhibitors, ashless dispersants, multifunctional agents, dyes, extreme pressure agents and the like and mixtures thereof. A variety of the additives are known and commercially available. These additives, or their analogous compounds, can be employed for the preparation of the lubricating oil compositions of the disclosure by the usual blending procedures.

[0082] In the preparation of lubricating oil formulations it is common practice to introduce the additives in the form of 10 to 100 wt. % active ingredient concentrates in hydrocarbon oil, e.g. mineral lubricating oil, or other suitable solvent.

[0083] Usually these concentrates may be diluted with 3 to 100, e.g., 5 to 40, parts by weight of lubricating oil per part by weight of the additive package in forming finished lubricants, e.g. crankcase motor oils. The purpose of concentrates, of course, is to make the handling of the various materials less difficult and awkward as well as to facilitate solution or dispersion in the final blend.

[0084] Each of the foregoing additives, when used, is used at a functionally effective amount to impart the desired properties to the lubricant. Thus, for example, if an additive is a friction modifier, a functionally effective amount of this friction modifier would be an amount sufficient to impart the desired friction modifying characteristics to the lubricant.

[0085] In general, the concentration of each of the additives in the lubricating oil composition, when used, may range from about 0.001 wt. % to about 20 wt. %, from about 0.01 wt. % to about 15 wt. %, or from about 0.1 wt. % to about 10 wt. %, from about 0.005 wt.% to about 5 wt.%, or from about 0.1 wt.% to about 2.5 wt.%, based on the total weight of the lubricating oil composition. Further, the total amount of the additives in the lubricating oil composition may range from about 0.001 wt.% to about 20 wt.%, from about 0.01 wt.% to about 10 wt.%, or from about 0.1 wt.% to about 5 wt.%, based on the total weight of the lubricating oil composition.

Oil of lubricating viscosity

[0086] The oil of lubricating viscosity (sometimes referred to as “base stock” or “base oil”) is the primary liquid constituent of a lubricant, into which additives and possibly other oils are blended, for example to produce a final lubricant (or lubricant composition). A base oil is useful for making concentrates as well as for making lubricating oil compositions therefrom, and may be selected from natural and synthetic lubricating oils and combinations thereof.

[0087] Natural oils include animal and vegetable oils, liquid petroleum oils and hydrotreated, solvent-treated mineral lubricating oils of the paraffinic, naphthenic and mixed paraffinic-naphthenic types. Oils of lubricating viscosity derived from coal or shale are also useful base oils.

[0088] Synthetic lubricating oils include hydrocarbon oils such as polymerized and interpolymers of olefins (e.g., polybutylenes, polypropylenes, propylene-isobutylene copolymers, chlorinated polybutylenes, poly(1-hexenes), poly(1-octenes), poly(1-decenes); alkylbenzenes (e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di(2-ethylhexyl)benzenes; polyphenols (e.g., biphenyls, terphenyls, alkylated polyphenols); and alkylated diphenyl ethers and alkylated diphenyl sulfides and the derivatives, analogues and homologues thereof.

[0089] Another suitable class of synthetic lubricating oils comprises the esters of dicarboxylic acids (e.g., malonic acid, alkyl malonic acids, alkenyl malonic acids, succinic acid, alkyl succinic acids and alkenyl succinic acids, maleic acid, fumaric acid, azelaic acid, suberic acid, sebacic acid, adipic acid, linoleic acid dimer, phthalic acid) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol). Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl) sebacate, di-*n*-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid.

[0090] Esters useful as synthetic oils also include those made from C₅ to C₁₂ monocarboxylic acids and polyols, and polyol ethers such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol and tripentaerythritol.

[0091] The base oil may be derived from Fischer-Tropsch synthesized hydrocarbons. Fischer-Tropsch synthesized hydrocarbons are made from synthesis gas containing H₂ and CO using a Fischer-Tropsch catalyst. Such hydrocarbons typically require further processing in order to be useful as the base oil. For example, the hydrocarbons may be hydroisomerized; hydrocracked and hydroisomerized; dewaxed; or hydroisomerized and dewaxed; using processes known to those skilled in the art.

[0092] Unrefined, refined and re-refined oils can be used in the present lubricating oil composition. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. For example, a shale oil obtained directly from

retorting operations, a petroleum oil obtained directly from distillation or ester oil obtained directly from an esterification process and used without further treatment would be unrefined oil. Refined oils are similar to the unrefined oils except they have been further treated in one or more purification steps to improve one or more properties. Many such purification techniques, such as distillation, solvent extraction, acid or base extraction, filtration and percolation are known to those skilled in the art.

[0093] Re-refined oils are obtained by processes similar to those used to obtain refined oils applied to refined oils which have been already used in service. Such re-refined oils are also known as reclaimed or reprocessed oils and often are additionally processed by techniques for approval of spent additive and oil breakdown products.

[0094] Hence, the base oil which may be used to make the present lubricating oil composition may be selected from any of the base oils in Groups I-V as specified in the American Petroleum Institute (API) Base Oil Interchangeability Guidelines (API Publication 1509). Such base oil groups are summarized in Table 1 below:

Table 1

Group ^(a)	Base Oil Properties		
	Saturates ^(b) , wt. %	Sulfur ^(c) , wt. %	Viscosity Index ^(d)
Group I	<90 and/or	>0.03	80 to <120
Group II	≥90	≤0.03	80 to <120
Group III	≥90	≤0.03	≥120
Group IV	Polyalphaolefins (PAOs)		
Group V	All other base stocks not included in Groups I, II, III or IV		

^(a) Groups I-III are mineral oil base stocks.

^(b) Determined in accordance with ASTM D2007.

^(c) Determined in accordance with ASTM D2622, ASTM D3120, ASTM D4294 or ASTM D4927.

^(d) Determined in accordance with ASTM D2270.

[0095] Base oils suitable for use herein are any of the variety corresponding to API Group II, Group III, Group IV, and Group V oils and combinations thereof, preferably the Group III to Group V oils due to their exceptional volatility, stability, viscometric and cleanliness features.

[0096] The oil of lubricating viscosity for use in the lubricating oil compositions of this disclosure, also referred to as a base oil, is typically present in a major amount, e.g., an amount of greater than 50 wt. %, preferably greater than about 70 wt. %, more preferably from about 80 to about 99.5 wt. % and most preferably from about 85 to about 98 wt. %, based on the total weight of the composition. The expression “base oil” as used herein shall be understood to mean a base stock or blend of base stocks which is a lubricant component that is produced by a single manufacturer to the same specifications (independent of feed source or manufacturer's location); that meets the same manufacturer's specification; and that is identified by a unique formula, product identification number, or both. The base oil for use herein can be any presently known or later-discovered oil of lubricating viscosity used in formulating lubricating oil compositions for any and all such applications, e.g., engine oils, marine cylinder oils, functional fluids such as hydraulic oils, gear oils, transmission fluids, etc. Additionally, the base oils for use herein can optionally contain viscosity index improvers, e.g., polymeric alkylmethacrylates; olefinic copolymers, e.g., an ethylene-propylene copolymer or a styrene-butadiene copolymer; and the like and mixtures thereof.

[0097] As one skilled in the art would readily appreciate, the viscosity of the base oil is dependent upon the application. Accordingly, the viscosity of a base oil for use herein will ordinarily range from about 2 to about 2000 centistokes (cSt) at 100° Centigrade (C.). Generally, individually the base oils used as engine oils will have a kinematic viscosity range at 100° C. of about 2 cSt to about 30 cSt, preferably about 3 cSt to about 16 cSt, and most preferably about 4 cSt to about 12 cSt and will be selected or blended depending on the desired end use and the additives in the finished oil to give the desired grade of engine oil, e.g., a lubricating oil composition having an SAE Viscosity Grade of 0W, 0W-8, 0W-12, 0W-16, 0W-20, 0W-26, 0W-30, 0W-40, 0W-50, 0W-60, 5W, 5W-20, 5W-30, 5W-40, 5W-50, 5W-60, 10W, 10W-20, 10W-30, 10W-40, 10W-50, 15W, 15W-20, 15W-30, 15W-40, 30, 40 and the like.

Lubricating Oil Compositions

[0098] In general, the level of sulfur in the lubricating oil compositions of the present invention is less than or equal to about 0.7 wt. %, based on the total weight of the lubricating oil composition, e.g., a level of sulfur of about 0.01 wt. % to about 0.70 wt. %, 0.01 to 0.6 wt.%, 0.01 to 0.5 wt.%, 0.01 to 0.4 wt.%, 0.01 to 0.3 wt.%, 0.01 to 0.2 wt.%, 0.01 wt. % to 0.10 wt. %. In one embodiment, the level of sulfur in the lubricating oil compositions of the present invention is less than or equal to about 0.60 wt. %, less than or equal to about 0.50 wt. %, less than or equal to about 0.40 wt. %, less than or equal to about 0.30 wt. %, less than or

equal to about 0.20 wt. %, less than or equal to about 0.10 wt. % based on the total weight of the lubricating oil composition.

[0099] In one embodiment, the levels of phosphorus in the lubricating oil compositions of the present invention is less than or equal to about 0.12 wt. %, based on the total weight of the lubricating oil composition, e.g., a level of phosphorus of about 0.01 wt. % to about 0.12 wt. %. In one embodiment, the levels of phosphorus in the lubricating oil compositions of the present invention is less than or equal to about 0.11 wt. %, based on the total weight of the lubricating oil composition, e.g., a level of phosphorus of about 0.01 wt. % to about 0.11 wt. %. In one embodiment, the levels of phosphorus in the lubricating oil compositions of the present invention is less than or equal to about 0.10 wt. %, based on the total weight of the lubricating oil composition, e.g., a level of phosphorus of about 0.01 wt. % to about 0.10 wt. %. In one embodiment, the levels of phosphorus in the lubricating oil compositions of the present invention is less than or equal to about 0.09 wt. %, based on the total weight of the lubricating oil composition, e.g., a level of phosphorus of about 0.01 wt. % to about 0.09 wt. %. In one embodiment, the levels of phosphorus in the lubricating oil compositions of the present invention is less than or equal to about 0.08 wt. %, based on the total weight of the lubricating oil composition, e.g., a level of phosphorus of about 0.01 wt. % to about 0.08 wt. %. In one embodiment, the levels of phosphorus in the lubricating oil compositions of the present invention is less than or equal to about 0.07 wt. %, based on the total weight of the lubricating oil composition, e.g., a level of phosphorus of about 0.01 wt. % to about 0.07 wt. %. In one embodiment, the levels of phosphorus in the lubricating oil compositions of the present invention is less than or equal to about 0.05 wt. %, based on the total weight of the lubricating oil composition, e.g., a level of phosphorus of about 0.01 wt. % to about 0.05 wt. %.

[00100] In one embodiment, the level of sulfated ash produced by the lubricating oil compositions of the present invention is less than or equal to about 1.60 wt. % as determined by ASTM D 874, e.g., a level of sulfated ash of from about 0.10 to about 1.60 wt. % as determined by ASTM D 874. In one embodiment, the level of sulfated ash produced by the lubricating oil compositions of the present invention is less than or equal to about 1.00 wt. % as determined by ASTM D 874, e.g., a level of sulfated ash of from about 0.10 to about 1.00 wt. % as determined by ASTM D 874. In one embodiment, the level of sulfated ash produced by the lubricating oil compositions of the present invention is less than or equal to about 0.80 wt. % as determined by ASTM D 874, e.g., a level of sulfated ash of from about 0.10 to about 0.80 wt. % as determined by ASTM D 874. In one embodiment, the level of

sulfated ash produced by the lubricating oil compositions of the present invention is less than or equal to about 0.60 wt. % as determined by ASTM D 874, e.g., a level of sulfated ash of from about 0.10 to about 0.60 wt. % as determined by ASTM D 874.

[00101] The following examples are presented to exemplify embodiments of the invention but are not intended to limit the invention to the specific embodiments set forth. Unless indicated to the contrary, all parts and percentages are by weight. All numerical values are approximate. When numerical ranges are given, it should be understood that embodiments outside the stated ranges may still fall within the scope of the invention. Specific details described in each example should not be construed as necessary features of the invention.

EXAMPLES

[00102] The following examples are intended for illustrative purposes only and do not limit in any way the scope of the present disclosure.

[00103] The isomerization level was measured by an NMR method.

Isomerization level (I) and NMR method

[00104] The isomerization level (I) of the olefin was determined by hydrogen-1 (¹H) NMR. The NMR spectra were obtained on a Bruker Ultrashield Plus 400 in chloroform-d₁ at 400 MHz using TopSpin 3.2 spectral processing software.

[00105] The isomerization level (I) represents the relative amount of methyl groups (-CH₃) (chemical shift 0.30-1.01 ppm) attached to the methylene backbone groups (-CH₂-) (chemical shift 1.01-1.38 ppm) and is defined by Equation (1) as shown below,

$$I = m/(m+n) \quad \text{Equation (1)}$$

where m is NMR integral for methyl groups with chemical shifts between 0.30 ± 0.03 to 1.01 ± 0.03 ppm, and n is NMR integral for methylene groups with chemical shifts between 1.01 ± 0.03 to 1.38 ± 0.10 ppm.

Baseline Formulation 1

[00106] A 15W-40 lubricating oil composition was prepared that contained a major amount of a base oil of lubricating viscosity and the following additives:

- (1) an ethylene carbonate post-treated bis-succinimide;
- (2) a mixture of a primary zinc dialkyldithiophosphate and a secondary zinc dialkyldithiophosphate;
- (3) a diphenylamine antioxidant;
- (4) 45 ppm in terms of molybdenum content of a sulfur-containing molybdenum succinimide; and

(5) a foam inhibitor.

Baseline Formulation 2

[00107] A 15W-40 lubricating oil composition was prepared that contained a major amount of a base oil of lubricating viscosity and the following additives:

- (1) an ethylene carbonate post-treated bis-succinimide;
- (2) a secondary zinc dialkyldithiophosphate;
- (3) a diphenylamine antioxidants;
- (4) 380 ppm in terms of molybdenum content of a sulfur-containing molybdenum succinimide; and
- (5) a foam inhibitor.

Baseline Formulation 3

[00108] A 15W-40 lubricating oil composition was prepared that contained a major amount of a base oil of lubricating viscosity and the following additives:

- (1) an ethylene carbonate post-treated bis-succinimide;
- (2) a secondary zinc dialkyldithiophosphate;
- (3) a diphenylamine antioxidant;
- (4) 380 ppm in terms of molybdenum content of a sulfur-free molybdenum succinimide; and
- (5) a foam inhibitor.

Example A

[00109] An alkylated phenol and alkylated Ca alkylhydroxybenzoate were prepared in substantially the same manner as in U.S. Patent No. 8,993,499 using a C₂₀₋₂₄ isomerized normal alpha olefin available from CP Chem. The isomerization level of the alpha olefin is about 0.16. The resulting alkylated alkylhydroxybenzoate composition has a TBN of about 225 mgKOH/gm and Ca content of 8 wt.% on an oil-free basis.

Example B

[00110] An alkylated phenol and alkylated Ca alkylhydroxybenzoate were prepared in substantially the same manner as in U.S. Patent No. 8,993,499 using a C₂₀₋₂₄ isomerized normal alpha olefin available from CP Chem. The isomerization level of the alpha olefin is about 0.16. The resulting alkylated alkylhydroxybenzoate composition has a TBN of about 120 mgKOH/gm and Ca content of 4.2 wt.% on an oil-free basis.

Comparative Example A

[00111] An alkylated phenol and alkylated Ca alkylhydroxybenzoate were prepared in substantially the same manner as in U.S. Patent No. 8,030,258 using a C₂₀₋₂₈ normal alpha olefin available from CP Chem. The resulting alkylated alkylhydroxybenzoate composition has a TBN of about 230 and Ca content about 8 wt.% on an oil-free basis.

Comparative Example B

[00112] An alkylated alkylhydroxybenzoate was prepared from an alkylphenol with an alkyl group derived from C₁₄ - C₁₈ normal alpha olefin and a TBN about 300 mgKOH/gm and Ca content about 10.6 wt. % on an oil-free basis.

Comparative Example C

[00113] An alkylated alkylhydroxybenzoate was prepared from an alkylphenol with an alkyl group derived from C₂₀ - C₂₈ normal alpha olefin and a TBN about 115 mgKOH/gm and Ca content about 4 wt. % on an oil-free basis.

Comparative Example D

[00114] A highly overbased Ca Sulfonate having a TBN about 700 mgKOH/gm and Ca content about 26 wt. % on an oil-free basis.

Example 1

[00115] To baseline formulation 1 was added 0.35 wt.% in terms of Ca content of a Ca alkylhydroxybenzoate detergent of Example A. The lubricating oil composition has 0.21 wt% of S, 0.1 wt% of P, and 1.3 wt% of ash.

Comparative Example 1

[00116] To baseline formulation 1 was added 0.35 wt.% in terms of Ca content of a Ca alkylhydroxybenzoate detergent of Comparative Example A. The lubricating oil composition has 0.22 wt% of S, 0.1 wt% of P, and 1.3 wt% of ash.

Comparative Example 2

[00117] To baseline formulation 1 was added 0.35 wt.% in terms of Ca content of a Ca alkylhydroxybenzoate of Comparative Example B. The lubricating oil composition has 0.22 wt% of S, 0.1 wt% of P, and 1.3 wt% of ash.

Example 2

[00118] To baseline formulation 2 was added 0.35 wt.% in terms of Ca content of a Ca alkylhydroxybenzoate of Example A. The lubricating oil composition has 0.17 wt% of S, 0.07 wt% of P, and 1.3 wt% of ash.

Comparative Example 3

[00119] To baseline formulation 2 was added 0.35 wt.% in terms of Ca content of a Ca alkylhydroxybenzoate of Comparative Example B. The lubricating oil composition has 0.16 wt% of S, 0.07 wt% of P, and 1.3 wt% of ash.

Example 3

[00120] To baseline formulation 3 was added 0.35 wt% in terms of Ca content of a Ca alkylhydroxybenzoate of Example A. The lubricating oil composition has 0.17 wt% of S, 0.07 wt% of P, and 1.3 wt% of ash.

Comparative Example 4

[00121] To baseline formulation 3 was added 0.35 wt% in terms of Ca content of a Ca alkylhydroxybenzoate of Comparative Example B. The lubricating oil composition has 0.16 wt% of S, 0.07 wt% of P, and 1.3 wt% of ash.

[00122] Examples 1 to 3, and Comparative Examples 1 to 4 were evaluated in the TEOST MHT4 and HTCBT tests described below. Results are in Table 2.

TEOST MHT4

[00123] The ASTM D7097 TEOST MHT4 test is designed to predict the deposit-forming tendencies of engine oil in the piston ring belt and upper piston crown area. Correlation has been shown between the TEOST MHT procedure and the TU3MH Peugeot engine test in deposit formation. This test determines the mass of deposit formed on a specially constructed test rod exposed to repetitive passage of 8.5 g of engine oil over the rod in a thin film under oxidative and catalytic conditions at 285 deg C. Deposit-forming tendencies of an engine oil under oxidative conditions are determined by circulating an oil-catalyst mixture comprising a small sample (8.4 g) of the oil and a very small (0.1 g) amount of an organo-metallic catalyst. This mixture is circulated for 24 hours in the TEOST MHT instrument over a special wire-wound depositor rod heated by electrical current to a controlled temperature of

285 deg C at the hottest location on the rod. The rod is weighed before and after the test. Deposit weight of 35 mg is considered as pass/fail criteria.

HTCBT

[00124] The ASTM D6594 HTCBT test is used to test diesel engine lubricants to determine their tendency to corrode various metals, specifically alloys of lead and copper commonly used in cam followers and bearings. Four metal specimens of copper, lead, tin and phosphor bronze are immersed in a measured amount of engine oil. The oil, at an elevated temperature (170 °C), is blown with air (5 l/h) for a period of time (168 h). When the test is completed, the copper specimen and the stressed oil are examined to detect corrosion and corrosion products, respectively. The concentrations of copper, lead, and tin in the new oil and stressed oil and the respective changes in metal concentrations are reported. To be a pass the concentration of lead should not exceed 120 ppm and the copper 20 ppm.

Table 2 - HTCBT and TEOST MHT4

	HTCBT (lead in ppm)	TEOST MHT4
Example 1	6	25.7
Comparative Ex 1	32	25.2
Comparative Ex 2	68	74.6
Example2	14	11.8
Comparative Ex 3	104	33.4
Example 3	17	14.8
Comparative Ex 4	110	24.9

[00125] The Ca alkylhydroxybenzoate derived from C₂₀ - C₂₄ isomerized NAO has surprisingly better corrosion inhibition and deposit control performance than the Ca alkylhydroxybenzoate derived from non-isomerized NAO at equal Ca level. This effect is enhanced in the presence of an effective level of a molybdenum compound.

Baseline Formulation 4

[00126] A 5W-20 lubricating oil composition was prepared that contained a major amount of a base oil of lubricating viscosity and the following additives:

- (1) an ethylene carbonate post-treated bis-succinimide;
- (2) a borated bis-succinimide dispersant;
- (3) a mixture of a primary zinc dialkyldithiophosphate and a secondary zinc dialkyldithiophosphate;

- (4) a mixture of molybdenum succinimide and diphenylamine antioxidants; and
- (5) a foam inhibitor.

Example 4

[00127] To baseline formulation 4 was added 0.18 wt% in terms of Ca content of a Ca alkylhydroxybenzoate of Example A. The lubricating oil composition has 0.16 wt% of S, 0.077 wt% of P, and 0.75 wt% of ash.

Example 5

[00128] To baseline formulation 4 was added 0.18 wt% in terms of Ca content of a Ca alkylhydroxybenzoate of Example A and 68 ppm in terms of Boron content of a borated glycerol monooleate (Glymo) friction modifier. The lubricating oil composition has 0.16 wt% of S, 0.077 wt% of P, and 0.76 wt% of ash.

Comparative Example 8

[00129] To baseline formulation 4 was added 0.18 wt% in terms of Ca content of a highly overbased Ca sulfonate detergent and 68 ppm in terms of B content of a borated glycerol monooleate (Glymo) friction modifier. The lubricating oil composition has 0.18 wt% of S, 0.077 wt% of P, and 0.75 wt% of ash.

Comparative Example 9

[00130] To baseline formulation 4 was added 0.18 wt% in terms of Ca content of Comparative Example D. The lubricating oil composition has 0.18 wt% of S, 0.077 wt% of P, and 0.76 wt% of ash.

MTM TEST

[00131] Examples 4 to 5, and Comparative Examples 8 and 9 were tested for friction performance in a Mini-Traction Machine (MTM) bench test. The MTM is manufactured by PCS Instruments and operates with a ball (0.75 inches 8620 steel ball) loaded against a rotating disk (52100 steel). The conditions employ a load of approximately 10-30 Newtons, a speed of approximately 10-2000 mm/s and a temperature of approximately 125-150 °C. In this bench test, the boundary friction performance of a formulation under a rolling/sliding contact is measured by the low speed traction coefficient. The low speed traction coefficient is the average traction coefficient of the second *Stribeck* between 15 and 20mm/s. Lower low

speed traction coefficients correspond to better boundary friction performance of the oil.

Results are in Table 3.

[00132]

Table 3 - MTM Test

	Low Speed Traction Coefficient
Example 4	0.1268
Example 5	0.0885
Comparative Example 8	0.1150
Comparative Example 9	0.1269

[00133] The Ca alkylhydroxybenzoate derived from C₂₀ - C₂₄ isomerized NAO has similar boundary friction performance to the highly overbased Ca Sulfonate at equal Ca level. However, the combination of the alkylhydroxybenzoate derived from C₂₀ - C₂₄ isomerized NAO and a friction modifier has significantly better boundary friction performance than the combination of the highly overbased Ca Sulfonate and a friction modifier or the alkylhydroxybenzoate alone, indicating a synergistic effect between the alkylhydroxybenzoate and the friction modifier.

Baseline Formulation 5

[00134] A railroad lubricating oil composition was prepared that contained a major amount of a base oil of lubricating viscosity and the following additives:

- (1) an ethylene carbonate post-treated bis-succinimide;
- (2) a mixture of phenate detergents
- (3) a mixture of Moly succinimide and diphenylamine antioxidants;
- (4) a friction modifier
- (5) a foam inhibitor.
- (6) a viscosity modifier

Example 6

[00135] To baseline formulation 5 was added 0.05wt% in terms of Ca content of a Ca alkylhydroxybenzoate of Example A.

Comparative Example 10

[00136] To baseline formulation 5 was added 0.04wt% in terms of Ca content of a Ca alkylhydroxybenzoate of Comparative Example A.

[00137] Example 6 and Comparative Example 10 were evaluated in the B2-7 Oxidation Test and the B72-2 Ali Silver Lubricity Test as described below.

B2-7 Test

[00138] The B2-7 test is an oxidation test with the following conditions:

UP Oxidation (B2)	
Temp	149 C. (300 F.)
Duration	96 hr
Coupons	Cu, Fe, Pb
Flow	oxygen
Replenishing oil	At 48 hr (50 mL)
	72 hr (50 mL)
Comments	Trend data of BN, AN, pH and Pb ppm

[00139] According to the B2-7 test, the oil to be tested is heated at 300 °F for 96 hours with bubbling of oxygen. Copper, iron and lead coupons are suspended in the oil. Fifty milliliter samples are taken at 48, 72 and 96 hours. The samples at 48 and 72 hours are replenished with fresh oil. The oil test samples are evaluated for base number, acid number, pH and lead.

Comparative Example 10 and Example 6 of the invention were evaluated for Total Base Number (TBN) decrease. The results are in table 4.

Table 4 – B2-7 Test

TBN D4739	Comparative Example 10	Example 6
0hr	9.70	9.64
48hr	6.50	6.76
72 hr	6.21	6.49
96 hr	5.98	6.22
TBN decrease	3.72	3.42

[00140] Higher numbers for TBN decrease indicate greater depletion of the base in the oil and are considered less favorable. An oil for extended use in a locomotive diesel engine will ideally retain TBN.

[00141] The results show that the Ca alkylhydroxybenzoate detergent derived from C₂₀ - C₂₄ isomerized NAO provide better BN retention when compared with the Ca alkylhydroxybenzoate detergent derived from non-isomerized NAO, meaning better protection of the engine.

Baseline Formulation 6

[00142] A 5W-30 lubricating oil composition was prepared that contained a major amount of a base oil of lubricating viscosity and the following additives:

- (1) a borated bis-succinimide;
- (2) an ethylene carbonate-treated bissuccinimide;
- (3) a highly overbased Ca sulfonate detergent
- (4) a mixture of a primary zinc dialkyldithiophosphate and a secondary zinc dialkyldithiophosphate;
- (5) a mixture of Moly succinimide and diphenylamine antioxidants;
- (6) a friction modifier
- (7) a foam inhibitor
- (8) a pour point depressant
- (9) a viscosity modifier

Example 7

[00143] To baseline formulation 6 was added 0.1 wt% in terms of Ca content of a Ca alkylhydroxybenzoate of Example B.

Comparative Example 11

[00144] To baseline formulation 6 was added 0.1 wt% in terms of Ca content of a Ca alkylhydroxybenzoate of Comparative Example C.

[00145] Example 7 and Comparative Example 11 were evaluated in the MRV test as described below.

MRV (Mini Rotary Viscometer)

The ASTM D4684 MRV test covers the measurement of the yield stress ($0 < Y < 35$ max) and viscosity (60,000 cp max) of engine oils after cooling at controlled rates over a period not exceeding 45 h to a final test temperature between -10 and -40 °C. In the MRV test an engine

oil sample is held at 80 °C. and then cooled at a programmed cooling rate to a final test temperature. A low torque is applied to the rotor shaft to measure the yield stress. A higher torque is then applied to determine the apparent viscosity of the sample. The viscosity measurements are made at *shear* stress of 525 Pa over a *shear* rate of 0.4 to 15 s⁻¹.

Table 5. MRV Test @-35C (ASTM D-4684)

	<u>Apparent Viscosity (cP)</u>	<u>Yield Stress (Pa)</u>
<u>Example 7</u>	<u>43100</u>	<u><175</u>
<u>Comparative 11</u>	<u>Frozen</u>	<u>≥350</u>

[00146] The Ca alkylhydroxybenzoate derived from C₂₀ - C₂₄ isomerized NAO has surprisingly better low temperature performance than the Ca alkylhydroxybenzoate derived from non-isomerized NAO at equal Ca level.

Baseline Formulation 7

[00147] A 5W-20 lubricating oil composition was prepared that contained a major amount of a base oil of lubricating viscosity and the following additives:

- (1) a borated bis-succinimide;
- (2) an ethylene carbonate-treated bissuccinimide;
- (3) a mixture of a primary zinc dialkyldithiophosphate and a secondary zinc dialkyldithiophosphate;
- (4) a mixture of Moly succinimide and diphenylamine antioxidants;
- (5) a friction modifier
- (6) a foam inhibitor
- (7) a pour point depressant
- (8) a viscosity modifier

Example 8

- (9) To baseline formulation 7 was added 0.06 wt% in terms of Ca content of a Ca alkylhydroxybenzoate of Example A and 0.12 wt% in terms of Ca content of Comparative Example D

Example 9

- (10) To baseline formulation 7 was added 0.12 wt% in terms of Ca content of a Ca alkylhydroxybenzoate of Example A and 0.06 wt% in terms of Ca content of Comparative Example D

Comparative Example 12

- (11) To baseline formulation 7 was added 0.18 wt% in terms of Ca content of a Ca alkylhydroxybenzoate of Example A.

Comparative Example 13

- (12) To baseline formulation 7 was added 0.18 wt% in terms of Ca content of Comparative Example D.
- (13) Example 8, 9 and Comparative Example 12 and 13 were evaluated in the TE 77 test as described below.

Plint TE 77 High Frequency Friction Machine

Boundary friction coefficient measurements for the Examples 8 and 9, and Comparative Examples 12 and 13 were obtained using a Plint TE-77 High Frequency Friction Machine (commercially available from Phoenix Tribology).

A 5mL sample of test oil was placed in the apparatus for each test. The TE-77 was run at 100 °C and 56N of load was placed on the testing specimen. The reciprocating speed was swept from 10Hz to 1Hz, and coefficient of friction data was collected throughout the test. The friction coefficient measurements are shown in Table 6.

Table 6 Plint TE 77

	Example 8	Example 9	Comp Example 12	Comp Example 13
1 Hz	0.01	0.01	0.06	0.02
2 Hz	0.01	0.01	0.06	0.02
3 Hz	0.01	0.01	0.07	0.02
4 Hz	0.01	0.02	0.07	0.04
5 Hz	0.01	0.03	0.07	0.06

6 Hz	0.02	0.05	0.08	0.08
7 Hz	0.05	0.07	0.08	0.10
8 Hz	0.07	0.08	0.08	0.12
9 Hz	0.09	0.09	0.09	0.13
10 Hz	0.10	0.08	0.08	0.14

Coefficient of friction data collected for these oils at reciprocating speeds of 1 to 2 Hz are in a boundary friction regime.

The boundary friction regime is an important consideration in the design of low viscosity engine oils. Boundary friction occurs when the fluid film separating two surfaces becomes thinner than the height of asperities on the surfaces. The resulting surface to surface contact creates undesirable high friction and poor fuel economy in an engine. Boundary friction in an engine can occur under high loads, low engine speeds and at low oil viscosities. Low viscosity engine oils make the engine more susceptible to operating in boundary friction conditions due to the oil's thinner, less robust film. Because additives – not base oil – influence the coefficient of friction under boundary conditions, additives that demonstrate lower coefficients of friction under boundary conditions in the TE-77 will give superior fuel economy in a low viscosity oil in an engine.

Based on the boundary friction regime results from Examples 8 and 9, it is evident that there is synergistic effect when the alkylhydroxybenzoate derived from isomerized normal alpha olefin is used together with the overbased Ca sulfonate.

Baseline Formulation 8

A 5W-30 lubricating oil composition was prepared that contained a major amount of a base oil of lubricating viscosity and the following additives:

- (1) an ethylene carbonate-treated bissuccinimide;
- (2) a highly overbased Ca sulfonate detergent
- (3) a secondary zinc dialkyldithiophosphate;
- (4) a diphenylamine antioxidant
- (5) a foam inhibitor
- (6) a pour point depressant
- (7) a viscosity modifier

Example 10

- (8) To baseline formulation 8 was added 0.2 wt% in terms of Ca content of a Ca alkylhydroxybenzoate of Example A.

Comparative Example 13

- (9) To baseline formulation 8 was added 0.2 wt% in terms of Ca content of a Ca alkylhydroxybenzoate of Comparative Example B.

Sequence IVA Test

The lubricating oil compositions of Example 10 and Comparative Example 13 were evaluated for valve tram wear in a gasoline engine: Sequence IVA, ASTM D 6891, Average cam wear (7 position average, μm). The passing limit for this test is 90 μm maximum.

Table 7. Sequence IVA Test

	Example 10	Comp. Example 13
Camshaft Wear (μm)	67	96

[00148] The Ca alkylhydroxybenzoate derived from C₂₀ - C₂₄ isomerized NAO has surprisingly better valve tram wear performance than the Ca alkylhydroxybenzoate derived from non-isomerized NAO at equal Ca level.