

LUBRICATING OIL COMPOSITION

BACKGROUND OF THE DISCLOSURE

[0001] With the need to squeeze every ounce of fuel economy out of engines, engine downsizing has become a major trend in the automotive industry. However, this can create problems in certain instances through a phenomenon called low speed pre-ignition (LSPI). In some cases, this can lead to catastrophic failure of engine hardware. Calcium coming from calcium detergents present in the lubricant has largely been identified as the bad actor. However, calcium is utilized to provide detergency as well as anti-rust performance and must be present in an appreciable amount to provide these benefits (i.e., >1800 ppm Ca). Many in the industry have lowered calcium levels and substituted in magnesium containing detergents to compensate for the problem of LSPI. While magnesium detergents have better TBN retention in general, they are quite poor at neutralizing acids. Additionally, they can be difficult to handle at times, with crystal and gel formation occurring. Thus, the need for a substantially magnesium free lubricating oil which also provides adequate corrosion control exists. The inventors of the present application have found such a solution to this problem.

SUMMARY OF THE DISCLOSURE

[0002] 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 salicylate compound derived from isomerized normal alpha olefin (NAO) having from about 10 to about 40 carbon atoms, wherein the TBN of the salicylate compound is at least 600 mg KOH/g on an actives basis, wherein the lubricating oil composition contains from about 0.12 to about 0.17 wt.% of calcium and is substantially free of magnesium.

[0003] 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 salicylate compound derived from isomerized normal alpha olefin (NAO) having from about 10 to about 40 carbon atoms, wherein the TBN of the salicylate compound is at least 600 mg KOH/g on an actives basis,

wherein the lubricating oil composition contains from about 0.12 to about 0.17 wt.% of calcium and is substantially free of magnesium.

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] “Substantially free” means less than 50, less than 40, less than 30, less than 10, less than 50 wt. ppm.

[0010] “Active ingredients” or “actives” or “oil free” refers to additive material that is not diluent or solvent.

[0011] All percentages reported are weight % on an active ingredient basis (i.e., without regard to carrier or diluent oil) unless otherwise stated.

[0012] The abbreviation “ppm” means parts per million by weight, based on the total weight of the lubricating oil composition.

[0013] Total base number (TBN) was determined in accordance with ASTM D2896.

[0014] Metal – The term “metal” refers to alkali metals, alkaline earth metals, or mixtures thereof.

[0015] High temperature high shear (HTHS) viscosity at 150°C was determined in accordance with ASTM D4863.

[0016] Kinematic viscosity at 100°C (KV₁₀₀) was determined in accordance with ASTM D445.

[0017] Cold Cranking Simulator (CCS) viscosity at -35°C was determined in accordance with ASTM D5293.

[0018] 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, alkyl dienes, 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.

[0019] 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 beginning and end of the chain.

[0020] 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.

[0021] All ASTM standards referred to herein are the most current versions as of the filing date of the present application.

[0022] 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) an salicylate compound derived from isomerized normal alpha olefin (NAO) having from about 10 to about 40 carbon atoms, wherein the TBN of the salicylate compound is at least 600 mg KOH/g-on an actives basis,

wherein the lubricating oil composition contains from about 0.12 to about 0.17 wt.% of calcium and is substantially free of magnesium.

Oil of lubricating viscosity

[0023] 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.

[0024] 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.

[0025] 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.

[0026] 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.

[0027] 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.

[0028] 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.

[0029] 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.

[0030] 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.

[0031] 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

	Base Oil Properties		
Group ^(a)	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.

[0032] 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.

[0033] 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.

[0034] 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.

Salicylate Detergent compound derived from C₁₀ - C₄₀ isomerized Normal Alpha Olefin (NAO)

[0035] In one aspect of the present disclosure, the salicylate detergent compound derived from C₁₀ - C₄₀ isomerized NAO has a TBN of at least 600, 600 or greater, from 600 - 800, 600 - 750, 600 - 700 mgKOH/g on an actives basis.

[0036] In one aspect of the present disclosure, the salicylate detergent derived from C₁₀ - C₄₀ isomerized NAO with a TBN of 600 mgKOH/gram or greater on an oil-free basis can be prepared as described in US Patent 8,993,499 which is herein incorporated in its entirety.

[0037] In one aspect of the present disclosure, the salicylate detergent derived from C₁₀ - C₄₀ isomerized NAO is a Ca salicylate detergent.

[0038] In one aspect of the present disclosure, the salicylate detergent derived from C₁₀ - C₄₀ isomerized NAO can be an alkylated hydroxybenzoate detergent. In one embodiment, the detergent can be a salicylate detergent. In another embodiment, the detergent can be a carboxylate detergent. In one aspect of the present disclosure, the salicylate detergent with a TBN of 600 mgKOH/g or greater 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, or from about 20 to about 24 carbon atoms per molecule.

[0039] In one aspect of the present disclosure, the salicylate detergent derived from C₁₀ - C₄₀ isomerized NAO with a TBN of 600 mgKOH/g or greater on an actives 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. Preferably the one or more alkylphenols with an alkyl group different from C₁₀ - C₄₀ isomerized NAO has a highly branched alkyl group of at least 9 carbon atoms, from 9 to 24, and from 10-15 carbon atoms. In one aspect of the present disclosure, the lubricating oil composition comprises about 0.03 to 0.17 wt. %, 0.04 to 0.17 wt. %, 0.05 to 0.17 wt. %, 0.06 to 0.17 wt. %, preferably 0.07 to 0.1 wt. %, preferably 0.08 to 0.16 wt. %, preferably 0.09 to 0.16 wt. %, preferably 0.10 to 0.16 wt. %, preferably 0.11 to 0.16 wt. %, preferably 0.12 to 0.16 wt%, preferably 0.13 to 0.15 wt%, preferably 0.12 to 0.15 wt%, preferably 0.06 to 0.14, 0.07 to 0.14, 0.07 to 0.12, 0.08 to 0.14 wt%, in terms of Ca content of the salicylate detergent derived from C₁₀ - C₄₀ isomerized NAO with a TBN of 600 mgKOH/g or greater on an actives basis.

[0040] In one aspect of the present disclosure, the total amount of calcium in the lubricating oil composition is from 0.12 to 0.17 wt%, from 0.13 to 0.17 wt%, from 0.14 to 0.17 wt%, from 0.12 to 0.16 wt%, from 0.12 to 0.15 wt%, from 0.12 to 0.14 wt%, from 0.13 to 0.15 wt%, from 0.13 to 0.14 wt%, from 0.14 to 0.16 wt%, and from 0.14 to 0.15 wt%.

[0041] In one aspect of the present disclosure, the lubricating oil composition comprising the salicylate derived from C₁₀ - C₄₀ isomerized NAO with TBN 600 or more on an active basis is an automotive engine oil, a gas engine oil, a motorcycle oil, a dual fuel engine oil, a mobile gas engine oil, or a locomotive engine oil.

[0042] In another aspect of the present disclosure, the lubricating oil composition is for use in an internal combustion engine equipped with an EGR control system, naturally aspirated engines, a hybrid engine oil, a turbo charged gasoline direct engine (GDI) oil.

[0043] In internal combustion engines equipped with an EGR control system, the EGR gas is very corrosive.

[0044] In situations when the engine oil temperature is low, water builds up in the oil and contacts highly corrosive EGR gas causing corrosion of engine parts. In one aspect of the present disclosure, the lubricating oil composition prevents or reduce corrosion in internal combustion engines equipped with EGR control systems. In another aspect of the present disclosure, the lubricating oil composition prevents or reduce corrosion in internal combustion engines equipped with EGR control systems where low engine oil temperature leads to build up of water which contacts highly corrosive EGR gas causing corrosion of engine parts. Especially in the case of a hybrid vehicle, this vehicle can run by a driving force from the motor, with the internal combustion engine stopped from being supplied with the

fuel. It is difficult to warm up the engine in a short time when EV running is frequently used, and it is easy for water with dissolved EGR gas to collect and accumulate. The metal-containing detergent in the lubricating oil composition of the present invention is generally available in the form of an oily dispersion which comprises a metal salt of an organic acid (generally referred to as "soap component") and particles of basic inorganic salts (e.g., calcium carbonate particles) gathering around the organic acid metal salt in a base oil. Soap content is based on 1 Kg of oil.

[0045] 1) Measurement of Organic Acid Metal Salt Content (Soap Content): The mineral oil portion and low molecular weight compounds in the metal-containing detergent are removed by the conventional rubber membrane dialysis. The residue (A) remaining in the membrane is weighed. Separately, the content of carbon dioxide originating from carbonate in the metal-containing detergent is measured, and the quantitative analysis of metal elements is carried out. From the carbon dioxide content and the metal content, the amount (B) of over-base components such as calcium carbonate or magnesium carbonate is calculated. The soap content (namely, organic acid metal salt content) is calculated by deducing (B) from (A).

In one embodiment, the total SOAP content of the lubricating oil composition is less than 18 mM. In one embodiment, the total SOAP content of the lubricating oil composition is from 2 mM to 18 mM. In another embodiment, the total SOAP content of the lubricating oil composition is from 2 mM to 17 mM, from 2 mM to 16 mM, or from 3 mM to 16 mM.

Additional Detergents

[0046] Additional calcium detergents can be present such that the total calcium in the finished oil does not exceed 0.17 wt.%.

[0047] 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, 30-600, 50-600, 100-600, 150-600, 50-500, 150-500, 50-450, 200-450 mg KOH/g on an active basis.

[0048] Detergents that may be used include oil-soluble overbased sulfonate, non-sulfur containing phenate, sulfurized phenates, salixarate, salicylate, saligenin, complex detergents and naphthenate detergents and other oil-soluble salicylates 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.

[0049] Overbased metal detergents are generally produced by carbonating a mixture of hydrocarbons, detergent acid, for example: sulfonic acid, salicylate 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.

[0050] 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.

[0051] 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.

[0052] 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.

[0053] 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.

[0054] 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.

[0055] 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.

[0056] 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.

[0057] 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.

[0058] 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.

[0059] 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.

[0060] 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.

[0061] 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.

[0062] 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.

[0063] 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.

[0064] 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.

[0065] 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.

[0066] In one embodiment, the one or more overbased detergent can be a salicylate with an alkyl group having 20-28 carbon atoms, more preferably 20-24C carbon atoms. In another embodiment, the one or more overbased detergent can be a salicylate with an alkyl group derived from C₁₄₋₁₈ NAO and contribute less than 0.05 wt%, preferably less than 0.025 wt%, more preferably less than 0.01 wt% in terms of Ca content to the lubricating oil.

[0067] 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.

Antiwear Agents

[0068] The lubricating oil composition disclosed herein can comprise one or more antiwear agent. 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., R^1+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. 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. 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

[0069] The lubricating oil composition disclosed herein can comprise one or more antioxidant. 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.

[0070] 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'-methylenebis(2,6-di-*tert*-butylphenol). Other useful hindered phenol antioxidants include hindered phenol with sulfur antioxidants such as thio-

ethylene-bis-(3-(3, 5-di-tert-butyl-4-hydroxyphenyl) propionate (IRGANOX® L-115 from Ciba).

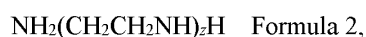
Typical aromatic amine antioxidants have at least two aromatic groups attached directly to one amine nitrogen. Typical aromatic amine antioxidants have alkyl substituent groups of at least 6 carbon atoms. Particular examples of aromatic amine antioxidants useful herein include 4,4'-dioctyldiphenylamine, 4,4'-dinonyldiphenylamine, *N*-phenyl-1-naphthylamine, *N*-(4-*tert*-octylphenyl)-1-naphthylamine, and *N*-(4-octylphenyl)-1-naphthylamine. Antioxidants may be present at 0.01 to 5 wt. % (e.g., 0.1 to 2 wt. %) of the lubricating oil composition.

Dispersants

[0071] The lubricating oil composition disclosed herein can comprise one or more dispersant. 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.

[0072] 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. 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.

[0073] 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. As is known in the art, the dispersants may be post-treated (e.g., with a boronating agent or a cyclic carbonate, ethylene carbonate etc).

[0074] 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. Dispersants may be present at 0.1 to 10 wt. % (e.g., 2 to 5 wt. %) of the lubricating oil composition.

Foam Inhibitors

[0075] The lubricating oil composition disclosed herein can comprise one or more foam inhibitor that can break up foams in oils. Non-limiting examples of suitable foam inhibitors or anti-foam inhibitors include silicone oils or polydimethylsiloxanes, fluorosilicones, alkoxyated aliphatic acids, polyethers (e.g., polyethylene glycols), branched polyvinyl ethers, alkyl acrylate polymers, alkyl methacrylate polymers, polyalkoxyamines and combinations thereof.

Additional Co-Additives

[0076] 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.

[0077] 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.

[0078] 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.

[0079] 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.

[0080] 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.

[0081] 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

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

Isomerization level (I) and NMR method

[0082] 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.

[0083] The isomerization level (I) represents the relative amount of methyl groups (-CH₃) (chemical shift 0.3-1.01 ppm) attached to the methylene backbone groups (-CH₂-) (chemical shift 1.01-1.38 ppm) and is defined by Equation (I) as shown below,

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

where m is NMR integral for methyl groups with chemical shifts between 0.3 ± 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.

[0084] The isomerized level (I) of the alpha olefin is between from about 0.1 to about 0.4, preferably from about 0.1 to about 0.3, more preferably from about 0.12 to about 0.3.

[0085] In one embodiment, the isomerization level of the NAO is about 0.16, and having from about 20 to about 24 carbon atoms.

[0086] In another embodiment, the isomerization level of the NAO is about 0.26, and having from about 20 to about 24 carbon atoms.

Baseline Formulation 1

[0087] A 0W-16 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
- (3) a mixture of primary and secondary zinc dialkyldithiophosphate in an amount of 0.077 wt.% phosphorus wherein the molar ratio of primary to secondary is 9:1;
- (4) a diphenylamine antioxidant;
- (5) a PMA comb polymer
- (6) a MoDTC compound in 0.085 wt.% of molybdenum;
- (7) a foam inhibitor; and

(8) the remainder Group III base oil.

Detergent 1

[0088] An alkylated phenol and a Ca salicylate was prepared in substantially the same manner as in U.S. Patent No. 8,993,499 using a C₂₀₋₂₄ isomerized normal alpha olefin. The isomerization level of the alpha olefin is about 0.16. The resulting salicylate composition has a TBN of about 630 and Ca content of about 22.4 wt.% on an oil-free basis.

Detergent 2

[0089] An overbased calcium sulfonate with a TBN of 690, and Ca content of about 26 wt.% on an actives basis, with an alkyl group derived from C₂₀₋₂₄ NAO.

Detergent 3

[0090] An salicylate was prepared with an alkyl group derived from C₁₄₋₁₈ NAO and a TBN about 300 and Ca content about 10.6 wt. % on an oil-free basis.

Detergent 4

[0091] An alkylated phenol and alkylated Ca salicylate 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 salicylate composition has a TBN of about 225 mgKOH/gm and Ca content of 8 wt.% on an oil-free basis.

Detergent 5

[0092] An alkylated phenol and alkylated Ca salicylate 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 salicylate composition has a TBN of about 120 mgKOH/gm and Ca content of 4.2 wt.% on an oil-free basis.

Detergent 6

[0093] An salicylate was prepared with an alkyl group derived from C₁₄₋₁₈ NAO and a TBN about 520 and Ca content about 18.7 wt. % on an oil-free basis.

Example 1

[0094] To baseline formulation 1 was added 0.14 wt.% in terms of Ca content of a detergent 1 (35 mM). Total SOAP from the detergent mixture is given below in Table 2.

Example 2

[0095] To baseline formulation 1 was added 0.14 wt.% in terms of Ca content of a mixture of mixture of detergent 1 (15.0 mM), detergent 4 (10.0 mM), and detergent 5 (10.0 mM) in approximately a 1.5:1:1 mixture based on mM of detergent. Total SOAP from the detergent mixture is given below in Table 2.

Example 3

[0096] To baseline formulation 1 was added 0.14 wt.% in terms of Ca content of a mixture of detergent 1 (23.0 mM), detergent 4 (6.0 mM), and detergent 5 (6.0 mM) in approximately a 3.83:1:1 mixture based on mM of detergent. Total SOAP from the detergent mixture is given below in Table 2.

Example 4

[0097] To baseline formulation 1 was added 0.12 wt.% in terms of Ca content of a mixture of detergent 1 (19.8 mM), detergent 4 (5.10 mM), and detergent 5 (5.10 mM) in approximately a 3.88:1:1 mixture based on mM of detergent. Total SOAP from the detergent mixture is given below in Table 3

Example 5

[0098] To baseline formulation 1 was added 0.12 wt.% in terms of Ca content of a mixture of detergent 1 (12.9 mM), detergent 4 (8.55 mM), and detergent 5 (8.55 mM) in approximately a 1.5:1:1 mixture based on mM of detergent. Total SOAP from the detergent mixture is given below in Table 3.

Example 6

[0099] To baseline formulation 1 was added 0.12 wt.% in terms of Ca content of a mixture of detergent 1 (4.2 mM), detergent 4 (12.9 mM), and detergent 5 (12.9 mM) in approximately a 0.33:1:1 mixture based on mM of detergent. Total SOAP from the detergent mixture is given below in Table 3

Example 7

[00100] To baseline formulation 1 was added 0.16 wt.% in terms of Ca content of detergent 1 (40 mM). Total SOAP from the detergent mixture is given below in Table 4.

Comparative Example A

[00101] To baseline formulation 1 was added 0.14 wt.% in terms of Ca content of detergent 2 (35 mM). Total SOAP from the detergent mixture is given below in Table 2.

Comparative Example B

[00102] To baseline formulation 1 was added 0.14 wt.% in terms of Ca content of detergent 3 (35 mM). Total SOAP from the detergent mixture is given below in Table 2.

Comparative Example C

[00103] To baseline formulation 1 was added 0.14 wt.% in terms of Ca content of a mixture of detergent 1 (5 mM), detergent 4 (15 mM), and detergent 5 (15 mM) in a 0.33:1:1 mixture based on mM of detergent. Total SOAP from the detergent mixture is given below in Table 2.

Comparative Example D

[00104] To baseline formulation 1 was added 0.14 wt.% in terms of Ca content of detergent 6 (35 mM). Total SOAP from the detergent mixture is given below in Table 2.

Ball Rust Test (BRT) - ASTM D6557

[00105] The Ball Rust test referred to herein is conducted using the method of ASTM-D-6557. The Ball Rust Test (BRT) is a procedure for evaluating the anti-corrosion ability of fluid lubricants. In accordance with ASTM D6557, a ball bearing is immersed in an oil. Air saturated with acidic contaminants is bubbled through the oil for 18 hours at 49° C. After the 18-hour reaction period, the ball is removed from the test oil and the amount of corrosion on the ball is quantified using a light reflectance technique. The amount of reflected light is reported as an average gray value (AGV). The AGV for a fresh un-corroded ball is approximately 140. A totally corroded ball has an AGV result of less than 20. A lubricating

oil composition which gives an AGV of at least 100 passes the BRT. A lubricating oil composition which gives an AGV of less than 100 fails the BRT.

Table 2 - BRT Test Results

	Ex 1	Ex 2	Ex 3	Comp Ex A	Comp Ex B	Comp Ex C	Comp Ex D
Ca (wt.%)	0.14	0.14	0.14	0.14	0.14	0.14	0.14
Total SOAP from detergents (mM)	3.96	13.4	9.62	1.96	12.25	18.12	4.9
BRT	126	113	112	91	81	86	81

Table 3 - BRT Test Results

	Ex 4	Ex 5	Ex 6
Ca (wt.%)	0.12	0.12	0.12
Total SOAP from detergents (mM)	8.2	11.46	15.57
BRT	117	132	113

Table 4 - BRT Test Results

	Ex 7
Ca (wt.%)	0.16
Total SOAP from detergents (mM)	4.52
BRT	122