

LUBRICATING OIL COMPOSITIONS

BACKGROUND OF THE DISCLOSURE

[0001] The requirements of engine lubricants have become more demanding to keep pace with modern engine designs. One such requirement is the need for stronger anti-oxidation which has heightened the search for new antioxidants. Oxidation of engine oils negatively impacts the performance of the lubricating oil additives and reduces the performance life of the engine oil.

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) one or more detergents comprising at least one alkylhydroxybenzoate compound derived from isomerized NAO having from about 10 to about 40 carbon atoms; and
- (c) an ashless sulfur compound, wherein the ashless sulfur compound is not a dithiocarbamate.

[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,
- (b) one or more detergents comprising at least one alkylhydroxybenzoate compound derived from isomerized NAO having from about 10 to 40 carbon atoms; and
- (c) an ashless sulfur compound, wherein the ashless sulfur compound is not a dithiocarbamate.

DETAILED DESCRIPTION OF THE DISCLOSURE

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

[0014] High temperature high shear (HTHS) viscosity at 150°C was determined in accordance with ASTM D4863.

[0015] Kinematic viscosity at 100°C (KV₁₀₀) was determined in accordance with ASTM D445.

[0016] Cold Cranking Simulator (CCS) viscosity at -35°C was determined in accordance with ASTM D5293.

[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, 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.

[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 beginning and end of the 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] This disclosure describes lubricating oil compositions comprising a combination of alkylhydroxybenzoate detergents and ashless sulfur compounds wherein the combination synergistically controls oxidation of engine oils.

[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) one or more detergents comprising at least one alkylhydroxybenzoate compound derived from isomerized normal alpha olefins having from about 10 to 40 carbon atoms; and
- (c) an ashless sulfur compound, wherein the ashless sulfur compound is not a dithiocarbamate.

[0023] In another aspect, 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) one or more detergents comprising at least one alkylhydroxybenzoate compound derived from isomerized normal alpha olefins having from about 10 to 40 carbon atoms, and
- (c) an ashless sulfur compound, wherein the ashless sulfur compound is not a dithiocarbamate.

[0024] Alkylhydroxybenzoate Detergent compound derived from C₁₀ - C₄₀ isomerized Normal Alpha Olefin (NAO)

[0025] In one aspect of the present disclosure, the TBN of the alkylhydroxybenzoate detergent derived from C₁₀-C₄₀ isomerized NAO is from about 100 to about 700, such as from about 100 to about 650, from about 100 to about 600, from about 100 to about 500, from about 100 to about 400, from about 100 to 300, from about 150 to 250, from about 175 to about 250, from about 175 to about 225 mg KOH/gram on oil free-basis.

[0026] In one aspect of the present disclosure, the alkylhydroxybenzoate detergent is derived from C₁₀-C₄₀ isomerized NAO and has a TBN of from about 10 to about 300, such as from about 50 to about 300, from about 100 to about 300, from about 150 to about 300, and from about 175 to about 250 mg KOH/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.

[0029] In one aspect of the present disclosure, the alkylhydroxybenzoate derived from C₁₀-C₄₀ isomerized NAO may be prepared as described in US Patent 8, 993,499 which is herein incorporated in its entirety.

[0030] In one aspect of the present disclosure, the alkylhydroxybenzoate detergent is made from an alkylphenol having an alkyl group derived from an isomerized alpha olefin having from about 10 to about 40 carbon atoms per molecules, such as from about 14 to about 28 carbon atoms per molecule, from about 20 to about 24 carbon atoms, from about 14 to about 18 carbon atoms, and 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 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, such as from about 0.10 to about 0.35, from about 0.10 to about 0.30, from about 0.12 to about 0.30 and from about 0.12 to about 0.20.

[0032] In one aspect of the present disclosure, the alkylhydroxybenzoate derived from C₁₀-C₄₀ isomerized NAO 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 the C₁₀-C₄₀ isomerized NAO.

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

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

[0035] The alkylhydroxybenzoate detergents derived from C₁₀-C₄₀ isomerized NAO may include 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.

[0036] In one aspect of the present disclosure, the lubricating oil composition comprises about 0.01 to about 2.0 wt.% in terms of Ca content of the alkylhydroxybenzoate derived from C₁₀-C₄₀ isomerized NAO, such as from about 0.1 to about 1.0 wt. %, from about 0.05 to about 0.5 wt. %, and from about 0.1 to about 0.5 wt.%.

[0037] In one aspect of the present disclosure, the lubricating oil composition comprises about 0.01 to about 2.0 wt.% in terms of Mg content of the alkylhydroxybenzoate derived from C₁₀-C₄₀ isomerized NAO, such as from about 0.1 to about 1.0 wt. % from about 0.05 to about 0.5 wt. %, and from about 0.1 to about 0.5 wt.%.

[0038] In one aspect of the present disclosure, the lubricating oil composition comprising the alkylhydroxybenzoate detergent derived from C₁₀-C₄₀ isomerized NAO 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.

[0039] In one aspect of the present disclosure, the lubricating oil composition comprising the alkylhydroxybenzoate detergent derived from C₁₀-C₄₀ isomerized NAO is a functional fluid for automotive and industrial applications, such as transmission oil, hydraulic oil, tractor fluid, gear oil, and the like.

[0040] In one aspect of the present disclosure, the lubricating oil composition comprising the alkylhydroxybenzoate detergent derived from C₁₀-C₄₀ isomerized NAO is a multi-grade oil or mono-grade oil.

[0041] In one aspect of the present disclosure, the lubricating oil composition comprising the alkylhydroxybenzoate detergent derived from C₁₀-C₄₀ isomerized NAO lubricates crankcases, gears, as well as clutches.

[0042] Ashless Sulfur Compounds

[0043] Sulfurized fatty esters

[0044] In one aspect, the ashless sulfur compound is a sulfurized fatty ester. The sulfurized fatty acid esters are prepared by reacting sulfur, sulfur monochloride, and/or sulfur dichloride with an unsaturated fatty ester under elevated temperatures. Typical esters include C₁-C₂₀ alkyl esters of C₈-C₂₄ unsaturated fatty acids, such as palmitoleic, oleic, ricinoleic, petroselinic, vaccenic, linoleic, linolenic, oleostearic, licanic, paranaric, tariric, gadoleic, arachidonic, cetoleic, etc. Particularly good results have been obtained with mixed unsaturated fatty acid esters, such as are obtained from animal fats and vegetable oils, such as tall oil, linseed oil, olive oil, castor oil, peanut oil, rape oil, fish oil, sperm oil, and so forth.

[0045] Exemplary fatty esters include lauryl tallate, methyl oleate, ethyl oleate, lauryl oleate, cetyl oleate, cetyl linoleate, lauryl ricinoleate, oleyl linoleate, oleyl stearate, and alkyl glycerides.

[0046] Sulfurized Olefins

[0047] In one aspect, the ashless sulfur compound is a sulfurized olefin. Cross-sulfurized ester olefins, such as a sulfurized mixture of C₁₀ to C₂₅ olefins with fatty acid esters of C₁₀ to C₂₅ fatty acids and C₁₀ to C₂₅ alkyl or alkenyl alcohols, wherein the fatty acid and/or the alcohol is unsaturated may also be used. Sulfurized olefins are usually derived from alpha olefins, isomerized alpha olefins, cyclic olefins, branched olefins, and polymeric olefins that are reacted with a sulfur source. Specific examples of olefins include but are not limited to; 1-butene, isobutylene, diisobutylene, 1-pentene, 1-hexene, 1-heptene, 1-octene, and more with longer carbon chains up to C₆₀ and beyond to polymeric olefins. Other examples of non-normal alpha olefins (NAOs) include cyclohexene, cyclooctene, amalyne, isoamylene, branched and internal olefin isomers of NAOs.

[0048] Examples of sulfur sources include sulfur, hydrogen sulfide, sodium hydrogen sulfide, sodium sulfide, sulfur chloride, and sulfur dichloride.

[0049] Also useful are the aromatic and alkyl sulfides, such as dibenzyl sulfide, dityl sulfide, dicetyl sulfide, diparaffin wax sulfide and polysulfide, cracked wax-olefin sulfides and so forth. They can be prepared by treating the starting material, e.g., olefinically unsaturated compounds, with sulfur, sulfur monochloride, and sulfur dichloride. Particularly preferred are the paraffin wax thiomers described in U.S. Pat. No. 2,346,156.

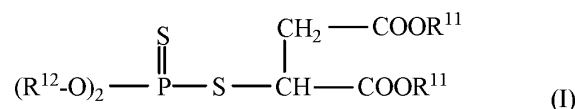
[0050] Thiadiazoles:

[0051] In one aspect, the ashless sulfur compound is a thiadiazole. Thiadiazoles include at least one of 2,5-dimercapto-1,3,4-thiadiazole; 2-mercapto-5-hydrocarbylthio-1,3,4-thiadiazoles; 2-mercapto-5-hydrocarbyldithio-1,3,4-thiadiazoles; 2,5-bis(hydrocarbylthio and

2,5-bis(hydrocarbyldithio)-1,3,4-thiadiazoles. Preferred compounds are the 1,3,4-thiadiazoles, especially the 2-hydrocarbyldithio-5-mercapto-1,3,4-dithiadiazoles and the 2,5-bis(hydrocarbyldithio)-1,3,4-thiadiazoles, a number of which are available as articles of commerce. Other preferred compounds include a non-polycarboxylate containing thiadiazole containing about 4.0 wt% 2,5-dimercapto-1,3,4-thiadiazole, which are commercially available as Hitec® 4313 from Afton Chemical (Richmond, Virginia) or Lubrizol® 5955A from Lubrizol Corporation (Wycliffe, Ohio).

[0052] Ashless Dithiophosphates:

[0053] In one aspect, the ashless sulfur compound is an ashless dithiophosphate. One class of suitable ashless dithiophosphates for use herein include those of represented by Formula (I):



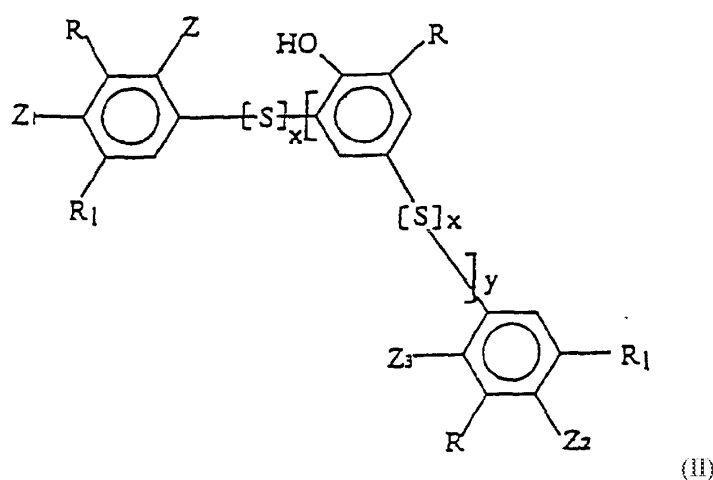
wherein R¹¹ and R¹² are independently an alkyl group having 3 to 8 carbon atoms. Suitable ashless dithiophosphates include VANLUBE® 7611M which is commercially available from R.T. Vanderbilt Co., Inc.

[0054] Another class of suitable ashless dithiophosphates for use herein include dithiophosphoric acid esters of carboxylic acid such as IRGALUBE® 63 which is commercially available from BASF.

[0055] Yet another class of suitable ashless dithiophosphates for use herein include triphenylphosphorothionates such as IRGALUBE® TPPT commercially available from BASF.

[0056] Sulfurized Hindered Phenols:

[0057] In one aspect, the ashless sulfur compound is a sulfurized hindered phenol. The sulfurized hindered phenols suitable for use in the present invention can be prepared by a number of known methods. The sulfurized hindered phenols are characterized by the type of hindered phenols used in their production and their final sulfur content. Hindered tert-butylphenols are preferred. The sulfurized hindered phenols may be chlorine-free, being prepared from chlorine-free sulfur sources such as elemental sulfur, sodium sulfide, or sodium polysulfide, or they may contain chlorine, being prepared from chlorinated sulfur sources such as sulfur monochloride and sulfur dichloride. Preferred sulfurized hindered phenols include those represented by Formula (II).



wherein R is an alkyl group, R₁ is an alkyl group or hydrogen, one of Z or Z₁ is -OH group with the other being hydrogen, one of Z₂ or Z₃ is -OH group with the other being hydrogen, x is in the range of from 1 to 6, and y is in the range of from 0 to 2.

[0058] Suitable chlorine-free, sulfurized hindered phenols may be prepared by the methods taught in U.S. Patent No. 3,929,654 or may be obtained by (a) preparing a mixture of (i) at least one chlorine-free hindered phenol, (ii) a chlorine-free sulfur source, and (iii) at least one alkali metal hydroxide promoter, in a polar solvent, and (b) causing components (i), (ii) and (iii) to react for sufficient time and at a sufficient temperature so as to form at least one chlorine-free sulfurized hindered phenol, as taught in co-pending applications 08/657,141 filed June 3, 1996 and 08/877,533 filed February 19, 1997.

[0059] Suitable sulfurized hindered phenol products prepared from a chlorinated sulfur source include those products taught in U.S. Patent Nos. 3,250,712 and 4,946,610, both of which are hereby incorporated by reference.

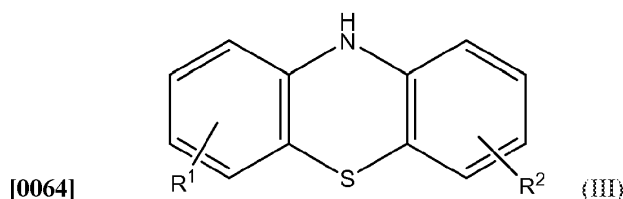
[0060] Examples of sulfurized hindered phenols that may be used in this invention include 4,4'-thiobis(2,6-di-t-butylphenol), 4,4'-dithiobis(2,6-di-t-butylphenol), 4,4'-thiobis(2-t-butyl-6-methylphenol), 4,4'-dithiobis(2-t-butyl-6-methylphenol), 4,4'-thiobis(2-t-butyl-5-methylphenol), and mixtures of these.

[0061] It is preferred that the sulfurized hindered phenols be a substantially liquid product. As used herein, substantially liquid refers to compositions that are chiefly liquid. In this regard, aged samples of the sulfurized hindered phenols may form a slight amount of crystallization, generally around the sides of the container where product comes in contact

with air and the glass container surface. It is further preferred that the sulfurized hindered phenols be chlorine-free, of low corrosivity and having a high content of monosulfide as described in co-pending applications 08/657,141 filed June 3, 1996 and 08/877,533 filed February 19, 1997. It is also preferred that the sulfur content of the sulfurized hindered phenol be in the range of about 4.0 wt. % to about 12.0 wt. % of the additive concentrate.

[0062] Phenothiazines:

[0063] In one aspect, the ashless sulfur compound is a phenothiazine. Phenothiazines useful in the practice of the invention include alkylated phenothiazine compounds represented by Formula (III):



[0065] wherein R¹ is a linear or branched group having from 4 to 24 carbon atoms, such as 4 to 10, carbon atoms and being an alkyl or alkylaryl group; and R² is, independently of R¹, a linear or branched group having from 4 to 24 carbon atoms, such as 4 to 10 carbon atoms and being an alkyl or alkylenyl group, or is a hydrogen atom.

[0066] As an example of the above Formula (III), R¹ is a nonyl group and R² is a hydrogen atom or a nonyl group.

[0067] In one aspect of the alkylated phenothiazine, R¹ is preferably an alkyl group having 4 to 10 carbon atoms and R² is a hydrogen atom or an alkyl group having 4 to 10 carbon atoms.

[0068] The alkylated phenothiazines preferably comprise mixtures of mono- and dialkylated phenothiazines, for example, wherein about 15 to about 85 mass % of the mixture is monalkylated.

[0069] Alkylated phenothiazines are known in the art and may be prepared by methods known in the art. For example, phenothiazine may be alkylated in the presence of an acid catalyst by reaction with a C₁ to C₁₀ olefin or mixture thereof, suitable such olefins including alpha olefins and internal olefins, for example isobutylene, diisobutylene, nonene and 1-decene.

Additional Detergents

[0070] The lubricating oil composition of the present invention can further contain one or more overbased detergents having a TBN of about 10 to about 800, such as from about 10 to

about 700, from about 30 to about 690, from about 100 to about 600, from about 150 to about 600, from about 150 to about 500, and from about 200 to about 450 mg KOH/g on an actives basis.

[0071] 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 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.

[0072] 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.

[0073] Overbased detergents may be low overbased, e.g., an overbased salt having a TBN below about 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.

[0074] In some embodiments, 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.

[0075] In some embodiments, overbased detergents may be high overbased, e.g., an overbased salt having a TBN above about 250. In one embodiment, the TBN of a high overbased salt may be from about 250 to about 800 on an actives basis.

[0076] 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.

[0077] 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.

[0078] 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.

[0079] 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. 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.

[0080] 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 about 20 to about 40 carbon atoms, preferably about 20 to about 28 carbon atoms, more preferably, isomerized NAO having about 20 to about 40 carbon atoms.

[0081] 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 include those obtained by alkylating benzene, toluene, xylene, naphthalene, diphenyl or their halogen derivatives. The alkyl group of 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 about 30 carbon atoms, and more preferably about 20 to about 24 carbon atoms.

[0082] 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. Neutral or overbased detergent 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 two or more phenols are bridged by sulfur containing bridges.

[0083] 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.

[0084] The reactants and reagents used in the present process may utilize all allotropic forms of sulfur. 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.

[0085] In certain circumstances, it may be desirable to use calcium hydroxide as the calcium base because of its excellent performance. Calcium hydroxide is considered more convenient to handle than, for example, calcium oxide. Other compatible calcium bases include, for example, calcium alkoxides.

[0086] 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.

[0087] 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 and having an isomerization 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.

[0088] In one embodiment, suitable alkyl phenolic compounds may be sourced from 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.

[0089] 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 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 being 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.

[0090] 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.

[0091] In one embodiment, the one or more overbased detergent can be a salicylate with an alkyl group having about 20 to about 28 carbon atoms, more preferably about 20 to about 24 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 about 0.05 wt%, preferably less than about 0.025 wt%, more preferably less than about 0.01 wt% in terms of Ca content to the lubricating oil.

[0092] 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.

Anti-wear Agents

[0093] The lubricating oil composition disclosed herein can comprise one or more anti-wear agent. Anti-wear agents reduce wear of metal parts. Suitable anti-wear agents include dihydrocarbyl dithiophosphate metal salts such as zinc dihydrocarbyl dithiophosphates (ZDDP) of Formula (IV):



wherein R¹ and R² may be the same or different hydrocarbyl group having from 1 to 18 (e.g., 2 to 12) carbon atoms. Suitable hydrocarbyl groups include, but are not limited to,

alkyl, alkenyl, aryl, arylalkyl, alkaryl and cycloaliphatic groups. Particularly preferred R^1 and R^2 groups include alkyl groups having from 2 to 8 carbon atoms (e.g., 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) should 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 about 3 wt. % or less (e.g., about 0.1 to about 1.5 wt. %, or about 0.5 to about 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

[0094] The lubricating oil composition disclosed herein can comprise one or more antioxidant. Antioxidants reduce the tendency of mineral oils to deteriorate during service. Oxidative deterioration can be evidenced by sludge in the lubricant, varnish-like deposits on the metal surfaces, and/or by viscosity growth. Suitable antioxidants include hindered phenols, aromatic amines, and sulfurized alkylphenols and alkali and alkaline earth metals salts thereof.

[0095] 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).

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 about 0.01 to about 5 wt. % (e.g., about 0.1 to about 2 wt. %) of the lubricating oil composition.

Dispersants

[0096] 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.

[0097] 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 about 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.

[0098] Particularly preferred ashless dispersants are the polyisobutenyl succinimides formed from polyisobutenyl succinic anhydride and a polyalkylene polyamine such as a polyethylene polyamine of Formula (V):



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 about 700 to about 3000 Daltons (e.g., about 900 to about 2500 Daltons). For example, the polyisobutenyl succinimide may be a bis-succinimide derived from a polyisobutenyl group having a M_n of about 900 to about 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).

[0099] 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 about 0.1 to about 10 wt. % (e.g., about 2 to about 5 wt. %) of the lubricating oil composition.

Foam Inhibitors

[00100] 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

[00101] 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.

[00102] In the preparation of lubricating oil formulations, it is common practice to introduce the additives in the form of about 10 to about 100 wt. % active ingredient concentrates in hydrocarbon oil, e.g. mineral lubricating oil, or other suitable solvent.

[00103] Usually these concentrates may be diluted with about 3 to about 100, e.g., about 5 to about 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.

[00104] 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.

[00105] 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

[00106] 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.

[00107] 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.

[00108] 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.

[00109] 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.

[00110] 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.

[00111] 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.

[00112] 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.

[00113] 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.

[00114] 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

	<u>Base Oil Properties</u>		
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.

[00115] 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.

[00116] 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 about 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.

[00117] 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

[00118] 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. %, about 0.01 to about 0.6 wt.%, about 0.01 to about 0.5 wt.%, about 0.01 to about 0.4 wt.%, about 0.01 to about 0.3 wt.%, about 0.01 to about 0.2 wt.%, about 0.01 wt. % to about 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.

[00119] 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. %.

[00120] 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.

[00121] In certain embodiments, the present disclosure provides lubricating oil compositions suitable for reducing friction in passenger car internal combustion engines, particularly spark-ignited, direct injection and/or port fuel injection engines. In certain embodiments, the engine may be coupled to an electric motor/battery system in a hybrid vehicle (e.g., a port fuel injection spark ignition engine coupled to an electric motor/battery system in a hybrid vehicle). In certain embodiments, the present disclosure provides lubricating oil compositions suitable for reducing friction in heavy duty diesel internal combustion engines.

[00122] 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

[00123] 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 at 400 MHz using TopSpin 3.2 spectral processing software. The NMR samples were dissolved in chloroform-d1.

[00124] 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 (1) as shown below,

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

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.

[00125] The isomerization 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.

[00126] In one embodiment, the isomerization level of the NAO is about 0.16, and having from about 20 to about 24 carbon atoms.

[00127] In another embodiment, the isomerization level of the NAO is about 0.26, and having from about 20 to about 24 carbon atoms.

Example A

[00128] An alkylated phenol and 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. The isomerization level of the alpha olefin is about 0.16. The resulting alkylhydroxybenzoate composition has a TBN of about 225 and Ca content of about 8 wt.% on an oil-free basis.

Comparative Example B

[00129] An alkylhydroxybenzoate was prepared from an alkylphenol 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.

Example C

[00130] Example C is a sulfurized olefin namely sulfurized isobutylene.

Example D

[00131] Example D is a sulfurized fatty ester which is (9-Octadecenoic acid (Z)-, isooctyl ester, reaction products with glycerol trioleate and sulfur).

Example E

[00132] Example E is an ashless dithiocarbamate, namely methylenebis (dibutyldithiocarbamate).

Example F

[00133] Example F is a thiadiazole with the tradename Hitec 4313.

Example G

[00134] Example G is an ashless dithiophosphate with the tradename Irgalube TPPT.

Example H

[00135] Example H is a sulfurized phenol with a sulfur content of 15.8 wt. %.

Baseline Formulation 1

[00136] A 15W-40 lubricating oil composition was prepared that contained a major amount of a group II base oil of lubricating viscosity and the following additives:

- (1) mixture of three dispersants
- (2) secondary zinc dialkyldithiophosphate in an amount of 0.077 wt. % phosphorus;

- (3) olefin copolymer viscosity index improver;
- (4) polymethacrylate pour point depressant; and
- (5) foam inhibitor

Example 1

[00137] To baseline 1 was added between 30 to 36 mM of Example A providing the lubricant with between 1200 to 1400 ppm of Ca. Also added was 0.29 wt.% of Example C providing the finished oil with approximately 1300 ppm of sulfur.

Example 2

[00138] To baseline 1 was added between 30 to 36 mM of Example A providing the lubricant with between 1200 to 1400 ppm of Ca. Also added was 1.35 wt.% of Example D providing the finished oil with approximately 1300 ppm of sulfur.

Example 3

[00139] To baseline 1 was added between 30 to 36 mM of Example A providing the lubricant with between 1200 to 1400 ppm of Ca. Also added was 0.375 wt.% of Example F providing the finished oil with approximately 1300 ppm of sulfur.

Example 4

[00140] To baseline 1 was added between 30 to 36 mM of Example A providing the lubricant with between 1200 to 1400 ppm of Ca. Also added was 1.452 wt.% of Example G providing the finished oil with approximately 1300 ppm of sulfur.

Example 5

[00141] To baseline 1 was added between 30 to 36 mM of Example A providing the lubricant with between 1200 to 1400 ppm of Ca. Also added was 0.854 wt.% of Example H providing the finished oil with approximately 1300 ppm of sulfur.

Comparative Example 1

[00142] To baseline 1 was added between 30 to 36 mM of Comparative Example B providing the lubricant with between 1200 to 1400 ppm of Ca. Also added was 0.29 wt.% of Example C providing the finished oil with approximately 1300 ppm of sulfur.

Comparative Example 2

[00143] To baseline 1 was added between 30 to 36 mM of Comparative Example B providing the lubricant with between 1200 to 1400 ppm of Ca. Also added was 1.35 wt.% of Example D providing the finished oil with approximately 1300 ppm of sulfur.

Comparative Example 3

[00144] To baseline 1 was added between 30 to 36 mM of Example A providing the lubricant with between 1200 to 1400 ppm of Ca. Also added was 0.45 wt.% of Example E providing the finished oil with approximately 1300 ppm of sulfur.

Comparative Example 4

[00145] To baseline 1 was added between 30 to 36 mM of Comparative Example B providing the lubricant with between 1200 to 1400 ppm of Ca. Also added was 0.45 wt.% of Example E providing the finished oil with approximately 1300 ppm of sulfur.

Example I

[00146] Example I is prepared by a slurry of MgO (82 grams) in MeOH (81.4 grams) and xylene (500 grams) is prepared and introduced into a reactor. Then the hydroxybenzoic acid made from isomerized alpha olefin (C20-24, 0.16 isomerization level), (1774 grams, 43% active in xylene) is loaded into the reactor and the temperature kept at 40°C for 15 minutes. Then dodecenylanhdyride (DDSA, 7.6 grams) followed by AcOH (37.3 grams) then H₂O (69 grams) are introduced in the reactor over 30 minutes while the temperature is ramped up to 50°C. CO₂ is then introduced in the reactor under strong agitation (96 grams). Then a slurry consisting of MgO (28 grams) in xylene (200 grams) is introduced in the reactor and a further quantity of CO₂ is bubbled through the mixture. At the end of CO₂ introduction, distillation of the solvent is accomplished by heating to 132 °C . 500 grams of base oil is then introduced in the reactor. The mixture is then centrifuged in a lab centrifuge to remove unreacted magnesium oxide and other solid. Finally, the mixture is heated at 170°C under vacuum (15 mbar) to remove the xylene and to lead to the final product containing 4.3% Magnesium as a C₂₀-C₂₄ magnesium alkylhydroxybenzoate detergent, made

from isomerized NAO with isomerization level of 0.16. Properties: TBN (mgKOH/g) = 199 in 35 wt% of diluent oil.

Comparative Example J

[00147] Comparative Example J is C₁₄-C₁₈ magnesium alkylhydroxybenzoate detergent, made from alpha olefin. Properties: TBN (mgKOH/g) = 236; Mg (wt.%) = 5.34.

Comparative Example 5

[00148] To baseline 1 was added between 38 to 46 mM of Example I providing the lubricant with between 900 to 1200 ppm of Mg. Also added was 0.45 wt.% of Example E providing the finished oil with approximately 1300 ppm of sulfur.

Comparative Example 6

[00149] To baseline 1 was added between 38 to 46 mM of Comparative Example J providing the lubricant with between 900 to 1100 ppm of Mg. Also added was 0.45 wt.% of Example E providing the finished oil with approximately 1300 ppm of sulfur.

Comparative Example 7

[00150] To baseline 1 was added between 30 to 36 mM of Comparative Example B providing the lubricant with between 1200 to 1400 ppm of Ca. Also added was 0.375 wt.% of Example F providing the finished oil with approximately 1300 ppm of sulfur.

Comparative Example 8

[00151] To baseline 1 was added between 30 to 36 mM of Comparative Example B providing the lubricant with between 1200 to 1400 ppm of Ca. Also added was 1.452 wt.% of Example G providing the finished oil with approximately 1300 ppm of sulfur.

Comparative Example 9

[00152] To baseline 1 was added between 30 to 36 mM of Comparative Example B providing the lubricant with between 1200 to 1400 ppm of Ca. Also added was 0.854 wt.% of Example H providing the finished oil with approximately 1300 ppm of sulfur.

Example K

[00153] An alkylated phenol and 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. The isomerization level of the alpha olefin is about 0.15. The resulting alkylhydroxybenzoate composition has a TBN of about 225 and Ca content of about 8 wt.% on an oil-free basis.

Example L

[00154] An alkylated phenol and 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. The isomerization level of the alpha olefin is about 0.219. The resulting alkylhydroxybenzoate composition has a TBN of about 225 and Ca content of about 8 wt.% on an oil-free basis.

Example M

[00155] An alkylated phenol and 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. The isomerization level of the alpha olefin is about 0.23. The resulting alkylhydroxybenzoate composition has a TBN of about 225 and Ca content of about 8 wt.% on an oil-free basis.

Example 6

[00156] To baseline 1 was added between 30 to 36 mM of Example K providing the lubricant with between 1200 to 1400 ppm of Ca. Also added was 0.29 wt.% of Example C providing the finished oil with approximately 1300 ppm of sulfur.

Example 7

[00157] To baseline 1 was added between 30 to 36 mM of Example L providing the lubricant with between 1200 to 1400 ppm of Ca. Also added was 0.29 wt.% of Example C providing the finished oil with approximately 1300 ppm of sulfur.

Example 8

[00158] To baseline 1 was added between 30 to 36 mM of Example M providing the lubricant with between 1200 to 1400 ppm of Ca. Also added was 0.29 wt.% of Example C providing the finished oil with approximately 1300 ppm of sulfur.

The Oxidation-Nitration Test

[00159] The Oxidation-Nitration bench test demonstrates the capacity of lubricating oil to resist oxidation and nitration. This test is an additional tool to help determine the performance of oils as they relate to the actual service of lubricating engines that use natural gas as a fuel source. The lower the value for oxidation and nitration at the end of the test, the superior the product's performance. The Oxidation-Nitration bench test was designed to simulate Caterpillar 3500 series engine conditions as related to actual field performance of the Caterpillar 3516 model. Oxidation-Nitration tests were performed on Examples 1-8 and Comparative Examples 1-9. The lubricating oil compositions from these Examples were placed in a heated glassware bath and subjected to calibrated levels of nitrous oxide gas over a specific period of time. The tests were run on each sample in duplicate and the results are an average of the two runs. The samples were evaluated using differential infra-red spectroscopy before placing them in the heated glassware bath to determine a base line for each sample. The samples were reevaluated at the end of testing period. The differential between the base line data, absorbance units at 5.8 and 6.1 microns, and the data taken at the end of test cycle provides an indication of the oxidation-nitration resistance of the samples.

[00160] Differential infra-red spectroscopy measures the amount of light that is absorbed by an oil sample and provides a unit of measure called an absorbance unit. DIR (Differential Infrared) spectra was determined by subtracting the fresh oil spectra from the used oil spectra to observe changes that have occurred due to oxidation, nitration, fuel dilution, soot accumulation, and or contamination. Typically a 0.1 millimeter (mm) cell is used; however an ATR crystal setup may be used after determining its associated path length. If the instrument does not have software that determines path length, the path length may be back calculated by measuring oxidation with a calibrated 0.1 mm cell. The variation between ATR and vertical

cell measurements is minimal if restricted to the narrow area of oxidation and nitration (~ 1725 to 1630 cm^{-1}).

[00161] DIR Oxidation was measured from peak maximum at $\sim 1715 \pm 5\text{ cm}^{-1}$ to the spectra baseline (in units of absorbance).

[00162] DIR Nitration was measured from peak maximum at $\sim 1630 \pm 1\text{ cm}^{-1}$ to peak baseline (in units of absorbance).

[00163] Oxidation levels of 5.8 microns and Nitration levels of 6.1 microns were used as peak height comparisons.

[00164] The Examples which contain the ashless sulfur compound and isomerized NAO detergent performed superior to its counterpart Comparative Examples which contain the same ashless sulfur compound and non-isomerized detergent, with respect to oxidation. This test, which quantify the resistance to oxidation of lubricating oils, are used to determine whether samples are good candidates for extending the life of lubricating oils. Oxidation is undesirable for lubricating oil.

[00165] Examples 1-8 and Comparative Examples 1-9 were tested separately by using each one as a lubricant in the bench test.

[00166] The oxidation performance of the samples was analyzed using differential IR as described above.

[00167] The following table shows the Oxidation performance.

Table 2
Oxidation Performance Evaluation

	Oxidation
Example 1	59.0
Comparative Example 1	153.62
Example 2	42.95
Comparative Example 2	92.35
Comparative Example 3	49.08
Comparative Example 4	36.83
Comparative Example 5	115.31
Comparative Example 6	83.44
Example 3	10
Example 4	59.17
Example 5	21
Comparative Example 7	105
Comparative Example 8	125.61
Comparative Example 9	56
Example 6	84
Example 7	66
Example 8	112