

US 20150191671A1

# (19) United States

# (12) Patent Application Publication MAYERNICK

## (10) Pub. No.: US 2015/0191671 A1

## (43) **Pub. Date:** Jul. 9, 2015

#### (54) LUBRICATING COMPOSITION

- (71) Applicant: **SHELL OIL COMPANY**, Houston, TX (US)
- (72) Inventor: **Adam David MAYERNICK**, Houston, TX (US)
- (21) Appl. No.: 14/589,032
- (22) Filed: Jan. 5, 2015

#### Related U.S. Application Data

(60) Provisional application No. 61/924,501, filed on Jan. 7, 2014.

### Publication Classification

(51) **Int. Cl.** (2006.01)

#### (57) ABSTRACT

A lubricating oil composition that includes a base oil comprising a Fischer-Tropsch derived base oil and an anti-corrosive compound. The anti-corrosive compound can be present in an amount between 0.001 and 8% by weight, preferably between 1 and 5% by weight.

#### **LUBRICATING COMPOSITION**

[0001] The present invention relates to a lubricating composition, in particular a lubricating composition having improved oxidation stability, demulsibility, filterability, corrosion reduction, and deposit reduction.

[0002] As is disclosed in for example D. J. Wedlock et al., "Gas-to-Liquids Base Oils to assist in meeting OEM requirements 2010 and beyond", presented at the 2nd Asia-Pacific base oil Conference, Beijing, China, 23-25 Oct. 2007, the use of Fischer-Tropsch derived base oils in lubricating compositions such as engine oils, transmission fluids, and industrial lubricants can result in various performance benefits. Examples of performance benefits by the use of Fischer-Tropsch derived base oils mentioned in the above article include: improved oxidation properties, improved engine cleanliness, improved wear protection, improved emissions and improved after-treatment device compatibility. Also the Fischer-Tropsch base oils allow for the formulation of low-viscosity energy conserving formulations.

[0003] Fischer-Tropsch derived base oils are highly paraffinic API group III base oils (API Base Oil Interchangeability Guidelines) exhibiting very good cold flow properties, high oxidative stability, and high viscosity indices. However, due to the high paraffin content the solvency of the base oils is generally low, often resulting in incompatibility with other lubricant components and additives.

[0004] Fischer-Tropsch base oils may have relatively low solvency. As used herein the term "solvency" in relation to a base oil means the ability of that base oil to dissolve various performance additives or, for that matter, dissolve any component that may potentially "desolvate" and form solids or a second liquid phase, including oxidation byproducts. Thus, in one embodiment, it would be desirable to develop lubricating compositions having increased solvency at the same time as exhibiting the other performance benefits mentioned above, in particular improved oxidation stability and reduced piston deposits.

[0005] One or more of the above or other objects can be obtained by a lubricating oil composition comprising:

- (a) a base oil selected from Group III base oils, Group IV polyalphaolefins, or a combination thereof; and
- (b) between 0.0001 and 10 wt % of a corrosion inhibiting compound.

[0006] In certain embodiments, the lubricating oil composition can include a solvent in which the corrosion inhibiting compound can be dissolved. In certain embodiments, the lubricating oil composition can further include an antioxidant, wherein the antioxidant can be selected from aminic antioxidants, phenolic antioxidants, and mixtures thereof. In certain embodiments, the lubricant composition can further include one or more detergent compounds having a TBN (total base number equivalent, as determined by ASTM D2896) in the range of from 0-400.

[0007] It has surprisingly been found that the lubricating compositions according to the present invention exhibit improved oxidation stability, foaming performance, air release, demulsibility, filterability, corrosion reduction, engine oil rust reduction, copper corrosion reduction and deposit reduction.

[0008] The lubricant composition described herein can find a variety of uses as a lubricant, including but not limited to, passenger car engine oils, heavy duty diesel engine oils, trans-

mission lubricants, turbine oils, air compressor lubricants, hydraulic fluids, gear oils, greases, transformer oils, marine lubricants, and the like.

[0009] The base oil used in the lubricating composition according to the present invention is selected from a Group III base oil, a polyalphaolefin, and mixtures thereof. The base oil used in the present invention may conveniently comprise mixtures of one or more Group III base oils and/or polyalphaolefins, thus, according to the present invention, the term "base oil" may refer to a mixture containing more than one base oil. Suitable base oils for use in the lubricating oil composition of the present invention are Group III mineral base oils, Group IV poly-alpha olefins (PAOs), Group III Fischer-Tropsch derived base oils, and mixtures thereof.

[0010] By "Group III" and "Group IV" base oils in the present invention are meant lubricating oil base oils according to the definitions of American Petroleum Institute (API) for category III and IV. These API categories are defined in API Publication 1509, 15th Edition, Appendix E, April 2002. [0011] Fischer-Tropsch derived base oils are known in the art. By the term "Fischer-Tropsch derived" is meant that a base oil is, or is derived from, a synthesis product of a Fischer-Tropsch process. A Fischer-Tropsch derived base oil may also be referred to as a GTL (Gas-To-Liquids) base oil. Suitable Fischer-Tropsch derived base oils that may be conveniently used as the base oil in the lubricating composition of the present invention include those, for example, disclosed in EP 0 776 959, EP 0 668 342, WO 97/21788, WO 00/15736, WO 00/14188, WO 00/14187, WO 00/14183, WO 00/14179, WO 00/08115, WO 99/41332, EP 1 029 029, WO 01/18156 and WO 01/57166.

[0012] Typically, the aromatics content of a Fischer-Tropsch derived base oil, as determined by ASTM D 4629, will be less than about 1 wt. %, alternatively less than about 0.5 wt. % or in alternate embodiments, less than about 0.1 wt. %. The base oil can have a total paraffin content of at least about 80 wt. %, alternatively at least about 85 wt. %, alternatively at least about 90 wt. %, alternatively at least about 95 wt. %, or, in certain embodiments, at least about 99 wt. %. The Fischer-Tropsch derived base oil can have a saturates content (as measured by IP-368, ASTM D2007, ASTM D7419, or any other chromatographic method that will yield similar results) of greater than about 98 wt. %, alternatively greater than about 99 wt. %, or alternatively greater than about 99.5 wt. %. The Fischer-Tropsch derived base oil can further include a maximum n-paraffin content of about 0.5 wt. % and naphthenic compound content of from 0 to less than 20 wt. %, alternatively from about 0.5 to 10 wt. %, alternatively from about 1-5 wt. %, or alternatively from about 5-10 wt. %.

[0013] Typically, the Fischer-Tropsch derived base oil or base oil blend has a kinematic viscosity at 100° C. (as measured by ASTM D 7042) in the range of from 1 to 35 mm²/s (cSt), alternatively from 1 to 25 mm²/s (cSt), alternatively from 2 to 20 mm²/s (cSt), or alternatively from 2 mm²/s to 12 mm²/s. The Fischer-Tropsch derived base oil can have a kinematic viscosity at 100° C. (as measured by ASTM D 7042) of at least 2.5 mm²/s, alternatively at least 3.0 mm²/s (e.g., "GTL 3". In certain embodiments of the present invention, the Fischer-Tropsch derived base oil can have a kinematic viscosity at 100° C. of not greater than 5.0 mm²/s, alternatively not greater than 4.5 mm²/s, alternatively not greater than 4.2 mm²/s (e.g., "GTL 4"). In certain embodiments of the present invention, the Fischer-Tropsch derived base oil has a kinematic viscosity at 100° C. of not greater than 8.5 mm²/s,

alternatively not greater than  $8~\text{mm}^2/\text{s}$  (e.g., "GTL 8"). Other grades of GTL products would also be possible, based upon the specific distillation process utilized to produce the GTL product.

[0014] Further, the Fischer-Tropsch derived base oil can have a kinematic viscosity at  $40^{\circ}$  C. (as measured by ASTM D 7042) of from 10 to  $100 \text{ mm}^2/\text{s}$  (cSt), alternatively from 15 to  $50 \text{ mm}^2/\text{s}$ , alternatively from 50 to  $80 \text{ mm}^2/\text{s}$ , alternatively greater than  $100 \text{ mm}^2/\text{s}$ .

[0015] Also, in certain embodiments, the Fischer-Tropsch derived base oil can have a pour point (as measured according to ASTM D 5950) of less than about  $-10^{\circ}$  C., alternatively less than about  $-20^{\circ}$  C., alternatively less than about  $-30^{\circ}$  C., alternatively less than about  $-40^{\circ}$  C., and alternatively less than about  $-45^{\circ}$  C.

[0016] The flash point (as measured by ASTM D92) of the Fischer-Tropsch derived base oil can be greater than  $120^{\circ}$  C., alternatively greater than  $130^{\circ}$  C., alternatively greater than  $140^{\circ}$  C.

[0017] The Fischer-Tropsch derived base oil can have a viscosity index (according to ASTM D 2270) in the range of from about 100 to 200. Alternativley, the Fischer-Tropsch derived base oil can have a viscosity index of at least 125, alternatively at least 130. In certain embodiments, the viscosity index is less than 180, alternatively less than 160, alternatively less than 150. In certain embodiments, the viscosity index can be between 125 and 180, alternatively between 130 and 160.

[0018] In the event the Fischer-Tropsch derived base oil contains a blend of two or more Fischer-Tropsch derived base oils, the above values apply to the blend of the two or more Fischer-Tropsch derived base oils.

[0019] Poly-alpha olefin base oils (PAOs) and their manufacture are well known in the art. In certain embodiments, the poly-alpha olefin base oils used in the lubricating compositions of the present invention may be derived from linear  $C_2$  to  $C_{32}$ , preferably  $C_6$  to  $C_{16}$ , alpha olefins. Alternatively, feedstocks for said poly-alpha olefins can be 1-octene, 1-decene, 1-dodecene and 1-tetradecene.

[0020] In certain embodiments, the base oil as used in the lubricating composition can include a first GTL base oil, and may optionally include one or more of the oils selected from PAO, or Group I, II, III or V base oils.

[0021] In certain embodiments, it may be preferable to use a Fischer-Tropsch derived base oil instead of a PAO base oil, in view of the high cost to manufacture PAOs. Thus, preferably, the base oil contains more than 50 wt. %, preferably more than 60 wt. %, more preferably more than 70 wt. %, even more preferably more than 80 wt. %, and most preferably more than 90 wt. % of a Fischer-Tropsch derived base oil. In an alternate embodiment, not more than 5 wt. %, alternatively not more than 2 wt. %, of the base oil is not a Fischer-Tropsch derived base oil. In certain preferred embodiments, 100 wt % of the base oil is based on one or more Fischer-Tropsch derived base oils.

[0022] Preferably the base oil or base oil blend that includes the Fischer-Tropsch derived base oil has a kinematic viscosity at 100° C. of between 2 and 35 cSt, alternatively between 2 and 10.5 cSt (according to ASTM D 445).

[0023] In addition to the Group III base oil and/or polyal-phaolefin base oil, the lubricating composition may include one or more other types of mineral derived or synthetic base oils, including Group I, II, IV and V base oils according to the

definitions of American Petroleum Institute (API). These API categories are defined in API Publication 1509, 15th Edition, Appendix E, July 2009.

[0024] In certain embodiments, the total amount of base oil that is incorporated in the lubricating composition of the present invention is preferably an amount in the range of from 60 to 99 wt. %, alternatively an amount in the range of from 65 to 90 wt. %, and in certain preferred embodiments, in an amount in the range of from 70 to 85 wt. %, with respect to the total weight of the lubricating composition.

[0025] The lubricating oil composition also includes an oil soluble organic dye. The organic dye can include functional groups that serves as chromophores that absorb and transmit wavelengths in the visible spectrum. In certain embodiments the organic dyes can be first dissolved in an organic solvent prior to being added to the base oil. The organic dyes can be present in an amount of between about 0.0001 wt. % and 0.001 wt. % as measured relative to the total weight of the lubricant composition.

[0026] Optionally, the lubricating oil compositions of the present invention can also include a solvency booster. As used herein, the term "solvency booster" means a component which enhances the solvency of the Group III/PAO base oil with respect to certain additives that are included in the formulation. The use of a solvency booster in the lubricating composition of the present invention can be particularly useful when the base oil is selected from a Fischer-Tropsch derived base oil. In certain embodiments, the solvency booster is present in an amount of between about 1 and 30 wt %, alternatively in an amount of between about 2 and 20 wt %, or alternatively in an amount between about 5 and 15 wt %. Compounds suitable for use as a solvency booster can be selected from alkylated aromatic compounds, naphthenic base oils, ester base oils, and mixtures thereof.

[0027] Alkylated naphthalenes may be produced by any suitable means known in the art, from naphthalene itself or from substituted naphthalenes which may contain one or more short chain alkyl groups having up to about eight carbon atoms, for example methyl, ethyl, and propyl. Suitable alkyl-substituted naphthalenes include alphamethylnaphthalene, dimethylnaphthalene, and ethylnaphthalene. Naphthalene itself is especially suitable since the resulting mono-alkylated products have better thermal and oxidative stability than the more highly alkylated materials. Suitable alkylated naphthalene lubricant compositions are described in U.S. Pat. No. 3,812,036, and U.S. Pat. No. 5,602,086. The preparation of alkylnaphthalenes is further disclosed in U.S. Pat. No. 4,714,794

[0028] The alkylated aromatic compound for use herein can be selected from alkylbenzene compounds, alkylnaphthalene compounds, and mixtures thereof.

[0029] The alkylaromatic component preferably has a kinematic viscosity at  $100^{\circ}$  C. in the range of from 3 to  $12 \text{ mm}^2/\text{s}$ , more preferably in the range of from 3.8 to  $7 \text{ mm}^2/\text{s}$ . The viscosity index of the alkylaromatic component is above 40, preferably at or above 70.

[0030] An exemplary alkylated aromatic compound for use herein is an alkylnaphthalene compound. Examples of commercially available alkylnaphthalene compounds are those under the tradename NA-Lube (King Industries), such as NA-Lube KR 008, NA-Lube KR019, and the like, and those under the tradename Mobil MCP (ExxonMobil).

[0031] Examples of commercially available alkyl benzenes include those available under the tradename Fusyn-22 (For-

mosan), those available under the tradename Janex HAL (Janex), and those available under the tradename ZEROL (Shreive Chemical Products, Inc. (SCP)).

[0032] Suitable naphthenic base oils for use as a solvency booster herein includes naphthenic base oils having low viscosity index (VI), typically between about 40-80, and a low pour point, for example, a temperature of less than -20° C. Such base oils can be produced from feedstocks rich in naphthenes and low in wax content. There is no particular limitation on the type of mineral-derived naphthenic base oil which can be used in the base oil composition herein. Any mineralderived naphthenic base oil which is suitable for use in a lubricating oil composition can be used herein. Naphthenic base oils are defined as Group V base oils according to API. Such mineral-derived base oils can be obtained by refinery processes starting from naphthenic crude feeds. Mineral-derived naphthenic base oils for use herein preferably have a pour point of below -20° C. and a viscosity index of less than 70. Such base oils can be produced from feedstocks rich in naphthenes and low in wax content. Mineral-derived naphthenic base oils are well known and described in more detail in "Lubricant base oil and wax processing", Avilino Sequeira, Jr., Marcel Dekker, Inc, New York, 1994, ISBN 0-8247-9256-4, pages 28-35. Methods of manufacture of naphthenic base oils can be found in "Lubricants and Lubrication (Second, Completely Revised and Extended Edition)", published by Wiley-VCH Verlag GmbH & Co. KgaA, Chapter 4, pages

[0033] An example of a suitable naphthenic base oil for use as a solvency booster herein is that commercially available under the tradename KN4006 (China National Petroleum Corporation). Other examples of suitable naphthenic base oils for use as a solvency booster herein include those available under the tradenames Hydrocal, Hydrosol and HR Tufflo (Calumet Specialty Products), and those commercially available under the tradename Nynas (Nynas Oil Company).

[0034] Suitable esters for use as a solvency booster herein include natural and synthetic esters such as diesters and polyol esters. An example of a suitable ester for use as a solvency booster herein is the saturated polyol ester commercially available under the tradename Priolube 3970 (Croda International PLC). Other suitable esters for use as a solvency booster herein include those available under the tradename Radialube (Oleon), those available under the tradename Emery (from Emery) and those available under the tradename Esterex (ExxonMobil Chemical).

[0035] The lubricating oil compositions of the present invention can include one or more detergent compounds having a TBN (total base number equivalent, as determined by ASTM D2896) of between about 0 and 400. In certain embodiments, the detergent compound can include one or more alkaline earth metal salicylate. Suitable alkaline earth metal salicylates, and mixtures thereof, preferably calcium salicylates.

[0036] In certain embodiments of the present invention, the lubricant composition can include from 0.001 to 8% by weight of a corrosion inhibitor. In certain embodiments, exemplary corrosion inhibitors include, but are not limited to, thiazoles, triazoles, benzodiazoles, benzotriazoles, and thiodiazoles. In alternate embodiments, exemplary corrosion inhibitors can include, but are not limited to, sodium sulfonates barium sulfonate, neutral barium dinonylnaphthalene sulfonate (also calcium and zinc), and overbased sulfonates.

In other embodiments, exemplary corrosion inhibitors can include, but are not limited to, ethoxylated phenols, substituted succinic acids, fatty carboxylic acids, carboxylic acid derivatives, and fatty amines such as alkyl imidazoline. In yet other embodiments, exemplary corrosion inhibitors can include, but are not limited to, phosphate esters, borate esters, and polyethers. In other embodiments, exemplary corrosion inhibitors can include, but are not limited to, zinc diamyldithiocarbamate and zinc dithiocarbamates. In other embodiments, exemplary corrosion inhibitors can include, but are not limited to, thiophosphates, phosphoric acid derivatives, and zinc dithiophosphates. In yet other embodiments, exemplary corrosion inhibitors can include, but are not limited to, zinc naphthenate and bismuth naphthenate. In other embodiments, exemplary corrosion inhibitors can include, but are not limited to, mercapto-thiadiazole derivatives. In other embodiments, exemplary corrosion inhibitors can include, but are not limited to, sarcosines. Alternatively, in certain embodiments, exemplary corrosion inhibitors can include, but are not limited to, salts of carboxylic acid and alkanolamine, amine phosphate, and fatty acid alkanolamines. In other embodiments, exemplary corrosion inhibitors can include, but are not limited to, hexamine, phenylenediamine, dimethylethanolamine, and derivatives thereof. Alternatively, exemplary corrosion inhibitors can include, but are not limited to, triethanolamine salt of phosphate esters. In other embodiments, an exemplary corrosion inhibitors include, but are not limited to, oil soluble complex chelating agents, such as N-salicylidene-propylenediamine.

[0037] Exemplary commercial corrosion inhibitors for use in the lubricant compositions of the present invention include, but are not limited to, Irgamet 30 (BASF), Bismuth naphthenate B (PCAS), Lubad 1365 (Mirachema Nuodex), Valirex Bi 17% naphthenate (Unicore), Dailube Z500 (Zn 5.2%, DIC), Soligen Zinc 11-12% S (OMG), Sarkosyl O (BASF), Irgamet 39 (BASF), Irgacor NPA (BASF), and Irgacor L12 (BASF).

[0038] The lubricating oil compositions of the present invention preferably include from 0.01 wt % to 9 wt %, more preferably from 1 wt % to 6 wt %, even more preferably from 3.5 wt % to 5.5 wt %, of a detergent, by weight of the lubricating oil composition.

[0039] The level of an alkaline earth metal salicylate having a TBN in the range of from 150 to 250 is preferably in the range of 0.01 wt % to 5 wt %, more preferably from 1 wt % to 3 wt %, by weight of the lubricating oil composition.

**[0040]** In certain embodiments, the detergent can be an alkaline earth metal salicylate having a TBNE (total base number equivalent, as determined by ASTM D2896) in the range of from 250 to 400, and is preferably in the range of 0.01 wt % to 3 wt %, more preferably from 1 wt % to 2 wt %, by weight of the lubricating oil composition.

[0041] In certain embodiments, the lubricating oil compositions of the present invention can include one or more antioxidants. Suitable anti-oxidants for use herein include phenolic antioxidants and/or aminic antioxidants.

[0042] In one embodiment, said antioxidants are present in an amount in the range of from 0.1 to 5.0 wt. %, preferably in an amount in the range of from 0.3 to 3.0 wt. %, and more preferably in an amount of in the range of from 0.5 to 1.5 wt. %, based on the total weight of the lubricating oil composition.

[0043] Examples of aminic antioxidants which may be conveniently used include alkylated diphenylamines, phenyl-□-naphthylamines, phenyl-β-naphthylamines and alkylated □-naphthylamines.

[0044] Exemplary aminic antioxidants include dialkyl-diphenylamines, such as p,p'-dioctyl-diphenylamine, p,p'-di-α-methylbenzyl-diphenylamine, and N-p-butylphenyl-N-p'-octylphenylamine, monoalkyldiphenylamines, such as mono-t-butyldiphenylamine and mono-octyldiphenylamine, bis(dialkylphenyl)amines, such as di-(2,4-diethylphenyl) amine and di(2-ethyl-4-nonylphenyl)amine, alkylphenyl-1-naphthylamines, such as octylphenyl-1-naphthylamine and n-t-dodecylphenyl-1-naphthylamine, 1-naphthylamine, aryl-naphthylamines, such as phenyl-1-naphthylamine, phenyl-2-naphthylamine, N-hexylphenyl-2-naphthylamine and N-octylphenyl-2-naphthylamine, phenylenediamines, such as N,N'-diisopropyl-p-phenylenediamine and N,N'-diphenyl-p-phenylenediamine, and phenothiazines, such as phenothiazine and 3,7-dioctylphenothiazine.

[0045] Preferred aminic antioxidants include those available under the following trade designations: "Sonoflex OD-3" (Seiko Kagaku Co.), "Irganox L-57" (Ciba Specialty Chemicals Co.) and phenothiazine (Hodogaya Kagaku Co.).

[0046] Exemplary phenolic antioxidants that may be used include C7-C9 branched alkyl esters of 3,5-bis(1,1-dimethylethyl)-4-hydroxy-benzenepropanoic acid, 2-t-butylphenol, 2-t-butyl-4-methylphenol, 2-t-butyl-5-methylphenol, 2,4-dit-butylphenol, 2,4-dimethyl-6-t-butylphenol, 2-t-butyl-4methoxyphenol, 3-t-butyl-4-methoxyphenol, 2,5-di-t-butylhydroquinone, 2,6-di-t-butyl-4-alkylphenols such as 2,6-dit-butylphenol, 2,6-di-t-butyl-4-methylphenol and 2,6-di-tbutyl-4-ethylphenol, 2,6-di-t-butyl-4-alkoxyphenols such as 2.6-di-t-butyl-4-methoxyphenol and 2,6-di-t-butyl-4-ethoxyphenol, 3,5-di-t-butyl-4-hydroxybenzylmercaptooctylacetate, alkyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionates such as n-octadecyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate, n-butyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate and 2'-ethylhexyl-3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate, 2,6-d-t-butyl-α-dimethylamino-p-cresol, 2,2'methylene-bis(4-alkyl-6-t-butylphenol) such methylenebis(4-methyl-6-t-butylphenol, 2,2and methylenebis(4-ethyl-6-t-butylphenol), bisphenols such as 4,4'-butylidenebis(3-methyl-6-t-butylphenol, 4,4'-methylenebis(2,6-di-t-butylphenol), 4,4'-bis(2,6-di-t-butylphenol), 2,2-(di-p-hydroxyphenyl)propane, 2,2-bis(3,5-di-t-butyl-4hydroxyphenyl)propane, 4,4'-cyclohexylidenebis(2,6-t-butylphenol), hexamethyleneglycol-bis[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate], triethyleneglycolbis[3-(3-t-butyl-4-hydroxy-5-methylphenyl)propionate], 2,2'-thio-[diethyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate], 3,9-bis{1,1dimethyl-2-[3-(3-t-butyl-4-hydroxy-5-methyl-phenyl) propionyloxy]ethyl}2,4,8,10-tetraoxaspiro[5,5]undecane, 4,4'-thiobis(3-methyl-6-t-butylphenol) and 2,2'-thiobis(4,6di-t-butylresorcinol), polyphenols such as tetrakis[methylene-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate]methane, 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl)butane, 1,3,5-trimethyl-2,4,6-tris(3,5-di-t-butyl-4-hydroxybenzyl) benzene, bis-[3,3'-bis(4'-hydroxy-3'-t-butylphenyl)butyric acid]glycol ester, 2-(3',5'-di-t-butyl-4-hydroxyphenyl)methyl-4-(2",4"-di-t-butyl-3"-hydroxyphenyl)methyl-6-t-butylphenol and 2,6-bis(2'-hydroxy-3'-t-butyl-5'-methylbenzyl)-4-methylphenol, and p-t-butylphenol-formaldehyde condensates and p-t-butylphenol-acetaldehyde condensates.

[0047] Phenolic antioxidants include those available under the following trade designations: "Irganox L-135" (Ciba Specialty Chemicals Co.), "Yoshinox SS" (Yoshitomi Seiyaku Co.), "Antage W-400" (Kawaguchi Kagaku Co.), "Antage W-500" (Kawaguchi Kagaku Co.), "Antage W-300" (Kawaguchi Kagaku Co.), "Irganox L-109" (Ciba Speciality Chemicals Co.), "Tominox 917" (Yoshitomi Seiyaku Co.), "Irganox L-115" (Ciba Speciality Chemicals Co.), "Sumilizer GA80" (Sumitomo Kagaku), "Antage RC" (Kawaguchi Kagaku Co.), "Irganox L-101" (Ciba Speciality Chemicals Co.), "Yoshinox 930" (Yoshitomi Seiyaku Co.).

[0048] The lubricating oil composition of the present invention may include mixtures of one or more phenolic antioxidants with one or more aminic antioxidants.

[0049] According to the present invention, the lubricating composition preferably includes up to about 30 wt % of a viscosity modifier, based on the total weight of the lubricating composition. In one embodiment, the lubricating composition comprises from 20 wt % to 30 wt % of a viscosity modifier. In another embodiment, the lubricating composition includes up to about 20 wt % of a viscosity modifier. In an alternate embodiment, the lubricating composition includes between about 10 and 20 wt % of a viscosity modifier. In yet another embodiment, the lubricating composition includes between about 1 and 10 wt % of a viscosity modifier. In a preferred embodiment of the present invention, the lubricating composition is essentially free of viscosity modifier. In a particularly preferred embodiment of the present invention, the lubricating composition comprises 0 wt % of a viscosity modifier.

[0050] Examples of viscosity index improvers include copolymers of alpha-olefins and dicarboxylic acid esters such as those described in U.S. Pat. No. 4,931,197. Commercially available copolymers of alpha-olefins and dicarboxylic acid diesters include the Ketjenlube polymer esters available from Italmatch (and previously Akzo Nobel Chemicals). Other suitable examples of viscosity index improvers are polyisobutylenes; commercially available polyisobutylenes include the Oloa® products (Chevron Oronite).

**[0051]** Further examples of viscosity index improvers which may conveniently be used in the lubricating compositions of the present invention include the styrene-butadiene stellate copolymers, styrene-isoprene stellate copolymers and the polymethacrylate copolymers and ethylene-propylene copolymers (also known as olefin copolymers) of the crystalline and non-crystalline type.

[0052] Suitable olefin copolymers include those commercially available under the trade designation "PARATONE®" (such as "PARATONE® 8921" and "PARATONE® 8941") (Chevron Oronite Company LLC); those commercially available under the trade designation "HiTEC®" (such as "HiTEC® 5850B") (Afton Chemical Corporation); and those commercially available under the trade designation "Lubrizol® 7067C" (The Lubrizol Corporation). Suitable polyisoprene polymers include those commercially available under the trade designation "SV200" (Infineum International Ltd.). Suitable diene-styrene copolymers include those commercially available under the trade designation "SV 260" (Infineum International Ltd.).

[0053] The compositions herein may also include one or more anti-wear additives. Suitable anti-wear additives for use herein include zinc dithiophosphate compounds selected from zinc dialkyl-, diaryl- and/or alkylaryl-dithiophosphates,

molybdenum-containing compounds, and ashless anti-wear additives such as substituted or unsubstituted thiophosphoric acids, and salts thereof.

[0054] Examples of ashless thiophosphates are known in the art. These compounds are metal-free organic compounds. Suitable ashless thiophosphates for use in the lubricating oil composition of the present invention may include esters and/or salts of thiophosphoric acids, and substituted thiophosphoric acids. Preferably, the ashless thiophosphates are substituted by one or more hydrocarbyl groups which hydrocarbyl groups can optionally contain an acid, a hydroxy and/or an ester group. The hydrocarbyl moiety preferably is an alkyl group containing up to 12 carbon atoms. The hydrocarbyl-substituted thiophosphate preferably contains 2 or 3 hydrocarbyl groups, or is a mixture of thiophosphates containing 2 and 3 hydrocarbyl groups.

[0055] The ashless thiophosphates can contain any number of sulphur atoms directly linked to the phosphorus atom. Preferably, the thiophosphates are monothiophosphates and/or dithiophosphates.

[0056] Examples of ashless thiophosphates which may be conveniently used in the lubricating oil composition of the present invention are described in EP-A-0375324, U.S. Pat. Nos. 5,922,657, 4,333,841 and 5,093,016, and may be conveniently made according to the methods described therein.

[0057] Examples of commercially available ashless thiophosphates that may be conveniently used in the lubricating oil composition of the present invention include those available under the trade designations "IRGALUBE L-63" and "IRGALUBE 353" (Ciba Specialty Chemicals) and that available under the trade designation "LZ 5125" (Lubrizol).

[0058] In certain embodiments, the lubricating composition can include one or more anti-wear additives selected from one or more zinc dithiophosphates. The or each zinc dithiophosphate may be selected from zinc dialkyl-, diaryl- or alkylaryl-dithiophosphates.

[0059] Examples of zinc dithiophosphates which are commercially available include those available under the trade designations "Lz 677A", "Lz 1095", "Lz 1097", "Lz 1370", "Lz 1371", "Lz 1373" and "Lz 1395" (Lubrizol Corp.), those available under the trade designations "OLOA 260", "OLOA 262", "OLOA 267" and "OLOA 269R" (Chevron Oronite), and those available under the trade designation "HITEC 7169" and "HITEC 7197" (Afton Chemical).

[0060] In certain embodiments, the lubricating composition according to the present invention includes a phosphorus containing compound, preferably selected from the group consisting of phosphonates, phosphates, phosphorothionates and dithiophosphates, and combinations thereof. Examples of commercially available dithiophosphates and phosphates are "IRGALUBE 63" and IRGALUBE 349", respectively, both available from Ciba Specialty Chemicals.

[0061] The lubricating oil composition of the present invention has a kinematic viscosity at 40° C. in the range of from 2 mm<sup>2</sup>/s to 220 mm<sup>2</sup>/s, preferably in the range of from 32 mm<sup>2</sup>/s to 220 mm<sup>2</sup>/s.

[0062] In addition to the components mentioned above, the lubricating composition according to the present invention may further include one or more additional additives such as anti-oxidants, dispersants, detergents, extreme-pressure additives, friction modifiers, viscosity index improvers, pour

point depressants, metal passivators, corrosion inhibitors, demulsifiers, anti-foam agents, seal compatibility agents and additive diluent base oils, etc.

[0063] As the person skilled in the art is familiar with the above and other additives, these are not further discussed here in detail.

[0064] Specific examples of such additives are described in for example Kirk-Othmer Encyclopedia of Chemical Technology, third edition, volume 14, pages 477-526.

[0065] The above-mentioned additives are typically present in an amount in the range of from 0.01 to 35.0 wt. %, based on the total weight of the lubricating composition, preferably in an amount in the range of from 0.05 to 25.0 wt. %, more preferably from 0.1 to 20.0 wt. %, based on the total weight of the lubricating composition.

[0066] The lubricating compositions of the present invention may be conveniently prepared by admixing the one or more additives with the base oil(s).

[0067] The lubricating composition according to the present invention may be used in various applications, such as a transmission oil, a grease, a hydraulic oil, an industrial gear oil, a turbine oil, a compressor oil, and the like.

[0068] In another aspect, the present invention provides a method for improving one or more of oxidation stability and deposit reduction properties, which method includes lubricating with a lubricating composition according to one aspect of the invention. In another aspect, the present invention provides the use of a lubricating composition as described herein, for improving one or more of oxidation stability properties (for example, as determined by ASTM D6186-98) and deposit reduction properties (for example, as determined according to ASTM D7097-09 or JPI-5S-55-99).

**[0069]** The present invention is described below with reference to the following Examples, which are not intended to limit the scope of the present invention in any way.

[0070] In one embodiment is provided a lubricating oil composition that includes: (a) a base oil that includes a Fischer-Tropsch derived base oil; and (b) an anti-corrosive compound. In certain embodiments, the anti-corrosive compound is present in an amount of between 0.001 and 8%, preferably between 0.01 and 8% by weight of the lubricant composition, alternatively in an amount of between 1 and 8% by weight of the lubricant composition, alternatively in an amount of between 1 and 3% by weight of the lubricant composition, alternatively in an amount of between 1 and 5% by weight of the lubricant composition, alternatively in an amount of between 3 and 5% by weight of the lubricant composition, or alternatively in an amount of between 5 and 8% by weight of the lubricant composition.

[0071] In another embodiment, is provided a lubricating oil composition that includes (a) a base oil that includes a Fischer-Tropsch derived base oil; and (b) an anti-corrosive compound. In certain embodiments, the anti-corrosive compound is selected from the group consisting of thiazoles, triazoles, benzodiazoles, benzotriazoles, and thiodiazoles; alternatively the anti-corrosive compound is selected from the group consisting of sodium sulfonates, barium sulfonate, neutral barium dinonylnaphthalene sulfonate (also calcium and zinc), and overbased sulfonates; alternatively the anti-corrosive compound is selected from the group consisting of zinc diamyldithiocarbamate and zinc dithiocarbamates; alternatively the anti-corrosive compound is selected from the group consisting of hexamine, phenylenediamine, dimethylethanolamine, and derivatives thereof; alternatively the anti-corrosive-corrosive corrosively the anti-corrosive thereof; alternatively the anti-corrosive-corrosive thereof; alternatively the anti-corrosive-corrosive thereof; alternatively the anti-corrosive-corro

sive compound is selected from the group consisting of phosphate esters, borate esters and polyethers; alternatively the anti-corrosive compound is selected from the group consisting of ethoxylated phenols, substituted succinic acids, fatty carboxylic acids, carboxylic acid derivatives, and fatty amines such as alkyl imidazoline; alternatively the anti-corrosive compound is selected from the group consisting of thiophosphates, phosphoric acid derivatives, and zinc dithiophosphates; alternatively the anti-corrosive compound is selected from the group consisting of zinc naphthenate and bismuth naphthenate; alternatively the anti-corrosive compound is selected from mercapto-thiadiazole derivatives; alternatively the anti-corrosive compound is a sarcosine; alternatively the anti-corrosive compound is selected from the group consisting of salts of carboxylic acid and alkanolamine, amine phosphate, and fatty acid alkanolamines; alternatively the anti-corrosive compound is selected from the group consisting of triethanolamine salts of phosphate esters; or alternatively the anti-corrosive compound is an oil soluble complex chelating agent.

[0072] In certain embodiments of the lubricant oil compositions of the present invention, the Fischer-Tropsch derived base oil has a kinematic viscosity at 100° C. of from 1 mm<sup>2</sup>/s to 35 mm<sup>2</sup>/s. In certain other embodiments of the lubricant oil compositions of the present invention, the base oil contains more than 50 wt. %, preferably more than 60 wt. %, more preferably more than 70 wt. %, even more preferably more than 80 wt. %, most preferably more than 90 wt. % Fischer-Tropsch derived base oil. In yet other embodiments, the lubricant oils of the present invention provide improved antioxidation properties, as determined by ASTM D6186-08; alternatively providing improved rust prevention, as determined by ASTM D6557, or alternatively providing improved copper corrosion prevention, as determined by ASTM D130. [0073] Also provided is a method for lubricating an engine, the method comprising the step of lubricating said engine with the oil compositions described, wherein the step of lubricating the engine results in a reduction of the amount of oxidation products that are formed, alternatively wherein the step of lubricating the engine results in a reduction in the amount of deposits that are formed; alternatively wherein the step of lubricating the engine results in a reduction in the amount of engine rust that is formed; alternatively wherein the step of lubricating the engine results in a reduction in the amount of copper corrosion; or alternatively wherein the step of lubricating the engine results in a reduction in the amount of copper corrosion. In certain instances, the lubricant oil compositions of the present invention can be utilized in a passenger car engine, alternatively in a heavy duty diesel engine, alternatively in a transmission, alternatively in a turbine, alternatively in an air compressor, alternatively as a hydraulic fluid, alternatively as a gear oil, alternatively as a grease, alternatively in a transformer, or alternatively in marine applications.

#### **EXAMPLES**

#### Lubricating Oil Compositions

[0074] Various combinations of additives, base oils and solvency boosters were formulated. Table 1 shows the properties of the base oils.

[0075] "Base oil 1" (or "BO1" or "GTL 4") was a Fischer-Tropsch derived base oil having a kinematic viscosity at 100° C. (ASTM D445) of approximately 3.89 cSt (mm²s¹). Base

oil 1 may be conveniently manufactured by the process described in e.g. WO-A-02/070631, the teaching of which is hereby incorporated by reference.

[0076] "Base oil 2" (or "BO2") was a commercially available Group III base oil having a kinematic viscosity at 100° C. (ASTM D445) of approximately 4.3 cSt. Base oil 2 is commercially available from e.g. SK Energy (Ulsan, South Korea) under the trade designation Yubase 4.

[0077] "Base oil 3" or (GTL 3) was a Fischer-Tropsch derived base oil having a kinematic viscosity at 100° C. (ASTM D445) of approximately 2.700 cSt (mm²s⁻¹). Base oil 3 may be conveniently manufactured by the process described in e.g. WO-A-02/070631, the teaching of which is hereby incorporated by reference.

[0078] "Base oil 4" or (GTL 8) was a Fischer-Tropsch derived base oil having a kinematic viscosity at 100° C. (ASTM D445) of approximately 4.000 cSt (mm²s⁻¹). Base oil 4 may be conveniently manufactured by the process described in e.g. WO-A-02/070631, the teaching of which is hereby incorporated by reference.

TABLE 1

|  | Base oil 1<br>(GTL 4) | Base oil 2<br>(Yubase 4) | Base oil 3<br>(GTL 3) | Base oil 4<br>(GTL 8) |
|--|-----------------------|--------------------------|-----------------------|-----------------------|
| Kinematic viscosity at 40° C. <sup>1</sup> [cSt]     | 16.91                 | 19.49                    | 9.930                 | 43.51                 |
| Kinematic viscosity<br>at 100° C. <sup>1</sup> [cSt] | 3.89                  | 4.3                      | 2.707                 | 7.613                 |
| VI Index <sup>2</sup>                                | 127                   | 126                      | 112                   | 144                   |
| Pour point <sup>3</sup> [° C.]                       | -39                   | -18                      | -39                   | -21                   |
| Noack volatility4                                    | 11.2                  | 14.2                     | 46.8                  | 2.1                   |
| [wt. %]  |                       |                          |                       |                       |
| Saturates <sup>5</sup> [wt. %]                       | 99.2                  | 99.3                     | 99.9                  | 99.9                  |
| Tertiary Carbon, %6                                  | 18.1                  | n.d.                     | n.d.                  | n.d.                  |
| Secondary Carbon, %6                                 | 66.7                  | n.d.                     | n.d.                  | n.d.                  |
| Primary Carbon, %6                                   | 14.3                  | n.d.                     | n.d.                  | n.d.                  |
| Epsilon carbon                                       | 12.1                  | n.d.                     | n.d.                  | n.d.                  |
| content, %6  |                       |                          |                       |                       |
| n- and iso- paraffins7                               | 92.35                 | n.d.                     | n.d.                  | n.d.                  |
| Mono-naphthenics <sup>7</sup>                        | 6.85                  | n.d.                     | n.d.                  | n.d.                  |
| di- and poly-  | 0.87                  | n.d.                     | n.d.                  | n.d.                  |
| naphthenics <sup>7</sup>                             |                       |                          |                       |                       |
| Aromatics <sup>5</sup>                               | 0.5                   | n.d.                     | n.d.                  | n.d.                  |
| Dynamic viscosity                                    | n.d.                  | 713                      | n.d.                  | n.d.                  |
| at -20° C.8 [cP]                                     |                       |                          |                       |                       |
| Dynamic viscosity                                    | n.d.                  | 931                      | n.d.                  | n.d.                  |
| at -25° C.8 [cP]                                     |                       |                          |                       |                       |
| Dynamic viscosity                                    | 948                   | n.d.                     | n.d.                  | 5010                  |
| at -30° C.8 [cP]                                     |                       |                          |                       |                       |
| Dynamic viscosity                                    | 1580                  | n.d.                     | n.d.                  | 9340                  |
| at -35° C.8 [cP]                                     |                       |                          |                       |                       |

<sup>1</sup>According to ASTM D 445

#### Copper Corrosion Test

[0079] In order to measure the copper corrosion prevention performance of the various lubricating compositions set out herein, the lubricating compositions were subjected to the ASTM D130 test at a temperature of 250° C. and a period of 1 hour. In this test method, a polished copper strip is immersed in a specific volume of the sample being tested and

<sup>&</sup>lt;sup>2</sup>According to ASTM D 2270

<sup>&</sup>lt;sup>3</sup>According to ASTM D 5950

<sup>&</sup>lt;sup>4</sup>According to CEC L-40-A-93/ASTM D 5800

<sup>&</sup>lt;sup>5</sup>According to IP 368 (modified)

<sup>&</sup>lt;sup>6</sup>According to 13C NMR

<sup>&</sup>lt;sup>7</sup>According to FIMS

<sup>&</sup>lt;sup>8</sup>According to ASTM D 5293

n.d. = not determined

heated under conditions of temperature and time that are specific to the class of material being tested. At the end of the heating period, the copper strip is removed, washed and the colour and tarnish level assessed against the ASTM Copper Strip Corrosion Standard.

[0080] Improved copper corrosion prevention is evidenced by a lower copper corrosion designation number.

#### Examples 1-3 and Comparative Examples 1-3

[0081] Table 2 below shows the formulations of Examples 1-3 and Comparative Examples 1-3 and the results when these formulations were subjected to the copper corrosion test ATSM D130. In Table 2, Irgamet 30, Irgacor NPA and Sarkosyl O are all corrosion inhibitors. Irgamet 30 and Irgacor NPA are commercially available from BASF and Sarkosyl O is available from CIBA.

- 7. The lubricating oil composition according to claim 1, wherein the anti-corrosive compound is selected from the group consisting of phosphate esters, borate esters and polyethers.
- 8. The lubricating composition according to claim 1, wherein the anti-corrosive compound is selected from the group consisting of ethoxylated phenols, substituted succinic acids, fatty carboxylic acids, carboxylic acid derivatives, and fatty amines such as alkyl imidazoline.
- **9**. The lubricating composition according to claim **1**, wherein the anti-corrosive compound is selected from the group consisting of thiophosphates, phosphoric acid derivatives, and zinc dithiophosphates.
- 10. The lubricating composition according to claim 1, wherein the anti-corrosive compound is selected from the group consisting of zinc naphthenate and bismuth naphthenate

TABLE 2

| Component:                       | Example 1<br>(wt %) | Example 2 (wt %) | Example 3 (wt %) | Comparative<br>Example 1<br>(wt %) | Comparative<br>Example 2<br>(wt %) | Comparative<br>Example 3<br>(wt %) |
|----------------------------------|---------------------|------------------|------------------|------------------------------------|------------------------------------|------------------------------------|
| Base Oil 1 (GTL 4)               | 99.9                | 99.99            | 99.95            |                                    |                                    |                                    |
| Base Oil 2 (Yubase 4)            |                     |                  |                  | 99.95                              | 99.99                              | 99.9                               |
| Irgamet 30                       | 0.1                 |                  |                  |                                    |                                    | 0.1                                |
| Sarkosyl O                       |                     | 0.01             |                  |                                    | 0.01                               |                                    |
| Irgacor NPA                      |                     |                  | 0.05             | 0.05                               |                                    |                                    |
| Total                            | 100                 | 100              | 100              | 100                                | 100                                | 100                                |
| ASTM D130<br>(1 hour at 150° C.) | 1A                  | 1A               | 1A               | 1A                                 | 1B                                 | 1A                                 |

#### DISCUSSION

[0082] In the copper corrosion test ASTM D130, 1A is the lowest copper corrosion designation number in this test (the lower the copper corrosion designation number the lower the corrosion). From Table 2 it can be seen that Comparative Example 2 gives a worse result (1B) (i.e. more corrosion) than the other examples.

- 1. A lubricating oil composition comprising:
- (a) a base oil comprising a Fischer-Tropsch derived base oil; and
- (b) an anti-corrosive compound.
- 2. The lubricating oil composition according to claim 1, wherein the anti-corrosive compound is present in an amount of between 0.01 and 8% by weight of the lubricant composition
- 3. The lubricating oil composition according to claim 1, wherein the anti-corrosive compound is selected from the group consisting of thiazoles, triazoles, benzodiazoles, benzotriazoles, and thiodiazoles.
- **4**. The lubricating oil composition according to claim **1**, wherein the anti-corrosive compound is selected from the group consisting of sodium sulfonates, barium sulfonate, neutral barium dinonylnaphthalene sulfonate (also calcium and zinc), and overbased sulfonates.
- 5. The lubricating oil composition according to claim 1, wherein the anti-corrosive compound is selected from the group consisting of zinc diamyldithiocarbamate and zinc dithiocarbamates.
- **6**. The lubricating oil composition according to claim **1**, wherein the anti-corrosive compound is selected from the group consisting of hexamine, phenylenediamine, dimethylethanolamine, and derivatives thereof.

- 11. The lubricating composition according to claim 1, wherein the anti-corrosive compound is selected from mercapto-thiadiazole derivatives.
- 12. The lubricating composition according to claim 1, wherein the anti-corrosive compound is a sarcosine.
- 13. The lubricating composition according to claim 1, wherein the anti-corrosive compound is selected from the group consisting of salts of carboxylic acid and alkanolamine, amine phosphate, and fatty acid alkanolamines.
- 14. The lubricating composition according to claim 1, wherein the anti-corrosive compound is selected from the group consisting of triethanolamine salts of phosphate esters.
- **15**. The lubricating composition according to claim 1, wherein the anti-corrosive compound is an oil soluble complex chelating agent.
- **16**. A lubricating oil composition according to claim **1** wherein the Fischer-Tropsch derived base oil has a kinematic viscosity at 100° C. of from 1 mm²/s to 35 mm²/s.
- 17. A lubricating oil composition according to claim 1 wherein the base oil contains more than 50 wt. %, preferably more than 60 wt. %, more preferably more than 70 wt. %, even more preferably more than 80 wt. %, most preferably more than 90 wt. % Fischer-Tropsch derived base oil.
- **18**. A method for lubricating an engine, the method comprising lubricating said engine with the oil composition of claim **1**, wherein the step of lubricating the engine results in a reduction in the amount of copper corrosion.
- 19. The method of claim 18, wherein the engine is a passenger car engine.
- 20. The method of claim 18, wherein the engine is a heavy duty diesel engine.

\* \* \* \* \*