

TITLE

Fuel Efficient Lubricating Composition

BACKGROUND

[0001] There is increasing interest in improving the fuel efficiency of internal combustion engines. Vehicle manufacturers have improved fuel economy through engine design, improvements which take advantage of advances in lubricating oils which provide better oxidative stability, wear protection, and reduced friction.

[0002] Lubricant viscosity and base oil viscosity are two of the primary drivers of lubricant mediated fuel economy. Lower lubricant viscosity often translates into improved fuel efficiency for internal combustion engines. However, there are practical limits that govern the available viscosity ranges available for lubricant compositions.

[0003] Lubricant life is limited by many factors, including exposure to combustion gases, high temperatures, and pressures. In addition, oil consumption, that is the loss of lubricant from the crankcase during normal operation of the engine, is a major factor impacting low viscosity fluids. While base oil volatility may be one of many factors governing oil consumption, the move to lower viscosity lubricants to achieve improvements in fuel economy may result in significant reduction in oil life.

[0004] The instant disclosure relates to lubricants for internal combustion engines, that may, at least, provide improved fuel economy without reducing the effective life of the lubricant and/or impacting the cleanliness and durability performance of the engine. This may be achieved through the use of low viscosity, low volatility base oils in combination with ashless succinimide dispersants.

SUMMARY

[0005] The instant disclosure is directed to low viscosity, low volatility lubricating compositions having an oil of lubricating viscosity that includes a lubricating base oil and a hydrocarbon oil, the hydrocarbon oil being at least 20 wt % of the oil of lubricating viscosity and has a kinematic viscosity of less than 3.7 cSt at 100°C and a NOACK volatility (measured by ASTM D5800) of less than 25 wt %; and from 1.2 to 4 wt % of a polyalkenyl succinimide

dispersant where the lubricating composition is a 0W-XX multi-grade composition according to SAE J300 and XX is selected from 8, 12, 16, and 20.

[0006] In another embodiment, the instant disclosure relates to a low viscosity, low volatility lubricating compositions having an oil of lubricating viscosity that includes a lubricating base oil and a hydrocarbon oil, the hydrocarbon oil being from 20 to 95 wt % of the oil of lubricating viscosity and has a kinematic viscosity of less than 3.7 cSt at 100°C and a NOACK volatility (measured by ASTM D5800) of less than 20 wt %; and from 1.2 to 4 wt % of a polyalkenyl succinimide dispersant where the lubricating composition is a 0W-XX multi-grade composition according to SAE J300 and XX is selected from 8, 12, 16, and 20.

[0007] In another embodiment, the instant disclosure relates to a low viscosity, low volatility lubricating compositions having an oil of lubricating viscosity that includes a lubricating base oil and a hydrocarbon oil, the hydrocarbon oil being at least 20 wt % of the oil of lubricating viscosity and has a kinematic viscosity of less than 3.7 cSt at 100°C and a NOACK volatility (measured by ASTM D5800) of less than 25 wt %; from 1.2 to 4 wt % of a polyisobutylene succinimide dispersant; from 0.1 to 3 wt % of an antiwear agent, such as zinc dialkyldithiophosphate; from 0.5 to 3 wt % of a metal-containing detergent selected from one or more of an overbased calcium salicylate detergent and a magnesium salicylate detergent; and from 0.08 to 1.2 wt % of a polymeric viscosity modifier; where the lubricating composition is a 0W-XX multi-grade composition according to SAE J300 and XX is selected from 8, 12, 16, and 20.

[0008] The instant disclosure further relates to methods of lubricating an internal combustion engine where the method includes supplying a composition as described herein to at least one lubricating system within the internal combustion engine.

[0009] The instant disclosure also relates to the use of any one of the lubricating compositions described herein to improve fuel economy in an internal combustion engine without reducing the effective life of the lubricating composition and/or impacting the cleanliness and durability performance of the engine.

DETAILED DESCRIPTION

[0010] Various features and embodiments will be described below by way of non-limiting illustration. The instant disclosure relates to methods for lubricating an internal combustion engine.

[0011] The disclosed technology provides a low volatility lubricating composition, a method for lubricating an internal combustion engine with a low volatility lubricating composition, and the use as disclosed above. The term “low volatility” when used in reference to a hydrocarbon oil means that the hydrocarbon oil has an evaporative loss of less than 25 wt % as measured by ASTM D5800 Noack test. The lubricating composition disclosed herein includes an oil of lubricating viscosity that includes a lubricating base oil and a hydrocarbon oil, the hydrocarbon oil being at least 20 wt % of the oil of lubricating viscosity and having a kinematic viscosity measured at 100 °C of no more than 3.7 cSt and an evaporative loss of less than 25 wt % as measured by ASTM D5800 Noack test. The oil of lubricating viscosity may further include one or more suitable lubricating base oils, different from that of the hydrocarbon oil.

Lubricating Base Oil

[0012] Lubricating base oils (in addition to and different from the hydrocarbon oil) include natural and synthetic oils, oil derived from hydrocracking, hydrogenation, and hydrofinishing, unrefined, refined, re-refined oils or mixtures thereof. A more detailed description of unrefined, refined and re-refined oils is provided in International Publication WO2008/147704, paragraphs [0054] to [0056] (a similar disclosure is provided in US Patent Publication 2010/0197536, see [0072] to [0073]). A more detailed description of natural and synthetic lubricating oils is described in paragraphs [0058] to [0059] respectively of WO2008/147704 (a similar disclosure is provided in US Patent Publication 2010/0197536, see [0075] to [0076]). Synthetic oils may also be produced by Fischer-Tropsch reactions and typically may be hydroisomerised Fischer-Tropsch hydrocarbons or waxes. In one embodiment, oils may be prepared by a Fischer-Tropsch gas-to-liquid synthetic procedure as well as other gas-to-liquid oils.

[0013] Lubricating base oils may also be defined as specified in the April 2008 version of "Appendix E - API Base Oil Interchangeability Guidelines for Passenger Car Motor Oils and Diesel Engine Oils", section 1.3 Sub-heading 1.3. "Base Stock Categories". The API Guidelines are also summarized in US Patent US 7,285,516 (see column 11, line 64 to column 12, line 10). In one embodiment, the lubricating base oil may be an API Group II, Group III, or Group IV oil, or mixtures thereof. The five base oil groups are as follows:

Base Oil Category	Sulfur (%)	Saturates (%)	Viscosity Index
Group I	>0.03 and/or	<90	80 to 120
Group II	≤ 0.03 and	≥ 90	80 to 120
Group III	≤ 0.03 and	≥ 90	≥ 120
Group IV	All polyalphaolefins (PAO)		
Group V	All others not included in Groups I, II, III, or IV		

[0014] The amount of the oil of lubricating base oil present in the lubricating composition is typically the balance remaining after subtracting from 100 weight % (wt %) the sum of the amount of instantly disclosed hydrocarbon oil and the other performance additives.

[0015] In one embodiment, the lubricating base oil comprises at least 30 wt % of Group II or Group III base oil. In another embodiment, the base oil comprises at least 60 weight % of Group II or Group III base oil, or at least 80 wt % of Group II or Group III base oil. In one embodiment, the lubricant composition comprises less than 20 wt % of Group IV (i.e. polyalphaolefin) base oil. In another embodiment, the lubricant composition comprises less than 10 wt % of Group IV base oil. In one embodiment, the lubricating composition is substantially free of (i.e. contains less than 0.5 wt %) of Group IV base oil.

[0016] Ester base fluids, which are characterized as Group V oils, have high levels of solvency as a result of their polar nature. Addition of low levels (typically less than 10 wt %) of ester to a lubricating composition may significantly increase the resulting solvency of the base oil. Esters may be broadly grouped into two categories: synthetic and natural. An ester base fluid would have a kinematic viscosity at 100°C suitable for use in an engine oil lubricant, such as between 2 cSt and 30 cSt, or from 3 cSt to 20 cSt, or even from 4 cSt to 12 cSt. In one embodiment, the lubricating composition comprises at least 2 weight % of an ester base fluid. In one embodiment the lubricating composition comprises at least 4 weight % of an ester base fluid, or at least 7 weight % of an ester base fluid, or even at least 10 weight % of an ester base fluid.

Hydrocarbon Oil

[0017] The hydrocarbon oil of the invention comprises one or more saturated hydrocarbons containing at least one hydrocarbyl branch, sufficient to provide fluidity to both very low and high temperatures. Hydrocarbons of the invention may include natural and synthetic oils, oil derived from hydrocracking, hydrogenation, and hydrofinishing, refined, bio-derived, re-refined oils or combinations or mixtures thereof.

[0018] Synthetic hydrocarbon oils may be produced by isomerization of predominantly linear hydrocarbons to product branched hydrocarbons. Linear hydrocarbons may be naturally sourced, synthetically prepared, or derived from Fischer-Tropsch reactions or similar processes. Hydrocarbon oil may be derived from hydro-isomerized wax and typically may be hydroisomerised Fischer-Tropsch hydrocarbons or waxes. In one embodiment oils may be prepared by a Fischer-Tropsch gas-to-liquid synthetic procedure as well as other gas-to-liquid oils.

[0019] Suitable hydrocarbon oils may also be obtained from natural, renewable, sources. Natural (or bio-derived) oils refer to materials derived from a renewable biological resource, organism, or entity, distinct from materials derived from petroleum or equivalent raw materials. Natural sources of hydrocarbon oil include fatty acid triglycerides, hydrolyzed or partially hydrolyzed triglycerides, or transesterified triglyceride esters, such as fatty acid methyl ester (or FAME). Suitable triglycerides include, but are not limited to, palm oil, soybean oil, sunflower oil, rapeseed oil, olive oil, linseed oil, and related materials. Other sources of triglycerides include, but are not limited to algae, animal tallow, and zooplankton. Linear and branched hydrocarbons may be rendered or extracted from vegetable oils and hydrorefined and/or hydroisomerized in a manner similar to synthetic oils to produce hydrocarbon oil. In some embodiments, at least 50 wt % of the hydrocarbon oil is bio-derived. In other embodiments, at least 55 wt %, or at least 60 wt %, or at least 65 wt %, or at least 70 wt %, or at least 80 wt % or at least 90 wt % of the hydrocarbon oil is bio-derived. In one embodiment, the hydrocarbon oil is bio-derived and is substantially free, i.e., less than 0.5 wt % based on the weight of the hydrocarbon oil, of ester functionality.

[0020] Hydrocarbons are generally understood to consist essentially of carbon and hydrogen atoms but may often contain low amounts of heteroatoms. The hydrocarbon oil of the invention is free of or substantially free of heteroatoms, except for impurities and contaminants that may carry over from processing or manufacture.

[0021] The hydrocarbon oil of the invention comprises a hydrocarbon compound containing 16 carbon atoms up to a maximum of 60 carbon atoms and at least one hydrocarbyl branch containing at least one carbon atom. In one embodiment, the hydrocarbon compound comprises at least 18 or at least 22 carbon atoms with the proviso that the longest continuous chain of carbon atoms is no more than 24 carbons in length. In one embodiment, the hydrocarbon oil comprises a hydrocarbon compound containing 22 to 38 carbon atoms with the proviso that the longest continuous chain of carbon atoms is no more than 24 carbons in length. In one embodiment, the hydrocarbon oil is bio-derived and includes a hydrocarbon compound having a continuous chain of no more than 24 carbon atoms and at least 30 total carbon atoms.

[0022] Alternatively, the hydrocarbon oil may be described as a paraffinic or iso-paraffinic compound.

[0023] Mineral oils often contain cyclic structures, i.e., aromatics or cycloparaffins also called naphthenes. In one embodiment, the hydrocarbon oil comprises a saturated hydrocarbon compound free of or substantially free of cyclic structures. In one embodiment, the hydrocarbon oil is substantially aliphatic (95 wt % and greater) and contains less than 5 wt % of cyclic hydrocarbons.

[0024] In one embodiment, the hydrocarbon oil has a kinematic viscosity, measured at 100 °C, of at least 0.7 cSt, or at least about 0.9 cSt, or at least about 1.1 cSt. In one embodiment, the hydrocarbon oil has a kinematic viscosity less than 3.7 cSt at 100° C, or less than 3.6 cSt at 100° C, or less than 3.5 cSt at 100° C, or less than 3.4 cSt, or less than 3.2 cSt at 100° C. In a further embodiment, the hydrocarbon oil has a closed cup flash point of at least 50 °C, or at least 60 °C, or at least 75 °C, or at least 100 °C.

[0025] In one embodiment, the hydrocarbon oil has an evaporative loss (also called Noack volatility) of less than 25 wt %wt %, as measured by ASTM D5800. In one embodiment the evaporative loss is less than 20 wt %wt % or less than 18 wt %wt %, or less than 15 wt %. In one embodiment, the hydrocarbon oil has a kinematic viscosity of less than 3.7 cSt at 100°C and an evaporative loss of less than 25 wt %.

[0026] The lubricating composition comprises oil of lubricating viscosity that includes at least 20 wt % of the hydrocarbon oil based on the weight of the oil of lubricating viscosity. In one embodiment, the oil of lubricating viscosity may comprise at least 30 wt % of the hydrocarbon oil, or at least 35 wt %, or at least 40 wt %, or at least 50 wt %, or at least 60 wt %, or at least 70 wt %

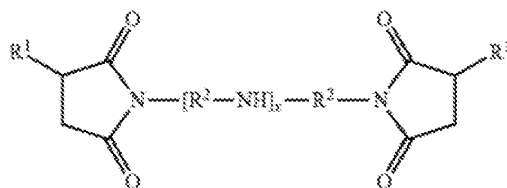
of the hydrocarbon oil. In another embodiment, the oil of lubricating viscosity is at least 90 wt % of the hydrocarbon oil, based on the weight of the oil of lubricating viscosity. In one embodiment, the oil of lubricating viscosity is 100 wt % of the hydrocarbon oil, based on the weight of the oil of lubricating viscosity.

[0027] In some embodiments, the oil of lubricating viscosity may include at least 20 wt % of the hydrocarbon oil, based on the weight of the oil of lubricating viscosity. In another embodiment, the oil of lubricating viscosity may comprise 20 wt % to 95 wt % of the hydrocarbon oil, or 25 wt % to 75 wt %, or 30 wt % to 60 wt % of the hydrocarbon oil.

[0028] The oil of lubricating viscosity containing the lubricating base oil and hydrocarbon oil can have a viscosity index of greater than 100. In some embodiments, the viscosity index is greater than 115, or greater than 125. In other embodiments, the viscosity index is from 110 to 130, or 115 to 125, or from 117 to 122.

Polyalkenyl Succinimide Dispersant

[0029] The lubricating composition of the instant disclosure further includes a polyalkenyl succinimide dispersant. Dispersants, generally, are well known in the field of lubricants and include primarily what is known as ashless dispersants and polymeric dispersants. Ashless dispersants are so-called because, as supplied, they do not contain metal and thus do not normally contribute to sulfated ash when added to a lubricant. However, they may, interact with ambient metals once they are added to a lubricant which includes a metal-containing species. Ashless dispersants are characterized by a polar group attached to a relatively high molecular weight hydrocarbon chain. Typical ashless dispersants include N-substituted long chain alkenyl succinimides, having a variety of chemical structures, including those represented by Formula (I)



Formula (I)

where each R^1 is independently an alkyl group, frequently a polyisobutylene group with a molecular weight (M_n) of 500-5000 based on the polyisobutylene precursor, and R^2 are alkylene groups, commonly ethylene (C_2H_4) groups.

[0030] Such molecules are commonly derived from reaction of an alkenyl acylating agent with a polyamine, and a wide variety of linkages between the two moieties is possible beside the simple imide structure shown above, including a variety of amides and quaternary ammonium salts. In the above Formula (I), the amine portion is shown as an alkylene polyamine, although other aliphatic and aromatic mono- and polyamines may also be used. Also, a variety of modes of linkage of the R^1 groups onto the imide structure are possible, including various cyclic linkages. The ratio of the carbonyl groups of the acylating agent to the nitrogen atoms of the amine may be 1:0.5 to 1:3, and in other instances 1:1 to 1:2.75 or 1:1.5 to 1:2.5. Succinimide dispersants are more fully described in U.S. Pat. Nos. 4,234,435 and 3,172,892 and in EP 0355895.

[0031] In certain embodiments, the dispersant is prepared by a process that involves the presence of small amounts of chlorine or other halogen, as described in U.S. Pat. No. 7,615,521 (see, e.g., col. 4, lines 18-60 and preparative example A). Such dispersants typically have some carbocyclic structures in the attachment of the hydrocarbyl substituent to the acidic or amidic "head" group. In other embodiments, the dispersant is prepared by a thermal process involving an "ene" reaction, without the use of any chlorine or other halogen, as described in U.S. Pat. No. 7,615,521; dispersants made in this manner are often derived from high vinylidene (i.e. greater than 50% terminal vinylidene) polyisobutylene (See col. 4, line 61 to col. 5, line 30 and preparative example B). Such dispersants typically do not contain the above-described carbocyclic structures at the point of attachment. In certain embodiments, the dispersant is prepared by free radical catalyzed polymerization of high-vinylidene polyisobutylene with an ethylenically unsaturated acylating agent, as described in U.S. Pat. No. 8,067,347.

[0032] Some dispersants for use in the instant lubricating compositions may be derived from, as the polyolefin, high vinylidene polyisobutylene, that is, having greater than 50, 70, or 75% terminal vinylidene groups (.alpha. and .beta. isomers). In certain embodiments, the succinimide dispersant may be prepared by the direct alkylation route. In other embodiments, it may comprise a mixture of direct alkylation and chlorine-route dispersants.

[0033] Suitable dispersants for use in the instant lubricating compositions include succinimide dispersants. In one embodiment, the dispersant may be present as a single dispersant.

In one embodiment, the dispersant may be present as a mixture of two or three different dispersants, wherein at least one may be a succinimide dispersant.

[0034] The succinimide dispersant may be a derivative of an aliphatic polyamine, or mixtures thereof. The aliphatic polyamine may be aliphatic polyamine such as an ethylenepolyamine, a propylenepolyamine, a butylenepolyamine, or mixtures thereof. In one embodiment, the aliphatic polyamine may be ethylenepolyamine. In one embodiment, the aliphatic polyamine may be selected from the group consisting of ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, polyamine still bottoms, and mixtures thereof.

[0035] The succinimide dispersant may be a derivative of an aromatic amine, an aromatic polyamine, or mixtures thereof. The aromatic amine may be 4-aminodiphenylamine (ADPA) (also known as N-phenylphenylenediamine), derivatives of ADPA (as described in United States Patent Publications 2011/0306528 and 2010/0298185), a nitroaniline, an aminocarbazole, an amino-indazolinone, an aminopyrimidine, 4-(4-nitrophenylazo)aniline, or combinations thereof. In one embodiment, the dispersant is derivative of an aromatic amine wherein the aromatic amine has at least three non-continuous aromatic rings.

[0036] The succinimide dispersant may be a derivative of a polyether amine or polyether polyamine. Typical polyether amine compounds contain at least one ether unit and will be chain terminated with at least one amine moiety. The polyether polyamines can be based on polymers derived from C₂-C₆ epoxides such as ethylene oxide, propylene oxide, and butylene oxide. Examples of polyether polyamines are sold under the Jeffamine[®] brand and are commercially available from Hunstman Corporation located in Houston, Texas.

[0037] The dispersant may also be post-treated by conventional methods by a reaction with any of a variety of agents. Among these are boron compounds, urea, thiourea, dimercapthiadiazoles, carbon disulfide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, maleic anhydride, nitriles, epoxides, and phosphorus compounds. In one embodiment, the succinimide dispersant may be post-treated with boron, resulting in a borated dispersant. In one embodiment, the succinimide dispersant comprises at least one boron-containing dispersant and at least one boron-free dispersant. In one embodiment, the lubricating composition is free of or substantially free of a boron-containing succinimide dispersant.

[0038] The polyalkenyl succinimide dispersant may be present in an amount of from 1.2 wt % to 4 wt % of the lubricating composition, or 1.5 wt % to 3.8 wt % of the composition, or 1.2 wt % to 3 wt %, or 2.0 wt % to 3.5 wt % of the composition. It is understood that if a mixture of two or more dispersants comprises the succinimide dispersant, each of those dispersants may be independently present in the composition at 0.01 wt % to 4 wt %, or 0.1 wt % to 3.5 wt %, or 0.5 wt % to 3.5 wt %, or 1.0 wt % to 3.0 wt %, or 0.5 wt % to 2.2 wt % of the lubricating composition, with the proviso that the total amount of dispersant is as described above. In one embodiment, the polyalkenyl succinimide dispersant is a polyisobutylene succinimide. In another embodiment, the polyalkenyl succinimide dispersant is a polyisobutylene succinimide and is present in the lubricating composition in an amount of from 1.2 to 4 wt %.

[0039] In one embodiment, the polyalkenyl succinimide dispersant is a boron-containing succinimide dispersant in an amount of from 1.2 to 4 wt % of the lubricating composition. In another embodiment, the polyalkenyl succinimide dispersant is a mixture of boron-free and boron-containing succinimide dispersants. When both boron-containing dispersants and boron-free dispersants are present, the ratio of the one or more boron-containing dispersants to the one or more boron-free dispersants may be 4:1 to 1:4 on a weight basis, or 3:1 to 1:3, or 2:1 to 1:3, or 1:1 to 1:4 on a weight basis. In another embodiment, one or more boron-containing dispersants is present in an amount 0.8 wt% up to 2.1 wt% and one or more boron-free dispersants is present in an amount 0.8 wt% up to 4 wt% of the lubricating composition.

Other Performance Additives

[0040] The compositions of the invention may optionally comprise one or more additional performance additives. These additional performance additives may include one or more metal deactivators, viscosity modifiers, detergents, friction modifiers, antiwear agents, corrosion inhibitors, dispersants (other than those of the invention), dispersant viscosity modifiers, extreme pressure agents, antioxidants, foam inhibitors, demulsifiers, pour point depressants, seal swelling agents, and any combination or mixture thereof. Typically, fully-formulated lubricating oil will contain one or more of these performance additives, and often a package of multiple performance additives.

[0041] In one embodiment, the invention provides a lubricating composition further comprising an anti-wear agent, a dispersant viscosity modifier, a friction modifier, a viscosity modifier, an antioxidant, an overbased detergent, a dispersant (different from that of the invention),

or a combination thereof, where each of the additives listed may be a mixture of two or more of that type of additive. In one embodiment, the invention provides a lubricating composition further comprising an anti-wear agent, a dispersant viscosity modifier, a friction modifier, a viscosity modifier (typically an olefin copolymer such as an ethylene-propylene copolymer), an antioxidant (including phenolic and aminic antioxidants), an overbased detergent (including overbased sulfonates and phenates), or a combination thereof, where each of the additives listed may be a mixture of two or more of that type of additive.

[0042] Another additive is an anti-wear agent. Examples of anti-wear agents include phosphorus-containing anti-wear/extreme pressure agents such as metal thiophosphates, phosphoric acid esters and salts thereof, phosphorus-containing carboxylic acids, esters, ethers, and amides, and phosphites. In certain embodiments a phosphorus antiwear agent may be present in an amount to deliver 0.01 to 0.2, or 0.015 to 0.15, or 0.02 to 0.1, or 0.025 to 0.08, or 0.01 to 0.05 percent phosphorus. Often the anti-wear agent is a zinc dialkyldithiophosphate (ZDDP or ZDP).

[0043] Zinc dialkyldithiophosphates may be described as primary zinc dialkyldithiophosphates or as secondary zinc dialkyldithiophosphates, depending on the structure of the alcohol used in its preparation. In some embodiments the compositions of the invention include primary zinc dialkyldithiophosphates. In some embodiments the compositions of the invention include secondary zinc dialkyldithiophosphates. In some embodiments the compositions of the invention include a mixture of primary and secondary zinc dialkyldithiophosphates. In some embodiments component (b) is a mixture of primary and secondary zinc dialkyldithiophosphates where the ratio of primary zinc dialkyldithiophosphates to secondary zinc dialkyldithiophosphates (one a weight basis) is at least 1:1, or even at least 1:1.2, or even at least 1:1.5 or 1:2, or 1:10. In some embodiments, component (b) is a mixture of primary and secondary zinc dialkyldithiophosphates that is at least 50 percent by weight primary, or even at least 60, 70, 80, or even 90 percent by weight primary. In some embodiments component (b) is free of primary zinc dialkyldithiophosphates.

[0044] The phosphorus anti wear agent may be present at 0 weight % to 3 weight %, or 0.1 to 3 wt % or 0.1 weight % to 1.5 weight %, or 0.5 weight % to 0.9 weight % of the lubricating composition.

[0045] In one embodiment, the invention provides a lubricating composition which further comprises ashless antioxidant. Ashless antioxidants may comprise one or more of arylamines, diarylamines, alkylated arylamines, alkylated diaryl amines, phenols, hindered phenols, sulfurized olefins, or mixtures thereof. In one embodiment, the lubricating composition includes an antioxidant, or mixtures thereof. The antioxidant may be present at 0 weight % to 15 weight %, or 0.1 weight % to 10 weight %, or 0.5 weight % to 5 weight %, or 0.5 weight % to 3 weight %, or 0.3 weight % to 1.5 weight % of the lubricating composition.

[0046] The diarylamine or alkylated diarylamine may be a phenyl- α -naphthylamine (PANA), an alkylated diphenylamine, or an alkylated phenylnaphthylamine, or mixtures thereof. The alkylated diphenylamine may include di-nonylated diphenylamine, nonyl diphenylamine, octyl diphenylamine, di-octylated diphenylamine, di-decylated diphenylamine, decyl diphenylamine and mixtures thereof. In one embodiment, the diphenylamine may include nonyl diphenylamine, dinonyl diphenylamine, octyl diphenylamine, dioctyl diphenylamine, or mixtures thereof. In one embodiment, the alkylated diphenylamine may include nonyl diphenylamine, or dinonyl diphenylamine. The alkylated diarylamine may include octyl, di-octyl, nonyl, di-nonyl, decyl or di-decyl phenylnaphthylamines.

[0047] The diarylamine antioxidant of the invention may be present on a weight basis of the lubrication composition at 0.1% to 10%, 0.35% to 5%, 0.4% to 1.2%, or even 0.5% to 2%.

[0048] The phenolic antioxidant may be a simple alkyl phenol, a hindered phenol, or coupled phenolic compounds.

[0049] 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 or 4-butyl-2,6-di-tert-butylphenol, 4-dodecyl-2,6-di-tert-butylphenol, or butyl 3-(3,5-ditert-butyl-4-hydroxyphenyl)propanoate. In one embodiment, the hindered phenol antioxidant may be an ester and may include, e.g., Irganox™ L-135 from BASF. In one embodiment, the phenolic antioxidant comprises a hindered phenol. In another embodiment the hindered phenol is derived from 2,6-ditertbutyl phenol.

[0050] In one embodiment, the lubricating composition of the invention comprises a phenolic antioxidant in a range of 0.01 weight % to 5 weight %, or 0.1 weight % to 4 weight %, or 0.2 weight % to 3 weight %, or 0.5 weight % to 2 weight % of the lubricating composition.

[0051] Sulfurized olefins are well known commercial materials, and those which are substantially nitrogen-free, that is, not containing nitrogen functionality, are readily available. The olefinic compounds which may be sulfurized are diverse in nature. They contain at least one olefinic double bond, which is defined as a non-aromatic double bond; that is, one connecting two aliphatic carbon atoms. These materials generally have sulfide linkages having 1 to 10 sulfur atoms, for instance, 1 to 4, or 1 or 2.

[0052] Ashless antioxidants may be used separately or in combination. In one embodiment of the invention, two or more different antioxidants are used in combination, such that there is at least 0.1 wt % of each of the at least two antioxidants and wherein the combined amount of the ashless antioxidants is 0.5 to 5 wt %. In one embodiment, there may be at least 0.25 to 3 wt % of each ashless antioxidant.

[0053] In one embodiment, the invention provides a lubricating composition further comprising a molybdenum compound. The molybdenum compound may be selected from the group consisting of molybdenum dialkyldithiophosphates, molybdenum dithiocarbamates, amine salts of molybdenum compounds, and mixtures thereof. The molybdenum compound may provide the lubricating composition with 0 to 1000 ppm, or 5 to 1000 ppm, or 10 to 750 ppm, or 5 ppm to 300 ppm, or 20 ppm to 250 ppm of molybdenum, or 350 ppm to 900 ppm.

[0054] In one embodiment, the lubricating composition of the invention further comprises a dispersant viscosity modifier. The dispersant viscosity modifier may be present at 0 weight % to 5 weight %, or 0 weight % to 4 weight %, or 0.05 weight % to 2 weight % of the lubricating composition.

[0055] Suitable dispersant viscosity modifiers include functionalized polyolefins, for example, ethylene-propylene copolymers that have been functionalized with an acylating agent such as maleic anhydride and an amine; polymethacrylates functionalized with an amine, or esterified styrene-maleic anhydride copolymers reacted with an amine. More detailed description of dispersant viscosity modifiers are disclosed in International Publication WO2006/015130 or U.S. Pat. Nos. 4,863,623; 6,107,257; 6,107,258; and 6,117,825. In one embodiment, the dispersant viscosity modifier may include those described in U.S. Pat. No. 4,863,623 (see column 2, line 15

to column 3, line 52) or in International Publication WO2006/015130 (see page 2, paragraph [0008] and preparative examples are described at paragraphs [0065] to [0073]).

[0056] In one embodiment, the invention provides a lubricating composition further comprising a metal-containing detergent. The metal-containing detergent may be an overbased detergent. Overbased detergents otherwise referred to as overbased or superbased salts are characterized by a metal content in excess of that which would be necessary for neutralization according to the stoichiometry of the metal and the particular acidic organic compound reacted with the metal. The overbased detergent may be selected from the group consisting of non-sulfur containing phenates, sulfur containing phenates, sulfonates, salixarates, salicylates, and mixtures thereof.

[0057] The overbased metal-containing detergent may be sodium salts, calcium salts, magnesium salts, or mixtures thereof of the phenates, sulfur-containing phenates, sulfonates, salixarates and salicylates. Overbased phenates and salicylates typically have a total base number of 180 to 450 TBN. Overbased sulfonates typically have a total base number of 250 to 600, or 300 to 500. Overbased detergents are known in the art. In one embodiment, the sulfonate detergent may be predominantly a linear alkylbenzene sulfonate detergent having a metal ratio of at least 8 as is described in paragraphs [0026] to [0037] of US Patent Publication 2005065045 (and granted as U.S. Pat. No. 7,407,919). The linear alkylbenzene sulfonate detergent may be particularly useful for assisting in improving fuel economy. The linear alkyl group may be attached to the benzene ring anywhere along the linear chain of the alkyl group, but often in the 2, 3 or 4 position of the linear chain, and in some instances, predominantly in the 2 position, resulting in the linear alkylbenzene sulfonate detergent. Overbased detergents are known in the art. The overbased detergent may be present at 0 weight % to 15 weight %, or 0.1 weight % to 10 weight %, or 0.2 weight % to 8 weight %, or 0.5 to 3 weight %, or 0.2 weight % to 3 weight %. For example, in a heavy-duty diesel engine, the detergent may be present at 2 weight % to 3 weight % of the lubricating composition. For a passenger car engine, the detergent may be present at 0.2 weight % to 1 weight % of the lubricating composition.

[0058] Metal-containing detergents contribute sulfated ash to a lubricating composition. Sulfated ash may be determined by ASTM D874. In one embodiment, the lubricating composition of the invention comprises a metal-containing detergent in an amount to deliver at least 0.4 wt % sulfated ash to the total composition. In another embodiment, the metal-containing detergent is

present in an amount to deliver at least 0.6 wt % sulfated ash, or at least 0.75 wt % sulfated ash, or even at least 0.9 wt % sulfated ash to the lubricating composition.

[0059] The lubricating composition may contain a polymeric viscosity modifier or mixtures thereof. The polymeric viscosity modifier may be an olefin (co)polymer, a poly(meth)acrylate (PMA), or mixtures thereof. In one embodiment, the polymeric viscosity modifier is an olefin (co)polymer.

[0060] The olefin polymer may be derived from isobutylene or isoprene. In one embodiment, the olefin polymer is prepared from ethylene and a higher olefin within the range of C3-C10 alpha-mono-olefins, for example, the olefin polymer may be prepared from ethylene and propylene.

[0061] In one embodiment, the olefin polymer may be a polymer of 15 to 80 mole percent of ethylene, for example, 30 mol percent to 70 mol percent ethylene and from and from 20 to 85 mole percent of C3 to C10 mono-olefins, such as propylene, for example, 30 to 70 mol percent propylene or higher mono-olefins. Terpolymer variations of the olefin copolymer may also be used and may contain up to 15 mol percent of a non-conjugated diene or triene. Non-conjugated dienes or trienes may have 5 to about 14 carbon atoms. The non-conjugated diene or triene monomers may be characterized by the presence of a vinyl group in the structure and can include cyclic and bicycle compounds. Representative dienes include 1,4-hexadiene, 1,4-cyclohexadiene, dicyclopentadiene, 5-ethylidene-2-norbornene, 5-methylene-2-norbornene, 1,5-heptadiene, and 1,6-octadiene.

[0062] In one embodiment, the olefin copolymer may be a copolymer of ethylene, propylene, and butylene. The polymer may be prepared by polymerizing a mixture of monomers comprising ethylene, propylene and butylene. These polymers may be referred to as copolymers or terpolymers. The terpolymer may comprise from about 5 mol % to about 20 mol %, or from about 5 mol % to about 10 mol % structural units derived from ethylene; from about 60 mol % to about 90 mol %, or from about 60 mol % to about 75 mol structural units derived from propylene; and from about 5 mol % to about 30 mol %, or from about 15 mol % to about 30 mol % structural units derived from butylene. The butylene may comprise any isomers or mixtures thereof, such as n-butylene, iso-butylene, or a mixture thereof. The butylene may comprise butene-1. Commercial sources of butylene may comprise butene-1 as well as butene-2 and butadiene. The butylene may comprise a mixture of butene-1 and isobutylene wherein the weight ratio of butene-1 to isobutylene

is about 1:0.1 or less. The butylene may comprise butene-1 and be free of or essentially free of isobutylene.

[0063] In one embodiment, the olefin copolymer may be a copolymer of ethylene and butylene. The polymer may be prepared by polymerizing a mixture of monomers comprising ethylene and butylene wherein, the monomer composition is free of or substantially free of propylene monomers (i.e., contains less than 1 wt % of intentionally added monomer). The copolymer may comprise 30 to 50 mol percent structural units derived from butylene; and from about 50 mol percent to 70 mol percent structural units derived from ethylene. The butylene may comprise a mixture of butene-1 and isobutylene wherein the weight ratio of butene-1 to isobutylene is about 1:0.1 or less. The butylene may comprise butene-1 and be free of or essentially free of isobutylene.

[0064] Useful olefin polymers, in particular, ethylene- α -olefin copolymers have a number average molecular weight ranging from 4500 to 500,000, for example, 5000 to 100,000, or 7500 to 60,000, or 8000 to 45,000.

[0065] In one embodiment, lubricating composition may comprise a poly(meth)acrylate polymeric viscosity modifier. As used herein, the term “(meth)acrylate” and its cognates means either methacrylate or acrylate, as will be readily understood.

[0066] In one embodiment, the poly(meth)acrylate polymer is prepared from a monomer mixture comprising (meth)acrylate monomers having alkyl groups of varying length. The (meth)acrylate monomers may contain alkyl groups that are straight chain or branched chain groups. The alkyl groups may contain 1 to 24 carbon atoms, for example 1 to 20 carbon atoms.

[0067] The poly(meth)acrylate polymers described herein are formed from monomers derived from saturated alcohols, such as methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, 2-methylpentyl (meth)acrylate, 2-propylheptyl (meth)acrylate, 2-butyloctyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, octyl (meth)acrylate, nonyl (meth)acrylate, isooctyl (meth)acrylate, isononyl (meth)acrylate, 2-tert-butylheptyl (meth)acrylate, 3-isopropylheptyl (meth)acrylate, decyl (meth)acrylate, undecyl (meth)acrylate, 5-methylundecyl (meth)acrylate, dodecyl (meth)acrylate, 2-methyldodecyl (meth)acrylate, tridecyl (meth)acrylate, 5-methyltridecyl (meth)acrylate, tetradecyl (meth)acrylate, pentadecyl (meth)acrylate, hexadecyl (meth)acrylate, 2-methylhexadecyl (meth)acrylate, heptadecyl (meth)acrylate, 5-isopropylheptadecyl (meth)acrylate, 4-tert-butyloctadecyl (meth)acrylate,

5-ethyloctadecyl (meth)acrylate, 3-isopropyloctadecyl-(meth)acrylate, octadecyl (meth)acrylate, nonadecyl (meth)acrylate, eicosyl (meth)acrylate, (meth)acrylates derived from unsaturated alcohols, such as oleyl (meth)acrylate; and cycloalkyl (meth)acrylates, such as 3-vinyl-2-butylcyclohexyl (meth)acrylate or bornyl (meth)acrylate.

[0068] Other examples of monomers include alkyl (meth)acrylates with long-chain alcohol-derived groups which may be obtained, for example, by reaction of a (meth)acrylic acid (by direct esterification) or methyl (meth)acrylate (by transesterification) with long-chain fatty alcohols, in which reaction a mixture of esters such as (meth)acrylate with alcohol groups of various chain lengths is generally obtained. These fatty alcohols include Oxo Alcohol® 7911, Oxo Alcohol® 7900 and Oxo Alcohol® 1100 of Monsanto; Alphanol® 79 of ICI; Nafol® 1620, Alfol® 610 and Alfol® 810 of Condea (now Sasol); Epal® 610 and Epal® 810 of Ethyl Corporation; Linevol® 79, Linevol® 911 and Dobanol® 25 L of Shell AG; Lial® 125 of Condea Augusta, Milan; Dehydad® and Lorol® of Henkel KGaA (now Cognis) as well as Linopol® 7-11 and Acropol® 91 of Uguine Kuhlmann.

[0069] In one embodiment, the poly(meth)acrylate polymer comprises a dispersant monomer; dispersant monomers include those monomers which may copolymerize with (meth)acrylate monomers and contain one or more heteroatoms in addition to the carbonyl group of the (meth)acrylate. The dispersant monomer may contain a nitrogen-containing group, an oxygen-containing group, or mixtures thereof.

[0070] The nitrogen-containing compound may be a (meth)acrylamide or a nitrogen containing (meth)acrylate monomer. Examples of a suitable nitrogen-containing compound include N,N-dimethylacrylamide, N-vinyl carbonamides such as N-vinyl-formamide, vinyl pyridine, N-vinylacetoamide, N-vinyl propionamides, N-vinyl hydroxy-acetoamide, N-vinyl imidazole, N-vinyl pyrrolidinone, N-vinyl caprolactam, dimethylaminoethyl acrylate (DMAEA), dimethylaminoethyl methacrylate (DMAEMA), dimethylaminobutyl acrylamide, dimethylaminopropyl meth-acrylate (DMPMA), dimethylaminopropyl acrylamide, dimethylaminopropyl methacrylamide, dimethylaminoethyl acrylamide or mixtures thereof.

[0071] Dispersant monomers may be present in an amount up to 5 mol percent of the monomer composition of the (meth)acrylate polymer. In one embodiment, the poly(meth)acrylate is present in an amount 0 to 5 mol percent, 0.5 to 4 mol percent, or 0.8 to 3 mol percent of the

polymer composition. In one embodiment, the poly(meth)acrylate is free of or substantially free of dispersant monomers.

[0072] In one embodiment, the poly(meth)acrylate comprises a block copolymer or tapered block copolymer. Block copolymers are formed from a monomer mixture comprising one or more (meth)acrylate monomers, wherein, for example, a first (meth)acrylate monomer forms a discrete block of the polymer joined to a second discrete block of the polymer formed from a second (meth)acrylate monomer. While block copolymers have substantially discrete blocks formed from the monomers in the monomer mixture, a tapered block copolymer may be composed of, at one end, a relatively pure first monomer and, at the other end, a relatively pure second monomer. The middle of the tapered block copolymer is more of a gradient composition of the two monomers.

[0073] In one embodiment, the poly(meth)acrylate polymer (P) is a block or tapered block copolymer that comprises at least one polymer block (B₁) that is insoluble or substantially insoluble in the base oil and a second polymer block (B₂) that is soluble or substantially soluble in the base oil.

[0074] In one embodiment, the poly(meth)acrylate polymers may have an architecture selected from linear, branched, hyper-branched, cross-linked, star (also referred to as “radial”), or combinations thereof. Star or radial refers to multi-armed polymers. Such polymers include (meth)acrylate-containing polymers comprising 3 or more arms or branches, which, in some embodiments, contain at least about 20, or at least 50 or 100 or 200 or 350 or 500 or 1000 carbon atoms. The arms are generally attached to a multivalent organic moiety which acts as a “core” or “coupling agent.” The multi-armed polymer may be referred to as a radial or star polymer, or even a “comb” polymer, or a polymer otherwise having multiple arms or branches as described herein.

[0075] Linear poly(meth)acrylates, random, block or otherwise, may have weight average molecular weight (M_w) of 1000 to 400,000 Daltons, 1000 to 150,000 Daltons, or 15,000 to 100,000 Daltons. In one embodiment, the poly(meth)acrylate may be a linear block copolymer with a M_w of 5,000 to 40,000 Daltons, or 10,000 to 30,000 Daltons.

[0076] Radial, cross-linked or star copolymers may be derived from linear random or diblock copolymers with molecular weights as described above. A star polymer may have a weight average molecular weight of 10,000 to 1,500,000 Daltons, or 40,000 to 1,000,000 Daltons, or 300,000 to 850,000 Daltons.

[0077] The lubricating compositions may comprise 0.05 weight % to 2 weight %, or 0.08 weight % to 1.8 weight %, or 0.1 to 1.2 weight % of the one or more polymeric viscosity modifiers as described herein.

[0078] In one embodiment, the invention provides a lubricating composition further comprising a friction modifier. Examples of friction modifiers include long chain fatty acid derivatives of amines, fatty esters, or epoxides; fatty imidazolines such as condensation products of carboxylic acids and polyalkylene-polyamines; amine salts of alkylphosphoric acids; fatty alkyl tartrates; fatty alkyl tartrimides; or fatty alkyl tartramides. The term fatty, as used herein, can mean having a C8-22 linear alkyl group.

[0079] Friction modifiers may also encompass materials such as sulfurized fatty compounds and olefins, molybdenum dialkyldithiophosphates, molybdenum dithiocarbamates, sunflower oil or monoester of a polyol and an aliphatic carboxylic acid.

[0080] In one embodiment the friction modifier may be selected from the group consisting of long chain fatty acid derivatives of amines, long chain fatty esters, or long chain fatty epoxides; fatty imidazolines; amine salts of alkylphosphoric acids; fatty alkyl tartrates; fatty alkyl tartrimides; and fatty alkyl tartramides. The friction modifier may be present at 0 weight % to 6 weight %, or 0.05 weight % to 4 weight %, or 0.1 weight % to 2 weight % of the lubricating composition.

[0081] In one embodiment, the friction modifier may be a long chain fatty acid ester. In another embodiment the long chain fatty acid ester may be a mono-ester or a diester or a mixture thereof, and in another embodiment the long chain fatty acid ester may be a triglyceride.

[0082] Other performance additives such as corrosion inhibitors include those described in paragraphs 5 to 8 of US Application US05/038319, published as WO2006/047486, octyl octanamide, condensation products of dodecenyl succinic acid or anhydride and a fatty acid such as oleic acid with a polyamine. In one embodiment, the corrosion inhibitors include the Synalox[®] (a registered trademark of The Dow Chemical Company) corrosion inhibitor. The Synalox corrosion inhibitor may be a homopolymer or copolymer of propylene oxide. The Synalox corrosion inhibitor is described in more detail in a product brochure with Form No. 118-01453-0702 AMS, published by The Dow Chemical Company. The product brochure is entitled "SYNALOX Lubricants, High-Performance Polyglycols for Demanding Applications."

[0083] The lubricating composition may further include metal deactivators, including derivatives of benzotriazoles (typically tolyltriazole), dimercaptotriazole derivatives, 1,2,4-triazoles, benzimidazoles, 2-alkyldithiobenzimidazoles, or 2-alkyldithiobenzothiazoles; foam inhibitors, including copolymers of ethyl acrylate and 2-ethylhexylacrylate and copolymers of ethyl acrylate and 2-ethylhexylacrylate and vinyl acetate; demulsifiers including trialkyl phosphates, polyethylene glycols, polyethylene oxides, polypropylene oxides and (ethylene oxide-propylene oxide) polymers; and pour point depressants, including esters of maleic anhydride-styrene, polymethacrylates, polyacrylates or polyacrylamides.

[0084] Pour point depressants that may be useful in the compositions of the invention further include polyalphaolefins, esters of maleic anhydride-styrene, poly(meth)acrylates, polyacrylates or polyacrylamides.

[0085] In different embodiments, the lubricating composition may have a composition as described in the following table:

Additive	Embodiments (wt %)		
	A	B	C
Low volatility Hydrocarbon Base Oil	20 to 95	30 to 85	40 to 65
Polyalkenyl Succinimide Dispersant	1.2 to 4	1.5 to 3.6	2 to 3.4
Anti-wear Agents	0.15 to 4	0.2 to 2	0.5 to 1.5
Ashless Antioxidants	0 to 6	0.6 to 3	0.8 to 2.5
Metal Detergents	0 to 5	0.45 to 2.5	0.8 to 2
Viscosity Modifier	0 or 0.1 to 4.5	0.5 to 3	0.8 to 1.8
Dispersant Viscosity Modifier	0 or 0.1 to 4.5	0 or 0.1 to 2.5	0.5 to 1.6
Friction Modifier	0 or 0.05 to 2	0.05 to 1.6	0.1 to 1.2
Any Other Performance Additive	0 or 0.05 to 6	0 or 0.05 to 3	0 or 0.05 to 1.8
Other Oil of Lubricating Viscosity	Balance to 100 %		

[0086] The present invention provides a surprising ability to provide engine durability (i.e. resistance to wear) and increased fuel economy, without increasing oil consumption.

INDUSTRIAL APPLICATION

[0087] As described above, the invention provides for a method of lubricating an internal combustion engine comprising supplying to the internal combustion engine a lubricating

composition as disclosed herein. Generally, the lubricant is added to the lubricating system of the internal combustion engine, which then delivers the lubricating composition to the critical parts of the engine, during its operation, that require lubrication. Further, the instant disclosure relates to use of the described lubricant composition in an internal combustion engine for improving the fuel economy thereof.

[0088] The lubricating compositions described above may be utilized in an internal combustion engine. The engine components may have a surface of steel or aluminum (typically a surface of steel) and may also be coated for example with a diamond-like carbon (DLC) coating.

[0089] The internal combustion engine may be fitted with an emission control system or a turbocharger. Examples of the emission control system include diesel particulate filters (DPF), Gasoline Particulate Filters (GPF), three-way catalysts, or systems employing selective catalytic reduction (SCR).

[0090] The internal combustion engine may be spark ignited or compression ignited and would utilize fuels appropriate to the ignition sequence. A spark ignited internal combustion engine may be port fuel injected (PFI) or direct injected.

[0091] The internal combustion engine may be fueled by a normally liquid or gaseous fuel or combinations thereof. The liquid fuel is normally a liquid at ambient conditions e.g., room temperature (20 to 30°C.). The fuel can be a hydrocarbon fuel, a nonhydrocarbon fuel, or a mixture thereof. The hydrocarbon fuel may be a gasoline as defined by ASTM specification D4814. In an embodiment of the invention the fuel is a gasoline, and in other embodiments the fuel is a leaded gasoline, or a nonleaded gasoline.

[0092] The internal engine may be operated at a brake mean effective pressure (BMEP) of at least at least 12 bars, or at least 20 bars, or at least 22 bars, or at least 24 bars, or at least 26 bars. In one embodiment, high BMEP is achieved through operating the engine with one or more features comprising gasoline direct injection (GDI), turbochargers, superchargers, variable valve timing, homogeneous charge compression ignition (HCCI), lean burn, or combinations thereof.

[0093] The nonhydrocarbon fuel can be an oxygen containing composition, often referred to as an oxygenate, to include an alcohol, an ether, a ketone, an ester of a carboxylic acid, a nitroalkane, or a mixture thereof. The nonhydrocarbon fuel can include for example methanol, ethanol, methyl t-butyl ether, methyl ethyl ketone, transesterified oils and/or fats from plants and animals such as rapeseed methyl ester and soybean methyl ester, and nitromethane. Mixtures of

hydrocarbon and nonhydrocarbon fuels can include, for example, gasoline and methanol and/or ethanol. In an embodiment of the invention, the liquid fuel is a mixture of gasoline and ethanol, wherein the ethanol content is at least 5 volume percent of the fuel composition, or at least 10 volume percent of the composition, or at least 15 volume percent, or 15 to 85 volume percent of the composition. In one embodiment, the liquid fuel contains less than 15% by volume ethanol content, less than 10% by volume ethanol content, less than 5% ethanol content by volume, or is substantially free of (i.e. less than 0.5% by volume) of ethanol.

[0094] The gaseous fuel is normally a gas at ambient conditions e.g., room temperature (20 to 30°C.). Suitable gas fuels include natural gas, liquefied petroleum gas (LPG), compressed natural gas, or mixtures thereof. In one embodiment, the engine is fueled with natural gas.

[0095] The lubricant composition may be an engine oil having a kinematic viscosity of up to about 32.5 cSt at 100° C, or from about 4.5 to about 18.5 cSt at 100° C., or from about 5.3 to about 13.5 cSt at 100° C, or from about 6 to about 10.5 cSt at 100° C as measured by ASTM D445.

[0096] High temp high shear (HTHS) are viscosity measurements and represent a fluid's resistance to flow under conditions resembling highly-loaded journal bearings in internal combustion engines. The HTHS value of an oil and/or lubricating composition directly correlates to the oil film thickness in a bearing. HTHS values of a fluid may be obtained by using ASTM D4683 at 150.degree. C. The lubricating compositions of this invention may have a HTHS of between 1.8 cP and 3.2 cP, or between 2.3 cP and 2.6 cP, or less than 2.3 cP.

[0097] In one embodiment, the lubricating composition may be an engine oil, wherein the lubricating composition may be characterized as having at least one of (i) a sulfur content of 0.5 wt % or less, (ii) a phosphorus content of 0.1 wt % or less, (iii) a sulfated ash content of 1.5 wt % or less, or combinations thereof.

EXAMPLES

[0098] The invention will be further illustrated by the following examples, which set forth particularly advantageous embodiments. While the examples are provided to illustrate the invention, they are not intended to limit it.

Lubricating Base Oils

[0099] A series of fluids are evaluated as base fluids for preparing lubricants suitable for internal combustion engines. Materials include conventional mineral oils, polyalphaolefins, and bio-engineered hydrocarbon oils, as described in Table 1 below.

	Base Fluid Type	Kinematic Viscosity at 100°C (D445_100) (m ² /s)	Noack Volatility (D5800) (wt %)
4 cSt Group III	Mineral Oil	4.2	14
PAO-4 ¹	Polyalphaolefin	3.8	13
3 cSt Group III	Mineral Oil	3.0	42
PAO-2 ²	Polyalphaolefin	1.7	75
HC-A ³	Branched hydrocarbon	3.2	24
HC-B ⁴	Brnached hydrocarbon	2.8	28

1. Polyalpha olefin available from Chevron Phillips Chemical Company as Synfluid® PAO 4 cSt
2. Polyalpha olefin available as Durasyn® 162 from INEOS
3. Bio-derived branched hydrocarbon with average carbon no. of 28-34, with at least 30 mol% carbons on one or more branches
4. Bio-derived branched hydrocarbon with average carbon no. of 24-28, with at least 30 mol% carbons on one or more branches

Lubricating Compositions

[00100] A series of 0W-16 engine lubricants are prepared containing the base fluids described above as well as conventional additives including ashless succinimide dispersant, overbased detergents, antioxidants (combination of phenolic ester, diarylamine, and sulfurized olefin), zinc dialkyldithiophosphate (ZDDP), polymeric viscosity modifier, as well as other performance additives. All of the lubricants are prepared based on a common formulation as follows in Table 2.

Table 2 – Lubricating Oil Composition Formulations¹

	EX1	EX2	EX3	EX4	EX5	EX6	EX7
4 cSt Gp III	85	65	65	65	55	65	65
3 cSt Gp III	0	20	0	0	0	0	0
HC-A	0	0	0	20	30	20	20
PAO-2	0	0	20	0	0	0	0
PIBsuccinimide dispersant ²	2	2	2	2	3	2	2
C3/6 Secondary ZDDP	0.8	0.8	0.8	0.8	0.8	0.8	0.8

	EX1	EX2	EX3	EX4	EX5	EX6	EX7
Overbased Calcium Sulfonate ³	1.2	1.2	1.2	1.2	1.2	0	0.2
Calcium Salicylate ⁴	0	0	0	0	0	0.6	0
Ashless Antioxidant ⁵	1.2	1.2	1.2	1.2	1.2	1.2	1.2
Overbased Mg Sulfonate	0	0	0	0	0	0	1.0
E-P VI Improver ⁶	0.7	0.6	0.6	0.45	0.6	0.45	0.45
Additional Additives ⁷	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Noack (D5800) ⁸	14	24	35	18	20	18	18
Calcium (ppm) (calculated)	2300	2300	2300	2300	2300	1060	450
Magnesium (ppm) (calculated)	0	0	0	0	0	0	1400
Phosphorus (ppm) (calculated)	0.075	0.075	0.075	0.075	0.075	0.075	0.075

1 – All amounts shown above are in wt % and are on an oil-free basis unless otherwise noted.

2 – PIB Fsuccinimide prepared from 2000 Mn PIB with oil free TBN of 27 mg KOH/g

3 – 500 TBN (oil free) overbased calcium sulfonate

4 – 400 TBN overbased calcium alkylsalicylate

5 – Combination of alkylated diarylamine, hindered phenol, and sulfurized olefin antioxidants

6 – Ethylene-propylene copolymer

7 – The Additional Additives used in the examples include friction modifier, pourpoint depressants, anti-foam agents, emulsifier, titanium alkoxide, and includes some amount of diluent oil that may be present in additives as manufactured

8 – Calculated amount

Testing

[00101] The lubricants are evaluated for wear performance, fuel economy, friction reduction performance, and oil consumption. Many industry standard engine tests are used to evaluate engine lubricant performance and often have an oil consumption measurement. Engine tests include the BMW N20 Endurance Engine Oil Test. The N20 test is a 395-hour test that is used to evaluate the lubricating composition for piston cleanliness, engine sludge, turbocharger deposits, and wear iron; the New European Drive Cycle (NEDC) in two Mercedes Benz vehicles, OM 271FE and OM642FE; the API Sequence IIH for measuring oxidation deposit control; the API Sequence IVB for measuring engine durability; and many others as part of the API SN plus gasoline engine approval and the API CK-4 diesel engine approval.

[00102] The lubricants are evaluated for wear performance in a programmed temperature high frequency reciprocating rig (HFRR) available from PCS Instruments. HFRR conditions for the evaluations are 200 g load, 75-minute duration, 1000 micrometer stroke, 20 hertz frequency, and temperature profile of 15 minutes at 40° C. followed by an increase in temperature to 160° C. at a rate of 2° C. per minute. Wear scar in micrometers and film formation as percent film thickness

are then measured with lower wear scar values and higher film formation values indicating improved wear performance.

[00103] The percent film thickness is based on the measurement of electrical potential between an upper and a lower metal test plate in the HFRR. When the film thickness is 100%, there is a high electrical potential for the full length of the 1000 micrometer stroke, suggesting no metal to metal contact. Conversely for a film thickness of 0% there is no electrical potential suggesting continual metal to metal contact between the plates. For intermediate film thicknesses, there is an electrical potential suggesting the upper and lower metal test plate have a degree of metal to metal contact as well as other areas with no metal to metal contact.

[00104] The lubricating compositions are tested for deposit control in a Panel Coker heated to 325° C., with a sump temperature of 105° C., and a splash/bake cycle of 120 s/45 s. The airflow is 350 ml/min, with a spindle speed of 1000 rpm and the test lasts for 4 hours. The oil is splashed onto an aluminum panel which is then optically rated by computer. Performance ranges from 0% (black panel) to 100% (clean panel).

[00105] The propensity for a lubricating composition to resist deposit formation is evaluated in the Komatsu Hot Tube (KHT) test. This is an industry test used to evaluate performance of engine oils based on their deposit-forming tendencies by circulating a sample of the engine oil at 0.31 mL per hour and air at 10 mL per minute through a glass tube for 16 hours at a specified temperature, usually from 270° C. up to 310° C. After the test, the tubes are visually rated, with a higher number being a better rating: 10 representing a clean tube and 0 (zero) representing a tube with heavy deposits.

[00106] Deposit performance can be measured according to the Thermo-Oxidation Engine Oil Simulation Test (TEOST 33) as presented in ASTM D6335. The results of the TEOST 33 test show the milligrams of deposit after an engine oil is run at elevated temperatures. Lower TEOST 33 results are indicative of improved resistance to deposit formation

[00107] It is known that some of the materials described above may interact in the final formulation, so that the components of the final formulation may be different from those that are initially added. The products formed thereby, including the products formed upon employing lubricant composition of the present invention in its intended use, may not be susceptible of easy description. Nevertheless, all such modifications and reaction products are included within the

scope of the present invention; the present invention encompasses lubricant composition prepared by admixing the components described above.

[00108] Each of the documents referred to above is incorporated herein by reference, as is the priority document and all related applications, if any, which this application claims the benefit of Except in the Examples, or where otherwise explicitly indicated, all numerical quantities in this description specifying amounts of materials, reaction conditions, molecular weights, number of carbon atoms, and the like, are to be understood as modified by the word "about." Unless otherwise indicated, each chemical or composition referred to herein should be interpreted as being a commercial grade material which may contain the isomers, by-products, derivatives, and other such materials which are normally understood to be present in the commercial grade. However, the amount of each chemical component is presented exclusive of any solvent or diluent oil, which may be customarily present in the commercial material, unless otherwise indicated. It is to be understood that the upper and lower amount, range, and ratio limits set forth herein may be independently combined. Similarly, the ranges and amounts for each element of the invention may be used together with ranges or amounts for any of the other elements.

[00109] As used herein, the term "hydrocarbyl substituent" or "hydrocarbyl group" is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group having a carbon atom directly attached to the remainder of the molecule and having predominantly hydrocarbon character. Examples of hydrocarbyl groups include hydrocarbon substituents, that is, aliphatic (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl, cycloalkenyl) substituents, and aromatic-, aliphatic-, and alicyclic-substituted aromatic substituents, as well as cyclic substituents wherein the ring is completed through another portion of the molecule (e.g., two substituents together form a ring); (ii) substituted hydrocarbon substituents, that is, substituents containing non-hydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbon nature of the substituent (e.g., halo (especially chloro and fluoro), hydroxy, alkoxy, mercapto, alkylmercapto, nitro, nitroso, and sulfoxy); (iii) hetero substituents, that is, substituents which, while having a predominantly hydrocarbon character, in the context of this invention, contain other than carbon in a ring or chain otherwise composed of carbon atoms.

[00110] Heteroatoms include sulfur, oxygen, nitrogen, and encompass substituents as pyridyl, furyl, thienyl and imidazolyl. In general, no more than two, preferably no more than one,

non-hydrocarbon substituent will be present for every ten carbon atoms in the hydrocarbyl group; typically, there will be no non-hydrocarbon substituents in the hydrocarbyl group.

[00111] As used in this document, the singular forms "a," "an," and "the" include plural references unless the context clearly dictates otherwise. Unless defined otherwise, all technical and scientific terms used herein have the same meanings as commonly understood by one of ordinary skill in the art. Nothing in this disclosure is to be construed as an admission that the embodiments described in this disclosure are not entitled to antedate such disclosure by virtue of prior invention. As used in this document, the term "comprising" means "including, but not limited to."

[00112] While various compositions, methods, and devices are described in terms of "comprising" various components or steps (interpreted as meaning "including, but not limited to"), the compositions, methods, and devices can also "consist essentially of" or "consist of" the various components and steps, and such terminology should be interpreted as defining essentially closed-member groups.

[00113] While various compositions, methods, and devices are described in terms of "comprising" various components or steps (interpreted as meaning "including, but not limited to"), the compositions, methods, and devices can also "consist essentially of" or "consist of" the various components and steps, and such terminology should be interpreted as defining essentially closed-member groups.

[00114] It will be understood by those within the art that, in general, terms used herein, and especially in the appended claims (e.g., bodies of the appended claims) are generally intended as "open" terms (e.g., the term "including" should be interpreted as "including but not limited to," the term "having" should be interpreted as "having at least," the term "includes" should be interpreted as "includes but is not limited to," etc.). It will be further understood by those within the art that if a specific number of an introduced claim recitation is intended, such an intent will be explicitly recited in the claim, and in the absence of such recitation, no such intent is present. For example, as an aid to understanding, the following appended claims may contain usage of the introductory phrases "at least one" and "one or more" to introduce claim recitations. However, the use of such phrases should not be construed to imply that the introduction of a claim recitation by the indefinite articles "a" or "an" limits any particular claim containing such introduced claim recitation to embodiments containing only one such recitation, even when the same claim includes the introductory phrases "one or more" or "at least one" and indefinite articles such as "a" or "an" (e.g.,

"a" and/or "an" should be interpreted to mean "at least one" or "one or more"); the same holds true for the use of definite articles used to introduce claim recitations. In addition, even if a specific number of an introduced claim recitation is explicitly recited, those skilled in the art will recognize that such recitation should be interpreted to mean at least the recited number (e.g., the bare recitation of "two recitations," without other modifiers, means at least two recitations, or two or more recitations). Furthermore, in those instances where a convention analogous to "at least one of A, B, and C, etc." is used, in general, such a construction is intended in the sense one having skill in the art would understand the convention (e.g., "a system having at least one of A, B, and C" would include but not be limited to systems that have A alone, B alone, C alone, A and B together, A and C together, B and C together, and/or A, B, and C together, etc.). In those instances where a convention analogous to "at least one of A, B, or C, etc." is used, in general, such a construction is intended in the sense one having skill in the art would understand the convention (e.g., "a system having at least one of A, B, or C" would include but not be limited to systems that have A alone, B alone, C alone, A and B together, A and C together, B and C together, and/or A, B, and C together, etc.). It will be further understood by those within the art that virtually any disjunctive word and/or phrase presenting two or more alternative terms, whether in the description, claims, or drawings, should be understood to contemplate the possibilities of including one of the terms, either of the terms, or both terms. For example, the phrase "A or B" will be understood to include the possibilities of "A" or "B" or "A and B."

[00115] In addition, where features or aspects of the disclosure may be described in terms of Markush groups, those skilled in the art will recognize that the disclosure is also thereby described in terms of any individual member or subgroup of members of the Markush group.

[00116] As will be understood by one skilled in the art, for any and all purposes, such as in terms of providing a written description, all ranges disclosed herein also encompass any and all possible subranges and combinations of subranges thereof. Any listed range can be easily recognized as sufficiently describing and enabling the same range being broken down into at least equal halves, thirds, quarters, fifths, tenths, etc. As a non-limiting example, each range discussed herein can be readily broken down into a lower third, middle third and upper third, etc. As will also be understood by one skilled in the art all language such as "up to," "at least," and the like include the number recited and refer to ranges which can be subsequently broken down into subranges as discussed above. Finally, as will be understood by one skilled in the art, a range

includes each individual member. Thus, for example, a group having 1-3 wt % refers to groups having 1, 2, or 3 wt.%. Similarly, a group having 1-5 wt % refers to groups having 1, 2, 3, 4, or 5 wt %, and so forth, including all points therebetween.

[00117] As used herein, the term "about" means that a value of a given quantity is within $\pm 20\%$ of the stated value. In other embodiments, the value is within $\pm 15\%$ of the stated value. In other embodiments, the value is within $\pm 10\%$ of the stated value. In other embodiments, the value is within $\pm 5\%$ of the stated value. In other embodiments, the value is within $\pm 2.5\%$ of the stated value. In other embodiments, the value is within $\pm 1\%$ of the stated value.

[00118] Unless otherwise stated, "wt %" as used herein shall refer to the wt % (weight percent) based on the total weight of the lubricating composition.

[00119] While the invention has been explained in relation to its preferred embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.