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(54) ENGINE LUBRICANTS FOR SILOXANE DEPOSIT CONTROL

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(57) **ABSTRACT**

A zinc free or substantially zinc free lubricant having a sulfated ash content of less than about 1.0 percent and including (a) an oil of lubricating viscosity; (b) 0.03 to about 3.0 weight percent of a phosphite compound; (c) an metal containing detergent; (d) a polyisobutylene succinimide dispersant derived from an ethylene polyamine and having a carbonyl to nitrogen ratio equal or greater than 1; (e) at least one other dispersant; (f) a boron containing compound in amount to provide at least 25 ppm boron to the lubricant composition is useful for inhibiting siloxane deposits in a stationary gas engine fueled by natural gas having a high silicon concentration.

ENGINE LUBRICANTS FOR SILOXANE DEPOSIT CONTROL

BACKGROUND OF THE INVENTION

[0001] The disclosed technology relates to a lubricant for a sump-lubricated internal combustion engine, especially such an engine that is fueled by natural gas, and more particularly, engines fueled by natural gasses containing high levels of siloxanes and other silicon containing compounds, such as are commonly found in landfill gases.

[0002] Internal combustion engines may be fueled by a variety of liquid or gaseous fuels, including natural gas. While liquefied natural gas or compressed natural gas may sometimes be used to fuel small engines on vehicles, more typically natural gas is used to power large compression ignited or spark ignited "stationary gas" engines that may be fueled by natural gas supplied directly from a gas wellhead. One common application for stationary gas engines is at landfills, where the engines may be fueled by gas emanating from decomposition of refuse at the landfill.

[0003] Landfill gasses tend not to be very clean and often have elevated levels of silicon containing compounds and other corrosive materials. In an engine combusting landfill gas, the silicon containing compounds in the landfill gas will form siloxane macromolecules which will deposit on the engine component surfaces leading to increased wear in the cylinders, valve areas and bearings. Over time, this wear reduces engine performance, may cause valve seat recession, may increase oil consumption, and may ultimately necessitate refurbishment of the engine. Typically, lubricants are replaced once the silicon concentration in the lubricant approaches 120 to 125 parts per million (ppm).

[0004] To prevent siloxane deposit buildup in engines operating on landfill gases (or other natural gas feedstocks containing high concentrations of silicon compounds), one existing method involves scrubbing the gas feedstock through various filters and other media before using it as a fuel stock for the engine. Scrubbing silicon compounds from landfill gases requires additional equipment that must be maintained and generally complicates the feed stream. Alternatively, lubricant formulations containing detergents and anti-wear agents have been introduced specifically for natural gas and landfill gas engines. These lubricants are directed to cleaning the engine surface from siloxane deposits and/or providing a sacrificial wear layer, but their efficacy is limited as detergency loses effectiveness and particularly once the siloxane macromolecules have formed. Accordingly, these lubricant formulations require frequent replenishment/replacement leading to increased lubricant consumption and engine downtime.

[0005] The present invention is directed to lubricant compositions which are formulated, according to the theory of the invention, to chemically cleave siloxane macromolecules into smaller compounds that can be more readily dispersed, thus reducing the formation of deposits and rendering the silicon less detrimental in deposit formation even at lubricant silicon concentrations of 125 ppm and higher. The subject lubricating formulations may be effectively used in siloxane deposit control for longer periods of time at elevated silicon concentrations, thereby facilitating the use of unscrubbed natural and landfill gases and extending the oil change intervals, leading to less engine downtime.

[0006] Improved siloxane deposit control and extended cleanliness and performance benefits may be provided by the lubricant of the disclosed technology.

SUMMARY OF THE INVENTION

[0007] The disclosed technology provides a method for lubricating a sump-lubricated stationary gas engine, comprising supplying to the engine a substantially zinc-free lubricant comprising:

[0008] (a) an oil of lubricating viscosity;

[0009] (b) 0.03 to about 3.0 weigh percent with respect to the lubricant composition (or 0.05 to 2.8 wt. % or 0.05 to 2.5 wt. %) of a phosphite compound;

[0010] (c) a metal containing detergent;

[0011] (d) at least a first dispersant, wherein the first dispersant is a polyisobutylene succinimide dispersant derived from an ethylene polyamine and having a carbonyl to nitrogen ratio equal or greater than 1 or 1:1 to 4:3 or 1.1:1 to 4:3;

[0012] (e) at least one other dispersant selected from the group consisting of a succinimide dispersant having a carbonyl to nitrogen ratio less than 1, a Mannich dispersant, and a polyisobutylene succinic acid ester dispersant;

[0013] (f) boron containing compound in amount to provide at least 25 ppm boron to the lubricant composition;

[0014] wherein the lubricant composition is substantially free of zinc, and

[0015] wherein the lubricant composition has a sulfated ash content of less than about 1.0 wt. % (or 0.7 wt. %).

[0016] The disclosed technology further provides the lubricant as thus described, and also provides a lubricant comprising:

[0017] (g) an oil of lubricating viscosity;

[0018] (b) 0.03 to about 3.0 weigh percent with respect to the lubricant composition (or 0.05 to 2.8 wt. % or 0.05 to 2.5 wt. %) of a phosphite compound;

[0019] an metal containing detergent;

[0020] (d) at least a first dispersant, wherein the first dispersant is a polyisobutylene succinimide dispersant derived from an ethylene polyamine and having a carbonyl to nitrogen ratio equal or greater than 1 or 1:1 to 4:3 or 1.1:1 to 4:3;

[0021] at least one other dispersant selected from the group consisting of a succinimide dispersant having a carbonyl to nitrogen ratio less than 1, a Mannich dispersant, and a polyisobutylene succinic acid ester dispersant;

[0022] (f) a boron containing compound in amount to provide at least 25 ppm boron to the lubricant composition;

[0023] wherein the lubricant composition is substantially free of zinc, and

[0024] wherein the lubricant composition has a sulfated ash content of less than about 1.0 wt. %.

DETAILED DESCRIPTION OF THE INVENTION

[0025] Various preferred features and embodiments will be described below by way of non-limiting illustration.

[0026] The amount of each chemical component described is presented exclusive of any solvent or diluent oil, which may be customarily present in the commercial material, that is, on an active chemical basis, unless otherwise indicated. However, 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 that are normally understood to be present in the commercial grade.

[0027] Fuels

[0028] In the methods of the present invention, it is contemplated that the lubricant formulations will be employed in engines that are fueled with natural gas and in some preferred embodiments, landfill gas. Landfill gas refers primarily to the source of the gas, namely, gas created by the action of microorganisms within a landfill. Such landfill gas may comprise only about 30 to 80 percent methane. In a particularly useful embodiment, the method of operating the engine comprises operating the engine using as its primary or only fuel natural gas having a concentration of silicon that is in excess of 10 mg/m^3 or 15 mg/m^3 or 20 mg/m^3 or 25 mg/m^3 or 30 mg/m^3 as measured by gas chromatography mass spectrometry.

[0029] Base Oils

[0030] One element of the lubricating compositions of the present technology is an oil of lubricating viscosity. Such oils 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 more detailed description of natural and synthetic lubricating oils is provided in paragraphs [0058] to [0059] respectively of WO2008/147704. Synthetic oils may also be produced by Fischer-Tropsch reactions and typically may be hydroisomerized 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.

[0031] Oils of lubricating viscosity may also be selected from any of the base oils in Groups I-V as specified in the American Petroleum Institute (API) Base Oil Interchangeability Guidelines. The five base oil groups are as follows: Group I: >0.03% sulfur and/or <90% saturates and viscosity index 80 to 120; Group II: <0.03% S and ≥90% saturates and VI 80 to 120; Group III: ≤0.03% S and ≥90% saturates and VI>120; Group IV: all polyalphaolefins; Group V: all others. Groups I, II and III are mineral oil base stocks.

[0032] The amount of the oil of lubricating viscosity present is typically the balance remaining after subtracting from 100 wt % the sum of the amount of the compound of the invention and the other performance additives.

[0033] The lubricating composition may be in the form of a concentrate and/or a fully formulated lubricant. If the lubricating composition of the invention (comprising the additives disclosed hereinabove) is in the form of a concentrate which may be combined with additional oil to form, in whole or in part, a finished lubricant), the ratio of the of these additives to the oil of lubricating viscosity and/or to diluent oil include the ranges of 1:99 to 99:1 by weight, or 80:20 to 10:90 by weight.

[0034] Phosphite Antiwear Compounds

[0035] The lubricant compositions of the present invention will comprise at least one phosphite compound. In some embodiments, the phosphite compound will include at least one phosphite ester, and more usefully in some embodiments, at least one phosphite diester or triester compound. In one embodiment, the phosphite compound may comprise phosphorous acid (H_3PO_3).

[0036] It will be understood that the term phosphite includes the tautomer(s). Similarly it will be understood that phosphite esters may be referred to generally as alkyl phosphites or alkyl hydrogen phosphites and these terms may be used interchangeably.

[0037] Examples of suitable phosphite compounds may include compounds having the general Formula I

$$(R^1O)_3P \quad \text{(I)}$$

[0038] In the above formula, each le independently may be hydrogen or a hydrocarbyl group having 1 to 36, or 1 to 24, or 1 to 18 or 2 to 30 or 2 to 24 or 2 to 10 carbon atoms or 12 to 36 or 12 to 30 or 12 to 20 carbon atoms. The hydrocarbyl group may be a linear or branched, may be a substituted or unsubstituted, may be aromatic or aliphatic or alicylic or heterocyclic or may be saturated or unsaturated and each le may be the same or different.

[0039] Exemplary phosphite monoesters may include phosphite monesters comprising C_1 to C_{30} hydrocarbyl groups.

[0040] Exemplary phosphite diesters may include dimethyl hydrogen phosphite, diethyl hydrogen phosphite, dipropyl hydrogen phosphite, dibutyl hydrogen phosphite, diethylhexyl hydrogen phosphite, didecyl hydrogen phosphite, didodecyl hydrogen phosphite (dilauryl hydrogen phosphite), dioctadecyl hydrogen phosphite (distearyl hydrogen phosphite), di-9-octadecenyl hydrogen phosphite (dioleyl hydrogen phosphite), diphenyl hydrogen phosphite and the like.

[0041] Examples of the phosphite triesters include, for example, triphenyl phosphite, triethyl phosphite, tributyl phosphite, tripropyl phosphite, trioctyl phosphite, tri-isooctyl phosphite, tris 2-ethylhexyl phosphite, tri-isodecyl phosphite, tris tridecyl phosphite, trioleyl phosphite, etc. and the like.

[0042] In one embodiment, the phosphite ester may comprise a polyphosphite ester, which may be produced as the reaction product, e.g., condensation product, of a monomeric phosphorous acid or an ester thereof with at least two alkylene diols. Exemplary polyphosphite esters are more fully described in International Publication WO2016/089565.

[0043] In some embodiments, the phosphite compound may comprise a mixture of two or more phosphite compounds. In a particularly useful embodiment, the phosphite compound may comprise a first alkyl phosphite ester having C2 to C10 hydrocarbyl groups and a second alkyl phosphite ester having C12 to C30 hydrocarbyl groups. In one embodiment, the phosphite may comprise a mixture of two or more phosphite diesters, wherein one diester has C2 to C10 hydrocarbyl groups and a second diester has C12 to C30 hydrocarbyl groups. In such an embodiment, the ratio of the C2 to C10 diester to the C12 to C30 diester may be from 20:80 to 80:20 or 40:60 to 60:40 or 60:40 to 90:10. In still another embodiment, the phosphite may comprise dibutyl phosphite.

[0044] The phosphite compound may be present in the lubricating composition (on an oil free basis) in an amount from about 0.03 to about 3.0 weight percent with respect to the lubricant composition (or 0.05 to 2.8 wt. % or 0.05 to 2.5 wt. % or 0.1 to 2.5 wt. % or 0.5 to 2.5 wt. % or 1.0 to 2.5 wt. %).

[0045] In some embodiments, the phosphite compounds may be present in an amount to provide 0.001 wt. % to 0.05 wt. % phosphorus (or 10 to 500 ppm phosphorus), or 0.005 to 0.04 wt. % phosphorus, or 0.005 to about 0.03 wt. % phosphorus to the lubricant composition. In still other embodiments, the phosphite may contribute greater than 80% or 90% or 95% of the total phosphorous in the lubricant composition. In still another embodiment, the phosphite compound may constitute the only phosphorous containing antiwear additive in the lubricating composition. The lubricant composition may be free of or substantially free of other phosphorus containing antiwear compounds or other phosphorous containing compounds. In some embodiments, the total amount of phosphorus in the lubricant composition may be less than about 0.03 wt. %

[0046] Dispersants

[0047] Another component in the lubricant compositions is a dispersant. Dispersants are well known in the field of lubricants and include what are known as ashless-type dispersants and polymeric dispersants. Suitable dispersants may be chosen from a succinimide dispersant, a Mannich dispersant, a succinamide dispersant, a polyolefin (typically isobutylene) succinic acid ester, ester-amide, or mixtures thereof. The dispersant may be present as a single dispersant; however, a mixture of more than one type of dispersant is particularly useful. Metal containing (ash containing) dispersants may be used, but in some embodiments, the dispersant is free of or substantially free of ash containing dispersants.

[0048] Ashless type dispersants are characterized by a polar group attached to a relatively high molecular weight hydrocarbon chain. Typical ashless dispersants include nitrogen-containing dispersants such as N-substituted long chain alkenyl succinimides, also known as succinimide dispersants.

[0049] The succinimide dispersant may be derived from an aliphatic amine, aliphatic polyamine, or mixtures thereof. The aliphatic polyamine may include such compounds as 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 chosen from ethylenediamine, diethylenetriamine, tri ethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, polyamine still bottoms, and mixtures thereof. Succinimide dispersants are more fully described in U.S. Pat. Nos. 4,234,435 and 3,172,892.

[0050] In one embodiment, the dispersant may comprise the condensation product of a hydrocarbyl-substituted succinic anhydride or reactive equivalent thereof with an alkylene polyamine, wherein the alkylene polyamine is a condensed amine. Such dispersants derived from condensed amines are more fully described in U.S. Pat. Pub. 2009/0018040.

[0051] In one embodiment 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, a nitroaniline, an aminocarbazole, an amino-indazolinone, an aminopyrimidine, 4-(4-nitrophenylazo)aniline, or combinations thereof. In one embodiment, the dispersant may comprise a derivative of an aromatic amine wherein the aromatic amine has at least three non-continuous aromatic rings.

[0052] 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 polyetherpolyamines 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 Huntsman Corporation located in Houston, Tex.

[0053] Another class of ashless dispersant is high molecular weight esters, prepared by reaction of a hydrocarbyl acylating agent, such as a succinic anhydride or alkylated (typically polyisobutylene) succinic anhydride or their reactive equivalents, and a polyhydric aliphatic alcohol such as ethylene glycol, propylene glycol, butylene glycol, pentaerythritol, mannitol, sorbitol, glycerol, diglycerol, triglycerol, tetraglycerol, erythritol, 2-hydroxymethyl-2-methyl-1,3 propanediol (trimethylolethane), 2-ethyl-2-(hydroxymethyl)-1,3 propanediol (trimethylolpropane), 1,3,4-hexane triol and mixtures thereof. Such materials are described in more detail in U.S. Pat. No. 3,381,022.

[0054] A polyolefin succinic acid ester-amide may be a polyisobutylene succinic acid reacted with an alcohol (such as pentaerythritol) and an amine (such as a diamine, typically diethyleneamine).

[0055] Another class of ashless dispersant is Mannich bases. These are materials which are formed by the condensation of a higher molecular weight, alkyl substituted phenol, an alkylene polyamine, and an aldehyde such as formaldehyde and are described in more detail in U.S. Pat. No. 3,634,515. Other dispersants include polymeric dispersant additives, which are generally hydrocarbon-based polymers which contain polar functionality to impart dispersancy characteristics to the polymer.

[0056] Where the dispersants described above are derived from a polyisobutylene succinic acid or anhydride, the polyisobutylene may have a number average molecular weight of 350 to 5000, or 750 to 2500 or 500 to 1500 or 750 to 1250.

[0057] A succinimide dispersant may be obtained/obtainable from a chlorine-assisted process, often involving Diels-Alder chemistry, leading to formation of carbocyclic linkages from the hydrocarbon chain to the succinic moiety. The process is known to a person skilled in the art. The chlorine-assisted process may produce a dispersant that is a polyisobutylene succinimide having a carbocyclic ring present on 50 mole % or more, or 60 to 100 mole % of the non-borated dispersant molecules. Both the thermal and chlorine-assisted processes are described in greater detail in U.S. Pat. No. 7,615,521, columns 4-5 and preparative examples A and B.

[0058] Alternatively, a succinimide dispersant may be prepared/ obtained/obtainable from reaction of succinic anhydride by an "ene" or "thermal" reaction, by what is referred to as a "direct alkylation process." The "ene" reaction mechanism and general reaction conditions are summarized in "Maleic Anhydride", pages, 147-149, Edited by B.C. Trivedi and B.C. Culbertson and Published by Plenum Press in 1982. The dispersant prepared by a process that includes an "ene" reaction may be a polyisobutylene succinimide having a carbocyclic ring present of less than 50 mole %, or 0 to less than 30 mole %, or 0 to less than 20 mole %, or 0 mole % of the non-borated dispersant molecules. The "ene" reaction may have a reaction temperature of 180° C. to less than 300° C., or 200° C. to 250° C., or 200° C. to 220° C. The polyisobutene particularly useful in preparing an "ene" type succinimide dispersant may desirably have at least 50 percent terminal vinylidene groups, such as at least 60, or 70, or 80 percent.

[0059] In certain embodiments, the succinimide dispersant prepared by the "thermal" or "ene" route may be particularly useful.

[0060] The dispersants may also be post-treated by conventional methods by a reaction with any of a variety of agents. Among these are boron compounds (such as boric acid), urea, thiourea, dimercaptothiadiazoles, carbon disulphide, aldehydes, ketones, carboxylic acids such as terephthalic acid, hydrocarbon-substituted succinic anhydrides, maleic anhydride, nitriles, epoxides, and phosphorus compounds. In one embodiment the post-treated dispersant may be borated. In one embodiment the post-treated dispersant may be reacted with dimercaptothiadiazoles. In one embodiment the post-treated dispersant may be reacted with phosphoric or phosphorous acid. In one embodiment the post-treated dispersant may be reacted with terephthalic acid and boric acid (as described in U.S. Patent Application US2009/0054278.

[0061] In one embodiment, the ashless dispersant may be boron-containing, i.e., has incorporated boron and delivers said boron to the lubricant composition. The boron- containing dispersant may be present in an amount to deliver at least 25 ppm boron, or at least 50 ppm boron, or at least 100 ppm or at least 200 ppm or 300ppm or 500 ppm or 200 to 500 ppm or 300 to 500 ppm boron to the lubricant composition. In one embodiment, the lubricant composition may be free of a boron- containing dispersant, i.e. the boron containing dispersant delivers no more than 10 ppm boron to the final formulation.

[0062] The lubricant compositions of the present invention include at least one polyisobutylene succinimide dispersant derived from an ethylene polyamine and having a carbonyl to nitrogen ratio equal to or greater than 1:1 or between about 1:1 to 4:3 or about 1.1:1 to 4:3 or about 1:1 to about 6:5 or about 1.1:1 to about 6:5. This dispersant (on an oil free basis) may be present in an amount of 0.1 wt % to 2 wt % (or 0.1 to 1.5 wt %, or 0.2 wt % to 2 wt %, or 0.3 wt % to 1 wt %) of the lubricant composition.

[0063] The dispersant may typically comprise a dispersant package of two or more dispersants. In one embodiment, the dispersant package comprises at least one polyisobutylene succinimide dispersant derived from an ethylene polyamine and having a carbonyl to nitrogen ratio equal to or greater than 1:1 or between about 1:1 to 4:3 or about 1.1:1 to 4:3 or about 1:1 to about 6:5 or about 1.1:1 to about 6:5 and a second dispersant selected from dispersants having a carbonyl to nitrogen ratio less than 1:1 and succinic acid ester dispersants. In one embodiment, the second dispersant may be a conventional polyisobutylene succinimide dispersant. In another embodiment, the second dispersant may be a polyisobutylene succinic acid ester dispersant. The second dispersant may by a Mannich dispersant. The second dispersant may be a borated dispersant.

[0064] In still a further embodiment, the dispersant package may comprise three or more dispersants, including at least one polyisobutylene succinimide dispersant derived from an ethylene polyamine and having a carbonyl to nitrogen ratio equal to or greater than 1:1 or between about 1:1 to 4:3 or about 1.1:1 to 4:3 or about 1:1 to about 6:5 or about 1.1:1 to about 6:5, a second dispersant which is a polyisobutylene succinimide dispersant having a carbonyl to nitrogen ratio less than 1:1 and a third dispersant which is an alkenyl (typically polyisobutylene) succinic acid ester dispersant or a borated dispersant or a Mannich dispersant or mixtures thereof.

[0065] In a dispersant package comprising two or more dispersants, the polyisobutylene succinimide dispersant derived from an ethylene polyamine and having a carbonyl to nitrogen ratio equal to or greater than 1:1 or between about 1:1 to 4:3 or about 1.1:1 to 4:3 or about 1:1 to about 6:5 or about 1.1:1 to about 6:5 will typically comprise from about 5 to 80 wt. % or 10 to 60 wt. %, 15 to 50 wt. % and 15 to 30 wt. % of the total dispersant package.

[0066] The total dispersant or dispersant package (on an oil free basis) may be present it the lubricant composition in an amount of 1.0 wt % to 6.0 wt. % or 1.5 wt. % to 5.0 wt. %, 2.0 to 4.0 wt. %.

Detergents

[0067] The disclosed lubricant may include one or more alkaline or alkali earth metal-containing detergent. The metal-containing detergent which may be present as an additive component in the lubricant is, in one embodiment, an overbased detergent. It may, alternatively, be a neutral detergent. Overbased materials, otherwise referred to as overbased or superbased salts, are generally homogeneous Newtonian systems characterized by a metal content in excess of that which would be present for neutralization according to the stoichiometry of the metal and the particular acidic organic compound reacted with the metal. The overbased materials are prepared by reacting an acidic material (typically an inorganic acid or lower carboxylic acid, preferably carbon dioxide) with a mixture comprising an acidic organic compound (in this instance, a hydrocarbyl-substituted salicylic acid), a reaction medium comprising at least one inert, organic solvent (e.g., mineral oil, naphtha, toluene, xylene) for said acidic organic material, a stoichiometric excess of a metal base, and a promoter such as a phenol or alcohol and optionally ammonia. The acidic organic material will normally have a sufficient number of carbon atoms, for instance, as a hydrocarbyl substituent, to provide a reasonable degree of solubility in oil. The amount of excess metal is commonly expressed in terms of metal ratio. The term "metal ratio" is the ratio of the total equivalents of the metal to the equivalents of the acidic organic compound. A neutral metal salt has a metal ratio of one. A salt having 4.5 times as much metal as present in a normal salt will have metal excess of 3.5 equivalents, or a ratio of 4.5.

[0068] Overbased detergents are often characterized by Total Base Number (TBN). TBN is the amount of strong acid needed to neutralize all of the overbased material's basicity, expressed as potassium hydroxide equivalents (mg KOH per gram of sample). Since overbased detergents are commonly provided in a form which contains a certain amount of diluent oil, for example, 40-50% oil, the actual TBN value for such a detergent will depend on the amount of such diluent oil present, irrespective of the "inherent" basicity of the overbased material. For the purposes of the present invention, the TBN of an overbased detergent is to be recalculated to an oil-free basis. Detergents which are useful in the present invention typically have a TBN (oil-free basis) of 100 to 800, and in one embodiment 150 to 750, and in another, 400 to 700. If multiple detergents are employed, the overall TBN of the detergent component (that is, an average of all the specific detergents together) will typically be in the above ranges.

[0069] The metal compounds useful in making the basic metal salts are generally any Group 1 or Group 2 metal compounds (CAS version of the Periodic Table of the Elements). The Group 1 metals of the metal compound include Group 1a alkali metals such as sodium, potassium, and lithium, as well as Group 1b metals such as copper. The Group 1 metals can be sodium, potassium, lithium and copper, and in one embodiment sodium or potassium, and in another embodiment, sodium. The Group 2 metals of the metal base include the Group 2a alkaline earth metals such as magnesium, calcium, and barium, as well as the Group 2b metals such as zinc or cadmium. In one embodiment the Group 2 metals are magnesium, calcium, barium, or zinc, and in another embodiments magnesium or calcium. In certain embodiments the metal is magnesium, calcium or sodium or a mixture of calcium and magnesium. In some embodiments of the present invention, the lubricant is zinc free or substantially zinc free and thus will not include zinc containing detergents. Generally the metal compounds are delivered as metal salts. The anionic portion of the salt can be hydroxide, oxide, carbonate, borate, or nitrate.

[0070] In one embodiment the lubricants may contain an overbased sulfonate detergent. Oil-soluble sulfonates can be represented by one of the following formulas: R^2-T-$(SO_3)_a$ and R^3-$(SO_3$-$)_b$, where T is a cyclic nucleus such as typically benzene; R^2 is an aliphatic group such as alkyl, alkenyl, alkoxy, or alkoxyalkyl; (R^2)-T typically contains a total of at least 15 carbon atoms; and R^3 is an aliphatic hydrocarbyl group typically containing at least 15 carbon atoms. Examples of R^3 are alkyl, alkenyl, alkoxyalkyl, and carboalkoxyalkyl groups. In one embodiment the sulfonate detergent may be a predominantly linear alkylbenzenesulfonate detergent having a metal ratio of at least 8 as described in paragraphs [0026] to [0037] of U.S. Patent Application 2005-065045.

[0071] Another overbased material which can be present is an overbased phenate detergent. The phenols useful in making phenate detergents can be represented by the formula $(R^4)_a$-Ar-$(OH)_b$, wherein R^5 is an aliphatic hydrocarbyl group of 4 to 400 carbon atoms, or 6 to 80 or 6 to 30 or 8 to 25 or 8 to 15 carbon atoms; Ar is an aromatic group (which can be a benzene group or another aromatic group such as naphthalene); a and b are independently numbers of at least one, the sum of a and b being in the range of two up to the number of displaceable hydrogens on the aromatic nucleus or nuclei of Ar. In one embodiment, a and b are independently numbers in the range of 1 to 4, or 1 to 2. R^4 and a are typically such that there is an average of at least 8 aliphatic carbon atoms provided by the R^4 groups for each phenol compound. Phenate detergents are also sometimes provided as sulfur-bridged species. In some embodiments, the phenate detergent contains less than 20% or less than 10% or less than 5% or less than 2% or less than 1%, e.g., 0 or 0.05% to 0.5% of monomeric para-dodecylphenol or sulfurized monomer thereof or salt thereof, based on the active chemical amount of the phenate detergent. Methods for preparing phenolic dispersants of this type are disclosed in numerous applications or publications, including PCT/US2012/060839, PCT/US2013/024877, and U.S. Pat. No. 7,435,709.

[0072] In one embodiment, detergent may comprise a salicylate detergent such as an overbased calcium hydrocarbyl-substituted salicylate detergent. The presence of a salicylate detergent may be beneficial in providing oxidation resistance to the lubricant. In one embodiment the salicylate detergent has a Total Base Number of about 200 to about 700 or 250 to 500 or 250 to 400 or 300 to 700 or 450 to 700 or greater than about 400 on an oil free basis, that is, factoring out the effect of diluent oil. Salicylate detergents are known; see, for instance, U.S. Pat. Nos. 5,688,751 or 4,627,928. In a particularly useful embodiment, the detergent may comprise an overbased calcium salicylate detergent and in another embodiment, an overbased magnesium salicylate detergent and in still another embodiment a mixture of calcium and magnesium salicylate detergents.

[0073] In one embodiment, the overbased material is an overbased saligenin detergent. Overbased saligenin detergents are commonly overbased magnesium salts which are based on saligenin derivatives. Saligenin detergents are disclosed in greater detail in U.S. Pat. No. 6,310,009, with special reference to their methods of synthesis (Column 8 and Example 1) and suitable amounts of the various species of X and Y (Column 6).

[0074] Salixarate detergents may also be present. Salixarates and methods of their preparation are described in greater detail in U.S. Pat. No. 6,200,936 and PCT Publication WO 01/56968. It is believed that the salixarate derivatives have a predominantly linear, rather than macrocyclic, structure, although both structures are intended to be encompassed by the term "salixarate."

[0075] Patents describing techniques for making basic salts of sulfonic acids, carboxylic acids, (hydrocarbyl-substituted) phenols, phosphonic acids, and mixtures of any two or more of these include U.S. Pat. Nos. 2,501,731; 2,616,905;

[0076] 2,616,911; 2,616,925; 2,777,874; 3,256,186; 3,384,585; 3,365,396; 3,320,162; 3,318,809; 3,488,284; and 3,629,109.

[0077] Other overbased detergents can include overbased detergents having a Mannich base structure, as disclosed in U.S. Pat. No. 6,569,818.

[0078] Either a single detergent or multiple additional detergents can be present. The amount of the detergent or detergents (individually or in total) in the lubricants of the present technology may be 0.5 to 5 percent by weight, or 1 to 3 percent. The amount in a concentrate will be correspondingly higher. The total amount of detergents present in the lubricants of the disclosed technology may be an amount suitable to provide 1 to 5 TBN, or 2 to 4, or 2.5 to 3 TBN to the lubricant.

Boron Compound

[0079] The lubricant compositions of the present invention may comprise a boron containing compound or mixture of boron containing compounds in an amount to provide the lubricant composition with 25 ppm boron, or at least 50 ppm boron, or at least 100 ppm or at least 200 ppm or 300 ppm or 500 ppm or 200 to 500 ppm or 300 to 500 ppm boron to the lubricant composition. Useful boron containing compounds may include boric acid (including metaboric acid,

HBO_2, orthoboric acid, H_3BO_3, and a tetraboric acid, $H_2B_4O_7$) and borate esters, which may be prepared by the reaction of boric acid, a boric oxide, a boron trioxide or an alkyl borate and at least one compound selected from epoxy compounds, halohydrin compounds, epihalohydrin compounds, alcohols and mixtures thereof. Typically the alcohols include monohydric alcohols, dihydric alcohols, trihydric alcohols or higher alcohols. Borate esters may also be prepared from boron halides.

[0080] The borated ester may contains at least one hydrocarbyl group often containing about 4 to about 30, or 8 to about 30 carbon atoms.

[0081] In one embodiment, the boron containing compound may comprise a borate ester comprising at least one C8 to C30 hydrocarbyl group. The boron containing compound may comprise one or more borated dispersants discussed above. In one embodiment, it the boron containing compound may comprise a mixture of a borate ester and a boron containing dispersant.

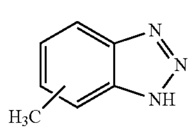
Other Performance Additives

[0082] The lubricant of the disclosed technology may also contain 3 to 80 ppm (or 5 to 70, or 10 to 60, or 20 to 50 ppm) of one or more silicon-containing antifoam agents. At least a small amount of such an antifoam agent is desirable to minimize foaming while the lubricant is lubricating the engine. However, an excessive amount may be deleterious to the anti-emulsion performance of the lubricant as it may be used for the lubrication of a compressor.

[0083] Silicon antifoam agents may be fluorinated molecules, or molecules without fluorine, or mixtures of such molecules. Such materials are commercially available and includes such species as polydimethylsiloxane and trimethyl, trifluoropropylmethyl siloxane. These materials may be provided commercially as oil-diluted compositions; the amounts reported herein are an oil-free basis.

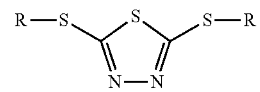
[0084] In certain embodiments, the disclosed lubricant may also contain a silicon-free polymeric antifoam agent. The amount of this agent, if it is present, may be up to 200 parts per million by weight, e.g., 10 to 200, or 20 to 100, or 25 to 80, or 30 to 70 ppm. The silicon-free polymeric antifoam agent may comprise an alkyl acrylate polymer, such as a copolymer of ethyl acrylate and 2-ethylhexyl acrylate. Such an antifoam agent may aid in improving anti-emulsion performance of the lubricant.

[0085] Another component that may be included in the lubricant is a corrosion inhibitor (which may also function as a rust inhibitor or a metal deactivator). Corrosion inhibitors typically may include nitrogen-containing materials such as triazoles and thiadiazoles and derivatives thereof. Suitable triazoles include aromatic triazoles such as benzotriazole or alkylbenzotriazoles such as tolutriazole.



(methyl-1-1H-benzo[d][1,2,3]triazole or tolutriazole)

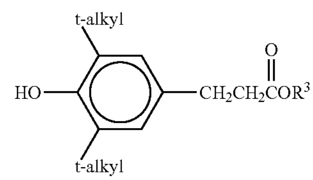
Thiadiazoles include dimercaptothiadiazoles and mono- or di-alkyl derivatives of dimercaptothiadiazoles.



(including species with multiple S atoms in a chain). The amount of the corrosion inhibitor (such as the amount of the aromatic triazole) may be 0.001 to 0.1 wt. %, or 0.003 to 0.03 wt. %, or 0.005 to 0.1 wt. %.

[0086] Additional conventional components may be used in preparing a lubricant according to the present technology, for instance, those additives typically employed in a crankcase lubricant. Crankcase lubricants may typically contain any or all of the following components hereinafter described.

[0087] One component is an antioxidant, sometimes referred to an ashless antioxidant if it is desired to distinguish metal-containing materials from metal-free (ashless) compounds. Antioxidants encompass phenolic antioxidants, which may comprise a butyl substituted phenol containing 2 or 3 t-butyl groups. The para position may also be occupied by a hydrocarbyl group or a group bridging two aromatic rings. They may also contain an ester group at the para position, for example, an antioxidant of the formula



wherein R^3 is a hydrocarbyl group such as an alkyl group containing, e.g., 1 to 18 or 2 to 12 or 2 to 8 or 2 to 6 carbon atoms; and t-alkyl can be t-butyl. Such antioxidants are described in greater detail in U.S. Pat. No. 6,559,105. Antioxidants also include aromatic amines, such as nonylated diphenylamines. Other antioxidants include sulfurized olefins, titanium compounds, and molybdenum compounds. U.S. Pat. No. 4,285,822, for instance, discloses lubricating oil compositions containing a molybdenum and sulfur containing composition. Typical amounts of antioxidants will, of course, depend on the specific antioxidant and its individual effectiveness, but illustrative total amounts can be 0.01 to 5 wt. % or 0.15 to 4.5 wt. % or 0.2 to 4 wt. %. Additionally, more than one antioxidant may be present, and certain combinations of these can be synergistic in their combined overall effect.

[0088] Viscosity improvers (also sometimes referred to as viscosity index improvers or viscosity modifiers) may be included in the disclosed compositions. Viscosity improvers are usually polymers, including polyisobutenes, polymethacrylic acid esters, diene polymers, polyalkylstyrenes, esterified styrene-maleic anhydride copolymers, alkenylarene-conjugated diene copolymers and polyolefins. Multifunctional viscosity improvers, which also have dispersant and/or antioxidancy properties are known and may optionally be used. Viscosity improvers may be used at, e.g., 0.1 to 0.8 wt. % or 0.3 to 0.6 wt. %.

[0089] The lubricant compositions of the present invention may include one or more antiwear agents other than the phosphite compounds disclosed above.

[0090] Examples of other anti-wear agents may include phosphorus-containing antiwear/extreme pressure agents such as metal thiophosphates, phosphoric acid esters and salts thereof, and phosphorus-containing carboxylic acids, esters, ethers, and amides. The present technology is particularly useful for formulations in which the total amount of phosphorus as delivered by various components including the antiwear agent, does not exceed 0.075% or 0.07% or 0.06%. Suitable amounts may include 0.005 to about 0.055 percent by weight or 0.01 to 0.05 percent or 0.02 to 0.05 percent. Non-phosphorus-containing anti-wear agents, which may also be used, include borate esters (including borated epoxides), dithiocarbamate compounds, molybdenum-containing compounds, and sulfurized olefins.

[0091] Other additives that may optionally be used in lubricating oils include pour point depressing agents, extreme pressure agents, and color stabilizers.

[0092] The present technology is particularly useful also when the total sulfated ash of a lubricant is relatively low, for instance, less than 1% or less than 0.8%, e.g., 0.01 to 0.8, or 0.1 to 0.75, or 0.2 to 0.7%.

[0093] In a particularly useful embodiment a lubricant formulation may be free or substantially free of any zinc containing compounds, such as the antiwear agent zinc dialkyldithiophosphate (ZDDP). In other embodiments, the lubricant may be free of or substantially free of any metal thiophosphates.

[0094] The lubricant formulations of the present invention are intended to effectively inhibit siloxane deposit formation and associated engine wear in engines fueled using natural or landfill gas having high concentrations of silicon, while also maintaining or improving seals performance and corrosion inhibition. Thus, in come embodiments of the method of the present invention, the lubricant composition may comprise greater than 120 ppm or 125 ppm or 130 ppm or 140 or 160 or 175 or 200 or 250 or 300 ppm of silicon. This silicon may be derived from contamination from silicon compounds in the fuel source or byproducts of combustion of the fuel source.

[0095] 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. For instance, metal ions (of, e.g., a detergent) can migrate to other acidic or anionic sites of other molecules. The products formed thereby, including the products formed upon employing the 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 technology; the present technology encompasses the composition prepared by admixing the components described above.

EXAMPLES

[0096] Reference Example 1 (RE1). A low-ash stationary-gas engine lubricant may be prepared comprising an oil of lubricating viscosity, 2.54 wt. % of a succinimide dispersant (chlorine-route); 0.74 wt. % of overbased Ca sulfonate detergent(s); 0.97 wt. % overbased Ca phenate detergent(s), 0.27 wt. % zinc dialkylthiophosphate(s); 2.85 wt. % antioxidants (phenolic, aminic, and/or sulfurized olefin); 0.35 wt. % of a borate ester, and 0.007 percent by weight of polydimethylsiloxane antifoam agent (commercial material, about 10% in oil, corresponding to 7 ppm antifoam agent on an active chemical basis).

[0097] Preparative Example 1 (PE1). A low-ash stationary-gas engine lubricant may be prepared comprising an oil of lubricating viscosity, 0.24 wt. % of a phosphite compound (s), 1.8 wt. % of a succinimide dispersant (chlorine-route); 0.6 wt. % of a polyisobutylene succinimide dispersant with a carbonyl to nitrogen ratio of 4:3, 0.34 wt.% of a borated succinimide dispersant, 0.28 wt. % succinic acid ester dispersant, 0.1 wt. % of a polypropylene oxide, 1.2 wt. % of overbased Ca salicylate detergent; 2.95 wt. % antioxidants (phenolic, aminic, and/or sulfurized olefin); 0.35 wt. % of a borate ester, 0.01 wt. % of a corrosion inhibitor, 0.05 wt. % of a titanium alkylate and 0.007 percent by weight of polydimethylsiloxane antifoam agent (commercial material, about 10% in oil, corresponding to 7 ppm antifoam agent on an active chemical basis).

[0098] Each of the documents referred to above is incorporated herein by reference. The mention of any document is not an admission that such document qualifies as prior art or constitutes the general knowledge of the skilled person in any jurisdiction. 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.” 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 can be used together with ranges or amounts for any of the other elements. As used herein, the expression “consisting essentially of” permits the inclusion of substances that do not materially affect the basic and novel characteristics of the composition under consideration.

[0099] As used herein, the term “substantially free of” means that the material in question is only present in amounts consistent with contamination and/or by-products present in commercial grades of desired components.

[0100] 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, including aliphatic, alicyclic, and aromatic substituents; 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; and hetero substituents, that is, substituents which similarly have a predominantly hydrocarbon character but contain other than carbon in a ring or chain. A more detailed definition of the term “hydrocarbyl substituent” or “hydrocarbyl group,” including permissible amounts of other atoms, is found in paragraphs [0118] to [0119] of International Publication WO2008147704 as well as paragraphs [0137] to [0141] of published application U.S. 2010-0197536.

1. A method for lubricating a natural gas fueled, sump-lubricated, stationary gas engine comprising supplying to the engine a lubricant composition comprising:

(a) an oil of lubricating viscosity;

(b) 0.03 to about 3.0 weight percent with respect to the lubricant of a phosphite compound;

(c) a metal containing detergent;

(d) at least a first dispersant, wherein the first dispersant is a polyisobutylene succinimide dispersant derived from an ethylene polyamine and having a carbonyl to nitrogen ratio equal or greater than 1;

(e) at least one other dispersant selected from the group consisting of a succinimide dispersant having a carbonyl to nitrogen ratio less than 1, a Mannich dispersant, a succinamide dispersant, and a polyisobutylene succinic acid ester dispersant;

a boron containing compound in amount to provide at least 25 ppm boron to the lubricant composition;

wherein the lubricant composition is free or substantially free of zinc, and

wherein the lubricant composition has a sulfated ash content of less than about 1.0 wt. %.

2. The method of claim **1** wherein the phosphite compound comprises a phosphite ester selected from the group consisting of phosphite diesters, phosphite triesters and mixtures thereof.

3. The method of claim **1** wherein the phosphite compound comprises a phosphite having the following formula

$$(R^1O)_3P$$

wherein each le independently is hydrogen or a hydrocarbyl group having 1 to 36 carbon atoms.

4. The method of claim **1** wherein the phosphite compound comprises a phosphite diester having ester groups of 2 to 10 carbon atoms and a phosphite diester having ester groups of 12 to 30 carbon atoms.

5. The method of claim **1**, wherein the phosphite compounds comprises dibutyl phosphite.

6. The method of claim **1** wherein the phosphite compound provides 0.001 wt. % to 0.05 wt. % phosphorus to the lubricant composition.

7. The method of claim **1**, wherein the total amount of dispersant is 1.0 wt % to 6.0 wt. % of the lubricant composition.

8. The method of claim **1**, wherein the first dispersant is present in an amount of 0.1 wt % to 2 wt % of the lubricant composition.

9. The method of claim **1**, wherein the second dispersant comprises a succinimide dispersant having a carbonyl to nitrogen ratio less than 1.

10. The method of claim **1**, wherein the metal containing detergent is selected from the group consisting of phenate detergents, sulphonate detergents, salicylate detergents, salixarate detergents, saligenin detergents and mixtures thereof.

11. The method of claim **1**, wherein the metal containing detergent comprises a salicylate detergent.

12. The method of claim **1**, wherein the salicylate detergent has a Total Base Number of about 200 to about 700 on an oil free basis.

13. The method of claim **1**, wherein the metal of the metal containing detergent is selected from the group consisting of magnesium, and calcium and mixtures thereof.

14. The method of claim **1**, wherein the lubricant composition comprises at least a third dispersant, wherein the third dispersant is a polyolefin succinic acid ester dispersant.

15. The method of claim **1**, wherein the lubricant composition has a silicon concentration greater than 125 ppm.

16. The method of claim **1**, wherein the engine is fueled by natural gas having a silicon concentration greater than about 10 mg/m^{3-} as measured by gas chromatography mass spectrometry.

17. The method of claim **1**, wherein the boron containing compound comprises a borate ester having at least one hydrocarbyl group of 8 to 30 carbon atoms.

18. The method of claim **1**, wherein the boron containing compound comprises a borated dispersant.

19. The method of claim **1**, wherein the lubricant composition has 50 to about 500 ppm phosphorus.

20-21. (canceled)

22. A lubricant comprising:

(a) an oil of lubricating viscosity;

(b) 0.03 to about 3.0 weigh percent with respect to the lubricant composition of a phosphite compound;

(c) a metal containing detergent;

(d) at least a first dispersant, wherein the first dispersant is a polyisobutylene succinimide dispersant derived from an ethylene polyamine and having a carbonyl to nitrogen ratio equal or greater than 1;

(e) at least one other dispersant selected from the group consisting of a succinimide dispersant having a carbonyl to nitrogen ratio less than 1, a Mannich dispersant, and a polyolefin succinic acid ester dispersant;

(f) a boron containing compound in amount to provide at least 25 ppm boron to the lubricant composition;

wherein the lubricant composition is substantially free of zinc,

wherein the lubricant composition has a sulfated ash content of less than about 1.0 percent.

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