

LUBRICATING OIL COMPOSITIONS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application No. 63/314,492, filed February 28, 2022, which is hereby incorporated herein by reference in its entirety.

BACKGROUND OF THE DISCLOSURE

[0002] Phosphorus-containing anti-wear agents are widely used as anti-wear agents in lubricating oils to provide protection against wear and/or corrosion. One issue associated with these components is that phosphorus can accumulate in an automobile's catalytic converter which can reduce the efficiency, effectiveness, and/or life of the converter unit. As a result, regulatory agencies and automotive industry have been pushing to reduce phosphorus content in lubricating oils. Accordingly, it would be desirable to reduce phosphorus content in lubricating oils while maintaining sufficient protection against wear and/or corrosion.

SUMMARY OF THE DISCLOSURE

[0003] In an embodiment, the present invention provides a low ash lubricating oil composition comprising: a major amount of an oil of lubricating viscosity; a detergent system comprising one or more magnesium-containing detergent and optionally, one or more calcium-containing detergent; and a boron-containing additive in an amount to provide at least 100 ppm of boron to the lubricating oil composition; wherein the lubricating oil composition is free of zinc and phosphorus; the total sulfated ash content of the lubricating oil composition is from 0.30 wt.% to 0.80 wt.%; and the total base number of the lubricating oil composition is from 4.0 to 9.5 mg KOH/g.

[0004] In another embodiment, the present invention provides a method for reducing corrosion in an engine, the method comprising providing a lubricating oil composition to the engine, wherein the lubricating oil composition comprises: a major amount of an oil of lubricating viscosity; a detergent system comprising one or more calcium overbased detergents and one or more overbased magnesium-containing detergents; zinc dithiophosphate in an amount to provide a phosphorus content from 0 to 300 ppm to the lubricating oil composition; boron-containing additive in an amount to provide less than 300 ppm of boron to the lubricating

oil composition; and molybdenum compound in an amount to provide from 50 to 500 ppm of molybdenum to the lubricating oil composition; wherein the lubricating oil composition has a calcium content of up to about 1300 ppm based on a total weight of the lubricating composition, and where the total sulfated ash content of the lubricating oil composition is from 0.40 wt.% to 0.80 wt.% and the total base number of the lubricating oil composition is from 4.0 to 9.0 mg KOH/g.

DETAILED DESCRIPTION OF THE DISLCOSURE

[0005] While the disclosure is susceptible to various modifications and alternative forms, specific embodiments thereof are herein described in detail. It should be understood, however, that the description herein of specific embodiments is not intended to limit the disclosure to the particular forms disclosed, but on the contrary, the intention is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the disclosure as defined by the appended claims.

[0006] To facilitate the understanding of the subject matter disclosed herein, a number of terms, abbreviations or other shorthand as used herein are defined below. Any term, abbreviation or shorthand not defined is understood to have the ordinary meaning used by a skilled artisan contemporaneous with the submission of this application.

DEFINITIONS

[0007] As used herein, the following terms have the following meanings, unless expressly stated to the contrary. In this specification, the following words and expressions, if and when used, have the meanings given below.

[0008] A “major amount” means in excess of 50 weight % of a composition.

[0009] A “minor amount” means less than 50 weight % of a composition, expressed in respect of the stated additive and in respect of the total mass of all the additives present in the composition, reckoned as active ingredient of the additive or additives.

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

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

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

[0013] High temperature high shear (HTHS) viscosity at 150°C was determined in accordance with ASTM D4683.

[0014] Kinematic viscosity at 100°C (KV₁₀₀) was determined in accordance with ASTM D445.

[0015] The term “metal” refers to alkali metals, alkaline earth metals, or mixtures thereof.

[0016] Throughout the specification and claims the expression oil soluble or dispersible is used. By oil soluble or dispersible is meant that an amount needed to provide the desired level of activity or performance can be incorporated by being dissolved, dispersed or suspended in an oil of lubricating viscosity. Usually, this means that at least about 0.001% by weight of the material can be incorporated in a lubricating oil composition. For a further discussion of the terms oil soluble and dispersible, particularly “stably dispersible”, see U.S. Pat. No. 4,320,019 which is expressly incorporated herein by reference for relevant teachings in this regard.

[0017] The term “sulfated ash” as used herein refers to the non-combustible residue resulting from detergents and metallic additives in lubricating oil. Sulfated ash may be determined using ASTM Test D874.

[0018] The term “Total Base Number” or “TBN” as used herein refers to the amount of base equivalent to milligrams of KOH in one gram of sample. Thus, higher TBN numbers reflect more alkaline products, and therefore a greater alkalinity. TBN was determined using ASTM D 2896 test. TBN numbers are based on the detergent concentrate.

[0019] The terminology “overbased” relates to metal salts, such as metal salts of sulfonates, salicylates, and phenates, wherein the amount of metal present exceeds the stoichiometric amount. Such salts may have a conversion level in excess of 100% (i.e., they may comprise more than 100% of the theoretical amount of metal needed to convert the acid to its “normal,” “neutral” salt). The expression “metal ratio,” often abbreviated as MR, is used to designate the ratio of total chemical equivalents of metal in the overbased salt to chemical equivalents of the metal in a neutral salt according to known chemical reactivity and stoichiometry. In a normal or neutral salt, the metal ratio is one and in an overbased salt, MR, is greater than one. They are commonly referred to as overbased, hyperbased, or superbased salts and may be salts of organic sulfur acids, salicylic acids, or phenols.

[0020] Boron, calcium, magnesium, molybdenum, phosphorus, sulfur, and/or zinc contents were determined in accordance with ASTM D5185.

[0021] Nitrogen content was determined in accordance with ASTM D4629.

[0022] All ASTM standards referred to herein are the most current versions as of the filing date of the present application.

[0023] Unless otherwise specified, all percentages are in weight percent.

[0024] While the disclosure is susceptible to various modifications and alternative forms, specific embodiments thereof are herein described in detail. It should be understood, however, that the description herein of specific embodiments is not intended to limit the disclosure to the particular forms disclosed, but on the contrary, the intention is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the disclosure as defined by the appended claims.

[0025] The specification and illustrations of the embodiments described herein are intended to provide a general understanding of the structure of the various embodiments.

[0026] The present invention provides a lubricating oil composition formulated to provide protection sufficient protection against wear and/or corrosion.

[0027] The lubricating oil composition comprises a major amount of an oil of lubricating viscosity, a detergent system comprising one or more magnesium-containing detergent and optionally, one or more calcium-containing detergent, and a boron-containing additive. The boron-containing additive is present in an amount to provide at least 100 ppm of boron to the lubricating oil composition. The lubricating oil composition is substantially free of zinc and phosphorus (less than or about 50 ppm). The total sulfated ash content of the lubricating oil composition is from 0.30 wt.% to 0.80 wt.%. The total base number of the lubricating oil composition is from 4.0 to 9.5 mg KOH/g.

Oil of Lubricating Viscosity

[0028] The oil of lubricating viscosity (sometimes referred to as “base stock” or “base oil”) is the primary liquid constituent of a lubricant, into which additives and possibly other oils are blended to produce a final lubricant (or lubricant composition). A base oil is useful for making concentrates as well as for making lubricating oil compositions therefrom and may be selected from natural and synthetic lubricating oils and combinations thereof.

[0029] Natural oils include animal and vegetable oils, liquid petroleum oils and hydrotreated, solvent-treated mineral lubricating oils of the paraffinic, naphthenic and mixed

paraffinic-naphthenic types. Oils of lubricating viscosity derived from coal or shale are also useful as base oils.

[0030] Synthetic lubricating oils include hydrocarbon oils such as polymerized and interpolymerized olefins (e.g., polybutylenes, polypropylenes, propylene-isobutylene copolymers, chlorinated polybutylenes, poly(1-hexenes), poly(1-octenes), poly(1-decenes); alkylbenzenes (e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di(2-ethylhexyl)benzenes; polyphenols (e.g., biphenyls, terphenyls, alkylated polyphenols); and alkylated diphenyl ethers and alkylated diphenyl sulfides and the derivatives, analogues and homologues thereof. Polymerized olefins can also be derived from bio-derived sources such as hydrocarbon terpenes such as myrcene, ocimene and farnesene which can also be co-polymerized with other olefins and further isomerized if desired.

[0031] Another suitable class of synthetic lubricating oils comprises the esters of dicarboxylic acids (e.g., malonic acid, alkyl malonic acids, alkenyl malonic acids, succinic acid, alkyl succinic acids and alkenyl succinic acids, maleic acid, fumaric acid, azelaic acid, suberic acid, sebacic acid, adipic acid, linoleic acid dimer, phthalic acid) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol). Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl) sebacate, di-*n*-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid.

[0032] Esters useful as synthetic oils also include those made from C₅ to C₁₂ monocarboxylic acids and polyols, and polyol ethers such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol and tripentaerythritol.

[0033] Also, esters from bio-derived sources are also useful as synthetic oils.

[0034] The base oil may be derived from Fischer-Tropsch synthesized hydrocarbons. Fischer-Tropsch synthesized hydrocarbons are made from synthesis gas containing H₂ and CO using a Fischer-Tropsch catalyst. Such hydrocarbons typically require further processing in order to be useful as the base oil. For example, the hydrocarbons may be hydroisomerized; hydrocracked and hydroisomerized; dewaxed; or hydroisomerized and dewaxed; using processes known to those skilled in the art.

[0035] Unrefined, refined and re-refined oils can be used in the present lubricating oil composition. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. For example, a shale oil obtained directly from retorting operations, a petroleum oil obtained directly from distillation or ester oil obtained directly from an esterification process and used without further treatment would be unrefined oil. Refined oils are similar to the unrefined oils except they have been further treated in one or more purification steps to improve one or more properties. Many such purification techniques, such as distillation, solvent extraction, acid or base extraction, filtration and percolation are known to those skilled in the art.

[0036] Re-refined oils are obtained by processes similar to those used to obtain refined oils applied to refined oils which have been already used in service. Such re-refined oils are also known as reclaimed or reprocessed oils and often are additionally processed by techniques for approval of spent additive and oil breakdown products.

[0037] Hence, the base oil which may be used to make the present lubricating oil composition may be selected from any of the base oils in Groups I-V as specified in the American Petroleum Institute (API) Base Oil Interchangeability Guidelines (API Publication 1509). Such base oil groups are summarized in Table 1 below:

Table 1

	<u>Base Oil Properties</u>		
Group ^(a)	Saturates ^(b) , wt. %	Sulfur ^(c) , wt. %	Viscosity Index ^(d)
Group I	<90 and/or	>0.03	80 to <120
Group II	≥90	≤0.03	80 to <120
Group III	≥90	≤0.03	≥120
Group IV	Polyalphaolefins (PAOs)		
Group V	All other base stocks not included in Groups I, II, III or IV		

^(a) Groups I-III are mineral oil base stocks.

^(b) Determined in accordance with ASTM D2007.

^(c) Determined in accordance with ASTM D2622, ASTM D3120, ASTM D4294 or ASTM D4927.

^(d) Determined in accordance with ASTM D2270.

[0038] Base oils suitable for use herein are any of the variety corresponding to API Group II, Group III, Group IV, and Group V oils and combinations thereof, preferably the Group III to Group V oils due to their exceptional volatility, stability, viscometric and cleanliness features.

[0039] The oil of lubricating viscosity for use in the lubricating oil compositions of this disclosure, also referred to as a base oil, is typically present in a major amount, e.g., an amount of greater than 50 wt. %, preferably greater than about 70 wt. %, more preferably from about 80 to about 99.5 wt. % and most preferably from about 85 to about 98 wt. %, based on the total weight of the composition. The expression "base oil" as used herein shall be understood to mean a base stock or blend of base stocks which is a lubricant component that is produced by a single manufacturer to the same specifications (independent of feed source or manufacturer's location); that meets the same manufacturer's specification; and that is identified by a unique formula, product identification number, or both. The base oil for use herein can be any presently known or later-discovered oil of lubricating viscosity used in formulating lubricating oil compositions for any and all such applications, e.g., engine oils, marine cylinder oils, functional fluids such as hydraulic oils, gear oils, transmission fluids, etc. Additionally, the base oils for use herein can optionally contain viscosity index improvers, e.g., polymeric alkylmethacrylates; olefinic copolymers, e.g., an ethylene-propylene copolymer or a styrene-butadiene copolymer; and the like and mixtures thereof.

[0040] As one skilled in the art would readily appreciate, the viscosity of the base oil is dependent upon the application. Accordingly, the viscosity of a base oil for use herein will ordinarily range from about 2 to about 2000 centistokes (cSt) at 100° Centigrade (C). Generally, individually the base oils used as engine oils will have a kinematic viscosity range at 100° C of about 2 cSt to about 30 cSt, preferably about 3 cSt to about 16 cSt, and most preferably about 4 cSt to about 12 cSt and will be selected or blended depending on the desired end use and the additives in the finished oil to give the desired grade of engine oil, e.g., a lubricating oil composition having an SAE Viscosity Grade of 0W, 0W-8, 0W-12, 0W-16, 0W-20, 0W-26, 0W-30, 0W-40, 0W-50, 0W-60, 5W, 5W-20, 5W-30, 5W-40, 5W-50, 5W-60, 10W, 10W-20, 10W-30, 10W-40, 10W-50, 15W, 15W-20, 15W-30, 15W-40, 30, 40 and the like.

[0041] In one embodiment, the level of sulfated ash produced by the lubricating oil compositions of the present disclosure is about 0.40 to about 0.80 wt. % as determined by ASTM D 874. In one embodiment, the level of sulfated ash produced by the lubricating oil

compositions of the present disclosure is about 0.40 to about 0.70 wt. % as determined by ASTM D 874. In one embodiment, the level of sulfated ash produced by the lubricating oil compositions of the present disclosure is about 0.40 to about 0.60 wt. % as determined by ASTM D 874. In one embodiment, the level of sulfated ash produced by the lubricating oil compositions of the present disclosure is about 0.50 to about 0.80 wt. % as determined by ASTM D 874. In one embodiment, the level of sulfated ash produced by the lubricating oil compositions of the present disclosure is about 0.60 to about 0.80 wt. % as determined by ASTM D 874.

[0042] The lubricating oil compositions of the present disclosure may have a total base number from 4.0 mg KOH/g to 9.0 mg KOH/g. In one embodiment, the total base number is from 4.0 mg KOH/g to 8.5 mg KOH/g. In one embodiment, the total base number is from 4.0 mg KOH/g to 8.0 mg KOH/g. In one embodiment, the total base number is from 4.0 mg KOH/g to 7.5 mg KOH/g. In one embodiment, the total base number is from 4.0 mg KOH/g to 7.0 mg KOH/g. In one embodiment, the total base number is from 4.0 mg KOH/g to 6.5 mg KOH/g. In one embodiment, the total base number is from 4.0 mg KOH/g to 6.0 mg KOH/g. In one embodiment, the total base number is from 4.5 mg KOH/g to 9.0 mg KOH/g. In one embodiment, the total base number is from 5.0 mg KOH/g to 9.0 mg KOH/g. In one embodiment, the total base number is from 5.5 mg KOH/g to 9.0 mg KOH/g. In one embodiment, the total base number is from 6.0 mg KOH/g to 9.0 mg KOH/g. In one embodiment, the total base number is from 5.0 mg KOH/g to 8.0 mg KOH/g.

Detergent System

[0043] The lubricating oil composition of the present invention includes a detergent system comprising a mixture of detergent components comprising one or more magnesium-containing detergent and optionally, one or more calcium-containing detergents. Suitable detergent components include magnesium-containing and/or calcium-containing overbased detergents.

[0044] Examples of overbased detergents include overbased sulfonates and overbased salicylates.

[0045] An overbased detergent has a TBN of about 250 mg KOH/gram or greater, or a TBN of about 300 mg KOH/gram or greater, or a TBN of about 350 mg KOH/gram or greater, or a TBN of about 375 mg KOH/gram or greater, or a TBN of about 400 mg KOH/gram or greater based on the detergent concentrate. In some embodiments, the detergent system includes

an overbased phenate detergent having a TBN of about or greater than 250 mg KOH/g and/or a low overbased sulfonate detergent having a TBN of up to about 180 mg KOH/g.

[0046] The magnesium-containing detergent(s) are present in an amount to provide about 50 to about 1000 ppm of magnesium to the lubricating oil composition, such as from about 100 to about 900 ppm, from about 150 ppm to about 850 ppm, from about 200 ppm to about 800 ppm, from about 250 ppm to about 750 ppm, from about 300 ppm to about 700 ppm, from about 350 ppm to about 650 ppm, from about 400 ppm to about 600 ppm, from about 50 ppm to about 950 ppm, from about 50 ppm to about 900 ppm, from about 50 ppm to about 850 ppm, from about 50 ppm to about 800 ppm, from about 50 ppm to about 750 ppm, from about 50 ppm to about 700 ppm, from about 50 ppm to about 650 ppm, from about 50 ppm to about 600 ppm, from about 50 ppm to about 550 ppm, from about 50 ppm to about 500 ppm, from about 100 ppm to about 800 ppm, from about 100 ppm to about 700 ppm, from about 100 ppm to about 600 ppm, from about 100 ppm to about 500 ppm, from about 150 ppm to about 1000 ppm, from about 150 ppm to about 900 ppm, from about 150 ppm to about 800 ppm, from about 150 ppm to about 700 ppm, from about 150 ppm to about 600 ppm, from about 200 ppm to about 1000 ppm, from about 200 ppm to about 900 ppm, from about 200 ppm to about 800 ppm, from about 200 ppm to about 700 ppm, from about 200 ppm to about 600 ppm, from about 300 ppm to about 1000 ppm, from about 300 ppm to about 900 ppm, from about 300 ppm to about 800 ppm, from about 300 ppm to about 700 ppm, and from about 300 ppm to about 600 ppm.

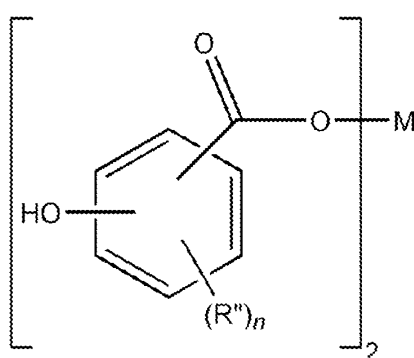
[0047] The optional calcium-containing detergent(s) are present in an amount to provide up to about 1300 ppm of calcium to the lubricating oil composition, such as up to about 1200 ppm, up to about 1100 ppm, up to about 1000 ppm, up to about 900 ppm, up to about 800 ppm, up to about 700 ppm, up to about 600 ppm, up to about 500 ppm, up to about 400 ppm, up to about 300 ppm, up to about 200 ppm, up to about 100 ppm, and up to about 50 ppm.

[0048] The ppm values are based on total weight of the lubricating oil composition.

[0049] Sulfonates may be prepared from sulfonic acids which are typically obtained by the sulfonation of alkyl-substituted aromatic hydrocarbons such as those obtained from the fractionation of petroleum or by the alkylation of aromatic hydrocarbons. Examples included those obtained by alkylating benzene, toluene, xylene, naphthalene, diphenyl or their halogen derivatives. The alkylation may be carried out in the presence of a catalyst with alkylating agents having from about 3 to more than 70 carbon atoms. The alkaryl sulfonates usually

contain from about 9 to 80 or more carbon atoms (e.g., about 16 to 60 carbon atoms) per alkyl substituted aromatic moiety.

[0050] Salicylates may be prepared by reacting a basic metal compound with at least one carboxylic acid and removing water from the reaction product. Detergents made from salicylic acid are one class of detergents prepared from carboxylic acids. Useful salicylates include long chain alkyl salicylates. One useful family of compositions is of the following structure:



wherein R'' is a C₁ to C₃₀ (e.g., C₁₃ to C₃₀) alkyl group; *n* is an integer from 1 to 4; and M is an alkaline earth metal (e.g., Ca or Mg).

[0051] Hydrocarbyl-substituted salicylic acids may be prepared from phenols by the Kolbe reaction (see U.S. Patent No. 3,595,791). The metal salts of the hydrocarbyl-substituted salicylic acids may be prepared by double decomposition of a metal salt in a polar solvent such as water or alcohol.

[0052] Phenates can be prepared by reacting an alkaline earth metal hydroxide or oxide (e.g., CaO, Ca(OH)₂, MgO, or Mg(OH)₂) with an alkyl phenol or sulfurized alkylphenol. Useful alkyl groups include straight or branched chain C₁ to C₃₀ (e.g., C₄ to C₂₀) alkyl groups, or mixtures thereof. Examples of suitable phenols include isobutylphenol, 2-ethylhexylphenol, nonylphenol, dodecyl phenol, and the like. It should be noted that starting alkylphenols may contain more than one alkyl substituent that are each independently straight chain or branched chain. When a non-sulfurized alkylphenol is used, the sulfurized product may be obtained by methods well known in the art. These methods include heating a mixture of alkylphenol and

sulfurizing agent (e.g., elemental sulfur, sulfur halides such as sulfur dichloride, and the like) and then reacting the sulfurized phenol with an alkaline earth metal base.

Overbased Sulfonate and/or Salicylate Detergent

[0053] The lubricating oil composition comprises one or more overbased calcium sulfonate and/or calcium salicylate detergents having a total base number of greater than 250 mg KOH/g, measured by the method of ASTM D-2896 present in an amount that provides 700 to 1300 ppm of calcium to the lubricating oil composition. In some embodiments, the one or more overbased calcium sulfonate and/or calcium salicylate detergents having a total base number of greater than 250 mg KOH/g, measured by the method of ASTM D-2896 is present in an amount that provides 800 to 1300 ppm of calcium, 800 to 1250 ppm of calcium, 850 to 1250 ppm of calcium, to the lubricating oil composition. In some embodiments, the one or more overbased calcium sulfonate and/or calcium salicylate detergents having a total base number of greater than 250 mg KOH/g, measured by the method of ASTM D-2896.

Magnesium-containing Detergent

[0054] The one or more magnesium-containing detergents may be overbased magnesium-containing detergents having a total base number of greater than 250 mg KOH/g, measured by the method of ASTM D-2896 and the one or more overbased magnesium-containing detergents may be selected from an overbased magnesium sulfonate detergent, an overbased magnesium phenate detergent, an overbased magnesium salicylate detergent and mixtures thereof. Alternatively, the magnesium-containing detergents may include one or more of the magnesium-containing detergents described above, including low-based/neutral magnesium-containing detergents.

[0055] Preferred magnesium-containing detergents include magnesium sulfonates, magnesium phenates, and magnesium salicylates, especially magnesium sulfonates.

Overbased Phenate Detergent

[0056] Optionally, the lubricating oil composition comprises an overbased phenate detergent having a total base number of greater than 250 mg KOH/g. In one embodiment, the overbased phenate is a calcium phenate. In one embodiment, the overbased calcium phenate is a sulfurized calcium phenate.

Boron-containing Additive

[0057] The lubricating oil composition comprises about 100 ppm or more of boron, based on the weight of the lubricating oil composition, such as about 120 ppm or more, about 150 ppm or more, about 175 ppm or more, about 200 ppm or more, and about 250 ppm or more.

[0058] The boron-containing additive may be any suitable oil-soluble compound or oil-dispersible compound. Boron-containing additives may be prepared by reacting a boron compound with an oil-soluble or oil-dispersible additive or compound. Boron compounds include boron oxide, boron oxidehydrate, boron trioxide, boron trifluoride, boron tribromide, boron trichloride, boron acid such as boronic acid, boric acid, tetraboric acid and metaboric acid, boron hydrides, boron amides and various esters of boron acids. For example, the boron-containing additive may be one or more of a borated dispersant; a borated dispersant viscosity index improver; an alkali metal or a mixed alkali metal or an alkaline earth metal borate; a borated overbased metal detergent; a borated epoxide; a borate ester; a sulfurised borate ester; and a borate amide. Preferably, the boron-containing additive is one or more of a borated dispersant, a borate ester or a borated overbased metal detergent. Optionally, the borated overbased metal detergent, if present, is a borated overbased metal detergent having a TBN of at least 150, such as a borated overbased calcium detergent having a TBN of at least 150.

[0059] Examples of borated dispersants include borated ashless dispersants such as borated polyalkenyl succinic anhydrides; borated non-nitrogen containing derivatives of a polyalkylene succinic anhydride; borated basic nitrogen compounds selected from the group consisting of succinimides, carboxylic acid amides, hydrocarbyl monoamines, hydrocarbyl polyamines, Mannich bases, thiazoles (e.g., 2,5-dimercapto-1,3,4-thiadiazoles, mercaptobenzothiazoles and derivatives thereof), triazoles (e.g., alkyltriazoles and benzotriazoles), copolymers which contain a carboxylate ester with one or more additional polar function, including amine, amide, imine, imide, hydroxyl, carboxyl, and the like (e.g., products prepared by copolymerization of long chain alkyl acrylates or methacrylates with monomers of the above function); and the like and combinations thereof. A preferred borated dispersant is a succinimide derivative of boron such as, for example, a borated polyisobutenyl succinimide.

[0060] Examples of borated ashless dispersants are the borated ashless hydrocarbyl succinimide dispersants prepared by reacting a hydrocarbyl succinic acid or anhydride with an

amine. Preferred hydrocarbyl succinic acids or anhydrides are those where the hydrocarbyl group is derived from a polymer of a C₃ or C₄ monoolefin, especially a polyisobutylene wherein the polyisobutenyl group has a number average molecular weight (Mn) of from 700 to 5,000, more preferably from 900 to 2,500. Such dispersants generally have at least 1, preferably 1 to 2, more preferably 1.1 to 1.8, succinic groups for each polyisobutenyl group. In one embodiment, the oil soluble or oil dispersible borated polyisobutylene succinimide dispersant, is derived from a polyisobutylene group having a number average molecular weight of from about 550 to about 5000. In one embodiment, the oil soluble or oil dispersible borated polyisobutylene succinimide dispersant, is derived from a polyisobutylene group having a number average molecular weight of about 550 to about 4000. In one embodiment, the oil soluble or oil dispersible borated polyisobutylene succinimide dispersant, is derived from a polyisobutylene group having a number average molecular weight of about 550 to about 3000. In one embodiment, the oil soluble or oil dispersible borated polyisobutylene succinimide dispersant is derived from a polyisobutylene group having a number average molecular weight of about 550 to about 2300. In one embodiment, the oil soluble or oil dispersible borated polyisobutylene succinimide dispersant, is derived from a polyisobutylene group having a number average molecular weight of about 950 to about 2300. In one embodiment, the oil soluble or oil dispersible borated polyisobutylene succinimide dispersant, is derived from a polyisobutylene group having a number average molecular weight of about 950 to about 1300. In one embodiment, the oil soluble or oil dispersible borated polyisobutylene succinimide dispersant is derived from a polyisobutylene group having a number average molecular weight of about 2300. In one embodiment, the oil soluble or oil dispersible borated polyisobutylene succinimide dispersant is derived from a polyisobutylene group having a number average molecular weight of about 1300. In one embodiment, the oil soluble or oil dispersible borated polyisobutylene succinimide dispersant, is derived from a polyisobutylene group having a number average molecular weight of about 1000.

[0061] Preferred amines for reaction to form the succinimide are polyamines having from 2 to 60 carbon atoms and from 2 to 12 nitrogen atoms per molecule, and particularly preferred are the polyalkyleneamines represented by the formula:



wherein n is 2 to 3 and m is 0 to 10. Illustrative are ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, tetrapropylene pentamine, pentaethylene hexamine and the like, as well as the commercially available mixtures of such polyamines.

Amines including other groups such as hydroxy, alkoxy, amide, nitride and imidazoline groups may also be used, as may polyoxyalkylene polyamines. The amines are reacted with the alkenyl succinic acid or anhydride in conventional ratios of about 1:1 to 10:1, preferably 1:1 to 3:1, moles of alkenyl succinic acid or anhydride to polyamine, and preferably in a ratio of about 1:1, typically by heating the reactants to from 100° to 250° C, preferably 125° to 175°C for 1 to 10, preferably 2 to 6, hours.

[0062] The boration of alkenyl succinimide dispersants is also well known in the art as disclosed in U.S. Pat. Nos. 3,087,936 and 3,254,025. The succinimide may for example be treated with a boron compound selected from the group consisting of boron, boron oxides, boron halides, boron acids and esters thereof, in an amount to provide from 0.1 atomic proportion of boron to 10 atomic proportions of boron for each atomic proportion of nitrogen in the dispersant.

[0063] The borated product will generally contain 0.1 to 2.0, preferably 0.2 to 0.8 weight percent boron based upon the total weight of the borated dispersant. Boron is considered to be present as dehydrated boric acid polymers attaching at the metaborate salt of the imide. The boration reaction is readily carried out adding from 1 to 3 weight percent (based on the weight of dispersant) of said boron compound.

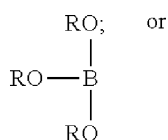
[0064] Examples of borated friction modifiers include, but are not limited to, borated fatty epoxides, borated alkoxyated fatty amines, borated glycerol esters and the like and mixtures thereof.

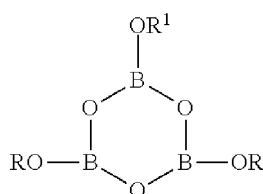
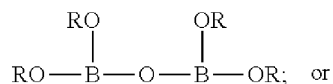
[0065] The hydrated particulate alkali metal borates are well known in the art and are available commercially. Representative examples of hydrated particulate alkali metal borates and methods of manufacture include those disclosed in, e.g., U.S. Pat. Nos. 3,313,727; 3,819,521; 3,853,772; 3,907,601; 3,997,454; 4,089,790; 6,737,387 and 6,534,450, the contents of which are incorporated herein by reference. The hydrated alkali metal borates can be represented by the following Formula: $M_2O \cdot mB_2O_3 \cdot nH_2O$ where M is an alkali metal of atomic number in the range of about 11 to about 19, e.g., sodium and potassium; m is a number from about 2.5 to about 4.5 (both whole and fractional); and n is a number from about 1.0 to about 4.8. Preferred are the hydrated sodium borates. The hydrated borate particles generally have a mean particle size of less than about 1 micron.

[0066] Examples of borated epoxides include borated epoxides obtained from the reaction product of one or more of the boron compounds with at least one epoxide. Suitable boron compounds include boron oxide, boron oxide hydrate, boron trioxide, boron trifluoride,

boron tribromide, boron trichloride, boron acids such as boronic acid, boric acid, tetraboric acid and metaboric acid, boron amides and various esters of boron acids. The epoxide is generally an aliphatic epoxide having from about 8 to about 30 carbon atoms and preferably from about 10 to about 24 carbon atoms and more preferably from about 12 to about 20 carbon atoms. Suitable aliphatic epoxides include dodecene oxide, hexadecene oxide and the like and mixtures thereof. Mixtures of epoxides may also be used, for instance commercial mixtures of epoxides having from about 14 to about 16 carbon atoms or from about 14 to about 18 carbon atoms. The borated epoxides are generally known and described in, for example, U.S. Pat. No. 4,584,115.

[0067] Examples of borate esters include those borate esters obtained by reacting one or more of the boron compounds disclosed above with one or more alcohols of suitable oleophilicity. Typically, the alcohols will contain from 6 to about 30 carbons and preferably from 8 to about 24 carbon atoms. The methods of making such borate esters are well known in the art. Representative examples of borate esters include those having the structures set forth in the following formulas:





wherein each R is independently a C₁-C₁₂ straight or branched alkyl group and R¹ is hydrogen or a C₁-C₁₂ straight or branched alkyl group.

[0068] Examples of borated fatty amines include borated fatty amines obtained by reacting one or more of the boron compounds disclosed above with one or more of fatty amines, e.g., an amine having from about fourteen to about eighteen carbon atoms.

[0069] Examples of borated amides include borated amides obtained from the reaction product of a linear or branched, saturated or unsaturated monovalent aliphatic acid having 8 to about 22 carbon atoms, urea, and polyalkylenepolyamine with a boric acid compound and the like and mixtures thereof.

[0070] Examples of borated sulfonates include borated alkaline earth metal sulfonates obtained by (a) reacting in the presence of a hydrocarbon solvent (i) at least one of an oil-soluble sulfonic acid or alkaline earth sulfonate salt or mixtures thereof; (ii) at least one source of an alkaline earth metal; (iii) at least one source of boron, and (iv) from 0 to less than 10 mole percent, relative to the source of boron, of an overbasing acid, other than the source of boron; and (b) heating the reaction product of (a) to a temperature above the distillation temperature of the hydrocarbon solvent to distill the hydrocarbon solvent and water from the reaction. Suitable borated alkaline earth metal sulfonates include those disclosed in, for example, U.S. Patent Application Publication No. 20070123437, the contents of which are incorporated by reference herein. Borated salicylates can be made in a similar fashion.

[0071] Preferably, at least a portion of the boron content of the lubricating oil composition is provided by a boron-containing dispersant additive, such as a major portion. In an embodiment of the invention, 100 wt.% of the boron in the lubricating oil composition, based on the weight of the boron in the lubricating oil composition, is provided by one or more boron-containing dispersant additives.

[0072] Alternatively or in addition, at least a portion of the boron content of the lubricating oil composition is provided by a borated detergent.

[0073] Additionally or alternatively, at least a portion of the boron content of the lubricating oil composition is provided by a borated glycerol ester.

[0074] In an embodiment of the invention, at least a portion of the boron content of the lubricating oil composition is provided by a boron-containing compound that is not a dispersant, such as a major portion.

[0075] Optionally, 100 wt.% of the boron in the lubricating oil composition, based on the weight of the boron in the lubricating oil composition is provided by one or more non-dispersant boron-containing compounds, such as a borated detergent and/or a borate ester. Optionally, from 20 wt.% to 100 wt.%, preferably from 40 wt.% to 80 wt.%, such as from 50 wt.% to 70 wt.%, of the boron in the lubricating oil composition, based on the weight of the boron in the lubricating oil composition, is provided by one or more borated detergent(s) and/or borated glycerol ester(s).

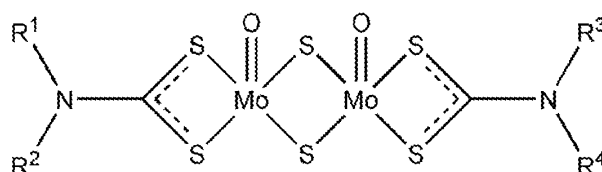
Organomolybdenum Compound

[0076] The lubricating oil composition comprises a molybdenum-containing compound in an amount of about 50 to about 500 ppm, for example, about 50 to about 450 ppm, about 50 to about 400 ppm, about 50 to about 350, or about 50 to about 300 ppm of molybdenum in terms of molybdenum content in the lubricating oil composition.

[0077] The lubricating oil compositions herein also may optionally contain one or more molybdenum-containing compounds. An oil-soluble molybdenum compound may have the functional performance of an antiwear agent, an antioxidant, a friction modifier, or mixtures thereof. An oil-soluble molybdenum compound may include molybdenum dithiocarbamates, , amine salts of molybdenum compounds, molybdenum xanthates, molybdenum thioxanthates, molybdenum sulfides, molybdenum carboxylates, molybdenum alkoxides, a trinuclear organo-molybdenum compound, molybdenum esters, molybdenum amides, and/or mixtures thereof. The molybdenum sulfides include molybdenum disulfide. The molybdenum disulfide may be

in the form of a stable dispersion. In one embodiment the oil-soluble molybdenum compound may be selected from the group consisting of molybdenum dithiocarbamates, molybdenum, amine salts of molybdenum compounds, and mixtures thereof. In one embodiment the oil-soluble molybdenum compound may be a molybdenum dithiocarbamate.

[0078] Molybdenum dithiocarbamate (MoDTC) is an organomolybdenum compound represented by the following structure:



wherein R^1 , R^2 , R^3 and R^4 are independently of each other, linear or branched alkyl groups having from 4 to 18 carbon atoms (e.g., 8 to 13 carbon atoms).

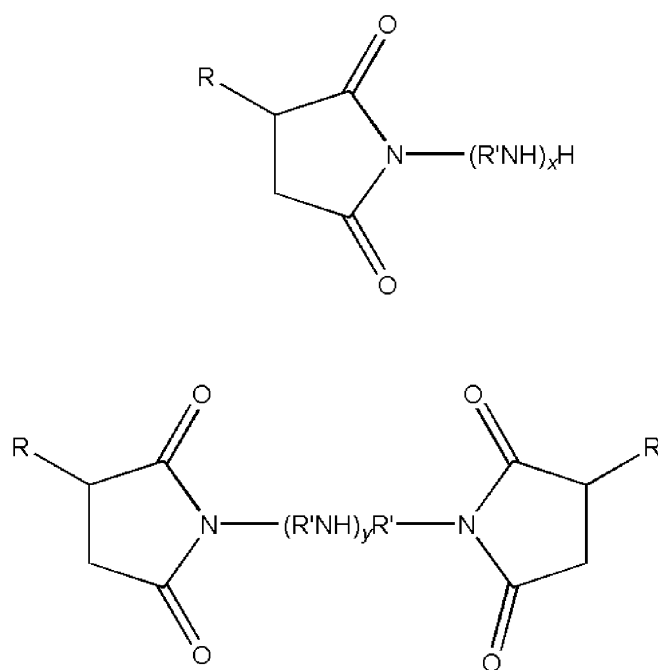
[0079] Suitable examples of molybdenum compounds which may be used include commercial materials sold under the trade names such as Molyvan 822™, Molyvan™ A, Molyvan 2000™ and Molyvan 855™ from R. T. Vanderbilt Co., Ltd., and Sakura-Lube™ S-165, S-200, S-300, S-310G, S-525, S-600, S-700, and S-710 available from Adeka Corporation, and mixtures thereof. Suitable molybdenum components are described in U.S. Pat. No. 5,650,381; US RE 37,363 E1; US RE 38,929 E1; and US RE 40,595 E1, incorporated herein by reference in their entireties.

[0080] Additionally, the molybdenum compound may be an acidic molybdenum compound. Included are molybdic acid, ammonium molybdate, sodium molybdate, potassium molybdate, and other alkaline metal molybdates and other molybdenum salts, e.g., hydrogen sodium molybdate, $MoOCl_4$, MoO_2Br_2 , $Mo_2O_3Cl_6$, molybdenum trioxide or similar acidic molybdenum compounds. Alternatively, the compositions can be provided with molybdenum by molybdenum/sulfur complexes of basic nitrogen compounds as described, for example, in U.S. Pat. Nos. 4,263,152; 4,285,822; 4,283,295; 4,272,387; 4,265,773; 4,261,843; 4,259,195 and 4,259,194; and US Patent Publication No. 2002/0038525, incorporated herein by reference in their entireties.

[0081] Another class of suitable organo-molybdenum compounds are trinuclear molybdenum compounds, such as those of the formula $Mo_3S_nL_mQ_z$ and mixtures thereof,

wherein S represents sulfur, L represents independently selected ligands having organo groups with a sufficient number of carbon atoms to render the compound soluble or dispersible in the oil, n is from 1 to 4, k varies from 4 through 7, Q is selected from the group of neutral electron donating compounds such as water, amines, alcohols, and ethers, and z ranges from 0 to 5 and includes non-stoichiometric values. At least 21 total carbon atoms may be present among all the ligands' organo groups, such as at least 25, at least 30, or at least 35 carbon atoms. Additional suitable molybdenum compounds are described in U.S. Pat. No. 6,723,685, herein incorporated by reference in its entirety.

[0082] In one embodiment, the molybdenum amine is a molybdenum-succinimide complex. Suitable molybdenum-succinimide complexes are described, for example, in U.S. Patent No. 8,076,275. These complexes are prepared by a process comprising reacting an acidic molybdenum compound with an alkyl or alkenyl succinimide of a polyamine of structures below or mixtures thereof:



wherein R is a C_{24} to C_{350} (e.g., C_{70} to C_{128}) alkyl or alkenyl group; R' is a straight or branched-chain alkylene group having 2 to 3 carbon atoms; x is 1 to 11; and y is 1 to 10.

[0083] The molybdenum compounds used to prepare the molybdenum-succinimide complex are acidic molybdenum compounds or salts of acidic molybdenum compounds. By “acidic” is meant that the molybdenum compounds will react with a basic nitrogen compound as measured by ASTM D664 or D2896. Generally, the acidic molybdenum compounds are hexavalent. Representative examples of suitable molybdenum compounds include molybdenum trioxide, molybdic acid, ammonium molybdate, sodium molybdate, potassium molybdate and other alkaline metal molybdates and other molybdenum salts such as hydrogen salts, (e.g., hydrogen sodium molybdate), MoOCl_4 , MoO_2Br_2 , $\text{Mo}_2\text{O}_3\text{Cl}_6$, and the like.

[0084] The succinimides that can be used to prepare the molybdenum-succinimide complex are disclosed in numerous references and are well known in the art. Certain fundamental types of succinimides and the related materials encompassed by the term of art “succinimide” are taught in U.S. Patent Nos. 3,172,892; 3,219,666; and 3,272,746. The term “succinimide” is understood in the art to include many of the amide, imide, and amidine species which may also be formed. The predominant product however is a succinimide and this term has been generally accepted as meaning the product of a reaction of an alkyl or alkenyl substituted succinic acid or anhydride with a nitrogen-containing compound. Preferred succinimides are those prepared by reacting a polyisobutenyl succinic anhydride of about 70 to 128 carbon atoms with a polyalkylene polyamine selected from triethylenetetramine, tetraethylenepentamine, and mixtures thereof.

[0085] The molybdenum-succinimide complex may be post-treated with a sulfur source at a suitable pressure and a temperature not to exceed 120°C to provide a sulfurized molybdenum-succinimide complex. The sulfurization step may be carried out for a period of from about 0.5 to 5 hours (e.g., 0.5 to 2 hours). Suitable sources of sulfur include elemental sulfur, hydrogen sulfide, organic polysulfides of formula R_2S_x where R is hydrocarbyl (e.g., C_1 to C_{10} alkyl) and x is at least 3, C_1 to C_{10} mercaptans, inorganic sulfides and polysulfides, thioacetamide, and thiourea.

Additional Lubricating Oil Additives

[0086] The lubricating oil compositions of the present disclosure may also contain other conventional additives that can impart or improve any desirable property of the lubricating oil composition in which these additives are dispersed or dissolved. Any additive known to a person of ordinary skill in the art may be used in the lubricating oil compositions disclosed herein. Some suitable additives have been described in Mortier et al., “Chemistry and

Technology of Lubricants”, 2nd Edition, London, Springer, (1996); and Leslie R. Rudnick, “Lubricant Additives: Chemistry and Applications”, New York, Marcel Dekker (2003), both of which are incorporated herein by reference. For example, the lubricating oil compositions can be blended with antioxidants, rust inhibitors, dehazing agents, demulsifying agents, metal deactivating agents, friction modifiers, pour point depressants, antifoaming agents, co-solvents, corrosion-inhibitors, ashless dispersants, multifunctional agents, dyes, extreme pressure agents and the like and mixtures thereof. A variety of the additives are known and commercially available. These additives, or their analogous compounds, can be employed for the preparation of the lubricating oil compositions of the disclosure by the usual blending procedures.

[0087] Dispersants maintain in suspension materials resulting from oxidation during engine operation that are insoluble in oil, thus preventing sludge flocculation and precipitation or deposition on metal parts. Dispersants useful herein include nitrogen-containing, ashless (metal-free) dispersants known to be effective to reduce formation of deposits upon use in gasoline and diesel engines.

[0088] Suitable dispersants include hydrocarbyl succinimides, hydrocarbyl succinamides, mixed ester/amides of hydrocarbyl-substituted succinic acid, hydroxyesters of hydrocarbyl-substituted succinic acid, and Mannich condensation products of hydrocarbyl-substituted phenols, formaldehyde and polyamines. Also suitable are condensation products of polyamines and hydrocarbyl-substituted phenyl acids. Mixtures of these dispersants can also be used.

[0089] Basic nitrogen-containing ashless dispersants are well-known lubricating oil additives and methods for their preparation are extensively described in the patent literature. Preferred dispersants are the alkenyl succinimides and succinimides where the alkenyl-substituent is a long-chain of preferably greater than 40 carbon atoms. These materials are readily made by reacting a hydrocarbyl-substituted dicarboxylic acid material with a molecule containing amine functionality. Examples of suitable amines are polyamines such as polyalkylene polyamines, hydroxy-substituted polyamines and polyoxyalkylene polyamines.

[0090] Particularly preferred ashless dispersants are the polyisobutenyl succinimides formed from polyisobutenyl succinic anhydride and a polyalkylene polyamine such as a polyethylene polyamine of formula:



wherein z is 1 to 11. The polyisobutenyl group is derived from polyisobutene and preferably has a number average molecular weight (M_n) in a range of 700 to 3000 Daltons (e.g., 900 to

2500 Daltons). For example, the polyisobutenyl succinimide may be a bis-succinimide derived from a polyisobutenyl group having a M_n of 900 to 2500 Daltons.

[0091] As is known in the art, the dispersants may be post-treated (e.g., with a boronating agent or a cyclic carbonate).

[0092] Nitrogen-containing ashless (metal-free) dispersants are basic, and contribute to the TBN of a lubricating oil composition to which they are added, without introducing additional sulfated ash.

[0093] Dispersants may be present at 0.1 to 10 wt. % (e.g., 2 to 5 wt. %) of the lubricating oil composition.

[0094] The lubricating oil composition of the present disclosure can contain one or more antioxidants that can reduce or prevent the oxidation of the base oil. Any antioxidant known by a person of ordinary skill in the art may be used in the lubricating oil composition. Non-limiting examples of suitable antioxidants include amine-based antioxidants (e.g., alkyl diphenylamines such as bis-nonylated diphenylamine, bis-octylated diphenylamine, and octylated/butylated diphenylamine, phenyl- α -naphthylamine, alkyl or arylalkyl substituted phenyl- α -naphthylamine, alkylated p-phenylene diamines, tetramethyl-diaminodiphenylamine and the like), phenolic antioxidants (e.g., 2-tert-butylphenol, 4-methyl-2,6-di-tert-butylphenol, 2,4,6-tri-tert-butylphenol, 2,6-di-tert-butyl-p-cresol, 2,6-di-tert-butylphenol, 4,4'-methylenebis-(2,6-di-tert-butylphenol), 4,4'-thiobis(6-di-tert-butyl-o-cresol) and the like), sulfur-based antioxidants (e.g., dilauryl-3,3'-thiodipropionate, sulfurized phenolic antioxidants and the like), phosphorous-based antioxidants (e.g., phosphites and the like), and combinations thereof. The amount of the antioxidant may vary from about 0.01 wt. % to about 10 wt. %, from about 0.05 wt. % to about 5 wt. %, or from about 0.1 wt. % to about 3 wt. %, based on the total weight of the lubricating oil composition.

[0095] The lubricating oil composition of the present disclosure can contain one or more friction modifiers that can lower the friction between moving parts. Any friction modifier known by a person of ordinary skill in the art may be used in the lubricating oil composition. Non-limiting examples of suitable friction modifiers include fatty carboxylic acids; derivatives (e.g., alcohol, esters, borated esters, amides, metal salts and the like) of fatty carboxylic acid; mono-, di- or tri-alkyl substituted phosphoric acids or phosphonic acids; derivatives (e.g., esters, amides, metal salts and the like) of mono-, di- or tri-alkyl substituted phosphoric acids or phosphonic acids; mono-, di- or tri-alkyl substituted amines; mono- or di-alkyl substituted amides and combinations thereof. In some embodiments examples of friction modifiers

include, but are not limited to, alkoxyated fatty amines; borated fatty epoxides; fatty epoxides, fatty amines, borated alkoxyated fatty amines, metal salts of fatty acids, fatty acid amides, glycerol esters, borated glycerol esters; and fatty imidazolines as disclosed in U.S. Patent No. 6,372,696, the contents of which are incorporated by reference herein; friction modifiers obtained from a reaction product of a C₄ to C₇₅, or a C₆ to C₂₄, or a C₆ to C₂₀, fatty acid ester and a nitrogen-containing compound selected from the group consisting of ammonia, and an alkanolamine and the like and mixtures thereof. The amount of the friction modifier may vary from about 0.01 wt. % to about 10 wt. %, from about 0.05 wt. % to about 5 wt. %, or from about 0.1 wt. % to about 3 wt. %, based on the total weight of the lubricating oil composition.

[0096] The lubricating oil composition of the present disclosure can contain one or more foam inhibitors or anti-foam inhibitors that can break up foams in oils. Any foam inhibitor or anti-foam known by a person of ordinary skill in the art may be used in the lubricating oil composition. Non-limiting examples of suitable foam inhibitors or anti-foam inhibitors include silicone oils or polydimethylsiloxanes, fluorosilicones, alkoxyated aliphatic acids, polyethers (e.g., polyethylene glycols), branched polyvinyl ethers, alkyl acrylate polymers, alkyl methacrylate polymers, polyalkoxyamines and combinations thereof. In some embodiments, the foam inhibitors or anti-foam inhibitors comprises glycerol monostearate, polyglycol palmitate, an ester of sulfonated ricinoleic acid, benzoylacetone, methyl salicylate, glycerol monooleate, or glycerol dioleate. The amount of the foam inhibitors or anti-foam inhibitors may vary from about 0.001 wt. % to about 5 wt. %, from about 0.05 wt. % to about 3 wt. %, or from about 0.1 wt. % to about 1 wt. %, based on the total weight of the lubricating oil composition.

[0097] The lubricating oil composition of the present disclosure can contain one or more pour point depressants that can lower the pour point of the lubricating oil composition. Any pour point depressant known by a person of ordinary skill in the art may be used in the lubricating oil composition. Non-limiting examples of suitable pour point depressants include polymethacrylates, alkyl acrylate polymers, alkyl methacrylate polymers, di(tetra-paraffin phenol)phthalate, condensates of tetra-paraffin phenol, condensates of a chlorinated paraffin with naphthalene and combinations thereof. In some embodiments, the pour point depressant comprises an ethylene-vinyl acetate copolymer, a condensate of chlorinated paraffin and phenol, polyalkyl styrene or the like. The amount of the pour point depressant may vary from about 0.01 wt. % to about 10 wt. %, from about 0.05 wt. % to about 5 wt. %, or from about 0.1 wt. % to about 3 wt. %, based on the total weight of the lubricating oil composition.

[0098] In one embodiment, the lubricating oil composition of the present disclosure does not contain one or more demulsifiers. In another embodiment, the lubricating oil composition of the present disclosure can contain one or more demulsifiers that can promote oil-water separation in lubricating oil compositions that are exposed to water or steam. Any demulsifier known by a person of ordinary skill in the art may be used in the lubricating oil composition. Non-limiting examples of suitable demulsifiers include anionic surfactants (e.g., alkyl-naphthalene sulfonates, alkyl benzene sulfonates and the like), nonionic alkoxylated alkyl phenol resins, polymers of alkylene oxides (e.g., polyethylene oxide, polypropylene oxide, block copolymers of ethylene oxide, propylene oxide and the like), esters of oil soluble acids, polyoxyethylene sorbitan ester and combinations thereof. The amount of the demulsifier may vary from about 0.01 wt. % to about 10 wt. %, from about 0.05 wt. % to about 5 wt. %, or from about 0.1 wt. % to about 3 wt. %, based on the total weight of the lubricating oil composition.

[0099] The lubricating oil composition of the present disclosure can contain one or more corrosion inhibitors that can reduce corrosion. Any corrosion inhibitor known by a person of ordinary skill in the art may be used in the lubricating oil composition. Non-limiting examples of suitable corrosion inhibitor include half esters or amides of dodecylsuccinic acid, alkyl imidazolines, sarcosines and combinations thereof. The amount of the corrosion inhibitor may vary from about 0.01 wt. % to about 5 wt. %, from about 0.05 wt. % to about 3 wt. %, or from about 0.1 wt. % to about 1 wt. %, based on the total weight of the lubricating oil composition.

[00100] The lubricating oil composition of the present disclosure can contain one or more extreme pressure (EP) agents that can prevent sliding metal surfaces from seizing under conditions of extreme pressure. Any extreme pressure agent known by a person of ordinary skill in the art may be used in the lubricating oil composition. Generally, the extreme pressure agent is a compound that can combine chemically with a metal to form a surface film that prevents the welding of asperities in opposing metal surfaces under high loads. Non-limiting examples of suitable extreme pressure agents include sulfurized animal or vegetable fats or oils, sulfurized animal or vegetable fatty acid esters, fully or partially esterified esters of trivalent or pentavalent acids of sulfurized olefins, dihydrocarbyl polysulfides, sulfurized Diels-Alder adducts, sulfurized dicyclopentadiene, sulfurized or co-sulfurized mixtures of fatty acid esters and monounsaturated olefins, co-sulfurized blends of fatty acid, fatty acid ester and alpha-olefin, functionally-substituted dihydrocarbyl polysulfides, thia-aldehydes, thia-ketones, epithio compounds, sulfur-containing acetal derivatives, co-sulfurized blends of terpene and

acyclic olefins, and polysulfide olefin products, and combinations thereof. The amount of the extreme pressure agent may vary from about 0.01 wt. % to about 5 wt. %, from about 0.05 wt. % to about 3 wt. %, or from about 0.1 wt. % to about 1 wt. %, based on the total weight of the lubricating oil composition.

[00101] The lubricating oil composition of the present disclosure can contain one or more rust inhibitors that can inhibit the corrosion of ferrous metal surfaces. Any rust inhibitor known by a person of ordinary skill in the art may be used in the lubricating oil composition. Non-limiting examples of suitable rust inhibitors include nonionic polyoxyalkylene agents, e.g., polyoxyethylene lauryl ether, polyoxyethylene higher alcohol ether, polyoxyethylene nonylphenyl ether, polyoxyethylene octylphenyl ether, polyoxyethylene octyl stearyl ether, polyoxyethylene oleyl ether, polyoxyethylene sorbitol monostearate, polyoxyethylene sorbitol monooleate, and polyethylene glycol monooleate; stearic acid and other fatty acids; dicarboxylic acids; metal soaps; fatty acid amine salts; metal salts of heavy sulfonic acid; partial carboxylic acid ester of polyhydric alcohol; (short-chain) alkenyl succinic acids; partial esters thereof and nitrogen-containing derivatives thereof; synthetic alkarylsulfonates, e.g., metal dinonylnaphthalene sulfonates; and the like and mixtures thereof. The amount of the rust inhibitor may vary from about 0.01 wt. % to about 10 wt. %, from about 0.05 wt. % to about 5 wt. %, or from about 0.1 wt. % to about 3 wt. %, based on the total weight of the lubricating oil composition.

[00102] The lubricating oil composition of the present disclosure can contain one or more viscosity index improvers. Non-limiting examples of suitable viscosity index improvers include, but are not limited to, olefin copolymers, such as ethylene-propylene copolymers, styrene-isoprene copolymers, hydrated styrene-isoprene copolymers, polybutene, polyisobutylene, polymethacrylates, vinylpyrrolidone and methacrylate copolymers and dispersant type viscosity index improvers. These viscosity modifiers can optionally be grafted with grafting materials such as, for example, maleic anhydride, and the grafted material can be reacted with, for example, amines, amides, nitrogen-containing heterocyclic compounds or alcohol, to form multifunctional viscosity modifiers (dispersant-viscosity modifiers). Other examples of viscosity modifiers include star polymers (e.g., a star polymer comprising isoprene/styrene/isoprene triblock). Yet other examples of viscosity modifiers include poly alkyl(meth)acrylates of low Brookfield viscosity and high shear stability, functionalized poly alkyl(meth)acrylates with dispersant properties of high Brookfield viscosity and high shear stability, polyisobutylene having a weight average molecular weight ranging from 700 to 2,500

Daltons and mixtures thereof. The amount of the viscosity index improvers may vary from about 0.01 wt. % to about 25 wt. %, from about 0.05 wt. % to about 20 wt. %, or from about 0.3 wt. % to about 15 wt. %, based on the total weight of the lubricating oil composition.

[00103] The lubricating oil composition of the present disclosure can contain one or more metal deactivators. Non-limiting examples of suitable metal deactivators include disalicylidene propylenediamine, triazole derivatives, thiadiazole derivatives, and mercaptobenzimidazoles.

[00104] In the preparation of lubricating oil formulations, it is common practice to introduce the additives in the form of 10 to 80 wt. % active ingredient concentrates in hydrocarbon oil, e.g. mineral lubricating oil, or other suitable solvent.

[00105] Usually these concentrates may be diluted with 3 to 100, e.g., 5 to 40, parts by weight of lubricating oil per part by weight of the additive package in forming finished lubricants, e.g. crankcase motor oils. The purpose of concentrates, of course, is to make the handling of the various materials less difficult and awkward as well as to facilitate solution or dispersion in the final blend.

[00106] Each of the foregoing additives, when used, is used at a functionally effective amount to impart the desired properties to the lubricant. Thus, for example, if an additive is a friction modifier, a functionally effective amount of this friction modifier would be an amount sufficient to impart the desired friction modifying characteristics to the lubricant.

[00107] In general, the concentration of each of the additives in the lubricating oil composition, when used, may range from about 0.001 wt. % to about 20 wt. %, from about 0.01 wt. % to about 15 wt. %, or from about 0.1 wt. % to about 10 wt. %, from about 0.005 wt.% to about 5 wt.%, or from about 0.1 wt.% to about 2.5 wt.%, based on the total weight of the lubricating oil composition. Further, the total amount of the additives in the lubricating oil composition may range from about 0.001 wt.% to about 20 wt.%, from about 0.01 wt.% to about 10 wt.%, or from about 0.1 wt.% to about 5 wt.%, based on the total weight of the lubricating oil composition.

[00108] The following examples are presented to exemplify embodiments of the disclosure but are not intended to limit the disclosure to the specific embodiments set forth. Unless indicated to the contrary, all parts and percentages are by weight. All numerical values are approximate. When numerical ranges are given, it should be understood that embodiments outside the stated ranges may still fall within the scope of the disclosure. Specific details described in each example should not be construed as necessary features of the disclosure.

[00109] It will be understood that various modifications may be made to the embodiments disclosed herein. Therefore, the above description should not be construed as limiting, but merely as exemplifications of preferred embodiments. For example, the functions described above and implemented as the best mode for operating the present disclosure are for illustration purposes only. Other arrangements and methods may be implemented by those skilled in the art without departing from the scope and spirit of this disclosure. Moreover, those skilled in the art will envision other modifications within the scope and spirit of the claims appended hereto.

EXAMPLES

[00110] The following examples are intended for illustrative purposes only and do not limit in any way the scope of the present disclosure.

The lubricating oil examples were prepared by blending a major amount of a Group III base oil of lubricating viscosity and a combination of the following additives, to provide a finished oil having a 0W-16 viscosity grade:

a mixture of borated and ethylene carbonate post-treated succinimide dispersant; a primary alkyl ZnDTP, a secondary alkyl ZnDTP, or both; a borated organic friction modifier; a molybdenum succinimide compound; a diphenylamine antioxidant;

one or more of an overbased calcium sulfonate detergent (TBN=410 mg KOH/g, Ca content=15.5 wt%), an overbased calcium phenate detergent (TBN=260 mg KOH/g, Ca content=9.6 wt%), an overbased calcium salicylate detergent (TBN=350 mg KOH/g, Ca content=12.5 wt%), and an overbased magnesium sulfonate detergent (TBN=400 mg KOH/g, Mg content=9.5 wt%);

and a minor amount of silicon-based foam inhibitor, pour point depressant, and olefin copolymer type viscosity modifier.

Ball Rust Test (BRT) - ASTM D6557

[00111] The Ball Rust Test (BRT) was conducted using ASTM-D-6557. BRT evaluates anti-corrosion ability of fluid lubricants. In accordance with ASTM D6557, a ball bearing was immersed in oil. Air saturated with acidic contaminants was bubbled through the oil for 18 hours at 49° C. After the 18-hour reaction period, the ball was removed from the test oil.

Degree of corrosion on the ball was quantified as reflected light using a light reflectance technique, wherein the reflected light is reported as an average gray value (AGV).

[00112] AGV for fresh un-corroded ball is approximately 140. AGV of fully corroded ball is typically less than 20. A lubricating oil composition which gives an AGV of at least 100 passes the BRT. A lubricating oil composition which gives an AGV of less than 100 fails the BRT. Obtained results of the BRT are summarized in Tables 2-4.

[00113] Table 2 indicates that the presence of ZnDTP is detrimental to BRT performance. In particular, comparative examples 1-5 which contain varying levels and types of ZnDTP all failed the BRT.

Table 2 – Effect of ZnDTP on BRT

	Example 1	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5
Ca content (ppm)	790	800	810	820	810	820
Ca detergent type	Sulfonate + phenate	Sulfonate + phenate	Sulfonate + phenate	Sulfonate + phenate	Sulfonate + phenate	Sulfonate + phenate
Mg content (ppm)	320	330	340	330	350	330
Total detergent (mmol/kg)	34	34	34	34	34	34
Phos. Content from ZnDTP (ppm)	0	390	170	100	360	360
ZnDTP alkyl group type	None	Primary + secondary	Primary + secondary	Primary + secondary	Primary only	Secondary only
Boron content (ppm)	110	110	110	110	100	100
Moly content (ppm)	190	180	180	180	180	180
Sulfated ash (wt%)	0.45	0.53	0.48	0.46	0.51	0.51
TBN (mg KOH/g)	6.1	6.0	6.2	6.2	6.4	6.2
BRT Rating	115	36	47	62	36	35
BRT Pass/Fail	Pass	Fail	Fail	Fail	Fail	Fail

Table 3 – Effect of Detergent on BRT

	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9	Comp. Ex. 6	Comp. Ex. 7
Ca content (ppm)	800	1330	820	620	610	0	850	820	610	1400
Ca detergent type	Salicylate only	Sulfonate + phenate	Sulfonate + phenate	Sulfonate + phenate	Sulfonate + phenate	None	Sulfonate + phenate	Sulfonate + phenate	Sulfonate + phenate	Sulfonate only
Mg Content (ppm)	330	350	970	340	220	810	230	50	100	0

Total detergent (mmol/kg)	34	46.5	61	29	24	34	29	22	19	34
Phos. Content from ZnDTP (ppm)	0	0	0	0	0	0	0	0	0	0
ZnDTP alkyl group type	None	None	None	None	None	None	None	None	None	None
Boron content (ppm)	100	110	110	100	110	90	100	100	110	100
Moly content (ppm)	180	180	180	180	180	180	190	180	180	180
Sulfated ash (wt%)	0.45	0.61	0.77	0.34	0.31	0.42	0.39	0.34	0.25	0.48
TBN (mg KOH/g)	6.4	7.5	9.1	5.7	5.1	6.3	5.9	5.2	4.2	6.2
BRT Rating	123	124	128	116	120	106	114	101	68	84
BRT Pass/Fail	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Fail	Fail

Table 4 – Effect of B/Mo on BRT

	Example 10	Example 11	Example 12	Comparative Example 8	Comparative Example 9	Comparative Example 10
Ca content (ppm)	810	810	820	820	820	830
Ca detergent type	Sulfonate + phenate	Sulfonate + phenate	Sulfonate + phenate	Sulfonate + phenate	Sulfonate + phenate	Sulfonate + phenate
Mg content (ppm)	330	330	330	330	340	330
Total detergent (mmol/kg)	34	34	34	34	34	34
Phos. Content from ZnDTP (ppm)	0	0	0	0	0	0
ZnDTP alkyl group type	None	None	None	None	None	None
Boron content (ppm)	300	110	100	0	40	70
Moly content (ppm)	180	60	500	180	180	180
Sulfated ash (wt%)	0.44	0.43	0.47	0.45	0.45	0.39
TBN (mg KOH/g)	7.5	6.1	6.5	5.9	6.1	5.8
BRT Rating	107	125	125	79	73	82
BRT Pass/Fail	Pass	Pass	Pass	Fail	Fail	Fail

Mg detergent (either alone or in combination with various Ca detergents) was shown to improve BRT performance. Ca detergent used alone in the absence of Mg was insufficient to give a passing BRT rating (comparative example 7). Furthermore, it was found that a minimum amount of detergent was necessary to achieve a passing rating as demonstrated by comparative example 6 (Table 3).

Table 4 shows the effect of boron and molybdenum on the BRT performance. While it was found that boron concentration has an effect on the BRT rating, the concentration of molybdenum did not exhibit an effect on the BRT.

WHAT IS CLAIMED IS:

1. A low ash lubricating oil composition comprising:
 - a major amount of an oil of lubricating viscosity;
 - a detergent system comprising one or more magnesium-containing detergent and optionally, one or more calcium-containing detergent; and
 - a boron-containing additive in an amount to provide at least 100 ppm of boron to the lubricating oil composition;wherein the lubricating oil composition is free of zinc and phosphorus; the total sulfated ash content of the lubricating oil composition is from 0.30 wt.% to 0.80 wt.%, and the total base number of the lubricating oil composition is from 4.0 to 9.5 mg KOH/g.
2. The lubricating oil composition of claim 1, wherein the composition contains at least 20 mmol/kg of calcium and/or magnesium detergent.
3. The lubricating oil composition of claim 1, wherein the one or more overbased detergents individually have a total base number of greater than 250 mg KOH/g.
4. The lubricating oil composition of claim 1, wherein the detergent system provides up to 1300 ppm of calcium to the lubricating oil composition.
5. The lubricating oil composition of claim 1, wherein the one or more magnesium-containing detergents is present in an amount to provide 50 to 1000 ppm of magnesium to the lubricating oil composition.
6. The lubricating oil composition of claim 1, further comprising:
 - antioxidant, foam inhibitor, viscosity modifier, pour point depressant, dispersant, extreme pressure agent, or metal deactivator.
7. The lubricating oil composition of claim 1, wherein the oil of lubricating viscosity is a Group III base oil.

8. The lubricating oil composition of claim 1, wherein the magnesium-containing detergent is a sulfonate or a salicylate.
9. The lubricating oil composition of claim 1, wherein the calcium-containing detergent is a sulfonate or a salicylate.
10. A method for reducing corrosion in an engine, the method comprising providing a lubricating oil composition to the engine, wherein the lubricating oil composition comprises:
- a major amount of an oil of lubricating viscosity;
 - a detergent system comprising one or more calcium overbased detergents and one or more overbased magnesium-containing detergents;
 - zinc dithiophosphate in an amount to provide a phosphorus content from 0 to 300 ppm to the lubricating oil composition;
 - boron-containing additive in an amount to provide less than 300 ppm of boron to the lubricating oil composition; and
 - molybdenum compound in an amount to provide from 50 to 500 ppm of molybdenum to the lubricating oil composition;
- wherein the lubricating oil composition has a calcium content of up to about 1300 ppm based on a total weight of the lubricating composition, and where the total sulfated ash content of the lubricating oil composition is from 0.40 wt.% to 0.80 wt.% and the total base number of the lubricating oil composition is from 4.0 to 9.0 mg KOH/g.
11. The method of claim 10, wherein the lubricating oil composition contains at least 20 mmol/kg of calcium and/or magnesium detergent.
12. The method of claim 10, wherein the one or more overbased detergents individually have a total base number of greater than 250 mg KOH/g.
13. The method of claim 10, wherein the detergent system provides up to 1300 ppm of calcium to the lubricating oil composition.

14. The method of claim 10, wherein the one or more magnesium-containing detergents is present in an amount to provide 50 to 1000 ppm of magnesium to the lubricating oil composition.
15. The method of claim 10, wherein the lubricating oil composition further comprises:
antioxidant, foam inhibitor, viscosity modifier, pour point depressant, dispersant, extreme pressure agent, or metal deactivator.
16. The method of claim 10, wherein the oil of lubricating viscosity is a Group III base oil.
17. The method of claim 10, wherein the magnesium-containing detergent is a sulfonate or a salicylate.
18. The method of claim 10, wherein the calcium-containing detergent is a sulfonate or a salicylate.