(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
11 May 2023 (11.05.2023)

WIPO | PCT

(10) International Publication Number
WO 2023/079475 A1

(51) International Patent Classification:
C10M 141/08 (2006.01)

(21) International Application Number:
PCT/IB2022/060589

(22) International Filing Date:
03 November 2022 (03.11.2022)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
63/275,074 03 November 2021 (03.11.2021) US

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CV, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, CV, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, ME, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:
— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

Published:
— *with international search report (Art. 21(3))*
— *in black and white; the international application as filed contained color or greyscale and is available for download from PATENTSCOPE*

(54) Title: LUBRICATING OIL COMPOSITIONS

(57) Abstract: The present application pertains to functional fluids or EV fluids. The functional fluids may comprise a major amount of an oil of lubricating viscosity, at least one overbased sulfonate detergent, and an anti-fatigue additive. The functional fluids or EV fluids provide surprising and unexpected fatigue properties.

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LUBRICATING OIL COMPOSITIONS

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FIELD OF THE DISCLOSURE

[0001] The present disclosure relates to lubricating oil compositions that provide enhanced protection against fatigue.

BACKGROUND

[0002] Modern lubricating oil formulations are formulated to exacting specifications often set by original equipment manufacturers. To meet such specifications, various additives are used, together with base oil of lubricating viscosity. Depending on the application, a typical lubricating oil composition may contain dispersants, detergents, antioxidants, wear inhibitors, rust inhibitors, corrosion inhibitors, foam inhibitors, and friction modifiers just to name a few.

[0003] Different applications will govern the type of additives that will go into a lubricating oil composition. For example, lubricants for conventional on-road automobiles are often required to meet certain anti-wear specifications but typically do not have similar requirements for anti-fatigue performance. However, other lubricating oil compositions may benefit from enhanced anti-fatigue properties. These include, for example, functional fluids and electric vehicle (EV) fluids which are used in strenuous load bearing environments. In such environments, metal surfaces are particularly susceptible to pitting or formation of cavities which is caused by repeated loading and contact stresses exceeding surface fatigue strength of the material.

[0004] A functional fluid is a term which encompasses a variety of fluids including but not limited to tractor hydraulic fluids, power transmission fluids including automatic transmission fluids (ATF), traction fluids, continuously variable transmission (CVT) fluids and manual transmission fluids, hydraulic fluids, including tractor hydraulic fluids, gear oils, power steering fluids, fluids used in wind turbines and fluids related to power train components. It

should be noted that within each of these fluids such as, for example, automatic transmission fluids, there are a variety of different types of fluids due to the various transmissions having different designs which have led to the need for fluids of markedly different functional characteristics.

[0005] With respect to tractor hydraulic fluids, these fluids are all-purpose products used for all lubricant applications in a tractor except for lubricating the engine. So-called Super Tractor Oil Universal fluids or "STOU" fluids also lubricate the engine. These lubricating applications may include lubrication of gearboxes, power take-off and clutch(es), rear axles, reduction gears, wet brakes, and hydraulic accessories. The components included within a tractor fluid must be carefully chosen so that the final resulting fluid composition will provide all the necessary characteristics required in the different applications. Such characteristics may include the ability to provide proper frictional properties for preventing wet brake chatter of oil immersed brakes while simultaneously providing the ability to actuate wet brakes and provide power take-off (PTO) clutch performance. A tractor fluid must provide sufficient anti-wear, anti-fatigue, and extreme pressure properties as well as water tolerance/filterability capabilities. As an example, existing approaches to tractor fluid formulating generally employ high levels of sulfur-containing phenates to provide adequate antifatigue properties to the fluid.

[0006] It is now recognized that what is needed are lubricating oil compositions with reduced levels of sulfur-containing phenates. It would also be desirable if such compositions could be used in functional fluids (e.g., construction machinery), electric vehicles, hybrid vehicles (including plug-in hybrids), and the like, while maintaining acceptable limits of fatigue protection of bearings and/or passing severe fatigue specification requirements. Advantageously, the compositions described in the present application meet one or more of the aforementioned needs and more.

SUMMARY OF THE INVENTION

[0007] In particular, the present application relates to a lubricant additive ("anti-fatigue additive") composition that is characterized by enhanced anti-fatigue properties. In some embodiments, the anti-fatigue additive imparts enhanced anti-fatigue properties to a lubricating oil composition such as those described herein. In some embodiments, the lubricating oil composition includes relatively low levels of sulfur-containing compounds that are typically used to provide anti-fatigue properties. These sulfur-containing compounds include sulfurized high overbased phenates and zinc dithiophosphates.

[0008] More specifically, the application relates to lubricating oil compositions comprising 0.001% to 1.5% of an anti-fatigue additive and sulfonate detergent. In some embodiments, the lubricating oil composition comprises low levels of metal sulfur containing phenates (e.g., about 40 mmol or less of metal from the metal sulfurized phenates, such as 35 mmol or less, 30 mmol or less, 25 mmol or less, 20 mmol or less, 10 mmol or less, and 0 mmol) to provide improved fatigue protection and performance. The lubricating oil compositions exhibit improved fatigue performance even with low levels of sulfur containing additives by the addition of glycerol. The compositions described herein often lead to a reduction in material fatigue. The compositions also may achieve a reduction in the formation surface fatigue, micro-pitting or sub-surface fatigue, and/or pitting of bearings.

[0009] In one embodiment, the application pertains to a functional fluid or EV fluid comprising (a) a major amount of an oil of lubricating viscosity; (b) anti-fatigue additive comprising alkyl polyol comprising 2 to 20 carbon atoms or derivative thereof and (c) at least one high overbased sulfonate detergent and at least one non-sulfonate detergent. In another embodiment, the amount of anti-fatigue additive is from about 0.001 wt. % to about 1.5 wt. % based on the total weight of the functional fluid or EV fluid. In another embodiment, the anti-fatigue additive is added in an amount that increases the fatigue time of the functional fluid or EV fluid over a

comparable fluid without anti-fatigue additive thereof as determined by the ZF bearing pitting test. In another embodiment, the functional or EV fluids may be employed in methods of increasing the fatigue time of a bearing comprising contacting a metal surface with a functional fluid or EV fluid.

[0010] In an embodiment, the application pertains to hybrid vehicle fluid or plug-in hybrid vehicle fluid comprising (a) a major amount of an oil of lubricating viscosity; (b) anti-fatigue additive comprising alkyl polyol comprising 2 to 20 carbon atoms or derivative thereof and (c) at least one high overbased sulfonate detergent and at least one non-sulfonate detergent. In another embodiment, the amount of anti-fatigue additive is from about 0.001 wt. % to about 1.5 wt. % based on the total weight of the hybrid vehicle fluid or plug-in hybrid vehicle fluid. In another embodiment, the anti-fatigue additive is added in an amount that increases the fatigue time of the hybrid vehicle fluid or plug-in hybrid vehicle fluid over a comparable fluid without anti-fatigue additive thereof as determined by the ZF bearing pitting test. In another embodiment, the hybrid vehicle fluid or plug-in hybrid fluid may be employed in methods of increasing the fatigue time of a bearing comprising contacting a metal surface with a hybrid vehicle fluid or plug-in hybrid vehicle fluid.

DETAILED DESCRIPTION

Definitions

[0011] The following terms will be used throughout the specification and will have the following meanings unless otherwise indicated.

[0012] The term “a major amount” of a base oil refers to where the amount of the base oil is at least 40 wt. % of the lubricating oil composition. In some embodiments, “a major amount” of a base oil refers to an amount of the base oil more than 50 wt. %, more than 60 wt. %, more than 70 wt. %, more than 80 wt. %, or more than 90 wt. % of the lubricating oil composition.

[0013] In the following description, all numbers disclosed herein are approximate values, regardless of whether the word "about" or "approximate" is used in connection therewith. They may vary by 1 percent, 2 percent, 5 percent, or, sometimes, 10 to 20 percent.

[0014] The term “construction machines” refers to off-road heavy-duty vehicles and off-road vehicles and/or machinery including but not limited to excavators, dozers, loaders, chip spreaders, pavers, compactors, and cranes.

[0015] “HOB” refers to high overbased with a TBN above 250 on an actives basis and “LOB” refers to low overbased with a TBN below 100 on an actives basis.

[0016] “TPP” refers to tetrapropenyl phenol or a salt thereof.

[0017] The term "Total Base Number" or "TBN" refers to the level of alkalinity in an oil sample, which indicates the ability of the composition to continue to neutralize corrosive acids, in accordance with ASTM Standard No. D2896 or equivalent procedure. The test measures the change in electrical conductivity, and the results are expressed as mgKOH/g (the equivalent number of milligrams of KOH needed to neutralize 1 gram of a product). Therefore, a high TBN reflects strongly overbased products and, as a result, a higher base reserve for neutralizing acids.

[0018] As used herein, an EV fluid refers to an electric drive fluid used in electric vehicles equipped with wet EV motors. Electric drive fluids are analogous to transmission fluids (used in conventional vehicles) but with, usually, one or more added functionalities (e.g., acting as a coolant for the EV motor, providing electrical resistivity, etc.). The one or more added functionalities can provide unique challenges to formulating EV fluids.

[0019] In some embodiments, the lubricating oil composition of the present invention may provide anti-fatigue benefits for hybrid vehicles (hybrid vehicle fluids) or plug-in hybrid vehicles (plug-in hybrid vehicle fluids) which are equipped with electric motors.

The Oil of Lubricating Viscosity

[0020] The lubricating oil compositions disclosed herein generally comprise at least one oil of lubricating viscosity. Any base oil known to a skilled artisan can be used as the oil of lubricating viscosity disclosed herein. Some base oils suitable for preparing the lubricating oil compositions have been described in Mortier et al., "Chemistry and Technology of Lubricants," 2nd Edition, London, Springer, Chapters 1 and 2 (1996); and A. Sequeria, Jr., "Lubricant Base Oil and Wax Processing," New York, Marcel Decker, Chapter 6, (1994); and D. V. Brock, Lubrication Engineering, Vol. 43, pages 184-5, (1987), all of which are incorporated herein by reference. Generally, the amount of the base oil in the lubricating oil composition may be from about 70 to about 99.5 wt. %, based on the total weight of the lubricating oil composition. In some embodiments, the amount of the base oil in the lubricating oil composition is from about 75 to about 99 wt. %, from about 80 to about 98.5 wt. %, or from about 80 to about 98 wt. %, based on the total weight of the lubricating oil composition.

[0021] In certain embodiments, the base oil is or comprises any natural or synthetic lubricating base oil fraction. Some non-limiting examples of synthetic oils include oils, such as polyalphaolefins or PAOs, prepared from the polymerization of at least one alpha-olefin, such as ethylene, or from hydrocarbon synthesis procedures using carbon monoxide and hydrogen gases, such as the Fisher-Tropsch process. In certain embodiments, the base oil comprises less than about 10 wt. % of one or more heavy fractions, based on the total weight of the base oil. A heavy fraction refers to a lube oil fraction having a viscosity of at least about 20 cSt at 100° C. In certain embodiments, the heavy fraction has a viscosity of at least about 25 cSt or at least about 30 cSt at 100° C. In further embodiments, the amount of the one or more heavy fractions in the base oil is less than about 10 wt. %, less than about 5 wt. %, less than about 2.5 wt. %, less than about 1 wt. %, or less than about 0.1 wt. %, based on the total weight of the base oil. In still further embodiments, the base oil comprises no heavy fraction.

[0022] In certain embodiments, the lubricating oil compositions comprise a major amount of a base oil of lubricating viscosity. In some embodiments, the base oil has a kinematic viscosity at 100° C. from about 2.5 centistokes (cSt) to about 20 cSt, from about 4 centistokes (cSt) to about 20 cSt, or from about 5 cSt to about 16 cSt. The kinematic viscosity of the base oils or the lubricating oil compositions disclosed herein can be measured according to ASTM D 445, which is incorporated herein by reference.

[0023] In other embodiments, the base oil is or comprises a base stock or blend of base stocks. In further embodiments, the base stocks are manufactured using a variety of different processes including, but not limited to, distillation, solvent refining, hydrogen processing, oligomerization, esterification, and rerefining. In some embodiments, the base stocks comprise a rerefined stock. In further embodiments, the rerefined stock shall be substantially free from materials introduced through manufacturing, contamination, or previous use.

[0024] In some embodiments, the base oil comprises one or more of the base stocks in one or more of Groups I-V as specified in the American Petroleum Institute (API) Publication 1509, Fourteen Edition, December 1996 (i.e., API Base Oil Interchangeability Guidelines for Passenger Car Motor Oils and Diesel Engine Oils), which is incorporated herein by reference. The API guideline defines a base stock as a lubricant component that may be manufactured using a variety of different processes. Groups I, II and III base stocks are mineral oils, each with specific ranges of the amount of saturates, sulfur content and viscosity index. Group IV base stocks are polyalphaolefins (PAO). Group V base stocks include all other base stocks not included in Group I, II, III, or IV.

[0025] In some embodiments, the base oil comprises one or more of the base stocks in Group I, II, III, IV, V or a combination thereof. In other embodiments, the base oil comprises one or more of the base stocks in Group II, III, IV or a combination thereof. In further embodiments, the base oil comprises one or more of the base stocks in Group II, III, IV or a combination

thereof wherein the base oil has a kinematic viscosity from about 2.5 centistokes (cSt) to about 20 cSt, from about 4 cSt to about 20 cSt, or from about 5 cSt to about 16 cSt at 100° C.

[0026] The base oil may be selected from the group consisting of natural oils of lubricating viscosity, synthetic oils of lubricating viscosity and mixtures thereof. In some embodiments, the base oil includes base stocks obtained by isomerization of synthetic wax and slack wax, as well as hydrocrackate base stocks produced by hydrocracking (rather than solvent extracting) the aromatic and polar components of the crude. In other embodiments, the base oil of lubricating viscosity includes natural oils, such as animal oils, vegetable oils, mineral oils (e.g., liquid petroleum oils and solvent treated or acid-treated mineral oils of the paraffinic, naphthenic or mixed paraffinic-naphthenic types), oils derived from coal or shale, and combinations thereof. Some non-limiting examples of animal oils include bone oil, lanolin, fish oil, lard oil, dolphin oil, seal oil, shark oil, tallow oil, and whale oil. Some non-limiting examples of vegetable oils include castor oil, olive oil, peanut oil, rapeseed oil, corn oil, sesame oil, cottonseed oil, soybean oil, sunflower oil, safflower oil, hemp oil, linseed oil, tung oil, oiticica oil, jojoba oil, and meadow foam oil. Such oils may be partially or fully hydrogenated.

[0027] In some embodiments, the synthetic oils of lubricating viscosity include hydrocarbon oils and halo-substituted hydrocarbon oils such as polymerized and inter-polymerized olefins, alkylbenzenes, polyphenyls, alkylated diphenyl ethers, alkylated diphenyl sulfides, as well as their derivatives, analogues and homologues thereof, and the like. In other embodiments, the synthetic oils include alkylene oxide polymers, interpolymers, copolymers and derivatives thereof wherein the terminal hydroxyl groups can be modified by esterification, etherification, and the like. In further embodiments, the synthetic oils include the esters of dicarboxylic acids with a variety of alcohols. In certain embodiments, the synthetic oils include esters made from C_5 to C_{12} monocarboxylic acids and polyols and polyol ethers. In further embodiments, the

synthetic oils include tri-alkyl phosphate ester oils, such as tri-n-butyl phosphate and tri-iso-butyl phosphate.

[0028] In some embodiments, the synthetic oils of lubricating viscosity include silicon-based oils (such as the polyakyl-, polyaryl-, polyalkoxy-, polyaryloxy-siloxane oils and silicate oils). In other embodiments, the synthetic oils include liquid esters of phosphorus-containing acids, polymeric tetrahydrofurans, polyalphaolefins, and the like.

[0029] Base oil derived from the hydroisomerization of wax may also be used, either alone or in combination with the aforesaid natural and/or synthetic base oil. Such wax isomerate oil is produced by the hydroisomerization of natural or synthetic waxes or mixtures thereof over a hydroisomerization catalyst.

[0030] In further embodiments, the base oil comprises a poly-alpha-olefin (PAO). In general, the poly-alpha-olefins may be derived from an alpha-olefin having from about 2 to about 30, from about 4 to about 20, or from about 6 to about 16 carbon atoms. Non-limiting examples of suitable poly-alpha-olefins include those derived from octene, decene, mixtures thereof, and the like. These poly-alpha-olefins may have a viscosity from about 2 to about 15, from about 3 to about 12, or from about 4 to about 8 centistokes at 100° C. In some instances, the poly-alpha-olefins may be used together with other base oils such as mineral oils.

[0031] In further embodiments, the base oil comprises a polyalkylene glycol or a polyalkylene glycol derivative, where the terminal hydroxyl groups of the polyalkylene glycol may be modified by esterification, etherification, acetylation and the like. Non-limiting examples of suitable polyalkylene glycols include polyethylene glycol, polypropylene glycol, polyisopropylene glycol, and combinations thereof. Non-limiting examples of suitable polyalkylene glycol derivatives include ethers of polyalkylene glycols (e.g., methyl ether of polyisopropylene glycol, diphenyl ether of polyethylene glycol, diethyl ether of polypropylene glycol, etc.), mono- and polycarboxylic esters of polyalkylene glycols, and combinations

thereof. In some instances, the polyalkylene glycol or polyalkylene glycol derivative may be used together with other base oils such as poly-alpha-olefins and mineral oils.

[0032] In further embodiments, the base oil comprises any of the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids, alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkyl malonic acids, alkenyl malonic acids, and the like) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol, and the like). Non-limiting 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 like.

[0033] In further embodiments, the base oil comprises a hydrocarbon prepared by the Fischer-Tropsch process. The Fischer-Tropsch process prepares hydrocarbons from gases containing hydrogen and carbon monoxide using a Fischer-Tropsch catalyst. These hydrocarbons may require further processing in order to be useful as base oils. For example, the hydrocarbons may be dewaxed, hydroisomerized, and/or hydrocracked using processes known to a person of ordinary skill in the art.

[0034] In further embodiments, the base oil comprises an unrefined oil, a refined oil, a rerefined oil, or a mixture thereof. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. Non-limiting examples of unrefined oils include shale oils obtained directly from retorting operations, petroleum oils obtained directly from primary distillation, and ester oils obtained directly from an esterification process and used without further treatment. Refined oils are similar to the unrefined oils except the former have been further treated by one or more purification processes to improve one or more properties. Many such purification processes are known to those skilled in the art such as

solvent extraction, secondary distillation, acid or base extraction, filtration, percolation, and the like. Rerefined oils are obtained by applying to refined oils processes similar to those used to obtain refined oils. Such rerefined oils are also known as reclaimed or reprocessed oils and often are additionally treated by processes directed to removal of spent additives and oil breakdown products.

Anti-Fatigue Additive

[0035] The lubricating oil composition herein contains an anti-fatigue additive. The anti-fatigue additive is an alkyl polyol wherein the alkyl polyol has 2 to 20 carbon atoms such as from 2 to 19 carbon atoms, 2 to 18 carbon atoms, 2 to 17 carbon atoms, 2 to 16 carbon atoms, 2 to 15 carbon atoms, 2 to 14 carbon atoms, 2 to 13 carbon atoms, 2 to 12 carbon atoms, 2 to 11 carbon atoms, 2 to 10 carbon atoms, 2 to 9 carbon atoms, and 2 to 8 carbon atoms. The alkyl polyol includes 2 or more alcohol groups such as 3 or more alcohol groups, 4 or more alcohol groups, and 5 or more alcohol groups. The term "alkyl", as used herein, unless otherwise specified, includes a saturated straight, branched, cyclic, primary, secondary, or tertiary hydrocarbon of C1 to C20.

[0036] Suitable alkyl polyols include glycerol, ethylene glycol, 3-amino-1,2-propanediol, 1,2,4-butanetriol, 1,1,1,-tris(hydroxymethyl)propane, meso-erythritol, D-sorbitol, xylitol, 2,2-diethyl-1,3-propanediol, 3-methoxy-1,2,-propanediol, 2,2-dimethyl-1,3-propanediol, pentaerythritol, and polyvinyl alcohol. Suitable cyclic alkyl polyols include myo-inositol, D-(+)-xylose, and D-(+)-glucose. Other alkyl polyols include alcohol ethers such as diglycerol, triglycerol, diethylene glycol, triethylene glycol, dipentaerythritol, and tripentaerythritol.

[0037] In some embodiments, the alkyl polyol is added to the lubricating oil composition in an amount that increases the fatigue time of the lubricating oil composition over a comparable fluid without the alkyl polyol according to the ZF bearing pitting test.

[0038] The exact amount of the anti-fatigue additive may vary depending upon the composition and amount of the oil or lubricating viscosity, the specific detergents and amounts, and the other desired properties of the lubricating oil composition. In some embodiments the amount of anti-fatigue additive is at least about 0.001, or at least about 0.05, or at least about 0.1, or at least about 0.3, or at least about 0.4, or at least about 0.4, or at least about 0.5, or at least about 0.75, or at least about 1.0 wt. % up to about 1.5, or up to about 1.25, or up to about 1.0, or up to about 0.9, or up to about 0.8 wt. % based on the total weight of the lubricating oil composition.

Detergents

[0039] The lubricating oil composition comprises a metal sulfonate detergent. The metal can be any metal suitable for making sulfonate detergents. Non-limiting examples of suitable metals include alkali metals, alkaline earth metals and transition metals. In some embodiments, the metal is Ca, Mg, Ba, K, Na, Li or the like.

[0040] Generally, the amount of the detergent is from about 0.001 wt. % to about 10 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.

[0041] Optionally, the lubricating oil composition may comprise additional detergents generally known in the art. Some suitable detergents have been described in Mortier et al., "Chemistry and Technology of Lubricants," 2nd Edition, London, Springer, Chapter 3, pages 75-85 (1996); and Leslie R. Rudnick, "Lubricant Additives: Chemistry and Applications," New York, Marcel Dekker, Chapter 4, pages 113-136 (2003), both of which are incorporated herein by reference. Examples of these detergents include phenates, salicylates, phosphonates, and the like.

[0042] In some embodiments the detergent comprises at least one high overbased (TBN above 250 on an actives basis) sulfonate detergent such as high overbased calcium sulfonate.

[0043] Overbased metal detergents are generally produced by carbonating a mixture of hydrocarbons, detergent acid, for example: sulfonic acid, alkylhydroxybenzoate etc., metal oxide or hydroxides (for example calcium oxide or calcium hydroxide) and promoters such as xylene, methanol and water. For example, for preparing an overbased calcium sulfonate, in carbonation, the calcium oxide or hydroxide reacts with the gaseous carbon dioxide to form calcium carbonate. The sulfonic acid is neutralized with an excess of CaO or $Ca(OH)_2$, to form the sulfonate.

[0044] Generally speaking, overbased detergents may be low overbased (LOB), e.g., an overbased salt having a TBN below 100 on an actives basis. In one aspect, the TBN of a low overbased salt may be from about 10 to about 100. In another aspect, the TBN of a low overbased salt may be from about 10 to about 80. Overbased detergents may be medium overbased (MOB), e.g., an overbased salt having a TBN from about 100 to about 250 on an actives basis. In one aspect, the TBN of a medium overbased salt may be from about 100 to about 200. In another aspect, the TBN of a medium overbased salt may be from about 125 to about 175. Overbased detergents may be high overbased (HOB), e.g., an overbased salt having a TBN above 250 on an actives basis. In one aspect, the TBN of a high overbased salt may be from about 250 to about 800 on an actives basis.

[0045] In some embodiments, the lubricating oil composition comprises low levels of sulfur containing calcium phenates (e.g., about 40 mmol or less of Ca from sulfurized phenates such as 35 mmol or less, 30 mmol or less, 25 mmol or less, 20 mmol or less, 10 mmol or less, 5 mmol or less and 0 mmol).

Other Additives

[0046] Optionally, the lubricating oil composition may further comprise at least an additive or a modifier (hereinafter designated as "additive") that can impart or improve any desirable property of the lubricating oil composition. 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. In some embodiments, the additive can be selected from the group consisting of antioxidants, antiwear agents, detergents, rust inhibitors, demulsifiers, friction modifiers, multi-functional additives, viscosity index improvers, pour point depressants, foam inhibitors, metal deactivators, dispersants, corrosion inhibitors, lubricity improvers, thermal stability improvers, anti-haze additives, icing inhibitors, dyes, markers, static dissipaters, biocides and combinations thereof.

[0047] A particularly suitable combination of additives comprises anti-fatigue additive in the amounts described above, a dispersant additive such as ethylene carbonate post treated bissuccinimide, an antiwear additive such as zinc dialkyl diothiophosphate such as one derived from a primary alcohol, and a detergent composition as described above comprising at least one high overbased sulfonate detergent (e.g., a high overbased calcium sulfonate). Optionally, the lubricating oil composition may comprise an additional detergent (e.g., a phenate detergent). The zinc dialkyl dithiophosphate is a primary, secondary zinc dialkyl dithiophosphate, or a combination thereof and may be present at 3 wt. % or less (e.g., 0.1 to 1.5 wt. %, or 0.5 to 1.0 wt %) of the lubricating oil composition. The dispersant such as ethylene carbonate post treated bissuccinimide may be present at 0.1 to 10 wt. % (e.g., 0.5 to 8, 0.7 to 7, 0.7 to 6, 0.7 to 6, 0.7 to 5, 0.7 to 4 wt. %), based on the total weight of the lubricating oil composition.

[0048] 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 10 wt. %, from about 0.01 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.

Anti-wear agents

[0049] Optionally, the lubricating oil composition disclosed herein can comprise one or more anti-wear agents. In some embodiments, the lubricating oil composition is free or substantially free of sulfur-containing anti-wear composition.

[0050] Anti-wear agents reduce wear of metal parts. Suitable anti-wear agents include dihydrocarbyl dithiophosphate metal salts such as zinc dihydrocarbyl dithiophosphates (ZDDP) of the following structure:

$Zn[S\text{-}P(=S)(OR^1)(OR^2)]_2$

wherein R^1 and R^2 may be the same of different hydrocarbyl radicals having from 1 to 18 (e.g., 2 to 12) carbon atoms and including radicals such as alkyl, alkenyl, aryl, arylalkyl, alkaryl and cycloaliphatic radicals. Particularly preferred as R^1 and R^2 groups are alkyl groups having from 2 to 8 carbon atoms (e.g., the alkyl radicals may be ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, n-pentyl, isopentyl, n-hexyl, isohexyl, 2-ethylhexyl). In order to obtain oil solubility, the total number of carbon atoms (i.e., $R^1 + R^2$) will be at least 5. The zinc dihydrocarbyl dithiophosphate can therefore comprise zinc dialkyl dithiophosphates. The zinc dialkyl dithiophosphate is a primary, secondary zinc dialkyl dithiophosphate, or a combination thereof. ZDDP may be present at 3 wt. % or less (e.g., 0.1 to 1.5 wt. %, or 0.5 to 1.0 wt %) of the lubricating oil composition.

Dispersants

[0051] Optionally, the lubricating oil composition disclosed herein can further comprise a dispersant. Dispersants maintain in suspension materials resulting from oxidation during

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

[0052] Basic nitrogen-containing ashless dispersants are well-known lubricating oil additives and methods for their preparation are extensively described in the patent literature. Preferred dispersants are the alkenyl succinimides and succinamides where the alkenyl-substituent is a long-chain of preferably greater than 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. As is known in the art, the dispersants may be post-treated (e.g., with a boronating agent, ethylene carbonate, or a cyclic carbonate). Nitrogen-containing ashless (metal-free) dispersants are basic, and contribute to the TBN of a lubricating oil composition to which they are added, without introducing additional sulfated ash. Dispersants may be present at 0.1 to 10 wt. % (e.g., 0.5 to 8, 0.7 to 7, 0.7 to 6, 0.7 to 6, 0.7 to 5, 0.7 to 4 wt. %), based on an actives level, of the lubricating oil composition. Nitrogen from the dispersants is present from greater than 0.0050 to 0.30 wt. % (e.g., greater than 0.0050 to 0.10 wt. %, 0.0050 to 0.080 wt. %, 0.0050 to 0.060 wt. %, 0.0050 to 0.050 wt. %, 0.0050 to 0.040 wt. %, 0.0050 to 0.030 wt. %) based on the weight of the dispersants in the finished oil.

Antioxidants

[0053] Optionally, the lubricating oil composition disclosed herein can further comprise an additional antioxidant 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, phenyl-.alpha.-naphthylamine, alkyl or aralkyl substituted phenyl-.alpha.-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), zinc dithiophosphate, oil-soluble copper compounds 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. Some suitable antioxidants have been described in Leslie R. Rudnick, "Lubricant Additives: Chemistry and Applications," New York. Marcel Dekker, Chapter 1, pages 1-28 (2003), which is incorporated herein by reference.

Friction Modifiers

[0054] The lubricating oil composition disclosed herein can optionally comprise a friction modifier 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, the friction modifier is selected from the group consisting of aliphatic amines, ethoxylated aliphatic amines, aliphatic carboxylic acid amides, ethoxylated aliphatic ether amines, aliphatic carboxylic acids, glycerol esters, aliphatic carboxylic ester-amides, fatty imidazolines, fatty tertiary amines, wherein the aliphatic or fatty group contains more than about eight carbon atoms so as to render the compound suitably oil soluble. In other embodiments, the friction modifier comprises an aliphatic substituted succinimide formed by reacting an aliphatic succinic acid or anhydride with ammonia or a primary amine. 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. Some suitable friction modifiers have been described in Mortier et al., "Chemistry and Technology of Lubricants," 2nd Edition, London, Springer, Chapter 6, pages 183-187 (1996); and Leslie R. Rudnick, "Lubricant Additives: Chemistry and Applications," New York, Marcel Dekker, Chapters 6 and 7, pages 171-222 (2003), both of which are incorporated herein by reference.

Pour Point Depressants

[0055] The lubricating oil composition disclosed herein can optionally comprise a pour point depressant 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. Some suitable pour point depressants have been described in Mortier et al., "Chemistry and Technology of Lubricants," 2nd Edition, London, Springer, Chapter 6, pages 187-189 (1996); and Leslie R. Rudnick, "Lubricant Additives: Chemistry and Applications," New York, Marcel Dekker, Chapter 11, pages 329-354 (2003), both of which are incorporated herein by reference.

Demulsifiers

[0056] The lubricating oil composition disclosed herein can optionally comprise a demulsifier 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 alkylphenol 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. Some suitable demulsifiers have been described in Mortier et al., "Chemistry and Technology of Lubricants," 2nd Edition. London, Springer, Chapter 6, pages 190-193 (1996), which is incorporated herein by reference.

Foam Inhibitors

[0057] The lubricating oil composition disclosed herein can optionally comprise a foam inhibitor or an anti-foam 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 anti-foams include silicone oils or polydimethylsiloxanes, fluorosilicones, alkoxylated aliphatic acids, polyethers (e.g., polyethylene glycols), branched polyvinyl ethers, alkyl acrylate polymers, alkyl methacrylate polymers, polyalkoxyamines and combinations thereof. In some embodiments, the anti-foam comprises glycerol monostearate, polyglycol palmitate, a trialkyl monothiophosphate, an ester of sulfonated ricinoleic acid, benzoylacetone, methyl salicylate, glycerol monooleate, or glycerol dioleate. The amount of the anti-foam 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. Some suitable anti-foams have been described in Mortier et al., "Chemistry and Technology of Lubricants," 2nd Edition, London, Springer, Chapter 6, pages 190-193 (1996), which is incorporated herein by reference.

Corrosion Inhibitors

[0058] The lubricating oil composition disclosed herein can optionally comprise a corrosion inhibitor 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, phosphate esters, thiophosphates, 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. Some suitable corrosion inhibitors have been described in Mortier et al., "Chemistry and Technology of Lubricants," 2nd Edition, London, Springer, Chapter 6, pages 193-196 (1996), which is incorporated herein by reference.

Extreme Pressure Agents

[0059] The lubricating oil composition disclosed herein can optionally comprise an extreme pressure (EP) agent 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 phosphorus, 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, amine salts of phosphoric acid esters or thiophosphoric acid esters 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. Some suitable extreme pressure agents have been described in Leslie R. Rudnick, "Lubricant Additives: Chemistry and Applications," New York, Marcel Dekker, Chapter 8, pages 223-258 (2003), which is incorporated herein by reference.

Rust Inhibitors

[0060] The lubricating oil composition disclosed herein can optionally comprise a rust inhibitor 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 oil-soluble monocarboxylic acids (e.g., 2-ethylhexanoic acid, lauric acid, myristic acid, palmitic acid, oleic acid, linoleic acid, linolenic acid, behenic acid, cerotic acid and the like), oil-soluble polycarboxylic acids (e.g., those

produced from tall oil fatty acids, oleic acid, linoleic acid and the like), alkenylsuccinic acids in which the alkenyl group contains 10 or more carbon atoms (e.g., tetrapropenylsuccinic acid, tetradecenylsuccinic acid, hexadecenylsuccinic acid, and the like); long-chain alpha,omega-dicarboxylic acids having a molecular weight in the range of 600 to 3000 daltons and combinations 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.

[0061] Other non-limiting examples of suitable rust inhibitors include nonionic polyoxyethylene surface active agents such as polyoxyethylene lauryl ether, polyoxyethylene higher alcohol ether, polyoxyethylene nonyl phenyl ether, polyoxyethylene octyl phenyl ether, polyoxyethylene octyl stearyl ether, polyoxyethylene oleyl ether, polyoxyethylene sorbitol monostearate, polyoxyethylene sorbitol mono-oleate, and polyethylene glycol mono-oleate. Further non-limiting examples of suitable rust inhibitor include 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, and phosphoric ester.

Multifunctional Additives

[0062] In some embodiments, the lubricating oil composition comprises at least a multifunctional additive. Some non-limiting examples of suitable multifunctional additives include sulfurized oxymolybdenum dithiocarbamate, sulfurized oxymolybdenum organophosphorodithioate, oxymolybdenum monoglyceride, oxymolybdenum diethylate amide, amine-molybdenum complex compound, and sulfur-containing molybdenum complex compound.

Viscosity Index Improvers

[0063] In certain embodiments, the lubricating oil composition comprises at least a viscosity index improver. Some non-limiting examples of suitable viscosity index improvers include

polymethacrylate type polymers, ethylene-propylene copolymers, styrene-isoprene copolymers, hydrated styrene-isoprene copolymers, polyisobutylene, and dispersant type viscosity index improvers.

Metal Deactivators

[0064] In some embodiments, the lubricating oil composition comprises at least a metal deactivator. Some non-limiting examples of suitable metal deactivators include disalicylidene propylenediamine, triazole derivatives, thiadiazole derivatives, and mercaptobenzimidazoles.

Additive Concentrate Formulations

[0065] The additives disclosed herein may be in the form of an additive concentrate having more than one additive. The additive concentrate may comprise a suitable diluent, such as a hydrocarbon oil of suitable viscosity. Such diluent can be selected from the group consisting of natural oils (e.g., mineral oils), synthetic oils and combinations thereof. Some non-limiting examples of the mineral oils include paraffin-based oils, naphthenic-based oils, asphaltic-based oils and combinations thereof. Some non-limiting examples of the synthetic base oils include polyolefin oils (especially hydrogenated alpha-olefin oligomers), alkylated aromatic, polyalkylene oxides, aromatic ethers, and carboxylate esters (especially diester oils) and combinations thereof. In some embodiments, the diluent is a light hydrocarbon oil, both natural or synthetic. Generally, the diluent oil can have a viscosity from about 13 centistokes to about 35 centistokes at 40°C.

[0066] Generally, it is desired that the diluent readily solubilizes the lubricating oil soluble additive and provides an oil additive concentrate that is readily soluble in the lubricant base oil stocks or fuels. In addition, it is desired that the diluent not introduce any undesirable characteristics, including, for example, high volatility, high viscosity, and impurities such as heteroatoms, to the lubricant base oil stocks and thus, ultimately to the finished lubricant or fuel.

[0067] The present application further provides an oil soluble additive concentrate composition comprising an inert diluent and from 2.0% to 90% by weight, preferably 10% to 50% by weight based on the total concentrate, of an oil soluble additive composition according to the present application.

[0068] The functional fluids comprising the additives described above may be employed in a method of increasing the fatigue time of a bearing comprising contacting a metal surface with a functional fluid.

[0069] The following examples are presented to exemplify embodiments but are not intended to limit the application 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 application. Specific details described in each example should not be construed as necessary features.

EXAMPLES

[0070] The following examples are intended for illustrative purposes only and do not limit in any way the scope.

ZF Bearing Pitting Test

[0071] Bearing performance is evaluated using ZF specification 03C bearing pitting test 0000 702 232. This test uses FE 8 roller thrust bearings with an axial for of 68 kN revolving at 300 rpm. The temperature is 100 °C. In this test, the length of time to failure is measured and failure is determined when vibration becomes so severe that metal pieces get dislodged from the bearing or the case that contacts the bearing and the FE8 test rig automatically shuts down. The removed metal leaves pits in the bearing or the case. In order to pass the test for the ZF 03C specification, the minimal length of time to failure is 300 hours. The maximum amount

of time the test is allowed to run is 750 hours. The ZF bearing pitting test is available from Assmann Laboratories, Aachen, Germany.

Baseline Formulation

[0072] The baseline formulation includes the following:

(i) 1 wt. % of an ethylene carbonate capped dispersant;

(ii) 1.28 wt. % of an oil concentrate of a zinc dithiophosphate derived from a primary alcohol containing 7.3 wt. % phosphorus;

(iii) 0.79 wt. % of a 320 TBN oil concentrate of a Ca sulfonate detergent;

(iv) 0.5 wt. % of a pour point depressant;

(v) 0.6 wt. % of a seal swell additive;

(vi) 0.04 wt. % of foam inhibitors;

(vii) The balance, a Group II base oil at 10W viscosity.

COMPARATIVE EXAMPLE A

[0073] Comparative Example A was prepared using the above baseline formulation with the addition of 1.46% wt. % (35 mmol Ca) of a sulfurized highly overbased calcium phenate with a TBN of 263.

COMPARATIVE EXAMPLE B

[0074] Comparative example B was prepared using the above baseline formulation with the addition of 1.88 wt. % (45 mmol Ca) of a highly sulfurized overbased calcium phenate with a TBN of 263.

COMPARATIVE EXAMPLE C

[0075] Comparative example C was prepared using the above baseline formulation with the addition of 2.29 wt. % (55 mmol Ca) of a highly sulfurized overbased calcium phenate with a TBN of 263.

[0076] Table 1 summarizes Comparative Examples A, B, and C. Table 1 also shows that in the absence of glycerol, a threshold amount of sulfurized phenate detergent is required to pass the ZF FE 8 Bearing Pitting Test. Increasing the amount of sulfurized phenate improved the ZF test results.

TABLE 1

	Comparative Example A	Comparative Example B	Comparative Example C
% Sulfurized Phenate Concentration	1.46	1.88	2.29
mmol of Ca from Sulfurized Phenate	35	45	55
% glycerol	0	0	0
Hours to Failure	96, 94, 88	340, 287	464, 429
Average Hours to failure	93	314	447
ZF Test Pass/Fail	Fail	Pass	Pass

EXAMPLES 1 TO 6

[0077] A lubricating oil composition was prepared utilizing the above baseline formulation with the addition of 1.46 wt. % (35 mmol Ca) of a sulfurized highly overbased calcium phenate with a TBN of 263. Glycerol was added into the formulations as a wt. % as shown in Table 2 below.

TABLE 2

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6
% Sulfurized Phenate Concentration	1.46	1.46	1.46	1.46	1.46	1.46
mmol of Ca from Sulfurized Phenate	35	35	35	35	35	35
% glycerol	0.01	0.03	0.05	0.1	0.15	0.25
Hours to Failure	104, 119	309, 232	368, 498	750, 750, 691	750, 750	750, 750
Average Hours to failure	110	271	433	730	750	750
ZF Test Pass/Fail	Fail	Fail	Pass	Pass	Pass	Pass

[0078] Table 2 shows that the addition of glycerol at very low treat rates surprisingly and unexpectedly allowed the passing of the ZF FE 8 Bearing Pitting Test even at below threshold levels of sulfurized phenate. Increasing the glycerol treat rate significantly improved the ZF test performance to the maximum duration of the ZF test (750 hours).

EXAMPLE 7

[0079] Example 7 was prepared using the above baseline formulation with the addition of 1.04 wt. % (25 mmol Ca) of a highly sulfurized overbased calcium phenate with a TBN of 263 and 0.25 wt. % glycerol.

EXAMPLE 8

[0080] Example 8 was prepared using the above baseline formulation with the addition of 0.42 wt. % (10 mmol Ca) of a highly sulfurized overbased calcium phenate with a TBN of 263 and 0.25 wt. % glycerol.

EXAMPLE 9

[0081] Example 9 was prepared using the above baseline formulation with the addition of 0.25 wt. % of glycerol.

EXAMPLE 10

[0082] Example 10 was prepared using the above baseline formulation with the addition of 0.20 wt. % of glycerol.

EXAMPLE 11

[0083] Example 11 was prepared using the above baseline formulation with the addition of 0.15 wt. % of glycerol.

EXAMPLE 12

[0084] Example 12 was prepared using the above baseline formulation with the addition of 0.10% wt. % of glycerol.

EXAMPLE 13

[0085] Example 13 was prepared using the above baseline formulation with the addition of 0.05 wt. % of glycerol.

EXAMPLE 14

[0086] Example 14 was prepared using the above baseline formulation with the addition of 0.03 wt. % of glycerol.

[0087] Examples 7 to 14 are summarized in Table 3 below.

TABLE 3

	Example 7	Example 8	Example 9	Example 10	Example 11	Example 12	Example 13	Example 14
% Sulfurized Phenate Concentration	1.04	0.42	0	0	0	0	0	0
mmol of Ca from Sulfurized Phenate	25	10	0	0	0	0	0	0
% glycerol	0.25	0.25	0.25	0.2	0.15	0.1	0.05	0.03
Hours to Failure	750, 750	577, 750	750, 750	750, 750	750, 750	485, 498	264, 240	186, 170
Average Hours to failure	750	664	750	750	750	492	252	178
Pass/Fail	Pass	Pass	Pass	Pass	Pass	Pass	Fail	Fail

[0088] As shown in Table 3, the addition of glycerol allows passing of the ZF FE 8 Bearing Pitting test at very low treat rates of sulfurized phenate or even in the absence of sulfurized phenate altogether. In fact, maximum ZF test performance can be achieved with very little amounts of glycerol and complete removal of sulfurized phenate.

EXAMPLES 15 - 19

[0089] Examples 15 – 19 were prepared using the above baseline formulation without the presence of the zinc dithiophosphate and with the wt. % of glycerol as shown in Table 4.

[0090] Surprisingly, improved bearing pitting results were observed in samples containing low amounts of zinc dithiophosphate or even in the absence of zinc dithiophosphate. In these samples, glycerol is essentially the only anti-fatigue component. This was observed even at very low amounts of glycerol (e.g., down to 0.05% glycerol).

[0091] As shown in Table 4, equivalent amounts of glycerol, especially at the low treat rates gave the maximum 750 hours of performance in the ZF FE 8 Bearing Pitting Test. Also, for example, comparing Example 13 with 0.05 wt. % glycerol and with 1.28% Zn dithiophosphate gave a failing result of 252 hours, whereas the equivalent zinc-free Example 19 gave a maximum passing result of 750 hours.

TABLE 4

	Ex. 10	Ex. 11	Ex. 12	Ex. 13	Ex. 14	Ex. 15	Ex. 16	Ex. 17	Ex. 18	Ex. 19
% Sulfurized Phenate Concentration	0	0	0	0	0	0	0	0	0	0
% Zn dithiophosphate	1.28	1.28	1.28	1.28	1.28	0	0	0	0	0
Glycerol (wt %)	0.2	0.15	0.1	0.05	0.03	0.25	0.2	0.15	0.1	0.05
Hours to Failure	750, 750	750, 750	485, 498	264 240	186, 170	750, 750	750, 750	750, 750	750, 664	750, 750
Average hours to failure	750	750	492	252	178	750	750	750	707	750
ZF Test (Pass/Fail)	Pass	Pass	Pass	Fail	Fail	Pass	Pass	Pass	Pass	Pass

[0092] 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 embodiments of the invention. For example, the functions described above and implemented for operating 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 application. Moreover, those skilled in the art will envision other modifications within the scope and spirit of the claims appended hereto.

CLAIMS

1. A functional fluid or EV fluid comprising:

(a) a major amount of an oil of lubricating viscosity;

(b) an anti-fatigue additive comprising alkyl polyol having 2 to 20 carbon atoms; and

(c) at least one overbased sulfonate detergent;

wherein the amount of anti-fatigue additive is from about 0.001 wt. % to about 1.5 wt. % based on the total weight of the functional fluid or EV fluid.

2. The functional fluid or EV fluid of claim 1, wherein the at least one overbased sulfonate detergent is a high overbased calcium sulfonate.

3. The functional fluid or EV fluid of claim 1, further comprising a sulfurized calcium phenate detergent present in an amount to provide about 40 mmol or less of calcium.

4. The functional fluid or EV Fluid of claim 1, wherein the functional fluid further comprises at least one dispersant additive.

5. The functional fluid or EV Fluid of claim 4, wherein the at least one dispersant additive is an ethylene carbonate post treated bissuccinimide.

6. The functional fluid or EV fluid of claim 1, further comprising at least one anti-wear additive.

7. The functional fluid or EV fluid of claim 6, wherein the at least one anti-wear additive is a zinc dialkyl dithiophosphate.

8. The functional fluid or EV fluid of claim 7, wherein the zinc dialkyl dithiophosphate is derived from a primary alcohol.

9. The functional fluid or EV fluid of claim 1, wherein the anti-fatigue additive is glycerol, triglycerol, 1,2,4-butanetriol, 2,2-diethyl-1,3-propanediol, diglycerol, 3-methoxy-1,2-propanediol, myo-inositol, meso-erythritol, D-sorbitol, xylitol, D-(+)-xylose, D-(+)-glucose, pentaerythritol, dipentaerythritol; tripentaerythritol, ethylene glycol, diethylene glycol, triethylene glycol, 2,2-dimethyl-1,3-propanediol, or polyvinyl alcohol.

10. The functional fluid or EV fluid of claim 1, wherein the functional fluid or EV fluid includes 3 wt. % or less of zinc dithiophosphate based on total weight of the functional fluid or EV fluid.

11. A method of increasing the fatigue time of a bearing comprising contacting a metal surface with a functional fluid or EV fluid comprising:

a) a major amount of an oil of lubricating viscosity;

(b) an anti-fatigue additive comprising alkyl polyol having 2 to 20carbon atoms; and

(c) at least one overbased sulfonate detergent; wherein the amount of anti-fatigue additive is from about 0.001 wt. % to about 1.5 wt. %.

12. The method of claim 11, wherein the at least one overbased sulfonate detergent is a high overbased calcium sulfonate.

13. The method of claim 11, wherein the functional fluid or EV fluid further comprises a sulfurized calcium phenate detergent present in an amount to provide about 40 mmol or less of calcium.

14. The method of claim 11, wherein the functional fluid or EV fluid further comprises at least one dispersant additive.

15. The method of claim 11, wherein the anti-fatigue additive is glycerol, triglycerol, 1,2,4-butanetriol, 1,1,1,-tris(hydroxymethyl)propane, 2,2-diethyl-1,3-propanediol, diglycerol, 3-

methoxy-1,2,-propanediol, myo-inositol, meso-erythritol, D-sorbitol, xylitol, D-(+)-xylose, D-(+)-glucose, pentaerythritol, dipentaerythritol; tripentaerythritol, ethylene glycol, diethylene glycol, triethylene glycol, 2,2-dimethyl-1,3-propanediol, or polyvinyl alcohol.

16. The method of claim 11, wherein the functional fluid or EV fluid includes less than 3 wt. % of zinc dithiophosphate based on the total weight of the functional fluid or EV fluid.

17. A lubricating oil composition for hybrid vehicle or plug-in hybrid vehicles comprising:

(a) a major amount of an oil of lubricating viscosity;

(b) an anti-fatigue additive comprising alkyl polyol having 2 to 20 carbon atoms; and

(c) at least one overbased sulfonate detergent;

wherein the amount of anti-fatigue additive is from about 0.001 wt. % to about 1.5 wt. % based on the total weight of the lubricating oil composition.

18. The lubricating oil composition of claim 17, wherein the at least one overbased sulfonate detergent is a high overbased calcium sulfonate.

19. The lubricating oil composition of claim 17, wherein the lubricating oil composition includes 3 wt. % or less of zinc dithiophosphate based on total weight of the lubricating oil composition.

20. The lubricating oil composition of claim 17, wherein the lubricating oil composition includes calcium phenate detergent in an amount to provide about 40 mmol or less of calcium.

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2022/060589

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10M141/08
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10M C10N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 11 142 715 B2 (CHEVRON USA INC [US]; CHEVRON ORONITE CO [US]) 12 October 2021 (2021-10-12) column 1, line 6 - line 9 column 5, line 1 - column 8, line 29	1-20
A	EP 3 878 928 A1 (ENEOS CORP [JP]) 15 September 2021 (2021-09-15) paragraph [0003]; claim 1	1-20

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
3 January 2023	13/01/2023

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Klaes, Daphne

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/IB2022/060589

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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