

MARINE LUBRICANTS ENABLING FUTURE FUELS

CROSS REFERENCE TO RELATED APPLICATIONS

[01] This application claims the priority benefit of U.S. Provisional Application No. 63/450,822, filed March 8, 2023, the disclosure of which is incorporated herein by reference.

TECHNICAL FIELD

[02] This disclosure relates to marine lubricant additives and lubricating oil compositions containing the same. More particularly, the marine lubricant additives and the lubricating oil compositions perform well in marine engines operated using non-carbon based fuels.

BACKGROUND

[03] Non-carbon based fuels (e.g., ammonia, hydrogen) are increasingly being looked at as alternative sources of energy for the propulsion of marine vessels. Utilizing non-carbon based fuels, such as ammonia, requires the development of new engines or possibly the retrofitting of conventional engines to account for differences in the fuel and fuel combustion. Consequently, there is a need to develop lubricating oil formulations that provide good performance and fuel compatibility in alternative fueled marine engines.

SUMMARY

[04] In one aspect, there is provided a marine cylinder lubricating oil composition for a non-carbon based fueled marine engine comprising: a major amount of an oil of lubricating viscosity; and a mixture of overbased phenol-based detergent and overbased calcium sulfonate detergent; and wherein the marine cylinder lubricating oil composition has a TBN of less than 200 mg KOH/g, and further wherein the marine engine lubricating oil composition is a monograde lubricating oil

composition meeting the specifications for SAE J300 revised January 2015 requirements for a SAE 20, SAE 30, SAE 40, SAE 50 or SAE 60 monograde lubricating oil.

[05] In still yet another aspect, there is provided a method of lubricating a marine two-stroke engine operated using ammonia fuel, the method comprising lubricating the engine with a lubricating oil composition comprising: a major amount of an oil of lubricating viscosity; and a mixture of an overbased phenol-based detergent and an overbased calcium sulfonate detergent; and wherein the marine cylinder lubricating oil composition has a TBN of less than 200 mg KOH/g, and further wherein the marine engine lubricating oil composition is a monograde lubricating oil composition meeting the specifications for SAE J300 revised January 2015 requirements for a SAE 40, SAE 50 or SAE 60 monograde lubricating oil.

[06] In still further aspect, there is provided a method of improving or maintaining deposit control performance and/or oxidative stability of an ammonia-fueled marine engine, the method comprising: lubricating the engine with a lubricating oil composition comprising: a major amount of an oil of lubricating viscosity; and a mixture of an overbased phenol-based detergent and an overbased calcium sulfonate detergent; and wherein the marine cylinder lubricating oil composition has a TBN of less than 200 mg KOH/g, and further wherein the marine engine lubricating oil composition is a monograde lubricating oil composition meeting the specifications for SAE J300 revised January 2015 requirements for a SAE 40, SAE 50 or SAE 60 monograde lubricating oil.

DETAILED DESCRIPTION

[07] In this specification, the following words and expressions, if and when used, have the meanings ascribed below.

[08] A "major amount" means greater than 40 wt. % of a composition.

[09] A "minor amount" means less than 40 wt. % of a composition.

[010] The term “on an actives basis” refers to additive material that is not diluent oil or solvent. Weight percentages throughout the specification are on an actives basis unless stated otherwise, or diluent oil contents are provided.

[011] The term “Total Base Number” or “TBN” or “BN” 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 mg KOH/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. Where TBN values are introduced herein, it should be understood that they are represented in units of mg KOH/g.

[012] “Overbased” is used to describe metal detergents in which the ratio of the number of equivalents of the metal moiety to the number of equivalents of the acid moiety is greater than one.

[013] “Soap” refers to soap content and refers to the concentration of surfactant anion contributed to the formulation by one or more detergents within the composition. For the purposes of this invention, the surfactant concentration is reported in terms of millimoles of surfactant per kg of oil.

[014] It is understood that when combinations, subsets, groups, etc. of elements are disclosed (e.g., combinations of components in a composition, or combinations of steps in a method), that while specific reference of each of the various individual and collective combinations and permutations of these elements may not be explicitly disclosed, each is specifically contemplated and described herein.

[015] The present disclosure relates to marine engine lubricant additive compositions compatible with non-carbon based fueled engines. The present disclosure also relates to lubricant additive compositions having improved oxidative stability, oxidative stability retention, and/or deposit control capability, lubricating oil

compositions containing the lubricant additive compositions, and methods of using the composition(s).

[016] The compositions disclosed herein are particularly suitable for ammonia-fueled engines operating under sustained high load conditions. In some embodiments, the engine may be a "low-speed" or "slow-speed" marine engine. In some embodiments, the engine may be a two-stroke crosshead compression-ignited engine. The engine can be a novel-design or retrofitted low speed two-stroke marine engine fueled by ammonia. Engines classified as "low-speed" or "slow-speed" may refer to a compression-ignition internal combustion engine that is driven at rotational speed that is less than 500 revolutions per minute (rpm).

[017] For purposes of this disclosure, it is understood that the "ammonia-fueled" engine concept for a large bore compression-ignition engine could encompass an engine operated in a dual-fuel mode. In compression-ignition engines, ammonia can be successfully used in a dual-fuel mode with diesel, or another pilot fuel, where ammonia is introduced into a diesel engine via a dual-fuel mode whereby fumigated premixed ammonia (main fuel) in the combustion chamber is ignited by a pilot fuel (e.g. diesel, kerosene, etc.) as an ignition source.

[018] Formulating marine lubricating oils (e.g., marine cylinder lubricants) generally involves use of additive technologies in conventional or more recently, biobased base oils. Some considerations for ammonia-fueled engine formulation include ability to withstand exposure to ammonia and its reactive combustion products (e.g., NO, NO₂, H₂O) without sacrificing critical performance parameters.

[019] In some embodiments, the lubricating oil composition disclosed herein is suitable for use as a marine cylinder lubricant used to lubricate ammonia-fueled engines. Marine cylinder lubricants are typically made to the SAE 20, SAE 30, SAE 40, SAE 50, or SAE 60 monograde specification in order to provide a sufficiently thick lubricant film at high temperatures on the cylinder liner wall. Typically, marine cylinder lubricants have a TBN of less than 200 mg KOH/g, of up to 200 mg KOH/g, or ranging from 2 to 200 mg KOH/g (e.g., from 2 to 200 mg KOH/g, from 5 to 200 mg KOH/g,

from 10 to 200 mg KOH/g, from 20 to 200 mg KOH/g, from 30 to 200 mg KOH/g, from 40 to 200 mg KOH/g, from 50 to 200 mg KOH/g, from 60 to 200 mg KOH/g, from 70 to 200 mg KOH/g, from 80 to 200 mg KOH/g, from 90 to 200 mg KOH/g, from 100 to 200 mg KOH/g, from 110 to 200 mg KOH/g, from 120 to 200 mg KOH/g, from 130 to 200 mg KOH/g, from 140 to 200 mg KOH/g, from 150 to 200 mg KOH/g, from 160 to 200 mg KOH/g, from 170 to 200 mg KOH/g, from 180 to 200 mg KOH/g, from 190 to 200 mg KOH/g, from 2 to 190 mg KOH/g, from 5 to 190 mg KOH/g, from 10 to 190 mg KOH/g, from 20 to 190 mg KOH/g, from 30 to 190 mg KOH/g, from 40 to 190 mg KOH/g, from 50 to 190 mg KOH/g, from 60 to 190 mg KOH/g, from 70 to 190 mg KOH/g, from 80 to 190 mg KOH/g, from 90 to 190 mg KOH/g, from 100 to 190 mg KOH/g, from 110 to 190 mg KOH/g, from 120 to 190 mg KOH/g, from 130 to 190 mg KOH/g, from 140 to 190 mg KOH/g, from 150 to 190 mg KOH/g, from 160 to 190 mg KOH/g, from 170 to 190 mg KOH/g, from 180 to 190 mg KOH/g, from 2 to 180 mg KOH/g, from 5 to 180 mg KOH/g, from 10 to 180 mg KOH/g, from 15 to 180 mg KOH/g, from 20 to 180 mg KOH/g, from 30 to 180 mg KOH/g, from 40 to 180 mg KOH/g, from 50 to 180 mg KOH/g, from 60 to 180 mg KOH/g, from 70 to 180 mg KOH/g, from 80 to 180 mg KOH/g, from 90 to 180 mg KOH/g, from 100 to 180 mg KOH/g, from 110 to 180 mg KOH/g, from 120 to 180 mg KOH/g, from 130 to 180 mg KOH/g, from 140 to 180 mg KOH/g, from 150 to 180 mg KOH/g, from 160 to 180 mg KOH/g, from 2 to 170 mg KOH/g, from 5 to 170 mg KOH/g, from 10 to 170 mg KOH/g, from 15 to 170 mg KOH/g, from 20 to 170 mg KOH/g, from 30 to 170 mg KOH/g, from 40 to 170 mg KOH/g, from 50 to 170 mg KOH/g, from 60 to 170 mg KOH/g, from 70 to 170 mg KOH/g, from 80 to 170 mg KOH/g, from 90 to 170 mg KOH/g, from 100 to 170 mg KOH/g, from 110 to 170 mg KOH/g, from 120 to 170 mg KOH/g, from 130 to 170 mg KOH/g, from 140 to 170 mg KOH/g, from 150 to 170 mg KOH/g, from 160 to 170 mg KOH/g, from 2 to 160 mg KOH/g, from 5 to 160 mg KOH/g, from 10 to 160 mg KOH/g, from 15 to 160 mg KOH/g, from 20 to 160 mg KOH/g, from 30 to 160 mg KOH/g, from 40 to 160 mg KOH/g, from 50 to 160 mg KOH/g, from 60 to 160 mg KOH/g, from 70 to 160 mg KOH/g, from 80 to 160 mg KOH/g, from 90 to 160 mg

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[020] The lubricating oil composition disclosed herein may provide advantaged oxidation control performance. The lubricating oil composition disclosed herein can either maintain or improve the oxidative stability performance even in the face of nitrogen-based contaminants (e.g., ammonia, NO, NO₂, etc.) which are present or generated in ammonia-fueled engines. The lubricating oil composition disclosed herein may demonstrate deposit control capability.

[021] In some embodiments, the lubricating oil composition is contaminated with ammonia. In some embodiments, the lubricating oil composition is contaminated with NO, NO₂, and/or water.

Base Oil

[022] The lubricating oil composition disclosed herein includes a base oil. In some embodiments, the base oil is a Group I, II, III (including III+), IV, or V base oil. In some embodiments, the base oil includes bright stock. Bright stock can be used as a thickener to achieve the correct viscosity. In some embodiments, the lubricating oil composition disclosed herein comprises a major amount of Group II or higher base stocks.

[023] Groups I, II, III, IV and V are broad categories of base oil stocks developed and defined by the American Petroleum Institute (API Publication 1509—Appendix E) to create guidelines for lubricant base oils. Group I base stocks contain less than 90% saturates and/or greater than 0.03% sulfur and have a viscosity index greater than or equal to 80 and less than 120. Group II base stocks contain greater than or equal to 90% saturates and less than or equal to 0.03% sulfur and have a viscosity index greater than or equal to 80 and less than 120. Group III base stocks contain greater than or equal to 90% saturates and less than or equal to 0.03% sulfur and have a viscosity index greater than or equal to 120. Group IV base stocks are polyalphaolefins. Group V base stocks include all other base stocks not included in Groups I, II, III or IV. Table 1 summarizes properties of each of these five groups.

Table 1

Base Oil Properties			
Group	Saturates ⁽¹⁾	Sulfur ⁽²⁾	Viscosity Index ⁽³⁾
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

(1) ASTM D2007

(2) ASTM D2622, ASTM D3120, ASTM D4294 or ASTM D4927

(3) ASTM D2270

[024] In some embodiments, the lubricating oil composition disclosed herein comprises a major amount of base stock containing greater than or equal to 90% saturates and less than or equal to 0.03% sulfur.

[025] In some embodiments, the lubricating oil composition disclosed herein comprises a major amount of biobased base oil derived from renewable carbon sources.

Biobased Base Oil

[026] In some embodiments, the lubricating oil composition may include biobased base oil. A detailed discussion of biobased base oil can be found in WO/2021/205385, the contents of which are hereby incorporated by reference.

[027] In one aspect, the biobased oil can be described by the following. Base oils, and more particularly isoparaffins, derived from biobased hydrocarbon terpenes such as myrcene, ocimene and farnesene, have been described in PCT Patent Application No. PCT/US2012/024926, entitled "Base Oils and Methods for Making the Same," filed, February 13, 2012 and published as WO 2012/141784 on October 18, 2012, by Nicholas Ohler, et al., and assigned to Amyris, Inc. in Emeryville, California. WO 2012/141784 discloses that terpenes are capable of being derived from isopentyl pyrophosphate or dimethylallyl pyrophosphate and the term "terpene" encompasses hemiterpenes, monoterpenes, sesquiterpenes, diterpenes, sesterterpenes, triterpenes, tetraterpenes and polyterpenes. A hydrocarbon terpene contains only hydrogen and carbon atoms and no heteroatoms such as oxygen, and in some embodiments has the general formula $(C_5H_8)_n$, where n is 1 or greater. A "conjugated terpene" or "conjugated hydrocarbon terpene" refers to a terpene comprising at least

one conjugated diene moiety. The conjugated diene moiety of a conjugated terpene may have any stereochemistry (e.g., cis or trans) and may be part of a longer conjugated segment of a terpene, e.g., the conjugated diene moiety may be part of a conjugated triene moiety. Hydrocarbon terpenes also encompass monoterpenoids, sesquiterpenoids, diterpenoids, triterpenoids, tetraterpenoids, and polyterpenoids that exhibit the same carbon skeleton as the corresponding terpene but have either a lesser or greater number of hydrogen atoms than the corresponding terpene, e.g., terpenoids having 2 fewer, 4 fewer, or 6 fewer hydrogen atoms than the corresponding terpene, or terpenoids having 2-additional, 4-additional, or 6-additional hydrogen atoms than the corresponding terpene. Some non-limiting examples of conjugated hydrocarbon terpenes include isoprene, myrcene, α -ocimene, β -ocimene, α -farnesene, β -farnesene, β -springene, geranylarnesene, neophytadiene, *c/s*-phyta-1,3-diene, *trans*-phyta-1,3-diene, isodehydrosqualene, isosqualane precursor I, and isosqualane precursor II. The terms terpene and isoprenoids may be used interchangeably and are a large and varied class of organic molecules that can be produced by a wide variety of plants and some insects. Some terpenes or isoprenoid compounds can also be made from organic compounds such as sugars by microorganisms, including bioengineered microorganisms, such as yeast. Because terpenes or isoprenoid compounds can be obtained from various renewable sources, they are useful monomers for making eco-friendly and renewable base oils. In some embodiments, the conjugated hydrocarbon terpenes are derived from microorganisms using a renewable carbon source, such as a sugar. Further processing of certain of such biobased base oil stocks has been found to yield highly useful and superior engine oils. For example, C₁₅ hydrocarbons containing four double bonds such as Biofene™ β -farnesene, commercially available from Amyris, Inc. (Emeryville, California) may be pre-treated to eliminate impurities and then hydrogenated so that three of the four double bonds are reduced to single bonds. The partially hydrogenated intermediate product is then subjected to an oligomerization reaction with a linear α olefin (LAO) using a catalyst such as BF₃ or a BF₃ complex. A further intermediate product, consisting of a mixture of

hydrocarbons ranging from C10 to about C75, results. This oligomeric mixture of hydrocarbons is then hydrogenated to reduce the amount of unsaturation. The saturated hydrocarbon mixture is then distilled to obtain the targeted composition and finally blended to meet desirable base oil product specifications (such as kinematic viscosity at 40 °C) for the engine oil. Desirable examples of biobased base oil specifications that can be used to produce blends suitable for engine oil formulation for one embodiment are set forth in Table 2. In some embodiments in this disclosure, a commercially available biobased hydrocarbon base oil (a hydrogenated reaction product between a partially hydrogenated p-3,7,11-trimethyldodeca-1,3,6,10-tetraene and a linear C8-C16 alpha olefin, hydrogenated) sold under the commercial designation NOVASPEC (Nowvi LLC, Emeryville, CA, United States; (REACH registration number 01-2120031429-59-0000), is used.

Table 2
Example Biobased Base Oil Specifications

<i>Properties</i>	<i>Method</i>	<i>3cSt base oil</i>	<i>4cSt base oil</i>	<i>7cSt base oil</i>	<i>12cSt base oil</i>
Appearance	Visual	Bright and Clear	Bright and Clear	Bright and Clear	Bright and Clear
Color	ASTM D1500-12	0.5	0.5	0.5	0.5
Density, 15°C (kg/l)	ASTM D4052-11	0.82	0.82	0.82	0.82
Viscosity, 40°C (cSt)	ASTM D445-14E2	12.5	19.2	46.1	105.5
Viscosity, 100°C (cSt)	ASTM D445-14E2	3.1	4.2	7.5	12.3
Viscosity Index	ASTM D445-14E2	110	124	126	122
Pour point (°C)	ASTM D97-12	-60	-42	-51	-42
Flash point (°C)	ASTM D92-12b	188	226	254	280

[028] Advantageously, in certain embodiments, at least about 20% of the carbon atoms in the base oil comprised by an engine oil originate from renewable carbon sources. For example, in one such embodiment at least about 30% of the carbon atoms in the base oil comprised by an engine oil originate from renewable carbon sources. By way of further example, in one such embodiment at least about 40% of the carbon atoms in the base oil comprised by an engine oil originate from renewable carbon sources. By way of further example, in one such embodiment at least about 50% of the carbon atoms in the base oil comprised by an engine oil originate from renewable carbon sources. By way of further example, in one such embodiment at least about 60% of the carbon atoms in the base oil comprised by an engine oil originate from renewable carbon sources. By way of further example, in one such embodiment at least about 70% of the carbon atoms in the base oil comprised by an engine oil originate from renewable carbon sources. By way of further example, in one such embodiment at least about 80% of the carbon atoms in the base oil comprised by an engine oil originate from renewable carbon sources. By way of further example, in one such embodiment at least about 90% of the carbon atoms in the base oil comprised by an engine oil originate from renewable carbon sources. In some variations, the carbon atoms of the base oil component of the engine oil comprises at least about 95%, at least about 97%, at least about 99%, or about 100% of originate from renewable carbon sources. The origin of carbon atoms in the reaction product adducts may be determined by any suitable method, including but not limited to reaction mechanism combined with analytical results that demonstrate structure and/or molecular weight of adducts, or by carbon dating (e.g., according to ASTM D6866-12 "Standard Test Methods for Determining the Biobased Content of Solid, Liquid, and Gaseous Samples Using Radiocarbon Analysis," which is incorporated herein by reference in its entirety). For example, using ASTM D6866-12 or another suitable technique, a ratio of carbon 14 to carbon 12 isotopes in the biobased base oil can be measured by liquid scintillation counting and/or isotope ratio mass spectroscopy to determine the amount of modern carbon content in the sample. A

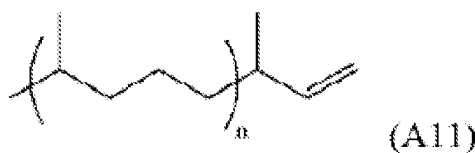
measurement of no modern carbon content indicates all carbon is derived from fossil fuels. A sample derived from renewable carbon sources will indicate a concomitant amount of modern carbon content, up to 100%.

[029] In some embodiments of this disclosure, one or more repeating units of biobased hydrocarbon base oil are specific species of partially hydrogenated conjugated hydrocarbon terpenes. Such specific species of partially hydrogenated conjugated terpenes may or may not be produced by a hydrogenation process. In certain variations, a partially hydrogenated hydrocarbon terpene species is prepared by a method that includes one or more steps in addition to or other than catalytic hydrogenation.

[030] In some embodiments of this disclosure, the biobased hydrocarbon base oil can be categorized as a Group III+ base oil having greater than or equal to 90% saturates and less than or equal to 0.03% sulfur and have a viscosity index greater than or equal to 120.

[031] Non-limiting examples of specific species partially hydrogenated conjugated hydrocarbon terpenes include any of the structures provided herein for dihydrofarnesene, tetrahydrofarnesene, and hexahydrofarnesene; any of the structures provided herein for dihydromyrcene and tetrahydromyrcene; and any of the structures provided herein for dihydroocimene and tetrahydroocimene.

[032] One example of a particular species of partially hydrogenated conjugated hydrocarbon terpene that may have utility as a feedstock is a terminal olefin having a saturated hydrocarbon tail with structure (A11):



where $n = 1, 2, 3, \text{ or } 4$.

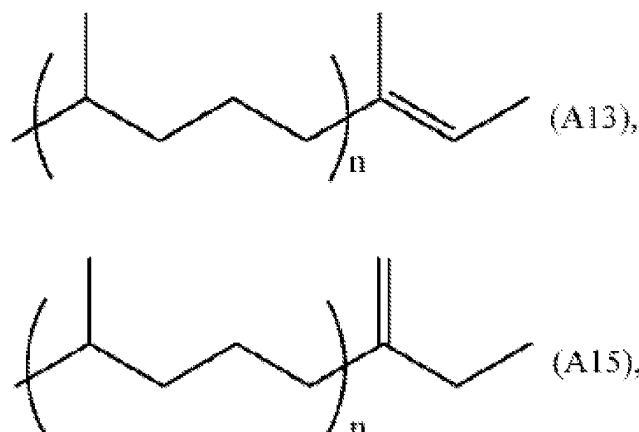
[033] In some variations, a mono-olefinic alpha-olefin having structure A11 may be derived from a conjugated hydrocarbon terpene wherein the conjugated diene is at the 1,3 -position of the terpene. Examples include alpha-olefins derived from a 1

,3- diene conjugated hydrocarbon terpene (e.g., a C₁₀-C₃₀ conjugated hydrocarbon terpene such as farnesene, myrcene, ocimene, springene, geranylfarnesene, neophytadiene, trans-phyta- 1,3 -diene, or cz's-phyta-l,3-diene). Another non-limiting example of an alpha-olefin having the general structure A11 includes 3,7,11-trimethyldodecene having structure A12.



[034] A mono-olefinic alpha-olefin having structure A11 may be prepared from the appropriate conjugated hydrocarbon terpene using any suitable method. In some variations, the mono-olefinic alpha-olefin having structure A11 is produced from primary alcohol of corresponding to the hydrocarbon terpene (e.g., farnesol in the case of farnesene, or geraniol in the case of myrcene). The methods comprise hydrogenating the primary alcohol, forming a carboxylic acid ester or carbamate ester from the hydrogenated alcohol, and pyrolyzing the ester (or heating the ester to drive the elimination reaction) to form the alpha-olefin with a saturated hydrocarbon tail, e.g., as described in Smith, L. E.; Rouault, G. F., J. Am. Chem. Soc. 1943, 65, 745-750, for the preparation of 3,7-dimethyloctene, which is incorporated by reference herein in its entirety. The primary alcohol of the corresponding hydrocarbon terpene may be obtained using any suitable method.

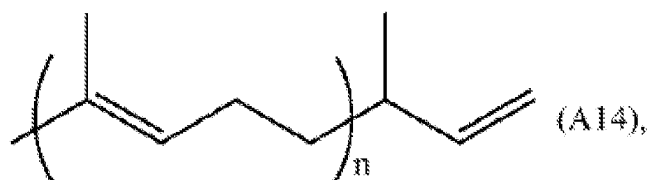
[035] Other examples of particular species of partially hydrogenated conjugated hydrocarbon terpene that may have utility as a feedstock are mono-olefins having a saturated hydrocarbon tail with structure (A13) or structure (A15):



where $n = 1, 2, 3$, or 4 . A mono-olefin having the general structure A13, A15 or A11 may in certain instances be derived from a conjugated hydrocarbon terpene having a 1,3-diene moiety, such as myrcene, farnesene, springene, geranylarnesene, neophytadiene, trans-phyta-1,3-diene, or c/Sup'/Sup-s-phyta-1,3-diene. Here again, the conjugated may be functionalized with a protecting group (e.g., via a Diels- Alder reaction) in a first step, exocyclic olefinic bonds hydrogenated in a second step, and the protecting group eliminated in a third step. In one non-limiting example of a method for making mono-olefins having the structure A13, A15 or A11, a conjugated hydrocarbon terpene having a 1,3-diene is reacted with SO_2 in the presence of a catalyst to form a Diels- Alder adduct. The Diels- Alder adduct may be hydrogenated with an appropriate hydrogenation catalyst to saturate exocyclic olefinic bonds. A retro Diels-Alder reaction may be carried out on hydrogenated adduct (e.g., by heating, and in some instances in the presence of an appropriate catalyst) to eliminate the sulfone to form a 1,3-diene. The 1,3-diene can then be selectively hydrogenated using a catalyst known in the art to result in a mono-olefin having structure A11, A13 or A15, or a mixture of two or more of the foregoing. Non-limiting examples of regioselective hydrogenation catalysts for 1,3- dienes are provided in Jong Tae Lee et al, "Regioselective hydrogenation of conjugated dienes catalyzed by hydridopentacyanocobaltate anion using β -cyclodextrin as the phase transfer agent and lanthanide halides as promoters," J. Org. Chem., 1990, 55 (6), pp. 1854-1856, in V.

M. Frolov et al, "Highly active supported palladium catalysts for selective hydrogenation of conjugated dienes into olefins," Reaction Kinetics and Catalysis Letters, 1984, Volume 25, Numbers 3-4, pp. 319-322, in Tungler, A., Hegedus, L., Fodor, K., Farkas, G., Furcht, A. and Karancsi, Z. P. (2003) "Reduction of Dienes and Polyenes," in The Chemistry of Dienes and Polyenes, Volume 2 (ed. Z. Rappoport), John Wiley & Sons, Ltd, Chichester, UK. , and in Tungler, A., Hegedus, L., Fodor, K., Farkas, G., Furcht, A. and Karancsi, Z. P., "Reduction of Dienes and Polyenes" in Patai's Chemistry of Functional Groups (John Wiley and Sons, Ltd, published online December 15, 2009,, each of which is incorporated herein by reference in its entirety. For example, a catalyst known in the art for 1,4 hydrogen addition to 1,3- dienes results in a mono-olefin having structure A13. In one non-limiting example, β - farnesene can be reacted with SO₂ in the presence of a catalyst to form a Diels-Alder adduct, which is subsequently hydrogenated, and the sulfone eliminated to form a 1,3- diene, which is subsequently selectively hydrogenated using a catalyst known in the art for regioselective hydrogen additions to 1,3-dienes to form 3,7,11-trimethyldodec-2-ene, 3,7,11 - trimethyldodec-1 -ene, or 3-methylene-7,11 -dimethyldodecane, or a mixture of any two or more of the foregoing.

[036] In yet another example of a particular species of partially hydrogenated hydrocarbon terpene that may have utility as a feedstock, a terminal olefin of the general structure A14 may be made from a conjugated hydrocarbon terpene having a 1,3-conjugated diene and at least one additional olefinic bond (e.g., myrcene, farnesene, springene, or geranylfarnesene):



where $n = 1, 2, 3$, or 4 . In one non-limiting variation, a compound having the structure A14 may be derived from an unsaturated primary alcohol corresponding to the relevant hydrocarbon terpene (e.g., farnesol in the case of farnesene, or geraniol in the

case of myrcene). The unsaturated primary alcohol may be exposed to a suitable catalyst under suitable reaction conditions to dehydrate the primary alcohol to form the terminal olefin A 14.

[037] An olefinic feedstock as described herein may comprise any useful amount of the particular species (e.g., alpha-olefinic species having structure A11, A12 or A15, mono-olefinic species having structure A13, or unsaturated terminal olefin species having structure A14), made either by a partial hydrogenation route or by another route, e.g., as described herein. In certain variations, an olefinic feedstock comprises at least about 1 %, at least about 5%, at least about 10%, at least about 20%, at least about 30%, at least about 40%, at least about 50%, at least about 60%, at least about 70%, at least about 80%, or at least about 90% species having structure A11, A12, A13, A14, or A15. In certain variations, an olefinic feedstock comprises at least about 1 %, at least about 5%, at least about 10%, at least about 20%, at least about 30%, at least about 40%, at least about 50%, at least about 60%, at least about 70%, at least about 80%, or at least about 90% 3,7,11-trimethyldodec-1-ene. In certain variations, an olefinic feedstock comprises at least about 1 %, at least about 5%, at least about 10%, at least about 20%, at least about 30%, at least about 40%, at least about 50%, at least about 60%, at least about 70%, at least about 80%, or at least about 90% 3-methylene-7,11-dimethyldodecane. In certain variations, an olefinic feedstock comprises at least about 1 %, at least about 5%, at least about 10%, at least about 20%, at least about 30%, at least about 40%, at least about 50%, at least about 60%, at least about 70%, at least about 80%, or at least about 90% 3,7,11-trimethyldodec-2-ene. In certain variations, an olefinic feedstock comprises at least about 1 %, at least about 5%, at least about 10%, at least about 20%, at least about 30%, at least about 40%, at least about 50%, at least about 60%, at least about 70%, at least about 80%, or at least about 90% 3,7,11-trimethyldodeca-1,6,10-triene. In certain variations, an olefinic feedstock comprises at least about 1 %, at least about 5%, at least about 10%, at least about 20%, at least about 30%, at least about 40%, at least about 50%, at least about 60%, at least about 70%, at least about 80%, or at least about 90% 3,7-dimethyloct-1

- ene. In certain variations, an olefinic feedstock comprises at least about 1 %, at least about 5%, at least about 10%, at least about 20%, at least about 30%, at least about 40%, at least about 50%, at least about 60%, at least about 70%, at least about 80%, or at least about 90% 3,7-dimethyloct-2-ene. In certain variations, an olefinic feedstock comprises at least about 1 %, at least about 5%, at least about 10%, at least about 20%, at least about 30%, at least about 40%, at least about 50%, at least about 60%, at least about 70%, at least about 80%, or at least about 90% 3,7-dimethylocta-1,6-diene.

[038] As described herein, in some variations, the hydrocarbon terpene feedstock comprising alpha-olefinic species or internal olefinic species of partially hydrogenated hydrocarbon terpenes are suitable for catalytic reaction with one or more alpha-olefins to form a mixture of isoparaffins comprising adducts of the terpene and the one or more alpha-olefins. In some variations, at least a portion of the mixture of isoparaffins so produced may be used as a base oil.

[039] In one embodiment, the biobased oil contains at least about 25% of the carbon atoms in the biobased base oil originate from renewable carbon sources as measured by ASTM-D6866-12, at least about 40% of the carbon atoms in the biobased base oil originate from renewable carbon sources as measured by ASTM-D6866-12, at least about 50% of the carbon atoms in the biobased base oil originate from renewable carbon sources as measured by ASTM-D6866-12, at least about 60% of the carbon atoms in the biobased base oil originate from renewable carbon sources as measured by ASTM-D6866-12, at least about 70% of the carbon atoms in the biobased base oil originate from renewable carbon sources as measured by ASTM-D6866-12, at least about 80% of the carbon atoms in the biobased base oil originate from renewable carbon sources as measured by ASTM-D6866-12, or at least about 90% of the carbon atoms in the biobased base oil originate from renewable carbon sources as measured by ASTM-D6866-12.

[040] In one embodiment the biobased base oil additionally has an average methyl branch index (methyl branches per 100 carbons) of at least 7, has an average methyl branch index (methyl branches per 100 carbons) of at least 8, has an average

methyl branch index (methyl branches per 100 carbons) of at least 9, has an average methyl branch index (methyl branches per 100 carbons) of at least 10, has an average methyl branch index (methyl branches per 100 carbons) of at least 11, has an average methyl branch index (methyl branches per 100 carbons) of at least 15, has an average methyl branch index (methyl branches per 100 carbons) of at least 20, has an average methyl branch index (methyl branches per 100 carbons) of at least 22, has an average methyl branch index (methyl branches per 100 carbons) of at least 24, has an average methyl branch index (methyl branches per 100 carbons) of at least 26, has an average methyl branch index (methyl branches per 100 carbons) of at least 27.

[041] In one embodiment, the molecular weight of the biobased base oil is in range of 300 g/mol to 800 g/mol, the molecular weight of the biobased base oil is in range of 390 g/mol to 510 g/mol.

[042] The biobased base oil comprises at least 95% non-cyclic isoparaffins having a molecular structure in which 25-34% of total carbon atoms are contained in the branches and less than half of the total isoparaffin branches contain two or more carbon atoms and the engine oil has a renewable hydrocarbon content greater than 25%, as measured by ASTM-D6866 method.

[043] In one embodiment, at least 95 wt% of the biobased base oil comprises acyclic isoparaffins and at least 25 wt% of the acyclic isoparaffins are hydrogenated sesquiterpenoid monomer units, at least 30 wt% of the acyclic isoparaffins are hydrogenated sesquiterpenoid monomer units, at least 35 wt% of the acyclic isoparaffins are hydrogenated sesquiterpenoid monomer units, or at least 45 wt% of the acyclic isoparaffins are hydrogenated sesquiterpenoid monomer units.

[044] In one embodiment, the biobased base oil has greater than 50% of biodegradation in 28 days according to OECD 301 B test method, the biobased base oil has greater than 60% of biodegradation in 28 days according to OECD 301 B test method, the biobased base oil has greater than 70% of biodegradation in 28 days according to OECD 301 B test method.

[045] In one embodiment, the biobased base oil is characterized by a viscosity index (VI) greater than 120, as measured in accordance with ASTM D2270-10, and has a branch ratio of less than 0.41.

[046] In one embodiment, the biobased base oil is characterized by a viscosity index (VI) greater than 120, as measured in accordance with ASTM D2270-10, and greater than 40% of the biobased base oil molecules have more than 3 methyl branch per molecule, at least 50% of the biobased base oil molecules have more than 3 methyl branch per molecule, at least 60% of the biobased base oil molecules have more than 3 methyl branch per molecule,

[047] In one embodiment, the biobased base oil is characterized by a viscosity index (VI) greater than 120, as measured in accordance with ASTM D2270-10, and greater than 25% of the biobased base oil molecules have more than 6 methyl branch per molecule, at least 30% of the biobased base oil molecules have more than 3 methyl branch per molecule, at least 40% of the biobased base oil molecules have more than 3 methyl branch per molecule, at least 50% of the biobased base oil molecules have more than 3 methyl branch per molecule, at least 60% of the biobased base oil molecules have more than 3 methyl branch per molecule.

[048] In one embodiment, the biobased base oil is characterized in having a renewable carbon content greater than 60% as measured by ASTM-D6866-12, greater than 70% as measured by ASTM-D6866-12, greater than 80% as measured by ASTM-D6866-12, greater than 90% as measured by ASTM-D6866-12.

[049] The base oil has a saturate content of at least 90% as determined by ASTM-D2007-1.

[050] In one embodiment at least 50% of hydrocarbon molecules comprised by the base oil comprise an odd number of carbon atoms per molecule, at least 60% of hydrocarbon molecules comprised by the base oil comprise an odd number of carbon atoms per molecule, at least 70% of hydrocarbon molecules comprised by the base oil comprise an odd number of carbon atoms per molecule, at least 80% of

hydrocarbon molecules comprised by the base oil comprise an odd number of carbon atoms per molecule.

[051] In one embodiment, the biobased base oil has greater than 60% of biodegradation in 28 days according to OECD 301 B test method, the biobased base oil has greater than 70% of biodegradation in 28 days according to OECD 301 B test method.

[052] The base oil comprises a biobased terpene selected from the group consisting of myrcene, ocimene, farnesene, and combinations thereof. In one embodiment, the base oil comprises farnesene. In one embodiment, the biobased base oil is derived from farnesene. In one embodiment the biobased base oil is derived from sugar.

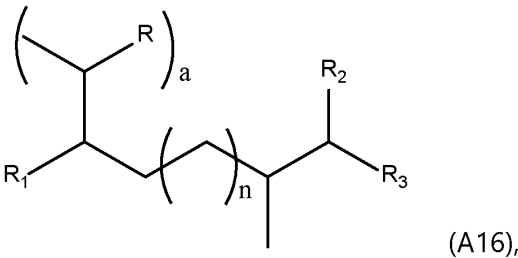
[053] In an aspect, the biobased base oil is a saturated hydrocarbon mixture having a unique branching structure as characterized by NMR that makes it suitable to be used as a high-quality synthetic base stock. The hydrocarbon mixture has outstanding properties including extremely low volatility, good low-temperature properties, etc., which are important performance attributes of high-quality base stocks. Specifically, the mixture comprises greater than 80% of the molecules with an even carbon number according to FIMS. The branching characteristics of the hydrocarbon mixture by NMR comprises a BP/BI in the range ≥ -0.6037 (Internal alkyl branching per molecule)+2.0. Moreover, on average, at least 0.3 to 1.5 of the internal methyl branches are located more than four carbons away from the end carbon..

[054] Biobased base oils may include oligomerization products of alpha-alkenes. In some embodiments, the oligomerization products may be hydrogenated and/or hydroisomerized.

[055] In one embodiment, the hydrocarbon mixtures described herein are the product of oligomerization of olefins and a subsequent hydroisomerization. C₁₄ to C₂₀ olefins are oligomerized to form an oligomer distribution consisting of unreacted monomer, dimers (C₂₈-C₄₀), and trimers and higher oligomers ($\geq$ C₄₂). The unreacted monomers are distilled off for possible re-use in a subsequent oligomerization. The

remaining oligomers are then hydroisomerized to achieve the final branching structures described herein.

[056] In one embodiment, the oligomerization product may have the following structure:



wherein

n = 1 (denotes C16 olefin) or 3 (denotes C18 olefin)

R = C16-C18 or H

R₁ = C9-C13

R₂ = C₄H₁₀ linear or branched

R₃ = C9-C13

a is a value which results in a molecular weight ranging from about 220 to 1020 g/mol.

Lubricating Oil Composition

[057] The lubricating oil composition of this disclosure can be identified by viscosity standards of the Society of Automotive Engineers (SAE) for engine oils (i.e., the SAE J300 standard). The SAE J300 viscosity grades are summarized in Table 3.

Table 3

SAE Viscosity Grade	Low Temp (°C) Cranking Viscosity ⁽¹⁾ , mPa*s Max	Low Temp (°C) Pumping Viscosity ⁽²⁾ , mPa*s Max with No Yield Stress	Low Shear Rate Kinematic Viscosity ⁽³⁾ (mm ² /s) at 100°C Min	Low Shear Rate Kinematic Viscosity ⁽³⁾ (mm ² /s) at 100°C Max	High Shear Rate Viscosity ⁽⁴⁾ , (mPa*s) at 150°C Min
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0W	6200 at -35	60000 at -40	3.8	-	-
5W	6600 at -30	60000 at -35	3.8	-	-
10W	7000 at -25	60000 at -30	4.1	-	-
15W	7000 at -20	60000 at -25	5.6	-	-
20W	9500 at -15	60000 at -20	5.6	-	-
25W	13000 at -10	60000 at -15	9.3	-	-
8	-	-	4.0	<6.1	1.7
12	-	-	5.0	<7.1	2.0
16	-	-	6.1	<8.2	2.3
20	-	-	6.9	<9.3	2.6
30	-	-	9.3	<12.5	2.9
40	-	-	12.5	<16.3	3.5 ⁽⁵⁾
40	-	-	12.5	<16.3	3.7 ⁽⁶⁾
50	-	-	16.3	<21.9	3.7
60	-	-	21.9	<26.1	3.7

(1) ASTM D5293

(2) ASTM D4684

(3) ASTM D445

(4) ASTM D4683, ASTM D4741, ASTM D5481 or CEC L-36-90

(5) For 0W-40, 5W-40 and 10W-40 grades

(6) For 15W-40, 20W-40, 25W-40 and 40 grades

[058] The lubricating oil composition of this disclosure may be a monograde engine oil, e.g., a SAE 20, SAE 30, SAE 40, SAE 50 or SAE 60 viscosity grade engine oil.

Additives

[059] The lubricating oil compositions of the present disclosure may contain one or more performance additives that can impart or improve any desirable property of the lubricating oil composition. Any additive known to those of skill in the art may be used in the lubricating oil composition disclosed herein. Some suitable additives have been described by R. M. Mortier et al. "Chemistry and Technology of Lubricants,"

3rd Edition, Springer (2010) and L. R. Rudnik "Lubricant Additives: Chemistry and Applications," Second Edition, CRC Press (2009).

[060] In general, the concentration of each of the additives in the lubricating oil composition, when used, may range from 0.001 to 60 wt. % (e.g., 0.01 to 50 wt. %, or 0.05 to 40 wt. %) of the lubricating oil composition. Further, the total amount of additives in the lubricating oil composition may range from 0.001 to 70 wt. % (e.g., 0.01 to 50 wt. % or 0.1 to 40 wt. %) of the lubricating oil composition.

[061] The present lubricating oil composition may additionally contain one or more of the other commonly used lubricating oil performance additives including antioxidants, anti-wear agent, metal detergents, dispersants, friction modifiers, corrosion inhibitors, demulsifiers, viscosity modifiers, pour point depressants, foam inhibitors, thickeners, and others.

Antioxidants

[062] Antioxidants retard the oxidative degradation of base oils during service. Such degradation may result in deposits on metal surfaces, the presence of sludge, or a viscosity increase in the lubricant. Useful antioxidants include hindered phenols, aromatic amines, and sulfurized alkylphenols and alkali and alkaline earth metal salts thereof.

[063] The hindered phenol antioxidant may contain a secondary butyl and/or a tertiary butyl group as a sterically hindering group. The phenol group may be further substituted with a hydrocarbyl group and/or a bridging group linking to a second aromatic group. Examples of suitable hindered phenol antioxidants include 2,6-di-tert-butylphenol, 4-methyl-2,6-di-tert-butylphenol, 2,2'-methylenebis(6-tert-butyl-4-methylphenol), 4,4'-bis(2,6-di-tert-butylphenol) and 4,4'-methylenebis(2,6-di-tert-butylphenol). The hindered phenol antioxidant may be an ester or an addition product derived from 2,6-di-tert-butylphenol and an alkyl acrylate, wherein the alkyl group may contain from 1 to 18 carbon atoms. The hindered phenol antioxidant may be a 2,6-di-alkyl-phenolic propionic ester derivative.

[064] Non-phenolic antioxidants which may be used include aromatic amine antioxidants such as diarylamines and alkylated diarylamines. Particular examples of aromatic amine antioxidants include diphenylamines (e.g. N-phenyl-2-naphthylamine, 4,4'-dioctyldiphenylamine, butylated/octylated diphenylamine, nonylated diphenylamine, and octylated N-phenyl-2-naphthylamine.)

[065] In one embodiment, the lubricating oil composition of this disclosure includes a hindered phenol antioxidant. The hindered phenol antioxidant can be present in the lubricating oil composition at 0 to 10.0 wt.% (e.g. at 0.5 to 10.0 wt.%, 0 to 5.0 wt.%, 0.5 to 4.0 wt.%, at 0.5 to 4.5 wt.%, at 0.5 to 4.0 wt.%, at 0.5 to 3.5 wt.%, at 0.5 to 3.0 wt.%, at 0.5 to 2.5 wt.%, at 1.0 to 10.0 wt.%, 1.0 to 4.5 wt.%, at 1.0 to 4.0 wt.%, at 1.0 to 3.5 wt.%, at 1.0 to 3.0 wt.%, or at 1.0 to 2.5 wt.%.)

[066] In one embodiment, the lubricating oil composition of this disclosure includes an aminic antioxidant. The aminic antioxidant can be present in the lubricating oil composition at 0 to 10.0 wt.% (e.g. at 0 to 5.0 wt.%, 0.5 to 5.0 wt.%, 0.5 to 4.0 wt.%, at 0.5 to 4.5 wt.%, at 0.5 to 4.0 wt.%, at 0.5 to 3.5 wt.%, at 0.5 to 3.0 wt.%, at 0.5 to 2.5 wt.%, at 1.0 to 4.5 wt.%, at 1.0 to 4.0 wt. %, at 1.0 to 3.5 wt.%, at 1.0 to 3.0 wt.%, or at 1.0 to 2.5 wt.%.)

[067] In accordance with the present disclosure, the lubricating oil composition can include a combination of hindered phenol antioxidant and aminic antioxidant. The combination may provide a ratio (in terms of mass percent) of phenolic antioxidant to aminic antioxidant of 1:1 to 100:1 (e.g., 1:1 to 75:1, 1:1 to 50:1, 1:1 to 25:1, 1:1 to 1:10, 1:1 to 8:1; 1:1 to 6:1; 1:1 to 5:1; 1:1 to 4:1; or of 1:1 to 3:1.)

[068] In some embodiments, the lubricating oil composition does not contain an aminic antioxidant. In some embodiments, the hindered phenol is the only antioxidant present in the lubricating oil composition.

Anti-Wear Agents

[069] Anti-wear agents reduce wear of metal parts. Examples of anti-wear agents include phosphorus-containing anti-wear/extreme pressure agents such as metal thiophosphates, phosphoric acid esters and salts thereof, phosphorus-

containing carboxylic acids, esters, ethers, and amides; and phosphites. The anti-wear agent may be a zinc dialkyldithiophosphate. Non-phosphorus-containing anti-wear agents include borate esters (including borated epoxides), dithiocarbamate compounds, molybdenum-containing compounds, and sulfurized olefins.

Metal Detergents

[070] A typical detergent is an anionic material that contains a long chain hydrophobic portion of the molecule and a smaller anionic or oleophobic hydrophilic portion of the molecule. The anionic portion of the detergent is typically derived from an organic acid such as a sulfur acid, carboxylic acid, phosphorous acid, phenol, or mixtures thereof. The counterion is typically an alkaline earth or alkali metal.

[071] In some embodiments, the lubricating oil composition provided herein comprises at least an overbased metal detergent as an additive, or additive components. The metal detergents in lubricating oil compositions can neutralize acidic products within the oil. The metal detergent can also prevent the formation of deposits on the surface of an engine. Depending on the nature of the acid used, the detergent may have additional functions, for example, antioxidant properties.

[072] In certain aspects, lubricating oil compositions contain metal detergents comprising either overbased detergents or mixtures of neutral and overbased detergents. The term "overbased" is intended to define additives which contain a metal content in excess of that required by the stoichiometry of the particular metal and the particular organic acid used. The excess metal exists in the form of particles of inorganic base (e.g., a hydroxide or carbonate) surrounded by a sheath of metal salt. The sheath serves to maintain the particles in dispersion in a liquid oleaginous vehicle. The amount of excess metal is commonly expressed as the ratio of total equivalence of excess metal to equivalence of organic acid and is typically in a range of 0.1 to 30.

[073] Overbased detergents may be further characterized as low overbased, medium overbased, or high overbased. Low overbased detergents may be, for example, an overbased salt having a TBN below 100 mgKOH/g on an active basis. Medium overbased detergents may be, for example, an overbased salt having a TBN

of 100 to 250 mgKOH/g on an actives basis. High overbased detergents may be, for example, an overbased salt having a TBN of greater than 250 mgKOH/g on an actives basis.

[074] Some examples of suitable metal detergents include sulfurized or unsulfurized alkyl toluene, sulfurized or unsulfurized alkyl or alkenyl phenates, alkyl or alkenyl aromatic sulfonates, borated sulfonates, sulfurized or unsulfurized metal salts of multi-hydroxy alkyl or alkenyl aromatic compounds, alkyl or alkenyl hydroxy aromatic sulfonates, sulfurized or unsulfurized alkyl or alkenyl naphthenates, metal salts of alkanolic acids, metal salts of an alkyl or alkenyl multiacid, and chemical and physical mixtures thereof. Other examples of suitable metal detergents include metal sulfonates, phenates, salicylates, phosphonates, thiophosphonates and combinations thereof. The metal can be any metal suitable for making sulfonate, phenate, salicylate or phosphonate detergents. Non-limiting examples of suitable metals include alkali metals, alkaline metals and transition metals. In some embodiments, the metal is Ca, Mg, Ba, K, Na, Li or the like.

[075] Metal salts of phenols and sulfurized phenols (e.g., phenate or sulfurized phenate detergents or calcium sulfurized phenate detergents) are prepared by reaction of the phenol or sulfurized phenol with an appropriate metal compound such as an oxide or hydroxide. Sulfurized phenols may be prepared by reacting a phenol with sulfur or a sulfur containing compound such as hydrogen sulfide, sulfur monohalide or sulfur dihalide, to form products which are generally mixtures of compounds in which two or more phenols are bridged by sulfur-containing bridges. Additional details regarding the general preparation of sulfurized phenates can be found in, for example, U.S. Pat. Nos. 2,680,096; 3,178,368 and 3,801,507, the contents of which are incorporated herein by reference.

[076] The sulfur employed for formation of a sulfurized compound may have any allotropic form of sulfur. The sulfur may be present either as molten sulfur or as a solid (e.g., powder or particulate) or as a solid suspension in a compatible hydrocarbon liquid.

[077] In some embodiments, it is desirable to use calcium hydroxide as the calcium base because of its handling convenience versus, for example, calcium oxide, and also because it affords excellent results. Other calcium bases can also be used, for example, calcium alkoxides.

[078] Suitable alkylphenols which can be used are those wherein the alkyl substituents contain a sufficient number of carbon atoms to render the resulting alkylphenate (e.g., overbased sulfurized calcium alkylphenate) composition oil-soluble. Oil solubility may be provided by a single long chain alkyl substitute or by a combination of alkyl substituents. Typically, the alkylphenol used in will be a mixture of different alkylphenols, e.g., C₂₀ to C₂₄ alkylphenol. In one embodiment, suitable alkyl phenolic compounds will be derived from isomerized normal alpha olefin alkyl groups having from about 10 to about 40 carbon atoms per molecule, having an isomerization level of the alpha olefin between from about 0.1 to about 0.4. Isomerization level can be determined by the method described in US11485928, the contents of which are incorporated herein by reference. In one embodiment, the isomerized normal alpha olefins have from about 20 to about 24 carbon atoms. In one embodiment, suitable alkyl phenolic compounds will be derived from alkyl groups which are branched olefinic propylene oligomers or mixture thereof having from about 9 to about 80 carbon atoms. In one embodiment, the branched olefinic propylene oligomer or mixtures thereof have from about 9 to about 40 carbon atoms. In one embodiment, the branched olefinic propylene oligomer or mixtures thereof have from about 9 to about 18 carbon atoms. In one embodiment, the branched olefinic propylene oligomer or mixtures thereof have from about 9 to about 12 carbon atoms.

[079] In one embodiment, suitable alkyl phenolic compounds include distilled cashew nut shell liquid (CNSL) or hydrogenated, distilled CNSL. Distilled CNSL is a mixture of biodegradable meta-hydrocarbyl substituted phenols, where the hydrocarbyl group is linear and unsaturated, including cardanol. Catalytic hydrogenation of distilled CNSL gives rise to a mixture of meta-hydrocarbyl substituted phenols predominantly rich in 3-pentadecylphenol.

[080] The alkylphenols can be para-alkylphenols, meta-alkylphenols or ortho alkylphenols. In certain embodiments, such as where overbased products are desired, the alkylphenol is preferably predominantly a para alkylphenol with no more than about 45 mole percent of the alkylphenol being ortho alkylphenols; and more preferably no more than about 35 mole percent of the alkylphenol is ortho alkylphenol. Alkyl-hydroxy toluenes or xylenes, and other alkyl phenols having one or more alkyl substituents in addition to at least one long chained alkyl substituent can also be used. In the case of distilled cashew nut shell liquid, the catalytic hydrogenation of distilled CNSL gives rise to a mixture of meta-hydrocarbyl substituted phenols.

[081] In general, the selection of alkylphenols can be based on the properties desired for the marine engine lubricating oil compositions, notably TBN, and oil solubility. Additional information regarding preparation of suitable alkylphenols can be found, for example, in U.S. Pat. Nos. 5,024,773, 5,320,763; 5,318,710; and 5,320,762, each of which are incorporated herein by reference.

[082] As noted, certain embodiments of lubricating oil formulations may utilize one or more sulfonate detergents, either alone or in combination with other sulfonates (e.g. combination of high overbased sulfonate and low overbased sulfonate) and other detergents. Sulfonates may be prepared from sulfonic acids which may be 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 of alkyl substituted aromatic hydrocarbons which may be sulfonated include 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 3 to more than 70 carbon atoms. The alkaryl sulfonates usually contain from 9 to 80 or more carbon atoms, preferably from 16 to 60, preferably from 16 to 30, most preferably from 20 to 24 carbon atoms per alkyl substituted aromatic moiety.

[083] In one embodiment, the lubricating oil formulations may utilize a combination of high overbased sulfonate and low overbased sulfonate derived from alkylation of toluene.

[084] The oil soluble sulfonates or alkaryl sulfonic acids may be neutralized with oxides, hydroxides, alkoxides, carbonates, carboxylate, sulfides, hydrosulfides, nitrates, borates and ethers of the metal. The amount of metal compound is chosen having regard to the desired TBN of the final product.

[085] Detergents may also include "hybrid" or "complex" detergents formed with mixed surfactant systems including phenate and/or sulfonate components, e.g., phenate/salicylates, sulfonate/phenates, sulfonate/salicylates, sulfonate/phenate/salicylates, as described for example in US Patents 6,429,178; 6,429,179; 6,153,565. Detergents may also include methylene-bridged polyphenol compositions prepared from the reaction of phenol with formaldehyde, or a reversible polymer thereof, optionally sulfurizing the methylene-bridged intermediate and subsequently reacting the intermediate with an excess of a metal base to produce a methylene bridged polyphenol phenate composition. In one embodiment the methylene bridged polyphenol phenate composition may be further reacted with an epoxide. In one embodiment the methylene bridged polyphenol phenate composition is not sulfurized.

[086] In one or more embodiments, the lubricating oil composition includes a phenol-based detergent which is an overbased sulfurized calcium phenate detergent. In one or more embodiments, the lubricating oil composition includes an overbased sulfurized calcium phenate detergent having a TBN of less than 250 mg KOH/g. In one or more embodiments, the lubricating oil composition includes an overbased sulfurized calcium phenate detergent that is not derived from tetrapropenyl phenol. In one or more embodiments, the lubricating oil composition includes a phenol-based detergent which is an overbased sulfurized calcium phenate detergent derived from

isomerized normal alpha olefin alkyl groups having from about 10 to about 40 carbon atoms per molecule.

[087] Generally, the amount of the detergent can be from about 0.001 wt. % to about 60 wt. %, such as from about 0.05 wt.% to about 40 wt.%, such as about 0.05 wt.% to about 30 wt. %, such as from about 0.05 wt. % to about 25 wt. %, from about 0.1 wt. % to about 20 wt. %, from about 0.01 to 15 wt. %, and from about 0.01 to about 10 wt. % based on the total weight of the marine lubricating oil composition.

[088] In one or more embodiments, the lubricating oil composition includes a low overbased calcium sulfonate detergent, a medium overbased calcium sulfonate detergent, and/or a high overbased calcium sulfonate detergent, or combinations thereof, which is present in an amount to provide a sulfonate soap content in the lubricating oil composition of 10 mmol/kg sulfonate soap or greater (e.g., 10 mmol/kg to 140 mmol/kg, 10 mmol/kg to 100 mmol/kg, 10 mmol/kg to 80 mmol/kg, 25 mmol/kg to 140 mmol/kg, 30 mmol/kg to 140 mmol/kg, 30 mmol/kg to 100 mmol/kg, 40 mmol/kg to 100 mmol/kg, 40 mmol/kg to 80 mmol/kg, or 50 mmol/kg to 100 mmol/kg sulfonate soap) to the lubricant composition.

[089] In one or more embodiments, the lubricating oil composition includes a low overbased calcium sulfonate detergent, a medium overbased calcium sulfonate detergent, and/or a high overbased calcium sulfonate detergent, or combinations thereof, wherein the TBN contribution from sulfonate detergents to total detergent BN contribution is greater than about 20%, greater than about 25% (e.g. 25 to 95%, 25 to 90%, 25 to 85%, 25 to 80%, 30 to 80%).

[090] In one or more embodiments, the lubricating oil composition includes a low overbased calcium sulfonate detergent, a medium overbased calcium sulfonate detergent, and/or a high overbased calcium sulfonate detergent, or combinations thereof, wherein the TBN contribution from sulfonate detergents to total detergent BN contribution is greater than about 20%; and further wherein the sulfonate detergents is present in an amount to provide a sulfonate soap content of 25 mmol/kg to 140 mmol/kg in the lubricating oil composition.

[091] In one or more embodiments, the lubricating oil composition includes a low overbased calcium sulfonate detergent, a medium overbased calcium sulfonate detergent, and/or a high overbased calcium sulfonate detergent, or combinations thereof, wherein the TBN contribution from sulfonate detergents to total detergent BN contribution is 20 to 95%; and further wherein the sulfonate detergents is present in an amount to provide a sulfonate soap content of 25 mmol/kg to 140 mmol/kg in the lubricating oil composition.

[092] In one embodiment, the contribution from the phenol-based detergent can be from one or more phenol-based detergents with similar or different TBN levels. In one embodiment, the sulfonate soap contribution can be from one or more sulfonate detergents with similar or different TBN levels (e.g. combination of low overbased and high overbased).

[093] Other additional detergents can be present in the lubricating oil composition at any appropriate amount, such as at 0.1 to 45 wt. %, or at 0.5 to 30 wt. % of the lubricating oil composition.

Ashless Dispersants

[094] A dispersant is an additive whose primary function is to hold solid and liquid contaminations in suspension, thereby passivating them and reducing engine deposits at the same time as reducing sludge depositions. For example, a dispersant maintains in suspension oil-insoluble substances that result from oxidation during use of the lubricant, thus preventing sludge flocculation and precipitation or deposition on metal parts of the engine.

[095] Dispersants are usually "ashless", being non-metallic organic materials that form substantially no ash on combustion, in contrast to metal-containing, and hence ash-forming materials. They comprise a long hydrocarbon chain with a polar head, the polarity being derived from inclusion of at least one nitrogen, oxygen or phosphorus atom. The hydrocarbon is an oleophilic group that confers oil-solubility, having, for example, 40 to 500 carbon atoms. Thus, ashless dispersants may comprise an oil-soluble polymeric backbone.

[096] A preferred class of olefin polymers is constituted by polybutylenes, specifically polyisobutylenes (PIB) or poly-n-butylenes, such as may be prepared by polymerization of a C4 refinery stream.

[097] Dispersants include, for example, derivatives of long chain hydrocarbon-substituted carboxylic acids, examples being derivatives of high molecular weight hydrocarbyl-substituted succinic acid. A noteworthy group of dispersants is constituted by hydrocarbon-substituted succinimides, made, for example, by reacting the above acids (or derivatives) with a nitrogen-containing compound, advantageously a polyalkylene polyamine, such as a polyethylene polyamine. Typical commercially available polyisobutylene-based succinimide dispersants contain polyisobutylene polymers having a number average molecular weight ranging from 900 to 2500, functionalized by maleic anhydride, and derivatized with polyamines having a molecular weight of from 100 to 350.

[098] Other suitable dispersants include succinic esters and ester-amides, Mannich bases, polyisobutylene succinic acid (PIBSA), and other related components.

[099] Succinic esters are formed by the condensation reaction between hydrocarbon-substituted succinic anhydrides and alcohols or polyols. For example, the condensation product of a hydrocarbon-substituted succinic anhydride and pentaerythritol is a useful dispersant.

[0100] Succinic ester-amides are formed by condensation reaction between hydrocarbon-substituted succinic anhydrides and alkanol amines. For example, suitable alkanol amines include ethoxylated polyalkylpolyamines, propoxylated polyalkylpolyamines and polyalkenylpolyamines such as polyethylene polyamines. One example is propoxylated hexamethylenediamine.

[0101] Mannich bases are made from the reaction of alkylphenols, formaldehyde, and a polyalkylene polyamines. Molecular weights of the alkylphenol may range from 800 to 2500.

[0102] Nitrogen-containing dispersants may be post-treated by conventional methods to improve their properties by reaction with any of a variety of agents. Among

these are boron compounds (e.g., boric acid) and cyclic carbonates (e.g., ethylene carbonate).

[0103] In one embodiment, the dispersant is polyalkenyl bis-succinimide dispersant, wherein the polyalkenyl substituent is derived from a polyalkene group having a number average molecular weight of from about 1500 to about 3000. In one embodiment, the dispersant is non-borated post-treated polyalkenyl bis-succinimide dispersant. In one embodiment the dispersant is post-treated with ethylene carbonate. In one embodiment the dispersant is a non post-treated polyalkenyl bis-succinimide dispersant, wherein the polyalkenyl substituent is derived from a polyalkene group having a number average molecular weight of from about 1000 to about 1500. In one embodiment the dispersant is present in the lubricating composition from 0.05 to 10.0 wt.% (e.g., 0.1 to 10.0 wt.%, 0.1 to 5.0 wt.%, 0.2 to 10 wt.%, or 0.2 to 5.0 wt.%).

Friction Modifiers

[0104] A friction modifier is any material or materials that can alter the coefficient of friction of a surface lubricated by any lubricant or fluid containing such material(s). Friction modifiers include alkoxylated fatty amines, borated fatty epoxides, fatty phosphites, fatty epoxides, fatty amines, borated alkoxylated fatty amines, metal salts of fatty acids, fatty acid amides, glycerol esters, borated glycerol esters and fatty imidazolines. As used herein, the term "fatty" means a hydrocarbon chain having 10 to 22 carbon atoms, typically a straight hydrocarbon chain.

[0105] Other known friction modifiers comprise oil-soluble organo-molybdenum compounds. Such organo-molybdenum friction modifiers also provide antioxidant and anti-wear credits to a lubricating oil composition. Suitable oil-soluble organo-molybdenum compounds have a molybdenum-sulfur core. As examples, there may be mentioned dithiocarbamates, dithiophosphates, dithiophosphinates, xanthates, thioxanthates, sulfides, and mixtures thereof. The molybdenum compound may be dinuclear or trinuclear.

Corrosion Inhibitors

[0106] Corrosion inhibitors protect lubricated metal surfaces against chemical attack by water or other contaminants. Suitable corrosion inhibitors include polyoxyalkylene polyols and esters thereof, polyoxyalkylene phenols, thiadiazoles and anionic alkyl sulfonic acids.

Viscosity Modifiers

[0107] Viscosity modifiers provide lubricants with high and low temperature operability. These additives increase the viscosity of the oil composition at elevated temperatures which increases film thickness, while having limited effect on viscosity at low temperatures.

[0108] Suitable viscosity improvers include high molecular weight hydrocarbons, polyesters and viscosity index improver dispersants that function as both a viscosity index improver and a dispersant. Typical molecular weights of these polymers are in a range of 1000 to 1,000,000 (e.g., 2000 to 500,000 or 25,000 to 100,000).

[0109] Examples of suitable viscosity improvers are polymers and copolymers of methacrylate, butadiene, olefins, or alkylated styrenes. Polyisobutylene is a commonly used viscosity modifier. Another suitable viscosity modifier is polymethacrylate (copolymers of various chain length alkyl methacrylates, for example), some formulations of which also serve as pour point depressants. Other suitable viscosity modifiers include copolymers of ethylene and propylene, hydrogenated block copolymers of styrene and isoprene, and polyacrylates (copolymers of various chain length acrylates, for example). Specific examples include styrene-isoprene or styrene-butadiene based polymers of 50,000 to 200,000 molecular weight.

Pour Point Depressants

[0110] Pour point depressants lower the minimum temperature at which a fluid will flow or can be poured. Suitable pour point depressants include C8 to C18 dialkyl fumarate/vinyl acetate copolymers, polyalkylmethacrylates and the like.

Foam Inhibitors

[0111] Foam inhibitors retard the formation of stable foams. Examples of suitable foam inhibitors include polysiloxanes, polyacrylates, and the like.

Thickener

[0112] A thickener can increase the viscosity of a lubricating oil composition in order to achieve a desired viscosity grade. Any suitable thickener such as bright stock (BS), polyisobutylene (PIB), polymethacrylate (PMA), or olefin copolymer (OCP) may be used.

[0113] PIB is a commercially available material from several manufacturers. Polyisobutylene is typically a viscous oil-miscible liquid having a number average molecular weight of 800 to 5000 (e.g., 1000 to 2500) and a kinematic viscosity at 100° C. of 200 to 5000 mm²/s (e.g., 200 to 1000 mm²/s). The amount of PIB added to the lubricating oil composition will normally be from 1 to 20 wt. % (e.g., 2 to 15 wt. % or 4 to 12 wt. % on an actives basis) of the finished oil.

[0114] Olefin copolymers will generally be present, on an actives basis, at 0.1 wt. % or greater, for example at 0.1 to 12 wt. % of the lubricating oil composition. In certain embodiments, the OCP is present, on an actives basis, at 0.2 to 10 wt. %, 0.3 to 9 wt. %, 0.4 to 8 wt. %, or 0.5 to 7 wt. % of the lubricating oil composition. In still further embodiments, the OCP is present, on an actives basis, at 0.5 to 12.0 wt.%, 0.5 to 5 wt. %, or 1 to 2 wt. % of the lubricating oil composition. In still further embodiments, the OCP is present, on an actives basis, at 1.0 wt. % or greater, for example at 1.0 to 12.0 wt. %, 1.0 wt. % to 5 wt. %, 1.3 wt. % to 4.5 wt. %, 1.5 wt. % to 4.0 wt. %, 2.0 to 12.0 wt.%, or 2.0 wt. % to 3.5 wt. % of the lubricating oil composition.

[0115] In certain embodiments, the olefin copolymers are copolymers based on ethylene units and units of an alpha olefin (e.g., a normal alpha olefin, an isomerized alpha olefin), such as ethylene-propylene copolymer compositions. Other alpha olefins suitable in place of propylene, or in combination with ethylene and propylene to form a terpolymer or tetrapolymer, for example, include: 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene; and branched chain alpha-olefins

such as 4-methyl-1-pentene, 4-methyl-1-hexene, 4-methyl pentene-1,4,4-dimethyl-1-pentene, 6-methylheptene-1, and mixtures thereof.

[0116] The following non-limiting examples are illustrative of the present invention. Brief descriptions of how the examples were prepared are provided.

EXAMPLES

[0117] The impact of ammonia fuel and its combustion products on MCL packages was investigated.

[0118] Fresh test oil samples containing MCL additive packages were contaminated with ammonia using an experimental aging method. The aging method mimics interactions between marine lubricants and ammonia in order to evaluate the impact on marine lubricant bench test performance. Wt.% nitrogen of the aged test oils was measured to demonstrate that an uptake of nitrogen occurred as a result of the ammonia exposure.

[0119] Both fresh test oils and aged test oils were evaluated using Differential Scanning Calorimetry (DSC), Modified IP-48 (MIP-48) and Komatsu Hot Tube (KHT) bench tests.

Marine Cylinder Lubricants

[0120] Marine Cylinder Lubricants were prepared by blending 15 and 40 BN MCL packages in various types of base oil mixtures.

[0121] Base oil mixture A consisted of a major amount of API Group I 600N base oil and minor amount of API Group I XOM 2500 bright stock as a thickener.

[0122] Base oil mixture B consisted of a major amount of biobased base oil SynNova9® (marketed as a Group III+ base oil 100% derived from renewable carbon sources, plant-derived sustainable synthetic base oil (SSBO) having a viscosity of 9.5 cSt @100°C) and minor amount of API Group I XOM 2500 bright stock thickener plus some high molecular weight polyisobutene (PIB2300) which serves to maintain equal

amount of bright stock and compensate for viscosity drop as a result of using the lower-viscosity SSBO.

[0123] Base oil mixture C consisted of a major amount of Chevron RLOP 600R API Group II base oil and minor amount of API Group I XOM 2500BS bright stock as a thickener.

[0124] The resulting test oil samples containing a marine additive package and a base oil mixture are summarized below.

Example 1 (40BN SAE 50 MCL with KV100°C of 18.5 cSt)

- a) Additive Package 1 – 9.0 wt.% oil concentrate of an overbased calcium sulfurized phenate (derived from propylene tetramer) having a TBN of 116BN (40 wt.% diluent oil), 60 mmol/kg sulfonate soap from a mixture of low overbased and high overbased calcium sulfonate detergents, bis-succinimide dispersant derived from 1000MW polyisobutylene, 1.5 wt.% of an antioxidant system having a combination of hindered phenolic antioxidant and diphenylamine aminic antioxidant. TBN contribution from sulfonate detergents was 72% of total detergent BN.
- b) Base oil mixture A – (78.1 wt.% base oil blend) contained 54.7 wt.% of API Group I 600N base oil and 23.4 wt.% API Group I XOM 2500BS bright stock as a thickener

Example 2 (40BN SAE 50 MCL with KV100°C of 18.5 cSt)

- a) Additive Package 1 – 9.0 wt.% oil concentrate of an overbased calcium sulfurized phenate (derived from propylene tetramer) having a TBN of 116BN (40 wt.% diluent oil), 60 mmol/kg sulfonate soap from a mixture of low overbased and high overbased calcium sulfonate detergents, bis-succinimide dispersant derived from 1000MW polyisobutylene, 1.5 wt.% of an antioxidant system having a combination of hindered phenolic

antioxidant and diphenylamine aminic antioxidant. TBN contribution from sulfonate detergents was 72% of total detergent BN.

- b) Base oil mixture B – (78.1 wt%) contained 50.2 wt.% of biobased base oil SynNova9® (a 100% renewable, plant-derived sustainable synthetic base oil (SSBO) having a viscosity of 9.5 cSt @100°C), 23.4 wt.% API Group I XOM 2500BS bright stock thickener, and 4.5 wt.% high molecular weight polyisobutene (PIB2300)

Example 3 (40BN SAE 50 MCL with KV100°C of 18.5 cSt)

- a) Additive Package 2 – 0.9 wt.% oil concentrate of an overbased calcium sulfurized phenate (derived from propylene tetramer) having a TBN of 260 (40 wt.% diluent oil), 9.0wt% oil concentrate of an overbased calcium sulfurized phenate (derived from propylene tetramer) having a TBN of 116BN (40 wt.% diluent oil), 70 mmol/kg sulfonate soap from a mixture of low overbased and high overbased calcium sulfonate detergents, bis-succinimide dispersant derived from 1000MW polyisobutylene, 1.5 wt.% of an antioxidant system having a combination of hindered phenolic antioxidant and diphenylamine aminic antioxidant. TBN contribution from sulfonate detergents was 70% of total detergent BN.
- b) Base oil mixture A – (75.8 wt.% base oil blend) contained 52.2 wt.% of API Group I 600N base oil and 23.6 wt.% API Group I XOM 2500BS bright stock as a thickener

Example 4 (40BN SAE 50 MCL with KV100°C of 18.5 cSt)

- a) Additive Package 2 – 0.9 wt.% oil concentrate of an overbased calcium sulfurized phenate (derived from propylene tetramer) having a TBN of 260 (40 wt.% diluent oil), 9.0wt% oil concentrate of an overbased calcium sulfurized phenate (derived from propylene tetramer) having a TBN of 116BN (40 wt.% diluent oil), 70 mmol/kg sulfonate soap from a mixture of

low overbased and high overbased calcium sulfonate detergents, bis-succinimide dispersant derived from 1000MW polyisobutylene, 1.5 wt.% of an antioxidant system having a combination of hindered phenolic antioxidant and diphenylamine aminic antioxidant. TBN contribution from sulfonate detergents was 70% of total detergent BN.

- b) Base oil mixture B - (75.8 wt%) contained 48.1 wt.% biobased base oil SynNova9® (a 100% renewable, plant-derived sustainable synthetic base oil (SSBO) having a viscosity of 9.5 cSt @100°C), 23.6 wt.% API Group I XOM 2500BS bright stock thickener, and 4.1 wt.% high molecular weight polyisobutene (PIB2300)

Example 5 (40BN SAE 50 MCL with KV100°C of 18.5 cSt)

- a) Additive Package 6 – 2.5 wt.% oil concentrate of an overbased calcium sulfurized phenate (derived from propylene tetramer) having a TBN of 260 (40 wt.% diluent oil), 14.0 wt.% oil concentrate of an overbased calcium sulfurized phenate (derived from propylene tetramer) having a TBN of 116BN (40 wt.% diluent oil), 30 mmol/kg sulfonate soap from a mixture of low overbased and high overbased calcium sulfonate detergents, bis-succinimide dispersant derived from 1000MW polyisobutylene. TBN contribution from sulfonate detergents was 43% of total detergent BN.
- b) Base oil mixture C – (77.6 wt.% base oil blend) 60.3 wt.% of Chevron RLOP 600R API Group II base oil and 17.4 wt.% of API Group I XOM 2500BS bright stock as a thickener.

Example 6 (40BN SAE 50 MCL with KV100°C of 18.5 cSt)

- a) Additive Package 7 – 23.5 wt.% oil concentrate of an overbased calcium sulfurized phenate (derived from C20-24 isomerized olefin) having a TBN of 95 (20 wt.% diluent oil), 27 mmol/kg sulfonate soap from a mixture of low overbased and high overbased calcium sulfonate detergents, bis-

succinimide dispersant derived from 1000MW polyisobutylene. TBN contribution from sulfonate detergents was 43% of total detergent BN.

- b) Base oil mixture C – (71.0 wt.% base oil blend) 57.3 wt.% of Chevron RLOP 600R API Group II base oil and 13.7 wt.% of API Group I XOM 2500BS bright stock as a thickener.

Example 7 (15BN SAE 50 MCL with KV100°C of 18.5 cSt)

- a) Additive Package 8 – 2.7 wt.% oil concentrate of an overbased calcium sulfurized phenate (derived from C20-24 isomerized olefin) having a TBN of 95 (20 wt.% diluent oil), 15 mmol/kg sulfonate soap from a mixture of low overbased and high overbased calcium sulfonate detergents, bis-succinimide dispersant derived from 1000MW polyisobutylene. TBN contribution from sulfonate detergents was 81% of total detergent BN.
- b) Base oil mixture C – (93.8 wt.% base oil blend) 52.4 wt.% of Chevron RLOP 600R API Group II base oil and 41.4 wt.% of API Group I XOM 2500BS bright stock as a thickener.

Example 8 (15BN SAE 50 MCL with KV100°C of 18.5 cSt)

- a) Additive Package 9 – 8.8 wt.% oil concentrate of an overbased calcium sulfurized phenate (derived from C20-24 isomerized olefin) having a TBN of 95 (20 wt.% diluent oil), 10 mmol/kg sulfonate soap from a mixture of low overbased and high overbased calcium sulfonate detergents, bis-succinimide dispersant derived from 1000MW polyisobutylene. TBN contribution from sulfonate detergents was 42% of total detergent BN.
- b) Base oil mixture C – (88.9 wt.% base oil blend) 53.0 wt.% of Chevron RLOP 600R API Group II base oil and 35.9 wt.% of API Group I XOM 2500BS bright stock as a thickener.

Comparative Example A (40BN SAE 50 MCL with KV100°C of 18.5 cSt)

- a) Additive Package 3 (sole phenate) – 14.8 wt.% oil concentrate of an overbased calcium sulfurized phenate (derived from propylene tetramer) having a TBN of 260 (40 wt.% diluent oil), 1.0 wt.% oil concentrate of an overbased calcium sulfurized phenate (derived from propylene tetramer) having a TBN of 116 (40 wt.% diluent oil), bis-succinimide dispersant derived from 1000MW polyisobutylene. TBN contribution from sulfonate detergents was 0% of total detergent BN.
- b) Base oil mixture C – (83.8 wt.% base oil blend) 55.2 wt.% of Chevron RLOP 600R API Group II base oil and 28.6 wt.% of API Group I XOM 2500BS bright stock as a thickener.

Comparative Example B (40BN SAE 50 MCL with KV100°C of 18.5 cSt)

- a) Additive Package 4 (sole sulfonate) – 50 mmol/kg sulfonate soap from a mixture of low overbased and high overbased calcium sulfonate detergents, bis-succinimide dispersant derived from 1000MW polyisobutylene. TBN contribution from sulfonate detergents was 100% of total detergent BN.
- b) Base oil mixture C – (89.2 wt.% base oil blend) 53.9 wt.% of Chevron RLOP 600R API Group II base oil and 35.4 wt.% of API Group I XOM 2500BS bright stock as a thickener.

Comparative Example C (15BN SAE 50 MCL with KV100°C of 18.5 cSt)

- a) Additive Package 5 (sole phenate) - 15.6 wt.% oil concentrate of an overbased calcium sulfurized phenate (derived from C20-24 isomerized olefin) having a TBN of 95 (20 wt.% diluent oil), bis-succinimide dispersant derived from 1000MW polyisobutylene. TBN contribution from sulfonate detergents was 0% of total detergent BN.
- b) Base oil mixture C – (84.0 wt.% base oil blend) 53.4 wt.% of Chevron RLOP 600R API Group II base oil and 30.6 wt.% of API Group I XOM 2500BS bright stock as a thickener.

Aging Protocol

[0125] To demonstrate the impact of ammonia fuel and its combustion products, the test oils were aged in a NH_3 atmosphere. Subsequent bench testing of the aged products provided insights about lubricant performance.

[0126] In the aging process, the 15 and 40BN marine cylinder lubricants were aged with gaseous ammonia (NH_3) at elevated temperature (180°C) for a prolonged period. After establishing an increased nitrogen content of at least about 600 ppm in the sample, a series of bench tests were run.

[0127] "Soap" refers to soap content and refers to the concentration in millimoles/kg of surfactant anion contributed to the formulation by one or more detergents within the composition. For the purposes of this invention, the surfactant concentration is reported in terms of millimoles of surfactant per kg of additive concentrate. Soap, or surfactant, content of a detergent additive can be measured as follows:

Step 1: Determine equivalence % Calcium as sulfonate soap (in mass %) in accordance with ASTM D4251. The value obtained is the [Wt. % calcium/100] in the expression below, or in other words, the wt.% equivalence of calcium as soap in 100 g of additive concentrate.

Step 2: Once % Calcium as sulfonate soap is determined, calculate the number of surfactant anion or "soap" in mmol/kg using the expression below:

$$[\text{Wt.\% calcium}/100] * [1000\text{g}/\text{Kg}] * [1\text{mole calcium}/40\text{g calcium}] * [2\text{ moles surfactant anion}/\text{mole calcium}] * [1000\text{ millimole}/\text{mole}] = \text{millimole surfactant "soap"}/\text{kg of additive concentrate}$$

DSC Oxidation Test

[0128] The DSC test is used to evaluate thin film oxidation stability of test oils, in accordance with ASTM D-6186. Heat flow to and from test oil in a sample cup is compared to a reference cup during the test. The Oxidation Onset Temperature is the temperature at which the oxidation of the test oil starts. The Oxidation Induction Time is the time at which the oxidation of the test oil starts. A higher oxidation induction time means better performance. The oxidation reaction is exothermic and is clearly shown by the heat flow. The Oxidation Induction Time (in minutes) is calculated to evaluate the thin film oxidation stability of the test oil.

Modified Institute of Petroleum 48 (MIP-48) Test

[0129] The MIP-48 Test measures the degree of stability against oxidation-based viscosity increase of the lubricant. The MIP-48 Test consists of a thermal part and an oxidative part. During both parts of the test the samples are heated for a period of time. In the thermal part of the test, nitrogen is passed through a heated oil sample for 24 hours and in parallel during the oxidative part of the test, air is passed through a heated oil sample for 24 hours. The samples are cooled and the viscosities of both samples are determined. The viscosity increase of the test oil caused by oxidation is determined and corrected for the thermal effect. The oxidation-based viscosity increase for each marine lubricating oil composition was calculated by subtracting the kinematic viscosity at 200 °C for the nitrogen-blown sample from the kinematic viscosity at 200 °C for the air-blown sample, and dividing the subtraction product by the kinematic viscosity at 200 °C for the nitrogen blown sample. This is done to correct for potential evaporation effects during the test, or any other thermal effect, thereby focusing on the impact of oxidation. This correction may result in a negative value. Test oils which exhibit better stability against oxidation-based viscosity increase will result in a lower % absolute value. The results of the MIP-48 Test are set forth in Table 1 below.

Komatsu Hot Tube (KHT) Test

[0130] The Komatsu Hot Tube test is a lubrication industry bench test that measures the degree of high temperature detergency and thermal and oxidative stability of a lubricating oil. During the test, a specified amount of test oil is pumped upwards through a glass tube that is placed inside an oven set at a certain temperature. Air is introduced in the oil stream before the oil enters the glass tube, and flows upward with the oil. Evaluations of the marine lubricating oils were conducted at temperatures between 300-320°C. After cooling and washing, the test result is determined by comparing the amount of lacquer deposited on the glass test tube to a rating scale ranging from 1.0 (very black) to 10.0 (perfectly clean). The result is reported in multiples of 0.5. In the case the glass tubes are completely blocked with deposits, the test result is recorded as “blocked”. Blockage is deposition below a 1.0 result, in which case the lacquer is very thick and dark but still allows fluid flow, although at a rate that is completely unsatisfactory for a usable oil.

[0131] Each of the finished oil lubricants of Examples 1-4 were evaluated for oxidation-based viscosity increase using the MIP-48 test, evaluating first the fresh oils and then the NH₃ aged oils. The results for each of the examples are set forth in Table 4 below.

Table 4

	Ex 1 Fresh oil	Ex 1 NH ₃ aging	Ex 2 Fresh oil	Ex 2 NH ₃ aging	Ex 3 Fresh oil	Ex 3 NH ₃ aging	Ex 4 Fresh oil	Ex 4 NH ₃ aging
Additive Package	1	1	1	1	2	2	2	2
Base oil Blend	Gr I/BS	Gr I/BS	SSBO/ PIB	SSBO/ PIB	Gr I/BS	Gr I/BS	SSBO/ PIB	SSBO/ PIB

N, wt%	470	870	450	890	460	910	410	880
MIP-48, % vis increase	25.7	28.5	8.1	7.0	30.3	26.3	9.1	8.6

[0132] Referring to Table 4, the impact of ammonia (NH₃) aging at 180°C had only marginal impacts on the marine cylinder lubricating compositions of the invention. Each ammonia aged test oil exhibited stability against oxidation-based viscosity increase relative to the fresh test oil prior to aging, as is evident by relatively stable % vis increase. This demonstrates that the cylinder lubricants of the invention are compatible with ammonia fuel. In some cases, as in Examples 2, 3 and 4, the test resulted in a smaller % vis increase of the ammonia aged oil than the fresh test oil indicating directionally improved stability against oxidation-based viscosity increase. Overall, the fresh and aged test oils which contained a major amount of SSBO base oil (Examples 2 and 4), over those that contained a major amount of conventional API Group I base oil, resulted in lower absolute value % vis increase indicating better stability against oxidation-based viscosity increase.

[0133] Each of the NH₃ aged Group II based finished oil lubricants of comparative examples A-B and examples 5-6 were evaluated for oxidation-based viscosity increase using the MIP-48 test, for high temperature detergency using the KHT test, and oxidative stability using the DSC test. The results for each of the examples are set forth in Table 5 below.

Table 5

	Comp A NH ₃ aging	Comp B NH ₃ aging	Ex 5 NH ₃ aging	Ex 6 NH ₃ aging
Additive Package	3	4	6	7

Sulfonate BN contribution, %	0	100	43	43
Base oil Blend	Gr II/BS	Gr II/BS	Gr II/BS	Gr II/BS
TBN, mgKOH/g	40	40	40	40
OIT, min	30.98	3.16	36.74	38.46
MIP-48, % vis increase	19.7	107.8	14.2	17.7
KHT (320C)	5.0	blocked	6.0	8.5

[0134] Referring to Table 5, Examples 5 and 6 resulted in lower % vis increase indicating better stability against oxidation-based viscosity increase, higher oxidation induction times and higher ratings in the KHT demonstrating improved oxidative stability and deposit performance over the comparative examples when exposed to ammonia aging.

[0135] Each of the NH₃ aged Group II based finished oil lubricants of comparative example C and examples 7-8 were evaluated for high temperature detergency using the KHT test. The results for each of the examples are set forth in Table 6 below.

Table 6

	Comp C NH ₃ aging	Ex 7 NH ₃ aging	Ex 8 NH ₃ aging
Additive Package	5	8	9
Sulfonate BN contribution, %	0	81	42
Base oil Blend	Gr II/BS	Gr II/BS	Gr II/BS
TBN, mgKOH/g	15	15	15
KHT (320C)	3.5	6.5	7.0

[0136] Referring to Table 6, the 15BN Group II based formulations of Examples 7 and 8 resulted in higher ratings in the KHT test demonstrating improved deposit performance over the comparative example when exposed to ammonia aging.

[0137] For the sake of brevity, only certain ranges are explicitly disclosed herein. However, ranges from any lower limit may be combined with any upper limit to recite a range not explicitly recited, as well as, ranges from any lower limit may be combined with any other lower limit to recite a range not explicitly recited, in the same way, ranges from any upper limit may be combined with any other upper limit to recite a range not explicitly recited. Additionally, within a range includes every point or individual value between its end points even though not explicitly recited. Thus, every point or individual value may serve as its own lower or upper limit combined with any other point or individual value or any other lower or upper limit, to recite a range not explicitly recited.

[0138] Likewise, the term "comprising" is considered synonymous with the term "including." Likewise, whenever a composition, an element or a group of elements is preceded with the transitional phrase "comprising," it is understood that we also contemplate the same composition or group of elements with transitional phrases "consisting essentially of," "consisting of," "selected from the group of consisting of," or "is" preceding the recitation of the composition, element, or elements and vice versa.

[0139] The terms "a" and "the" as used herein are understood to encompass the plural as well as the singular.

[0140] Various terms have been defined above. To the extent a term used in a claim is not defined above, it should be given the broadest definition persons in the pertinent art have given that term as reflected in at least one printed publication or issued patent. Furthermore, all patents, test procedures, and other documents cited in this application are fully incorporated by reference to the extent such disclosure is not inconsistent with this application and for all jurisdictions in which such incorporation is permitted.

[0141] The foregoing description of the disclosure illustrates and describes the present disclosure. Additionally, the disclosure shows and describes only the preferred embodiments but, as mentioned above, it is to be understood that the disclosure is capable of use in various other combinations, modifications, and environments and is capable of changes or modifications within the scope of the concept as expressed herein, commensurate with the above teachings and/or the skill or knowledge of the relevant art. While the foregoing is directed to embodiments of the present disclosure, other and further embodiments of the disclosure may be devised without departing from the basic scope thereof, and the scope thereof is determined by the claims that follow.

[0142] It is understood that when combinations, subsets, groups, etc. of elements are disclosed (e.g., combinations of components in a composition, or combinations of steps in a method), that while specific reference of each of the various individual and collective combinations and permutations of these elements may not be explicitly disclosed, each is specifically contemplated and described herein.

[0143] The embodiments described hereinabove are further intended to explain best modes known of practicing it and to enable others skilled in the art to utilize the disclosure in such, or other, embodiments and with the various modifications required by the particular applications or uses. Accordingly, the description is not intended to limit it to the form disclosed herein. Also, it is intended that the appended claims be construed to include alternative embodiments.

CLAIMS

1. A marine cylinder lubricating oil composition for a non-carbon based fueled marine engine comprising:

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

(b) a mixture of overbased phenol-based detergent and overbased calcium sulfonate detergent; and

wherein the marine cylinder lubricating oil composition has a TBN of less than 200 mg KOH/g, and further wherein the marine engine lubricating oil composition is a monograde lubricating oil composition meeting the specifications for SAE J300 revised January 2015 requirements for a SAE 20, SAE 30, SAE 40, SAE 50 or SAE 60 monograde lubricating oil.

2. The marine cylinder lubricating oil composition of claim 1, wherein the lubricating oil composition is contaminated with ammonia.

3. The marine cylinder lubricating oil composition of claim 1, wherein the oil of lubricating viscosity is a base oil having greater than or equal to 90% saturates and less than or equal to 0.03% sulfur and have a viscosity index greater than or equal to 120.

4. The marine cylinder lubricating oil composition of claim 1, further comprising an ashless dispersant.

5. The marine cylinder lubricating oil composition of claim 1, further comprising a mixture of phenolic antioxidant and aminic antioxidant.

6. The marine cylinder lubricating oil composition of claim 1, wherein the composition has a BN level of 15 to 80 mg KOH/g.

7. The marine cylinder lubricating oil composition of claim 1, wherein the phenol-based detergent in an overbased calcium sulfurized phenate.
8. The marine cylinder lubricating oil composition of claim 1, wherein the sulfonate detergent is one or more sulfonate detergents; wherein the TBN contribution from sulfonate detergents to total detergent BN contribution is 20 to 95%.
9. The marine cylinder lubricating oil composition of claim 1, wherein the sulfonate detergent is one or more sulfonate detergents; wherein the sulfonate detergents is present in an amount to provide a sulfonate soap content of 10 mmol/kg to 140 mmol/kg in the lubricating oil composition.
10. A method of lubricating a marine two-stroke engine operated using ammonia fuel, the method comprising lubricating the engine with a lubricating oil composition comprising:
- (a) a major amount of an oil of lubricating viscosity; and
 - (b) a mixture of an overbased phenol-based detergent and an overbased calcium sulfonate detergent; and
- wherein the marine cylinder lubricating oil composition has a TBN of less than 200 mg KOH/g, and further wherein the marine engine lubricating oil composition is a monograde lubricating oil composition meeting the specifications for SAE J300 revised January 2015 requirements for a SAE 40, SAE 50 or SAE 60 monograde lubricating oil.
11. The method of claim 10, wherein the oil of lubricating viscosity is a base oil having greater than or equal to 90% saturates and less than or equal to 0.03% sulfur and have a viscosity index greater than or equal to 120.

12. The method of claim 10, wherein the oil of lubricating viscosity contains greater than or equal to 90% saturates and less than or equal to 0.03 wt. % sulfur.
13. The method of claim 10, wherein the lubricating oil composition has a BN level of 15 to 80 mg KOH/g.
14. The method of claim 10, wherein the lubricating oil composition further comprises an ashless dispersant.
15. The method of claim 10, wherein the lubricating oil composition further comprises a mixture of phenolic antioxidant and aminic antioxidant.
16. The marine cylinder lubricating oil composition of claim 10, wherein the phenol-based detergent in an overbased calcium sulfurized phenate.
17. The marine cylinder lubricating oil composition of claim 10, wherein the sulfonate detergent is one or more sulfonate detergents; wherein the TBN contribution from sulfonate detergents to total detergent BN contribution is 20 to 95%.
18. The marine cylinder lubricating oil composition of claim 10, wherein the sulfonate detergent is one or more sulfonate detergents; wherein the sulfonate detergents is present in an amount to provide a sulfonate soap content of 10 mmol/kg to 140 mmol/kg in the lubricating oil composition.
19. A method of improving or maintaining deposit control performance and/or oxidative stability of an ammonia-fueled marine engine, the method comprising:
lubricating the engine with a lubricating oil composition comprising:
(a) a major amount of an oil of lubricating viscosity; and

(b) a mixture of an overbased phenol-based detergent and an overbased calcium sulfonate detergent; and

wherein the marine cylinder lubricating oil composition has a TBN of less than 200 mg KOH/g, and further wherein the marine engine lubricating oil composition is a monograde lubricating oil composition meeting the specifications for SAE J300 revised January 2015 requirements for a SAE 40, SAE 50 or SAE 60 monograde lubricating oil.

20. The method of claim 19, wherein the oil of lubricating viscosity is a base oil having greater than or equal to 90% saturates and less than or equal to 0.03% sulfur and have a viscosity index greater than or equal to 120.

21. The method of claim 19, wherein the oil of lubricating viscosity contains greater than or equal to 90% saturates and less than or equal to 0.03 wt. % sulfur.

22. The method of claim 19, wherein the lubricating oil composition has a BN level of 15 to 80 mg KOH/g.

23. The method of claim 19, wherein the lubricating oil composition further comprises an ashless dispersant.

24. The method of claim 19, wherein the lubricating oil composition further comprises a mixture of phenolic antioxidant and aminic antioxidant.

25. The marine cylinder lubricating oil composition of claim 19, wherein the phenol-based detergent is an overbased calcium sulfurized phenate.

26. The marine cylinder lubricating oil composition of claim 19, wherein the sulfonate detergent is one or more sulfonate detergents; wherein the TBN contribution from sulfonate detergents to total detergent BN contribution is 20 to 95%.

27. The marine cylinder lubricating oil composition of claim 19, wherein the sulfonate detergent is one or more sulfonate detergents; wherein the sulfonate detergents is present in an amount to provide a sulfonate soap content of 10 mmol/kg to 140 mmol/kg in the lubricating oil composition.