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(54) Lubricating oil composition for marine applications

(57) A lubricating oil and a lubricant additive composition suitable for use in marine gear applications, including the gears of two-cycle or four-cyale outboard marine engines or the gears of an outdrive of an inboard/outboard marine drivetrain. The lubricating oil and additive composition may exhibit improved water emulsification and wear properties.

EP 1 990 400 A2

Description

TECHNICAL FIELD

[0001] The present disclosure relates to lubricating oil compositions suitable for drivetrains used in marine applications. More particularly, the present invention relates to lubricating oil compositions which improve water tolerance in marine applications.

BACKGROUND

[0002] Outboard motors are self-contained units that include an engine, a drivetrain, and a propeller, and are designed to be mounted at the rear of a water craft. Gear oils are commonly used to lubricate the drivetrains of marine engines, for example the gears of a two-cycle or four-cycle outboard marine engine, or the gears of an outdrive of the inboard/ outboard marine drivetrain. Marine gear oils tend to lose certain performance characteristics and benefits over time in marine environments. Marine gear oils are particularly susceptible to performance deterioration due to the introduction of water into the marine drivetrain. Normally water separates from oil, and in an engine or drivetrain, should this occur, the water will induce corrosion and lead to the hydrolysis of certain lubricant additives leading to acidic byproducts that attack the engine or drivetrain further. The present invention has addressed this problem by creating a wear resistant marine lubricant that is also capable of emulsifying water.

SUMMARY

[0003] The present disclosure provides novel lubricating oils suitable for use in marine gear applications, such as gears of outboard motors. As an example, lubricating oils described herein may be suitable for use in the gears of two-cycle or four-cycle outboard engines, or the gears of the outdrive of an inboard/outboard marine drivetrain. Further, embodiments of the present disclosure may provide lubricating oils suitable for marine applications and having improvements in the following characteristics: antioxidancy, antiwear performance, rust inhibition, shear stability, water tolerance, air entrainment, extreme pressure, and foam reducing properties.

[0004] In an embodiment, a marine lubricant may comprise a major amount of a base oil, at least one metal-containing detergent, at least one phosphorus-based wear preventative, and at least on surfactant.

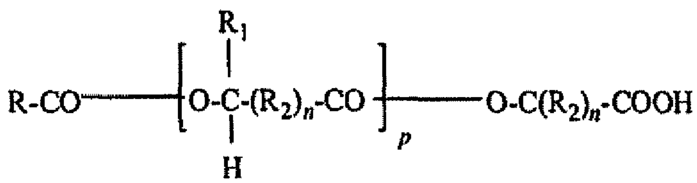
[0005] In some embodiments, the marine lubricant may further comprise a ratio of alkali and/or alkaline earth metal content (ppm) to phosphorus content (ppm). based on the total weight of the lubricant, ranging from about 0.025 to about 1.5 (ppm/ppm).

[0006] In some embodiments, the marine lubricant may achieve a score of about 5 mL or less water separation in a water emulsion test.

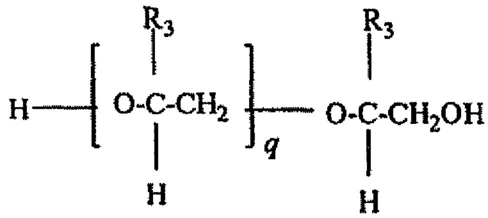
[0007] In some embodiments, the at least one metal detergent may comprise an overbased calcium phenate.

[0008] In some embodiments, the at least one phosphorus-based wear preventative may comprise at least one zinc dihydrocarbyl dithiophosphate compound.

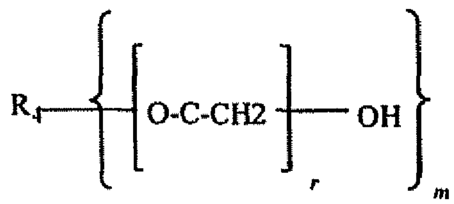
[0009] In some embodiments, the at least one surfactant agent may comprise a block or graft co-polymer of the general formula $(A\text{-}COO)_mB$, where m in an integer of at least 2 and, A is a polymeric component having a molecular weight of at least 500 and is the residue of an oil-soluble complex mono-carboxylic acid of the general structural formula:



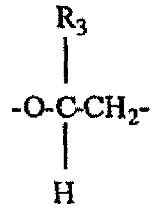
in which R is hydrogen or a monovalent hydrocarbon or substituted hydrocarbon group, R_1 is hydrogen or a monovalent C_1 to C_{24} hydrocarbon group, R_2 is a divalent C_1 to C_{24} hydrocarbon group, n is zero or 1 and p is zero or an integer of up to 200; and B is a polymeric component having a molecular weight of at least 500 and, in the case where m is 2, is the divalent residue of a water-soluble polyalkylene glycol of the general formula:



in which R_3 is hydrogen or a C_1 to C_3 alkyl group, q is an integer from 10 to 500, or, in the case where m is greater than 2, is the residue of valency *m* of a water-soluble polyether polyol of the general formula:



in which R_3 and *m* have their previous significance, *r* is zero or an integer from 1 to 500, provided that the total number of



units in the molecule is at least 10, and R_4 is the residue of an organic compound containing in the molecule m hydrogen atoms reactive with an alkylene oxide.

[0010] In some embodiments, the marine lubricant may contain from about 200 to about 2000 ppm phosphorus from the zinc dihydrocarbyl dithiophosphate compound.

[0011] In some embodiments, the marine lubricant may contain from about 200 to 600 ppm phosphorus from the zinc dihydrocarbyl dithiophosphate compound.

[0012] In some embodiments, the marine lubricant may contain from about 10 ppm to about 800 ppm metal from the metal-containing detergent.

[0013] In some embodiments, the marine lubricant may further comprise at least one component selected from the group consisting of: an extreme pressure agent, an antiwear agent, a friction modifier, a dispersant, a defoamant, an antioxidant, a viscosity index improver, and a pour point depressant.

[0014] In an embodiment, a gear component of a marine engine may be lubricated with a marine lubricant as described herein.

[0015] In another embodiment, an additive composition suitable for use in a lubricant used in a marine environment may comprise: a) at least one metal-containing detergent; b) at least one phosphorus-based wear preventative; and c) at least one surfactant agent.

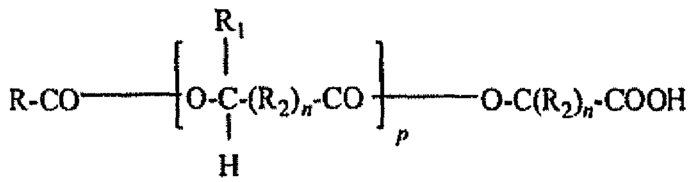
[0016] In some embodiments, the additive composition may further comprise a ratio of alkali and/or alkaline earth metal content (ppm) to phosphorus content (ppm), based on total mass of the lubricant, ranging from about 0.025 to about 1.5 (ppm/ppm).

[0017] In some embodiments, the lubricant may achieve a score of about 5 mL or less water separation in a water emulsion test.

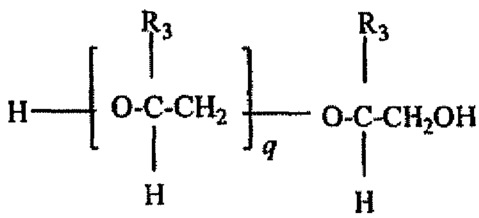
[0018] In some embodiments, the at least one metal detergent may comprise an overbased calcium phenate.

[0019] In some embodiments, the at least one phosphorus-based wear preventative may comprise at least one zinc dihydrocarbyl dithiophosphate compound.

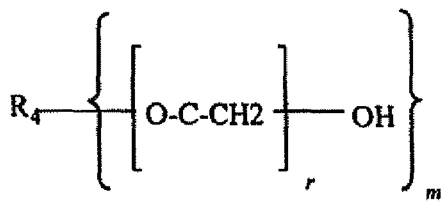
[0020] In some embodiments, the at least one surfactant agent may comprise a block or graft co-polymer of the general formula $(A\text{-}COO)_mB$, where m in an integer of at least 2 and, A is a polymeric component having a molecular weight of at least 500 and is the residue of an oil-soluble complex mono-carboxylic acid of the general structural formula:



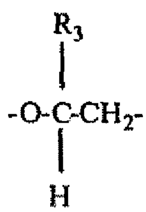
in which R is hydrogen or a monovalent hydrocarbon or substituted hydrocarbon group, R_1 is hydrogen or a monovalent C_1 to C_{24} hydrocarbon group, R_2 is a divalent C_1 to C_{24} hydrocarbon group, n is zero or 1 and *p* is zero or an integer of up to 200; and B is a polymeric component having a molecular weight of at least 500 and, in the case where m is 2, is the divalent residue of a water-soluble polyalkylene glycol of the general formula:



in which R_3 is hydrogen or a C_1 to C_3 alkyl group, q is an integer from 10 to 500, or, in the case where *m* is greater than 2, is the residue of valency m of a water-soluble polyether polyol of the general formula:



in which R_3 and *m* have their previous significance, *r* is zero or an integer from 1 to 500, provided that the total number of



units in the molecule is at least 10, and R_4 is the residue of an organic compound containing in the molecule m hydrogen atoms reactive with an alkylene oxide.

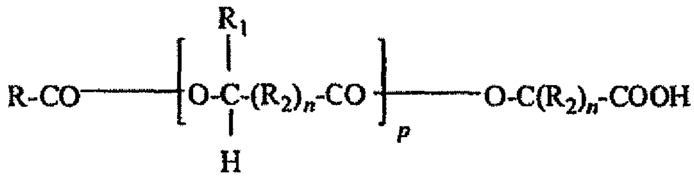
[0021] In some embodiments, the additive composition may further comprise at least one component selected from the group consisting of: an extreme pressure agent, an antiwear agent, a friction modifier, a dispersant, a defoamant, an antioxidant, a viscosity index improver, and a pour point depressant.

[0022] In another embodiment, a method for making a lubricant suitable for use in marine applications may comprise: adding to a major amount of a base oil, a minor amount of an additive composition, The additive composition may comprise at least one metal-containing detergent, and at least one phosphorus-based wear preventative, and at least one surfactant agent.

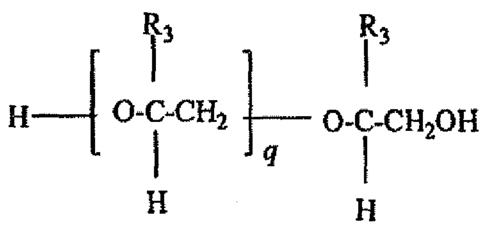
[0023] In some embodiments, the method for making a lubricant suitable for use in marine applications may further comprise adding to the major amount of a base oil, a minor amount of an additive composition wherein a ratio of alkali and/or alkaline earth metal content (ppm) to phosphorus content (ppm), based on total mass of the lubricant, ranging from about 0.025 to about 1.5 (ppm/ppm).

[0024] In some embodiments, the method for making a lubricant suitable for use in marine applications may further comprise adding to the major amount of a base oil, a minor amount of an additive composition wherein the lubricant achieves a score of about 5 mL or less water separation in a water emulsion test.

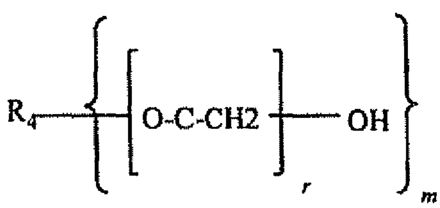
[0025] In some embodiments, the method for making a lubricant suitable for use in marine applications may further comprise adding to the major amount of a base oil, a minor amount of an additive composition, wherein said at least one surfactant agent comprises a block or graft co-polymer of the general formula $(A\text{-}COO)_mB$, where m in an integer of at least 2 and, A is a polymeric component having a molecular weight of at least 500 and is the residue of an oil-soluble complex mono-carboxylic acid of the general structural formula:



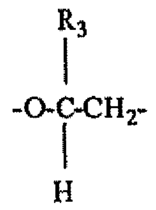
in which R is hydrogen or a monovalent hydrocarbon or substituted hydrocarbon group, R_1 is hydrogen or a monovalent C_1 to C_{24} hydrocarbon group, R_2 is a divalent C_1 to C_{24} hydrocarbon group, n is zero or 1 and *p* is zero or an integer of up to 200; and B is a polymeric component having a molecular weight of at least 500 and, in the case where m is 2, is the divalent residue of a water-soluble polyalkylene glycol of the general formula:



in which R_3 is hydrogen or a C_1 to C_3 alkyl group, q is an integer from 10 to 500, or, in the case where m is greater than 2, is the residue of valency m of a water-soluble polyether polyol of the general formula:



in which R_3 and m have their previous significance, r is zero or an integer from 1 to 500, provided that the total number of



units in the molecule is at least 10, and R_4 is the residue of an organic compound containing in the molecule m hydrogen atoms reactive with an alkylene oxide.

[0026] In another embodiment, a method of lubricating a marine engine gear component may comprise adding to the marine gear component a marine lubricant comprising a major amount of a base oil, at least one metal-containing detergent, at least one phosphorus-based wear preventative, and at least one surfactant agent, and then operating the engine.

[0027] In some embodiments, the method of lubricating a marine engine gear component may comprise adding to the marine gear component a marine lubricant further comprising a ratio of alkali and/or alkaline earth metal content (ppm) to phosphorus content (ppm), based on total mass of the lubricant, ranging from about 0.025 to about 1.5.

[0028] In some embodiments, the method of lubricating a marine engine gear component may comprise adding to the marine gear component a marine lubricant wherein the lubricant achieves a score of about 5 mL or less water separation in a water emulsion test.

[0029] In another embodiment, a method for improving the water tolerance of a gear oil suitable for use in a marine application may comprise combining a major amount of a base oil with at least one metal-containing detergent, at least one phosphorus-based wear preventative, and at least one surfactant agent.

[0030] In some embodiments, the method for improving the water tolerance of a gear oil suitable for use in a marine application may comprise combining a major amount of a base oil with at least one metal-containing detergent, at least one phosphorus-based wear preventative, and at least one surfactant agent, wherein the ratio of alkali and/or alkaline earth metal to phosphorus (in ppm), based on the total weight of the lubricant, ranges from about 0.025 to about 1.5.

[0031] In some embodiments, the method for improving the water tolerance of a gear oil suitable for use in a marine application may comprise combining a major amount of a base oil with at least one metal-containing detergent, at least one phosphorus-based wear preventative, and at least one surfactant agent, wherein the lubricant may achieve a score of about 5 mL or less water separation in a water emulsion test.

[0032] In another embodiment, a method for improving the extreme pressure properties of a gear oil suitable for use in a marine application may comprise combining a major amount of a base oil with at least one metal-containing detergent, at least one phosphorus-based wear preventative, and at least one surfactant agent.

[0033] In some embodiments, the method for improving the extreme pressure properties of a gear oil suitable for use in a marine application may comprise combining a major amount of a base oil with at least one metal-containing detergent, at least one phosphorus-based wear preventative, and at least one surfactant agent, wherein the ratio of alkali and/or alkaline earth metal to phosphorus (in ppm), based on the total weight of the lubricant, ranges from about 0.025 to about 1.5.

[0034] In some embodiments, the method for improving the extreme pressure properties of a gear oil suitable for use in a marine application may comprise combining a major amount of a base oil with at least one metal-containing detergent, at least one phosphorus-based wear preventative, and at least one surfactant agent, wherein the lubricant may achieve a score of greater than about 350 kgf in an extreme pressure weld point test.

[0035] In some embodiments, the method for improving the extreme pressure properties of a gear oil suitable for use in a marine application may comprise combining a major amount of a base oil with at least one metal-containing detergent, at least one phosphorus-based wear preventative, and at least one surfactant agent, wherein the lubricant may achieve a score of greater than about 375 kgf in an extreme pressure weld point test.

[0036] In another embodiment, a marine lubricant may comprise: a) a major amount of a base oil; b) an extreme pressure weld point improving effective amount of a phosphorus-based wear preventative; and c) wherein said marine lubricant achieves a four-ball extreme pressure weld point score of about 350 kgf or greater and a score of about 5 mL or less water separation in a water emulsion test.

[0037] In some embodiments, the marine lubricant may further comprise a metal-containing detergent.

[0038] In some embodiments, the marine lubricant may further comprise at least one surfactant agent.

[0039] In another embodiment, a marine lubricant may comprise a) a major amount of a base oil; b) a phosphorus-based wear preventative; and c) wherein said marine lubricant achieves a four-ball extreme pressure weld point score of about 350 kgf or greater, a passing L-42 score, and a score of about 5 mL or less water separation in a water emulsion test.

[0040] The following definitions of terms are provided in order to clarify the meanings of certain terms as used herein.

[0041] As used herein, the terms "oil composition," "lubrication composition," "lubricating oil composition," "lubricating oil," "lubricant composition." "lubricating composition." "fully formulated lubricant composition," and "lubricant" are considered synonymous, fully interchangeable terminology referring to the finished lubrication product comprising a major amount of a base oil plus a minor amount of an additive composition.

[0042] As used herein, the terms "additive package,' "additive concentrate," and "additive composition" are considered synonymous, fully interchangeable terminology referring the portion of the lubricating composition excluding the major amount of base oil stock mixture.

[0043] As used herein, the term "marine" is intended to encompass any body of water including saltwater and/or fresh water environments.

[0044] As used herein, the term "hydrocarbyl substituent" or "hydrocarbyl group" is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group having a carbon atom directly attached to the remainder of the molecule and having predominantly hydrocarbon character. Examples of hydrocarbyl groups include:

(1) hydrocarbon substituents, that is, aliphatic (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl, cycloalkenyl) substituents, and aromatic-, aliphatic-, and alicyclic-substituted aromatic substituents, as well as cyclic substituents wherein the ring is completed through another portion of the molecule (e.g., two substituents together form an alicyclic radical);
(2) substituted hydrocarbon substituents, that is, substituents containing non-hydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbon substituent (e.g., halo (especially chloro and fluoro), hydroxy, alkoxy, mercapto, alkylmercapto, nitro, nitroso, and sulfoxy);
(3) hetero substituents, that is, substituents which, while having a predominantly hydrocarbon character, in the context of this invention, contain other than carbon in a ring or chain otherwise composed of carbon atoms. Heteroatoms include sulfur, oxygen, nitrogen, and encompass substituents such as pyridyl, furyl, thienyl, and imidazolyl. In general, no more than two, for example, no more than one, non-hydrocarbon substituent will be present for every ten carbon atoms in the hydrocarbyl group; typically, there will be no non-hydrocarbon substituents in the hydrocarbyl group.

[0045] As used herein, the term "percent by weight", unless expressly stated otherwise, means the percentage the recited component represents to the weight of the entire composition.

[0046] The terms "oil-soluble" or "dispersible" used herein do not necessarily indicate that the compounds or additives are soluble, dissolvable, miscible, or capable of being suspended in the oil in all proportions. These do mean, however, that they are, for instance, soluble or stably dispersible in oil to an extent sufficient to exert their intended effect in the environment in which the oil is employed. Moreover, the additional incorporation of other additives may also permit incorporation of higher levels of a particular additive, if desired.

[0047] Marine lubricating oils of the present disclosure may be formulated by the addition of one or more additives, as described in detail below, to an appropriate base oil formulation. The additives may be combined with a base oil in the form of an additive package (or concentrate) or, alternatively, may be combined individually with a base oil. The fully formulated marine lubricant may exhibit improved performance properties, based on the additives added and their respective proportions.

[0048] Additional objects and advantages of the disclosure will be set forth in part in the description which follows, and/or can be learned by practice of the disclosure. The objects and advantages of the disclosure will be realized and attained by means of the elements and combinations particularly pointed out in the appended claims.

[0049] It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the disclosure, as claimed.

DESCRIPTION OF THE EXEMPLARY EMBODIMENTS

[0050] The present disclosure will now be described in the more limited aspects of embodiments thereof, including various examples of the formuiation and use of the present disclosure. It will be understood that these embodiments are presented solely for the purpose of illustrating the invention and shall not be considered as a limitation upon the scope thereof.

[0051] The environment and hardware configuration of a marine engine creates an undesirable condition where water may enter and become entrapped within the engine. Normally water separates from oil, and in the engine should this occur the water may induce corrosion of ferrous materials, as well as potential hydrolysis of additives leading to acidic byproducts that could attack the materials. So, to provide exceptional utility in this application it may be desirable for a marine lubricant oil to emulsify water. Lubricant compositions and/or additive compositions prepared according to embodiments disclosed herein may provide such benefits.

[0052] in one embodiment of the present disclosure, an additive composition may comprise at least one metal detergent and at least one phosphorus-based wear preventative. The additive composition may optionally include one or more of any of an emulsifier, a surfactant agent, an extreme pressure agent, an antiwear compound, a friction modifier, a dispersant, an anti-foam agent (also referred to as a "defoamant"), an antioxidant, a viscosity index improver, and a pour point depressant.

Base Oil

[0053] Base oils suitable for use in formulating marine lubricant fluid compositions may be selected from any of the synthetic or natural oils or mixtures thereof. Natural oils may include animal oils and vegetable oils (e.g., castor oil, lard oil) as well as mineral lubricating oils such as liquid petroleum oils and solvent treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic or mixed paraffinic-naphthenic types. Oils derived from coal or shale may also be suitable. The base oil typically may have a viscosity of about 2 to about 15 cSt or, as a further example, about 2 to about 10 cSt at 100° C. Further, an oil derived from a gas-to-liquid process is also suitable.

[0054] Suitable synthetic base oils may include alkyl esters of dicarboxylic acids, polyglycols and alcohols, poly-alpha-olefins, including polybutenes, alkyl benzenes, organic esters of phosphoric acids, and polysilicone oils. Synthetic oils include hydrocarbon oils such as polymerized and interpolymerized olefins (e.g., polybutylenes, polypropylenes, propylene isobutylene copolymers, etc.); po!y(1-hexenes), poly.(1-octenes), poly(1-decenes), etc. and mixtures thereof; alkylbenzenes (e.g., dodecylbenzenes, tetradecylbenzenes, di-nonylbenzenes, di-(2-ethylhexyl)benzenes, etc.); polyphenyls (e.g., biphenyls, terphenyl, alkylated polyphenyls, etc.); alkylated diphenyl ethers and alkylated diphenyl sulfides and the derivatives, analogs and homologs thereof and the like.

[0055] Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc., constitute another class of known synthetic oils that may be used. Such oils are exemplified by the oils prepared through polymerization of ethylene oxide or propylene oxide, the alkyl and aryl ethers of these polyoxyalkylene polymers (e.g., methyl-polyisopropylene glycol ether having an average molecular weight of about 1000, diphenyl ether of polyethylene glycol having a molecular weight of about 500-1000, diethyl ether of polypropylene glycol having a molecular weight of about 1000-1500, etc.) or mono- and polycarboxylic esters thereof, for example, the acetic acid esters, mixed C_3-C_8 fatty acid esters, or the C_{13} oxo-acid diester of tetraethylene glycol.

[0056] Another class of synthetic oils that may be used includes the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids, alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkyl malonic acids, alkenyl malonic acids, etc.) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol, etc.) Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl)sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid and the like.

[0057] Esters useful as synthetic oils also include those made from C_5 to C_{12} monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylol propane, pentaerythritol, dipentaerythritol, tripentaerythritol, etc.

[0058] Hence, the base oil used which may be used to make the transmission fluid compositions as described herein may be selected from any of the base oils in Groups I-V as specified in the American Petroleum Institute (API) Base Oil Interchangeability Guidelines. Such base oil groups are as follows:

Base Oil Group[1]	Sulfur (wt%)		Saturates (wt%)	Viscosity Index
Group I	>0.03	And/or	<90	80 to 120
Group II	≤0.03	And	≥90	80 to 120
Group III	≤0.03	And	≥90	≥ 120
Group IV	all polyalphaolefins (PAOs)			
Group V	all others not included in Groups I-IV			
[1]Groups I-III are mineral oil base stocks.				

[0059] As set forth above, the base oil may be a poly-alpha-olefin (PAO). Typically, the poly-alpha-olefins are derived from monomers having from about 4 to about 30, or from about 4 to about 20, or from about 6 to about 16 carbon atoms. Examples of useful PAOs include those derived from octene, decene, mixtures thereof, and the like. PAOs may have a viscosity of from about 2 to about 15, or from about 3 to about 12, or from about 4 to about 8 cSt at 100° C. Examples of PAOs include 4 cSt at 100° C poly-alpha-olefins, 6 cSt at 100° C poly-alpha-olefins, and mixtures thereof. Mixtures of mineral oil with the foregoing poly-alpha-olefins may be used.

[0060] The base oil may be an oil derived from Fischer-Tropsch synthesized hydrocarbons. Fischer-Tropsch synthesized hydrocarbons are made from synthesis gas containing H_2 and CO using a Fischer-Tropsch catalyst. Such hydrocarbons typically require further processing in order to be useful as the base oil. For example, the hydrocarbons may be hydroisomerized using processes disclosed in U.S. Pat. Nos. 6,103.099 or 6,180,575; hydrocracked and hydroisomerized using processes disclosed in U.S. Pat. Nos. 4,943,672 or 6,096,940; dewaxed using processes disclosed in U.S. Pat. No. 5,882,505; or hydroisomerized and dewaxed using processes disclosed in U.S. Pat. Nos. 6,013,171; 6,080,301; or 6,165,949.

[0061] Unrefined, refined, and rerefined oils, either natural or synthetic (as well as mixtures of two or more of any of these) of the type disclosed hereinabove can be used in the base oils. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. For example, a shale oil obtained directly from retorting operations, a petroleum oil obtained directly from primary distillation or ester oil obtained directly from an esterification process and used without further treatment would be an unrefined oil. Refined oils are similar to the unrefined oils except they have been further treated in one or more purification steps to improve one or more properties. Many such purification techniques are known to those skilled in the art such as solvent extraction, secondary distillation, acid or base extraction, filtration, percolation, etc. Rerefined oils are obtained by processes similar to those used to obtain refined oils applied to refined oils which have been already used in service. Such rerefined oils are also known as reclaimed or reprocessed oils and often are additionally processed by techniques directed to removal of spent additives, contaminants, and oil breakdown products.

[0062] The base oil may be combined with an additive composition as disclosed in embodiments herein to provide a marine lubricant fluid. The base oil may be present in the marine lubricant fluid in an amount from about 50 wt% to about 95 wt %.

Metal-Containing Detergents

[0063] Embodiments of the present disclosure may also comprise at least one metal detergent. Detergents generally comprise a polar head with a long hydrophobic tail where the polar head comprises a metal salt of an acidic organic compound. The salts may contain a substantially stoichiometric amount of the metal, in which case they are usually described as normal or neutral salts, and would typically have a total base number or TBN (as measured by ASTM D2896) of from about 0 to less than about 150. Large amounts of a metal base may be included by reacting an excess of a metal compound such as an oxide or hydroxide with an acidic gas such as carbon dioxide. The resulting overbased detergent comprises micelles of neutralized detergent surrounding a core of inorganic metal base (e.g., hydrated carbonates). Such overbased detergents may have a TBN of about 150 or greater, such as from about 150 to about 450 or more.

[0064] Detergents that may be suitable for use in the present embodiments include oil-soluble neutral or overbased sulfonates, phenates, sulfurized phenates, and salicylates of a metal, particularly the alkali or alkaline earth metals, e.g., sodium, potassium, lithium, calcium, and magnesium. More than one metal may be present, for example, both calcium and magnesium. Mixtures of calcium and/or magnesium with sodium may also be suitable. Suitable metal detergents may be neutral or overbased calcium or magnesium sulfonates having a TBN of from 20 to 450 TBN, neutral or overbased calcium or magnesium phenates or sulfurized phenates having a TBN of from 50 to 450, and neutral or overbased calcium or magnesium salicylates having a TBN of from 130 to 350. Mixtures of such salts may also be used.

[0065] The metal-containing detergent may be present in a lubricating composition in an amount of from about 0.01 wt % to about 3 wt %. As a further example, the metal-containing detergent may be present in an amount of from about 0.02 wt % to about 1 wt %. The metal-containing detergent may be present in a lubricating composition in an amount sufficient to provide from about 10 to about 800 ppm alkali and/or alkaline earth metal. As a further example, the metal-containing detergent may be present in a lubricating composition in an amount sufficient to provide from about 12 to about 755 ppm alkali and/or alkaline earth metal.

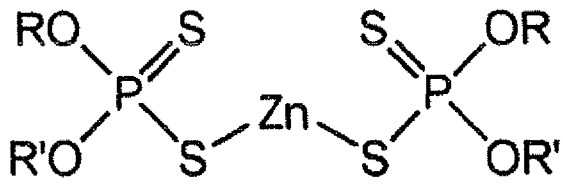
Phosphorus-Based Antiwear Agents

[0066] The phosphorus-based wear preventative may comprise a metal dihydrocarbyl dithiophosphate compound, such as but not limited to a zinc dihydrocarbyl dithiophosphate compound. Suitable metal dihydrocarbyl dithiophosphates may comprise dihydrocarbyl dithiophosphate metal salts wherein the metal may be an alkali or alkaline earth metal, or aluminum, lead, tin, molybdenum, manganese, nickel, copper, or zinc.

[0067] Dihydrocarbyl dithiophosphate metal salts may be prepared in accordance with known techniques by first forming a dihydrocarbyl dithiophosphoric acid (DDPA), usually by reaction of one or more alcohol or a phenol with P_2S_5

and then neutralizing the formed DDPA with a metal compound. For example, a dithiophosphoric acid may be made by reacting mixtures of primary and secondary alcohols. Alternatively, multiple dithiophosphoric acids can be prepared where the hydrocarbyl groups on one are entirely secondary in character and the hydrocarbyl groups on the others are entirely primary in character. To make the metal salt, any basic or neutral metal compound could be used but the oxides, hydroxides and carbonates are most generally employed. Commercial additives frequently contain an excess of metal due to the use of an excess of the basic metal compound in the neutralization reaction.

[0068] The zinc dihydrocarbyl dithiophosphates (ZDDP) are oil soluble salts of dihydrocarbyl dithiophosphoric acids and may be represented by the following formula:



[0069] wherein R and R' may be the same or different hydrocarbyl radicals containing from 1 to 18, for example 2 to 12, carbon atoms and including radicals such as alkyl, alkenyl, aryl, arylalkyl, alkaryl, and cycloaliphatic radicals. R and R' groups may be alkyl groups of 2 to 8 carbon atoms. Thus, the radicals may, for example, be ethyl, n-propyl, i-propyl, n-butyl, i-butyl, sec-butyl, amyl, n-hexyl, i-hexyl, n-octyl, decyl, dodecyl, octadecyl, 2-ethylhexyl, phenyl, butylphenyl, cyclohexyl, methylcyclopentyl, propenyl, butenyl. In order to obtain oil solubility, the total number of carbon atoms (i.e., R and R') in the dithiophosphoric acid will generally be about 5 or greater. The zinc dihydrocarbyl dithiophosphate can therefore comprise zinc dialkyl dithiophosphates.

[0070] Other suitable components that may be utilized as the phosphorus-based wear preventative include any suitable organophosphorus compound, such as but not limited to, phosphates, thiophosphates, di-thiophosphates, phosphites, and salts thereof and phosphonates. Suitable examples are tricresyl phosphate (TCP), di-alkyl phosphite (e.g., dibutyl hydrogen phosphite), and amyl acid phosphate.

[0071] Another suitable component is a phosphorylated succinimide such as a completed reaction product from a reaction between a hydrocarbyl substituted succinic acylating agent and a polyamine combined with a phosphorus source, such as inorganic or organic phosphorus acid or ester. Further, it may comprise compounds wherein the product may have amide, amidine, and/or salt linkages in addition to the imide linkage of the type that results from the reaction of a primary amino group and an anhydride moiety.

[0072] Another suitable component is a 2-ethyl hexyl acid phosphate (2-EHAP).

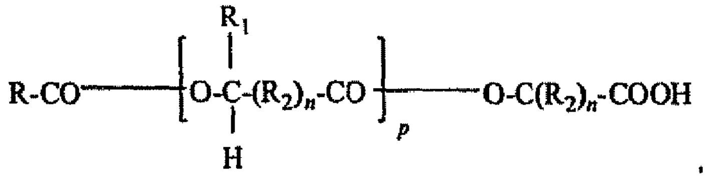
[0073] The phosphorus-based wear preventative may be present in a lubricating composition in an amount sufficient to provide from about 200 to about 2000 ppm phosphorus. As a further example, the phosphorus-based wear preventative may be present in a lubricating composition in an amount sufficient to provide from about 200 to about 600 ppm phosphorus.

[0074] The phosphorus-based wear preventative may be present in a lubricating composition in an amount sufficient to provide a ratio of alkali and/or alkaline earth metal content (ppm) based on the total amount of alkali and/or alkaline earth metal in the lubricating composition to phosphorus content (ppm) based on the total amount of phosphorus in the lubricating composition of from about 0.025 to about 1.5 (ppm/ppm).

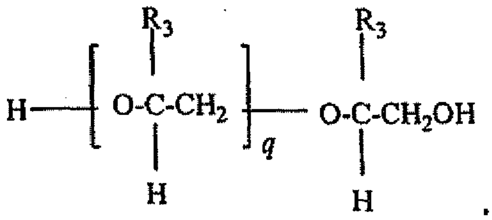
Emulsifying Agents (Surfactants)

[0075] Lubricating compositions and/or additive packages as described herein may comprise one or more emulsifying agents. Any suitable emulsifying agent may be used. An example of a series of suitable emulsifying agents is sold under the trade designation HYPERMER® and is available from Uniqema or its affiliated company Croda. These emulsifiers are described in U.S. Pat. Nos. 4,504,276; 4,509,950; and 4,776,966, herein incorporated by reference. Emulsifying agents are also known in the art by the term "surfactants", which terms are fully synonymous and interchangeable.

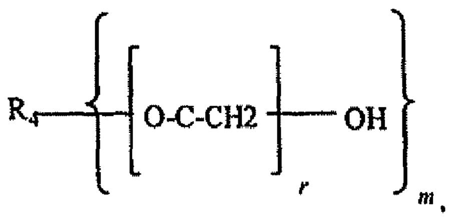
[0076] The emulsifying agents sold under the trade designation HYPERMER® are described as a block or graft copolymer of the general formula $(A\text{-}COO)_m B$, where *m* is an integer of at least 2 and, A is a polymeric component having a molecular weight of at least about 500 and is the residue of an oil-soluble complex mono-carboxylic acid of the general structural formula:



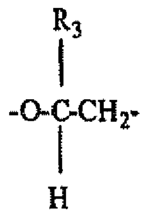
in which R is hydrogen or a monovalent hydrocarbon or substituted hydrocarbon group, R_1 is hydrogen or a monovalent C_1 to C_{24} hydrocarbon group, R_2 is a divalent C_1 to C_{24} hydrocarbon group, n is zero or 1 and p is zero or an integer of up to about 200; and (b) B is a polymeric component having a molecular weight of at least about 500 and, in the case where m is 2, is the divalent residue of a water-soluble polyalkylene glycol of the general formula:



In which R_3 is hydrogen or a C_1 to C_3 alkyl group, q is an integer from about 10 to about 500, or, in the case where m is greater than 2, is the residue of valency m of a water-soluble polyether polyol of the general formula:



in which R_3 and m have their previous significance, r is zero or an integer from 1 to 500, provided that the total number of



units in the molecule is at least about 10, and R_4 is the residue of an organic compound containing in the molecule m hydrogen atoms reactive with an alkylene oxide.

[0077] Additional HYPERMER emulsifiers include the reaction product of a polyalk(en)yl succinic anhydride with a polar compound containing In the molecule at least one hydroxyl or amino group. The preferred polyalk(en)yl succinic anhydride are poly (isobutenyl) succinic anhydrides having a molecular weight in the range of about 400 to about 5000. The preferred polar compound with which the anhydride is reacted may be a polyol such as ethylene glycol, propylene glycol, glycerol, trimethylol propane, pentaerythritol or sorbital; or with a polyamine, for example ethylene diamine, trimethylene diamine, hexamethylene diamine, dimethylaminopropylamine or diethylaminopropylamine or with a hydroxyamine for example monoethanolamine, diethanolamine, dipropanolamine, tris(hydroxymathyl)aminomethane or dimethylaminoethanol.

[0078] Suitable emulsifiers may comprise molecules having repeating hydrophilic and hydrophobic units. They tend to occupy a stable position at the interface, producing emulsions of high stability and controllable droplet size. When positioned at the interface, the extensive interactions of the polymer ensure a superior colloidal stability against coagulation or coalescence. In the systems, the hydrophilic portion of the molecule acts as an anchor group in the water phase and the hydrophobic polymeric chain portion penetrates into the oil providing a static stabilization barrier preventing strong interaction between droplets. For efficient static stabilization, the chemical structure of the polymeric chain required is determined by compatibility with the non-aqueous medium to be used. In addition the polymeric chain must have a molecular weight designed to the give optimum-size steric stabilization barrier. In principle, an almost infinite number of polymeric structures are suitable as sterically stabilizing surfactants. These include the following five basic structures: PEG alkyds with a fatty acid hydrophobe and polyethylene glycol hydrophile; long chain alkylene hydrophobe and polyethylene glycol hydrophile; polyhydroxy fatty acid hydrophobe and polyethylene glycol hydrophile; polymethacrylate hydrophobe and alkoxy polyethylene glycol hydrophile; and long-chain alkylene hydrophobe and anionic/nonionic (various) hydrophile. Examples of suitable surfactants include one of or combinations of one or more of: Hypermer® B210, A70, B206, and B246. For example, Hypermer B210 may be suitable for use with a mineral oil base oil and as a further example, a blend of B210 and another emulsifier may be suitable for use with synthetic base oils. As a further example, a suitable surfactant may be one having an HLB (hydrophilic/lipophilic balance) of between about 3 to about 6.

Extreme Pressure Agents

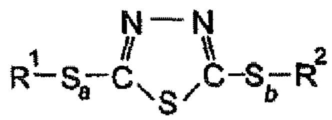
[0079] In some embodiments of the present disclosure, one or more extreme pressure agents may be included in the compositions. Extreme pressure agents may include a sulfur-containing compound. Suitable sulfur-containing extreme pressure additives include, but are not limited to, dihydrocarbyl polysulfides, sulfurized olefins, sulfurized fatty acid esters of both natural and synthetic origins, trithiones, sulfurized thienyl derivatives, sulfurized terpenes, sulfurized oligomers of C_2-C_8 monoolefins, and sulfurized Dieis-Alder adducts such as those disclosed in reissue U.S. Pat. No. 27,331, the disclosure of which is incorporated herein by reference. Specific examples include sulfurized polyisobutene, sulfurized isobutylene, sulfurized triisobutene, dicyclohexyl polysulfide, diphenyl and dibenzyl polysulfide, di-tert-butyl polysulfide and dinonyl polysulfide, among others.

[0080] Phosphorus-containing extreme pressure agents may also be used. Generally speaking there are two principal categories of phasphorus-containing extreme pressure agents: metal salts of phosphorus acids and metat-free phosphorus compounds. The metal salts are the oil-soluble salts of a metal such as copper, cadmium, calcium, magnesium, and most notably, zinc. and of a suitable acidic compound of phosphorus, such as a thiophosphoric acid, a dithiophosphoric acid, a trithiophosphoric acid, a tetrathiophosphoric acid or a complex acidic product formed by phosphosulfurizing a hydrocarbon such as one or more olefins or terpenes with a reactant such as phosphorus pentasulfide and hydrolyzing the resultant product. Methods of forming such metal salts are well known to those skilled in the art and are extensively described in the patent literature.

[0081] The oil-soluble metal-free phosphorus-containing extreme pressure agents are for the most part partially or fully esterified acids of phosphorus. Such compounds include for example phosphates, phosphites, phosphonates, phosphonites, and their various sulfur analogs. Examples include monohydrocarbyl phosphates, monohydrocarbyl phosphates, monohydrocarbyl mono-, di-, tri-, and tetrathiophosphites, monohydrocarbyl mono-, di-, tri-, and tetrathiophosphates, dihydrocarbyl phosphates, dihydrocarbyl phosphates, dihydrocarbyl mono-, di-, tri-, and tetrathiophosphites, dihydrocarbyl mono- di-, tri-, and tetrathiophosphates, trihydrocarbylphosphites, trihydrocarbylphosphates, trihydrocarbyl mono-, di-, tri-, and tetrathiophosphites, trihydrocarbyl mono-, di-, tri-, and tetrathiophosphates, the various hydrocarbyl phosphonates and thiophosphonates, the various hydrocarbyl phosphonites and thiophosphonites, and analogous oil-soluble derivatives of polyphosphoric and polythiophosphoric acids, and many others. A few specific examples of such compounds are tricresyl phosphate, tributyl phosphite, triphenyl phosphite, tri-(2-ethylhexyl) phosphate, dihexyl thiophosphite, diisooctyl butylphosphonate, tricyclohexyl phosphate, cresyl diphenyl phosphate, tris(2butoxyethyl) phosphite, diisapropyl dithiophosphate, tris(tridecyl)tetrathio-phosphate, bis(2-chloroethyl) phosphate, and like compounds.

[0082] In one embodiment, the sulfur-containing extreme pressure agent is at least one dimercaptothiadiazole or an oil-soluble derivative thereof. Such materials provide extreme pressure and/or antiwear properties to lubricating compositions described herein.

[0083] Dimercaptothiadiazoles which may be used in the lubricating compositions include, but are not limited to, 2,5-dimercapto-1,3,4-thiadiazoles (DMTD) of the following formula:



wherein R^1 and R^2 are selected from hydrogen and straight and branched chain alkyl groups having from 1 to 30 carbon atoms, and a and b are independently selected from integers ranging from 1 to 3. DMTD may be prepared by reacting one mole of hydrazine, or a hydrazine salt, with two moles of carbon disulfide in an alkaline medium, followed by acidification.

[0084] Lubricating fluid compositions described herein may include DMTD or derivatives of DMTD as set forth in the foregoing formula. For example, U.S. Pat. Nos. 2,719.125; 2,719,126; and 3,087,937 describe the preparation of various 2,5-bis(hydrocarbon dithio)-1,3,4-thiadiazoles.

[0085] The total amount of sulfur- and/or phosphorus-containing extreme pressure agent in the lubricating compositions described herein may range from about 0.01 to about 12.0 weight percent of the total lubricating composition, provided the active sulfur content of the lubricating composition may be greater than about 5,000 ppm. In another example, the active sulfur content of the lubricating composition may range from about 5,000 ppm to about 25,000 ppm, and as a further example, the active sulfur content of the lubricating composition may range from about 15,000 to about 25,000 ppm.

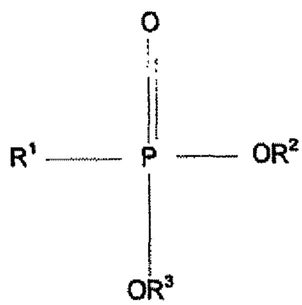
Anti-foam Agents

[0086] In some embodiments, a foam inhibitor may form another component suitable for use in the compositions. Foam inhibitors may be selected from silicones, polyacrylates, surfactants, and the like. One suitable acrylic defoamer material is PC-2544 available from Cytec Surface Specialties. The amount of antifoam agent in the marine gear oil fluid formulations described herein may range from about 0.01 wt% to about 0.5 wt% based on the total weight of the formulation. As a further example, antifoam agent may be present in an amount from about 0.01 wt% to about 0.1 wt%.

Friction Modifiers

[0087] Some embodiments of the present disclosure may include one or more friction modifiers. Suitable friction modifiers may comprise, but are not limited to, imidazolines, amides, amines, succinimides, alkoxylated amines, alkoxylated ether amines, amine oxides, amidoamines, nitriles, betaines, quaternary amines, imines, amine salts, amino guanadine, alkanolamides, phosphonates, metal-containing compounds, and the like.

[0088] The friction modifier may contain one or more phosphonates having the formula:



wherein R^1 is an alkyl or alkenyl group containing about 12 to about 30 carbon atoms and wherein R^2 and R^3 are each independently hydrogen, an alkyl, or an alkenyl group. As examples, suitable alkyl groups may include methyl, ethyl, propyl, isopropyl, n-butyl, t-butyl, isobutyl, or any combination thereof. Examples of these phosphonates are dimethyl triacontylphosphonate, dimethyl triacontenylphosphonate, dimethyl eicosylphosphonate, dimethyl hexadecylphosphonate, dimethyl hexadecenylphosphonate, dimethyl tetracontenylphosphonate, dimethyl hexacontylphosphonate, dimethyl dodecylphosphonate, dimethyl dodecenylphosphonate, and the like. In an embodiment R^1 is an alkyl or alkenyl group containing about 16 to about 20 carbon atoms. Examples of these phosphonates are dimethyl hexadecylphosphonate, dimethyl hexadecenylphosphonate, dimethyl octadecylphosphonate, dimethyl octadecenylphosphonate, dimethyl eicosylphosphonate, and the like. Suitable alkylphosphonate monoesters and processes for manufacturing the same are described in US 2004-0230068 and in US 4,108,889, herein incorporated by reference.

[0089] Suitable friction modifiers may contain hydrocarbyl groups that are selected from straight chain, branched chain, or aromatic hydrocarbyl groups or admixtures thereof, and may be saturated or unsaturated. The hydrocarbyl groups may be composed of carbon and hydrogen or hetero atoms such as sulfur or oxygen. The hydrocarbyl groups may range from about 12 to about 25 carbon atoms and may be saturated or unsaturated.

[0090] Another example of suitable friction modifiers includes amides of polyamines. Such compounds can have hydrocarbyl groups that are linear, either saturated or unsaturated, or a mixture thereof and may contain from about 12 to about 25 carbon atoms.

[0091] Further examples of suitable friction modifiers include alkoxylated amines and alkaxylated ether amines. Such compounds may have hydrocarbyl groups that are linear, either saturated, unsaturated, or a mixture thereof. They may contain from about 12 to about 25 carbon atoms. Examples include ethoxylated amines and ethoxylated ether amines.

[0092] The amines and amides may be used as such or in the form of an adduct or reaction product with a boron compound such as a boric oxide, boron halide, metaborate, boric acid or a mono-, di- or tri-alkyl borate. Other suitable friction modifiers are described in US 6,300,291, herein incorporated by reference.

[0093] Suitable friction modifiers may comprise an organic, ashless (metal-free), nitrogen-free organic friction modifier. Such friction modifiers may include esters formed by reacting carboxylic acids and anhydrides with alkanols. Other useful friction modifiers generally include a polar terminal group (e.g. carboxyl or hydroxyl) covalently bonded to an oleophilic hydrocarbon chain. Esters of carboxylic acids and anhydrides with alkanols are described in U.S. 4,702,850. Another example of an organic ashless nitrogen-free friction modifier is glycerol monooleate (GMO). Other suitable friction modifiers are described in US 6,723,685, herein incorporated by reference.

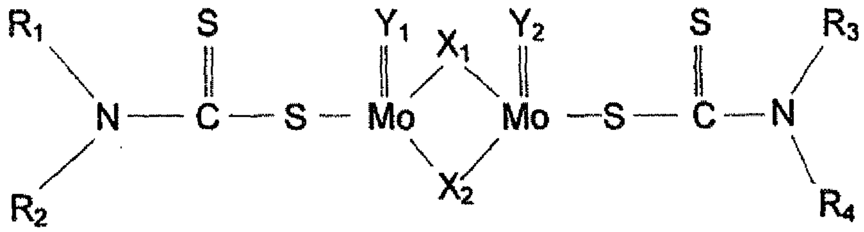
[0094] Suitable friction modifiers may comprise one or more molybdenum compounds. The molybdenum compound may comprise an organo-molybdenum compound. For example, the molybdenum compound may comprise, but is not limited to, one or more of a molybdenum dialkyldithiocarbamate, a molybdenum dialkyldithiophosphate, a molybdenum dialkyldithiophosphinate, a molybdenum xanthate, a molybdenum thioxanthate, and mixtures thereof.

[0095] The molybdenum compound may be mono-, di-, tri- or tetra-nuclear. The molybdenum compound may be an organo-molybdenum compound. The molybdenum compound may be selected from the group consisting of molybdenum dithiocarbamates (MoDTC), molybdenum dithiophosphates, molybdenum dithiophosphinates, molybdenum xanthates, molybdenum thioxanthates, molybdenum sulfides, a trinuclear organo-molybdenum compound and mixtures thereof.

[0096] Additionally, the molybdenum compound may be an acidic molybdenum compound. Included are molybdic acid, ammonium molybdate, sodium molybdate, potassium molybdate, and other alkaline metal molybdates and other molybdenum salts, e.g., hydrogen sodium molybdate, $MoOCl_4$, $Mo0_2Br_2$, $Mo_2O_3Cl_8$, molybdenum trioxide or similar acidic molybdenum compounds. Alternatively, the compositions can be provided with molybdenum by molybdenum/sulfur complexes of basic nitrogen compounds as described, for example, in U.S. Pat. Nos. 4,263,152; 4,285,822; 4,283,295: 4,272,387; 4,265,773; 4,261,843; 4,259,195 and 4,259,194; and WO 94/06897.

[0097] Among the molybdenum compounds useful in the present compositions are organo-molybdenum compounds of the formulae: $Mo(ROCS_2)_4$ and $Mo(RSCS_2)_4$, wherein R is an organo group selected from the group consisting of alkyl, aryl, aralkyl, and alkoxyalkyl, generally of from 1 to 30 carbon atoms, and preferably 2 to 12 carbon atoms and most preferably alkyl of 2 to 12 carbon atoms. An example is the dialkyldithiocarbamates of molybdenum.

[0098] Suitable molybdenum dithiocarbamates may be represented by the formula:



where R_1, R_2, R_3, and R_4 each independently represent a hydrogen atom, a C_1 to C_{20} alkyl group, a C_6 to C_{20} cycloalkyl, aryl, alkylaryl, or aralkyl group, or a C_3 to C_{20} hydrocarbyl group containing an ester, ether, alcohol, or carboxyl group; and X_1, X_2, Y_1, and Y_2 each independently represent a sulfur or oxygen atom.

[0099] Examples of suitable groups for each of R_1, R_2, R_3, and R_4 include 2-ethylhexyl, nonylphenyl, methyl, ethyl, n-propyl, iso-propyl, n-butyl, t-butyl, n-hexyl, n-octyl, nonyl, decyl, dodecyl, tridecyl, lauryl, oleyl, linoleyl, cyclohexyl and phenylmethyl, R_1 to R_4 may each have C_6 to C_{18} alkyl groups. X_1 and X_2 may be the same, and Y_1 and Y_2 may be the same. X_1 and X_2 may both comprise sulfur atoms, and Y_1 and Y_2 may both comprise oxygen atoms.

[0100] Further examples of molybdenum dithiocarbamates include C_6 - C_{18} dialkyl or diaryldithiocarbamates, or alkyl-aryldithiocarbamates such as dibutyl-, diamyl-di-(2-ethylhexyl)-, dilauryl-, dioleyl-, and dicyclohexyl-dithiocarbamate.

[0101] Another class of suitable organo-molybdenum compounds are trinuclear molybdenum compounds, such as those of the formula $Mo_3S_kL_nQ_z$ and mixtures thereof, wherein L represents independently selected ligands having organo groups with a sufficient number of carbon atoms to render the compound soluble or dispersible in the oil, n is from 1 to 4, k varies from 4 through 7, Q is selected from the group of neutral electron donating compounds such as water, amines, alcohols, phosphines, and ethers, and z ranges from 0 to 5 and includes non-stoichiometric values. At least 21 total carbon atoms may be present among all the ligands' organo groups, such as at least 25, at least 30, or at least 35 carbon atoms. Additional suitable molybdenum compounds are described in US 6,723,685, herein incorporated by reference.

[0102] The molybdenum compound may be present in a fully formulated marine lubricant in an amount to provide about 10 ppm to 200 ppm molybdenum. As a further example, the molybdenum compound may be present in an amount to provide about 75 to 125 ppm molybdenum.

[0103] Additives used in formulating the compositions described herein may be blended into the base oil individually or in various sub-combinations. However, it may be suitable to blend all of the components concurrently using an additive concentrate (i.e., additives plus a diluent, such as a hydrocarbon solvent). The use of an additive concentrate may take advantage of the mutual compatibility afforded by the combination of ingredients when in the form of an additive concentrate. Also, the use of a concentrate may reduce blending time and may lessen the possibility of blending errors.

[0104] The present disclosure provides novel lubricating oil blends specifically formulated for use in the gears of two-cycle or four-cycle outboard engines or the gears of an outdrive of an inboard/outboard marine drivetrain. Embodiments of the present disclosure may provide lubricating oils suitable for marine applications and having improvements in the following characteristics: antioxidancy, antiwear performance, rust inhibition, shear stability, water tolerance, air entrainment, and foam reducing properties.

[0105] Lubricants according to the present disclosure may be suitable for use as marine gear oils. Further, the present lubricants may be suitable for lubricating various gear components of a marine engine, including, but not limited to, rotating driveshafts, universal joints or equivalent, a bevel gear set with both forward and reverse gears and driving pinion, a bevel gearset with only one pair of gears, a dog clutch used to select forward or reverse gear, and bearings that support radial and thrust loads from these components.

EXAMPLES

Tests

Emulsion Test

[0106] Data from field samples of used marine gear oils, as well as manufacturer's requirements, indicating that water was introduced into the used marine gear oils created the need for a special emulsion test. The ASTM D1401 demulsion test, showing the separation of water from oil, provides a framework for the emulsion test, in which the thorough mixing of water with oil is evaluated.

[0107] A test for emulsification, modified from the ASTM D 1401 demulsion test, was performed to evaluate satisfactory emulsification properties. In general, during the emulsification test, a quantity of a test fluid and a quantity of one of distilled water, seawater, or synthetic seawater is combined and mechanically mixed in a graduated cylinder and held at a constant temperature, such as a temperature within the range of from about 30 °C to about 90 °C, for 24 hours ± 10 minutes. The graduated cylinder is then observed and measurements recorded of the volume of sample fluid, water, and emulsion layers present. If no water layer is present after about 24 hours, the sample fluid receives a score of 0 (zero), indicating complete emulsion after about 24 hours. If three mL of water has visibly separated then the sample fluid would receive a score of three (3) indicating that the fluid had failed to emulsify three mL of water.

[0108] In a specific embodiment of the Emulsion Test, 20 mL of synthetic sea water was introduced into a graduated cylinder, followed by 60 mL of a test fluid sample. Synthetic sea salt was prepared according to ASTM D-1141-52, Formula A, Table 1, Section 4. The ASTM D1401 test apparatus was then used to thoroughly stir and mix the two dissimilar liquids into an emulsion while heating the contents of the graduated cylinder to a desired temperature of about 82 °C. After five minutes of stirring with the flat-bladed paddle, the paddle was removed and the graduated cylinder and its contents were placed in the heated oil bath and held at a temperature of about 82 °C for about 24 hours. At the end of about 24 hours, the test fluid sample and water emulsion was evaluated for the quantity of test fluid, water, and emulsion present. The maximum emulsion present was 80 mL. The maximum water present was 20 mL. A test fluid that provided no emulsibility would be observed to have 60 mL test fluid separation, 20 mL water separation, and zero mL emulsion separation. A test fluid that maintained the emulsion would have 80 mL emulsion, zero mL test fluid separation, and zero mL water separation. A satisfactory score on the Emulsion Test has less than about 5 mL of water separation. As another example, a satisfactory score on the Emulsion Test has less than about 1 mL of water separation. As another example, a satisfactory score on the Emulsion Test has about 0 mL of water separation.

Four-Ball Extreme Pressure Weld Point Test

[0109] The test fluids and commercial fluids were subjected to a Four-Ball extreme pressure weld point test which was performed according to ASTM 2783, except the load intervals were diminished to 10 kgf to obtain more accurate values of the fluid performance. This test measures the ability of the lubricant to prevent the welding of a steel ball to three other steel balls under extremely high pressures. It is a simple test, commonly available in the lubrication industry. Higher extreme pressure weld points are desirable. For example, values below 200 kgf would indicate insufficient EP protection.

L-42 Shock Test

[0110] The products of Test Fluid Sample A and Comparative Examples H, t, and K were tested for anti-scoring properties under high speed and shock conditions using a DANA model 44 hypoid rear axle by the L-42 Axle Shock Test method described in ASTM publication STP 512A (available at the ASTM International Test Monitoring website: http://www.astmimc.cmu.edu/). Test results, in Table I, are based on the scored area of the pinion and ring gears and a pass/fail grade is provided based on comparison to a reference oil formulation. The pass/fail criteria requires that there be less quantity of scoring on the ring and pinion gears than on the associated pass reference oil test.

Test Fluids

[0111] Six inventive test fluids were prepared and tested in the Emulsion test and the Four-Ball EP Weld Point Test. Further, five comparative test fluids, which are commercially available gear oils, were also tested in the Emulsion test and the Four-Ball EP Weld Point Test. Each inventive test fluid comprised the following base fluid: a surfactant, a sulfur-containing extreme pressure agent, a phosphorus-containing antiwear compound, a ZDDP antiwear compound, a molybdenum-containing friction modifier, an oil-soluble phosphonate friction modifier, at least one dispersant, at least one anti-foam agent, an antioxidant, at least one viscosity index improver, at least one pour point depressant, and a major amount of at least one base oil. The surfactant used comprised a HYPERMER® B210 surfactant available from Uniqema or its affiliated company Croda. The additive composition of the base fluid for the following examples was held constant for each test fluid, except that levels of metal-containing detergent were varied for each inventive test fluid. The fluids tested and results are described below.

[0112] Test fluid sample A is an inventive test fluid that comprised about 0.022 wt% metal-containing detergent, about 28 total ppm alkali and/or alkali earth metal, and about 494 ppm phosphorus. The fluid had a ratio of alkali and/or alkali earth metal to phosphorus of about 0.06 ppm/ppm. The fluid had a passing emulsification test result because it had 0 mL water separation and 80 mL emulsification. The fluid had a Four-Ball EP weld point at about 390 kgf and passed the L-42 shock test.

[0113] Test fluid sample B is an inventive test fluid that comprised about 0.044 wt% metal-containing detergent, about 54 total ppm alkali and/or alkali earth metal, and about 495 ppm phosphorus. The fluid had a ratio of alkali and/or alkali earth metal to phosphorus of about 0.11 ppm/ppm. The fluid had a passing emulsification test result because it had 0 mL water separation and 80 mL emulsification. The fluid had a Four-Ball EP weld point at about 390 kgf.

[0114] Test fluid sample C is an inventive test fluid that comprised about 0.088 wt% metal-containing detergent, about 87 total ppm alkali and/or alkali earth metal, and about 495 ppm phosphorus. The fluid had a ratio of alkali and/or alkali earth metal to phosphorus of about 0.18 ppm/ppm. The fluid had a passing emulsification test result because it had 0 mL water separation and 80 mL emulsification. The fluid had a Four-Ball EP weld point at about 380 kgf.

[0115] Test fluid sample D is an inventive test fluid that comprised about 0.176 wt% metal-containing detergent, about 167 total ppm alkali and/or alkali earth metal, and about 499 ppm phosphorus. The fluid had a ratio of alkali and/or alkali earth metal to phosphorus of about 0.33 ppm/ppm. The fluid had a passing emulsification test result because it had 0 mL water separation and 80 mL emulsification. The fluid had a Four-Ball EP weld point at about 380 kgf.

[0116] Test fluid sample E is an inventive test fluid that comprised about 0.352 wt% metal-containing detergent, about 313 total ppm alkali and/or alkali earth metal, and about 502 ppm phosphorus. The fluid had a ratio of alkali and/or alkali earth metal to phosphorus of about 0.62 ppm/ppm. The fluid had a passing emulsification test result because it had 0 mL water separation and 80 mL emulsification. The fluid had a Four-Ball EP weld point at about 400 kgf.

[0117] Test fluid sample F is an inventive test fluid that comprised about 0.704 wt% metal-containing detergent, about 631 total ppm alkali and/or alkali earth metal, and about 499 ppm phosphorus. The fluid had a ratio of alkali and/or alkali earth metal to phosphorus of about 1.26 ppm/ppm. The fluid had a passing emulsification test result because it had 0 mL water separation and 80 mL emulsification. The fluid had a Four-Ball EP weld point at about 400 kgf.

[0118] Test fluid comparative sample G is a commercially available 80W90 grade fluid that comprised about 5 total ppm alkali and/or alkali earth metal and about 364 ppm phosphorus. The fluid had a ratio of alkali and/or alkali earth metal to phosphorus of about 0.01 ppm/ppm. The fluid had a failing emulsification test result because it had 20 mL water separation and 0 mL emulsification. The fluid had a Four-Ball EP weld point at about 230 kgf.

[0119] Test fluid comparative sample H is a commercially available 85 grade fluid that comprised about 2612 total ppm alkali and/or alkali earth metal and about 332 ppm phosphorus. The fluid had a ratio of alkali and/or alkali earth metal to phosphorus of about 7.87 ppm/ppm. The fluid had a failing emulsification test result because it had 20 mL water separation and 0 mL emulsification. The fluid had a Four-Ball EP weld point at about 315 kgf and failed the L-42 shock test.

[0120] Test fluid comparative sample I is a commercially available 75W90 synthetic fluid that comprised about 1 total ppm alkali and/or alkali earth metal and about 939 ppm phosphorus. The fluid had a ratio of alkali and/or alkali earth metal to phosphorus of about 0 ppm/ppm. The fluid had a failing emulsification test result because it had 20 mL water separation and 0 mL emulsification. The fluid had a Four-Ball EP weld point at about 290 kgf and passed the L-42 shock test.

[0121] Test fluid comparative sample J is a commercially available 80W90 grade fluid that comprised about 2 total ppm alkali and/or alkali earth metal and about 940 ppm phosphorus. The fluid had a ratio of alkali and/or alkali earth metal to phosphorus of about 0 ppm/ppm. The fluid had a passing emulsification test result because it had about 0 mL water separation and 80 mL emulsification. The fluid had a Four-Ball EP weld point at about 290 kgf.

[0122] Test fluid comparative sample K is a commercially available 80W90 grade fluid that comprised about 25 total ppm alkali and/or alkali earth metal and about 859 ppm phosphorus. The fluid had a ratio of alkali and/or alkali earth metal to phosphorus of about 0.03 ppm/ppm. The fluid had a passing emulsification test result because it had about 0 mL water separation and about 80 mL emulsification. The fluid had a Four-Ball EP weld point at about 315 kgf and failed the L-42 shock test.

Table I

Test Fluid Sample	Alkali or Alkaline Earth Metal/ Phosphorus Ratio	Emulsification Result*	4·Ball EP Weld Point [kgf]	L-42 Shock Test
A	0.06	Pass [0 mL water]	390	PASS
B	0.11	Pass [0 mL water]	390	
C	0.18	Pass [0 mL water]	380	
D	0.33	Pass [0 mL water]	380	
E	0.62	Pass [0 mL water]	400	
F	1.26	Pass [0 mL water]	400	
Comparative G	0.01	Fail [20 ml water]	230	
Comparative H	7.87	Fail [20 ml water]	315	FAIL
Comparative I	0.00	Fall [20 ml water]	290	PASS
Comparative J	0.00	Pass [0 mL water]	290	
Comparative K	0.03	Pass [0 mL water]	315	FAIL
* A "fail" in the emulsification test is achieved when after 24 hours at 82 °C, 5 mL or greater synthetic seawater is visible.				

[0123] As seen in the Table I, test fluid samples A-F, which have an alkali and/or alkali earth metal to phosphorus ratio ranging from about 0.06 to about 1.26 all passed the emulsification test. Further, not only did these samples provide passing emulsion test results, they are capable of achieving superior weld point test results compared to the comparative test fluids. The test fluid samples A-F provide weld point test results greater than about 3513 kgf. Further, surprisingly, the test fluid samples A-F provide weld point test results greater than about 375 kgf. None of the comparative samples were able to provide such superior extreme pressure weld points. Finally, in addition to the 4-ball EP weld point test, inventive test fluid Sample A was able to simultaneously pass an L-42 shock test and the water emulsification test.

[0124] At numerous places throughout this specification, reference has been made to a number of U.S. Patents. All such cited documents are expressly incorporated in full into this disclosure as if fully set forth herein.

[0125] Other embodiments of the present disclosure will be apparent to those skilled in the art from consideration of the specification and practice of the embodiments disclosed herein. As used throughout the specification and claims, "a" and/or "an" may refer to one or more than one. Unless otherwise indicated, all numbers expressing quantities of ingredients, properties such as molecular weight, percent, ratio, reaction conditions, and so forth used in the specification and claims are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the specification and claims are approximations that may vary depending upon the desired properties sought to be obtained by the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques. Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contains certain errors necessarily resulting from the standard deviation found in their respective testing measurements. It is intended that the specification and examples be considered as exemplary only, with a true scope and spirit of the invention being indicated by the following claims.

[0126] The foregoing embodiments are susceptible to considerable variation in practice. Accordingly, the embodiments are not intended to be limited to the specific exemplifications set forth hereinabove. Rather, the foregoing embodiments are within the spirit and scope of the appended claims, including the equivalents thereof available as a matter of law.

[0127] The patentees do not intend to dedicate any disclosed embodiments to the public, and to the extent any disclosed modifications or alterations may not literally fall within the scope of the claims, they are considered to be part hereof under the doctrine of equivalents.

1. A marine lubricant, comprising:

a) a major amount of a base oil;
b) at least one metal-containing detergent;
c) at least one phosphorus-based wear preventative; and
d) at least one surfactant agent.

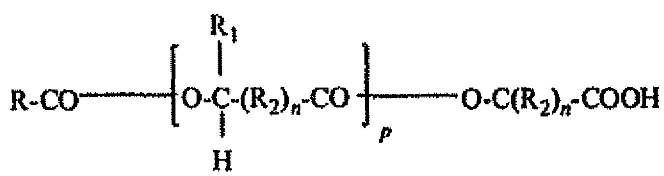
2. The marine lubricant of embodiment 1 further comprising a ratio of alkali and/or alkaline earth metal content (ppm) to phosphorus content (ppm), based an total mass of the lubricant, ranging from about 0.025 to about 9.5 (ppm/ppm).

3. The marine lubricant of embodiment 1 wherein the lubricant achieves a score of about 5 mL or less water separation in a water emulsion test.

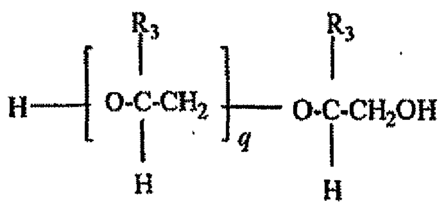
4. The marine lubricant according to embodiment 1, wherein said at least one metal detergent is an overbased calcium phenate.

5. The marine lubricant according to embodiment 1, wherein said at least one phosphorus-based wear preventative comprises at least one zinc dihydrocarbyl dithiophosphate compound.

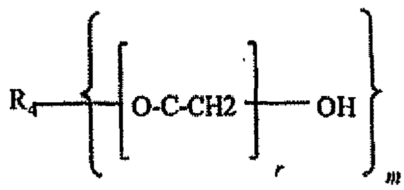
6. The marine lubricant according to embodiment 1, wherein said at least one surfactant agent comprises a block or graft co-polymer of the general formula $(A\text{-}COO)_mB$, where m in an integer of at least 2 and, A is a polymeric component having a molecular weight of at least 500 and is the residue of an oil-soluble complex mono-carboxylic acid of the general structural formula:



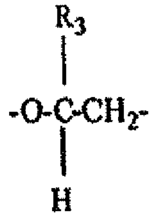
in which R is hydrogen or a monovalent hydrocarbon or substituted hydrocarbon group, R_1 is hydrogen or a monovalent C_1 to C_{24} hydrocarbon group, R_2 is a divalent C_1 to C_{24} hydrocarbon group, n is zero or 1 and p is zero or an integer of up to 200; and B is a polymeric component having a molecular weight of at least 500 and, in the case where m is 2, is the divalent residue of a water-soluble polyalkylene glycol of the general formula:



in which R_3 is hydrogen or a C_1 to C_3 alkyl group, q is an integer from 10 to 500, or, in the case where m is greater than 2, is the residue of valency m of a water-soluble polyether polyol of the general formula:



in which R_3 and m have their previous significance, r is zero or an integer from 1 to 500, provided that the total number of



units in the molecule is at least 10, and R_4 is the residue of an organic compound containing in the molecule m hydrogen atoms reactive with an alkylene oxide.

7. The marine lubricant according to embodiment 5, wherein said composition contains from about 200 to about 2000 ppm phosphorus from the zinc dihydrocarbyl dithiophosphate compound.

8. The marine lubricant according to embodiment 7, wherein said composition contains from about 200 to 600 ppm phosphorus from the zinc dihydrocarbyl dithiophosphate compound.

9. The marine lubricant according to embodiment 1, wherein said composition contains from about 10 ppm to about 800 ppm metal from the metal-containing detergent.

10. The marine lubricant according to embodiment 1, further comprising at least one component selected from the group consisting of: an extreme pressure agent, an antiwear agent, a friction modifier, a dispersant, a defoamant, an antioxidant, a viscosity index improver, and a pour point depressant.

11. A gear component of a marine engine lubricated with the composition according to embodiment 1.

12. An additive composition suitable for use in a lubricant used in a marine environment, comprising:

a) at least one metal-containing detergent;
b) at least one phosphorus-based wear preventative; and
c) at least one surfactant agent.

13. The additive composition of embodiment 12, further comprising a ratio of alkali and/or alkaline earth metal content (ppm) to phosphorus content (ppm), based an total mass of the lubricant, ranging from about 0.025 to about 1.5 (ppm/ppm).

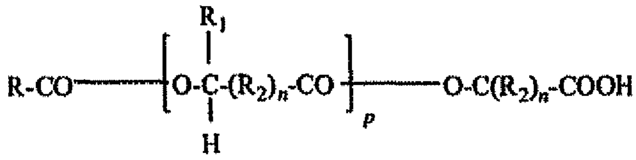
14. The additive composition of embodiment 12, wherein the lubricant achieves a score of about 5 mL or less water separation in a water emulsion test.

15. The additive composition according to embodiment 12, wherein said at least one metal detergent is an overbased calcium phenate.

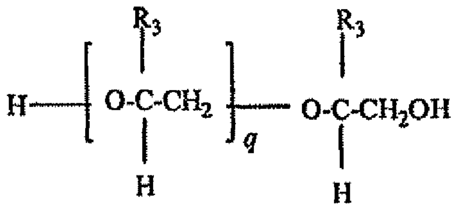
16. The additive composition according to embodiment 12, wherein said at least one phosphorus-based wear preventative comprises at least one zinc dihydrocarbyl dithiophosphate compound.

17. The additive composition according to embodiment 12, wherein said at least one surfactant agent comprises a

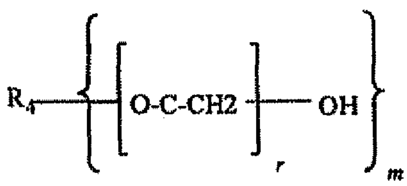
block or graft co-polymer of the general formula $(A\text{-}COO)_m,B$, where *m* in an integer of at least 2 and, A is a polymeric component having a molecular weight of at least 500 and is the residue of an oil-soluble complex mono-carboxylic acid of the general structural formula:



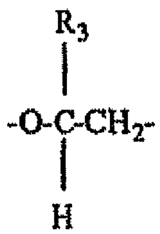
in which R is hydrogen or a monovalent hydrocarbon or substituted hydrocarbon group, R_1 is hydrogen or a monovalent C_1 to C_{24}hydrocarbon group, R_2 is a divalent C_1 to C_{24} hydrocarbon group, n is zero or 1 and p is zero or an integer of up to 200; and B is a polymeric component having a molecular weight of at least 500 and, in the case where m is 2, is the divalent residue of a water-soluble polyalkylene glycol of the general formula:



in which R_3 is hydrogen or a C_1 to C_3 alkyl group, q is an integer from 10 to 500, or, in the case where m is greater than 2, is the residue of valency m of a water-soluble polyether polyol of the general formula:



in which R_3 and m have their previous significance, *r* is zero or an integer from 1 to 500, provided that the total number of



units in the molecule is at least 10, and R_4 is the residue of an organic compound containing in the molecule m hydrogen atoms reactive with an alkylene oxide.

18. The additive composition according to embodiment 12, further comprising at least one component selected from the group consisting of: an extreme pressure agent, an antiwear agent, a friction modifier, a dispersant, a defoamant, an antioxidant, a viscosity index improver, and a pour point depressant.

19. A method of making a lubricant suitable for use in marine applications, comprising:

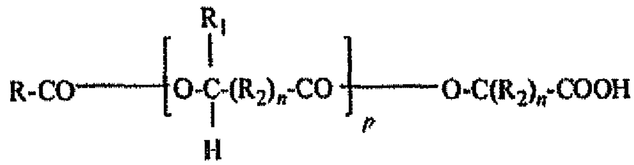
adding to a major amount of a base oil, a minor amount of an additive composition, comprising:

a) at least one metal-containing detergent;
b) at least one phosphorus-based wear preventative; and
c) at least one surfactant agent.

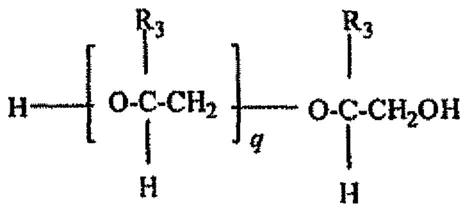
20. The method of embodiment 19, further comprising a ratio of alkali and/or alkaline earth metal content (ppm) to phosphorus content (ppm), based an total mass of the lubricant, ranging from about 0.025 to about 1.5 (ppm/ppm).

21. The method of embodiment 19, wherein the lubricant achieves a score of about 5 mL or less water separation in a water emulsion test.

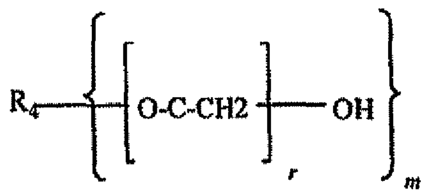
22. The method according to embodiment 19, wherein said at least one surfactant agent comprises a block or graft co-polymer of the general formula $(A\text{-}COO)_mB$, where *m* in an integer of at least 2 and, A is a polymeric component having a molecular weight of at least 500 and is the residue of an oil-soluble complex mono-carboxylic acid of the general structural formula:



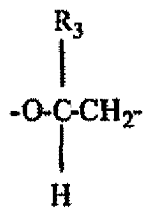
in which R is hydrogen or a monovalent hydrocarbon or substituted hydrocarbon group, R_1 is hydrogen or a monovalent C_1 to C_{24} hydrocarbon group, R_2 is a divalent C_1 to C_{24} hydrocarbon group, n is zero or 1 and p is zero or an integer of up to 200; and B is a polymeric component having a molecular weight of at least 500 and, in the case where m is 2, is the divalent residue of a watereoluble polyalkylene glycol of the general formula:



in which R_3 is hydrogen or a C_1 to C_3 alkyl group, q is an integer from 10 to 500, or, in the case where m is greater than 2, is the residue of valency m of a water-soluble polyether polyol of the general formula:



in which R_3 and *m* have their previous significance, *r* is zero or an integer from 1 to 500, provided that the total number of



units in the molecule is at least 10, and R_4 is the residue of an organic compound containing in the molecule m hydrogen atoms reactive with an alkylene oxide.

23. A method of lubricating a marine engine gear component, comprising:

adding to the marine engine gear component a marine lubricant, comprising:

a) a major amount of a base oil;
b) at least one metal-containing detergent;
c) at least one phosphorus-based wear preventative; and
d) at least one surfactant agent; and

operating the engine.

24. The method of embodiment 23 further comprising a ratio of alkali and/or alkaline earth metal content (ppm) to phosphorus content (ppm), based on total mass of the lubricant, ranging from about 0.025 to about 1.5.

25. The method of embodiment 23 wherein the lubricant achieves a score of about 5 mL or less water separation in a water emulsion test.

26. A method for improving the water tolerance of a gear oil suitable for use in marine applications, comprising combining a major amount of a base oil with at least one metal-containing detergent, at least one phosphorus-based wear preventative, and at least one surfactant agent.

27. The method of embodiment 26 further comprising a ratio of alkali and/or alkaline earth metal content (ppm) to phosphorus content (ppm), based on total mass of the lubricant, ranging from about 0.025 to about 1.5.

28. The method of embodiment 26, wherein the lubricant achieves a score of about 5 mL or less water separation in a water emulsion test.

29. A method for improving the extreme pressure properties of a gear oil suitable for use in marine applications, comprising combining a major amount of a base oil with at least one metal-containing detergent, at least one phosphorus-based wear preventative, and at least one surfactant agent.

30. The method of embodiment 29, further comprising a ratio of alkali and/or alkaline earth metal content (ppm) to phosphorus content (ppm), based a total mass of the lubricant, ranging from about 0.025 to about 1.5.

31. The method of embodiment 30, wherein the lubricant achieves a score of greater than about 350 kgf in an extreme pressure weld point test.

32. The method according to embodiment 31, wherein the lubricant achieves a score of greater than about 375 kgf in an extreme pressure weld point test.

33. A marine lubricant comprising:

a) a major amount of a base oil;
b) an extreme pressure weld point improving effective amount of a phosphorus-based wear preventative; and
c) wherein said marine lubricant achieves a four-ball extreme pressure weld point score of about 350 kgf or greater and a score of about 5 mL or less water separation in a water emulsion test.

34. The marine lubricant of embodiment 33, further comprising a metal-containing detergent.

35. The marine lubricant of embodiment 33, further comprising at least one surfactant agent.

36. A marine lubricant comprising:

a) a major amount of a base oil;
b) a phosphorus-based wear preventative; and
c) wherein said marine lubricant achieves a four-ball extreme pressure weld point score of about 350 kgf or greater, a passing L-42 score, and a score of about 5 mL or less water separation in a water emulsion test.

Claims

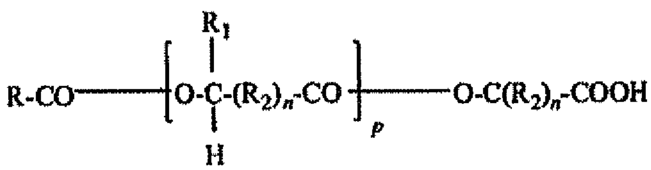
1. An additive composition suitable for use in a lubricant used in a marine environment, comprising:

   a) at least one metal-containing detergent;
   b) at least one phosphorus-based wear preventative; and
   c) at least one surfactant agent.

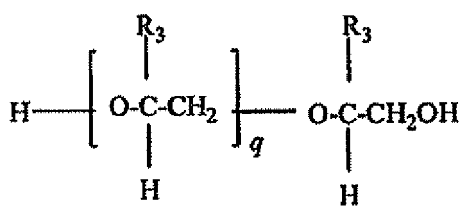
2. The additive composition according to claim 1, wherein said at least one metal detergent is an overbased calcium phenate.

3. The additive composition according to claim 1 or 2, wherein said at least one phosphorus-based wear preventative comprises at least one zinc dihydrocarbyl dithiophosphate compound.

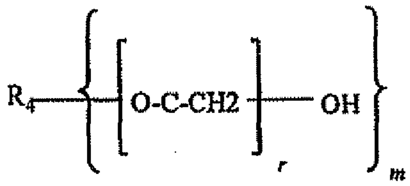
4. The additive composition according to any one of claims 1 to 3, wherein said at least one surfactant agent comprises a block or graft co-polymer of the general formula $(A\text{-}COO)_m$,B, where m in an integer of at least 2 and, A is a polymeric component having a molecular weight of at least 500 and is the residue of an oil-soluble complex mono-carboxylic acid of the general structural formula:



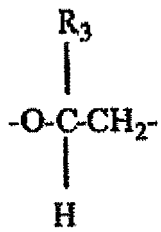
in which R is hydrogen or a monovalent hydrocarbon or substituted hydrocarbon group, R_1 is hydrogen or a monovalent C_1 to C_{24} hydrocarbon group, R_2 is a divalent C_1 to C_{24} hydrocarbon group, n is zero or 1 and p is zero or an integer of up to 200; and B is a polymeric component having a molecular weight of at least 500 and, in the case where m is 2, is the divalent residue of a water-soluble polyalkylene glycol of the general formula:



in which R_3 is hydrogen or a C_1 to C_3 alkyl group, q is an integer from 10 to 500, or, in the case where m is greater than 2, is the residue of valency m of a water-soluble polyether polyol of the general formula:



in which R_3 and m have their previous significance, r is zero or an integer from 1 to 500, provided that the total number of



units in the molecule is at least 10, and R_4 is the residue of an organic compound containing in the molecule m hydrogen atoms reactive with an alkylene oxide.

5. The additive composition according to any one of claims 1 to 4, further comprising at least one component selected from the group consisting of: an extreme pressure agent, an antiwear agent, a friction modifier, a dispersant, a defoamant, an antioxidant, a viscosity index improver, and a pour point depressant.

6. A marine lubricant, comprising:

a major amount of a base oil;
and an additive composition according to any one of claims 1 to 5.

7. The marine lubricant of claim 6 further comprising a ratio of alkali and/or alkaline earth metal content (ppm) to phosphorus content (ppm), based an total mass of the lubricant, ranging from about 0.025 to about 1.5 (ppm/ppm).

8. The marine lubricant of claim 6 or 7 wherein the lubricant achieves a score of about 5 mL or less water separation in a water emulsion test.

9. The marine lubricant according to any one of claims 6 to 8, wherein said composition contains from about 200 to about 2000 ppm, preferably from about 200 to 600 ppm phosphorus from the zinc dihydrocarbyl dithiophosphate compound.

10. The marine lubricant according to any one of claims 1 to 9, wherein said composition contains from about 10 ppm to about 800 ppm metal from the metal-containing detergent.

11. The lubricant according to any one of claims 6 to 10, wherein the lubricant achieves a score of greater than about 350 kgf, preferably of greater than about 375 kgf in an extreme pressure weld point test.

12. The lubricant according to any one of claims 6 to 11, wherein the lubricant achieves a passing L-42 score.

13. A method of making a lubricant according to any one of claims 6 to 12 suitable for use in marine applications, comprising:

adding to a major amount of a base oil, a minor amount of an additive composition, comprising:

a) at least one metal-containing detergent;
b) at least one phosphorus-based wear preventative; and

c) at least one surfactant agent.

14. Use of the composition according to any one of claims 1 to 5 or of the lubricant according to any one of claims 6 to 12 to lubricate a gear component of a marine engine.

15. Use according to claim 14, comprising

adding to the marine engine gear component a marine lubricant according to any one of claims 6 to 12; and operating the engine.

16. A method according to claim 13 for improving the water tolerance of a gear oil suitable for use in marine applications, comprising combining a major amount of a base oil with at least one metal-containing detergent, at least one phosphorus-based wear preventative, and at least one surfactant agent.

17. A marine lubricant comprising:

a) a major amount of a base oil;
b) an extreme pressure weld point improving effective amount of a phosphorus-based wear preventative; and
c) wherein said marine lubricant achieves a four-ball extreme pressure weld point score of about 350 kgf or greater and a score of about 5 mL or less water separation in a water emulsion test; wherein the phosphorus-based wear preventative is as defined in any one of claims 1, 3 or 9.

18. The marine lubricant of claim 17, further comprising a metal-containing detergent, and/or at least one surfactant agent and optionally at least one compound as defined in claim 5; wherein the metal-containing detergent is as defined in any one of claims 1, 2 or 10 and wherein the surfactant agent is as defined in any one of claims 1 or 4.

19. A marine lubricant comprising:

a) a major amount of a base oil;
b) a phosphorus-based wear preventative; and
c) wherein said marine lubricant achieves a four-ball extreme pressure weld point score of about 350 kgf or greater, a passing L-42 score, and a score of about 5 mL or less water separation in a water emulsion test; wherein the phosphorus-based wear preventative is as defined in any one of claims 1, 3 or 9.

REFERENCES CITED IN THE DESCRIPTION

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