TITLE

Marine Diesel Cylinder Lubricants for Improved Fuel Efficiency

BACKGROUND OF THE INVENTION

[0001] The disclosed technology relates to lubricants for internal combustion engines, and in particular marine diesel cylinder lubricants.

[0002] Improving fuel economy is of interest for the operation of nearly all engines from relatively small gasoline powered engines through large marine diesel engines. There are both economic and environmental advantages for improving fuel economy in the marine industry, the largest impact perhaps being from improvement in Marine Diesel Cylinder Lubricant (MDCL) technology, for instance, by improving the contact between the piston rings and cylinder liner in these engines. Particularly in the marine industry, much work has been done by original equipment manufacturers on improving fuel economy by engineering means.

[0003] In gasoline engines and smaller diesel engines, significant effort has been expended toward improving efficiency by means of reducing friction within the engine by modifying the lubricant. There are additional challenges, however, in attempting to apply such methods to lubricants for marine diesel engines because of the significantly higher operating temperatures of such engines, typically in excess of 150°C, e.g., 175-275°C in the area lubricated by a marine diesel cylinder lubricant (i.e., the cylinder liner), compared to the temperatures commonly encountered by lubricants in smaller engines, e.g., around 100°C or below. Natural gas-fueled engines (stationary engines) will also typically operate at high temperatures.

[0004] US Patent 4,683,069 discloses lubricating oil compositions containing 0.05 to 0.2 weight % of glycerol esters as fuel economy additives. The glycerol esters disclosed include GMO. The lubricating oil composition is suitable for either gasoline or diesel engines.

[0005] US Patent Application 2003/134758 discloses the use of an effective amount of one or more compounds capable of reducing friction coefficients under mixed lubrication or boundary lubrication conditions in a heavy duty diesel engine lubricating oil composition for improving the fuel economy of a heavy duty diesel engine. Example 1 contains glycerol monooleate.

[0006] US Patent Application 2003/134758 discloses heavy duty diesel engine lubricating oil compositions for improving the fuel economy. The treat

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rate may range from 0.01 to 5.0 wt %, or preferably 0.15 to 0.5 wt %. Example 1 discloses a composition with glycerol monooleate in an amount of 0.3 mass %, while Example 2 contains as a friction reducer a trinuclear molybdenum dithiocarbamate.

[0007] US Patent 6,074,993 discloses a lubricating composition which exhibits improved fuel economy. The composition contains amongst other materials at least one organic oil-soluble friction modifier. Claim 12 discloses ethoxylated amine. The lubricating composition may be used in the formulation of crankcases oils. Heavy-duty diesel motor oils are mentioned as a possible crankcase oil.

[0008] US Patent Application 2007/0015672 discloses a drive in terms of fuel economy for gasoline and diesel engines which has resulted in increased levels of organic friction modifiers being used in lubricating oil compositions; unfortunately, there are compatibility issues between the friction modifiers and overbased detergents, such as overbased calcium sulphonates. The invention described therein is therefore concerned with improving the compatibility between friction modifiers and overbased detergents in lubricating oil compositions. Examples therein include the use of GMO and/or ethoxylated tallow amine.

[0009] US Patent 6,333,298 discloses a molybdenum-free lubricating oil composition exhibiting improved fuel economy and fuel economy retention properties by employing at least one friction modifier. Claim 8 specifies the friction modifier is an ethoxylated amine. The lubricating oil composition is suitable for heavy duty diesel engines.

[0010] US Patent 6,074,993 discloses a lubricating oil composition which exhibits improved fuel economy and wet clutch friction properties, said composition comprising: an oil of lubricating viscosity; at least one overbased calcium; at least one organic oil soluble friction modifier; and at least one zinc dihydrocarbyldithiophosphate compound, wherein said composition has a TBN of at least 3.6. Ethoxylated amines are disclosed in claim 12. The lubricating oil composition is suitable for crankcase lubricating oils (i.e., passenger car motor oils, heavy duty diesel motor oils, and passenger car diesel oils) for spark-ignited and compression-ignited engines.

[0011] US Patent Application 2006/276354 discloses lubricant compositions for use in automotive engine oils comprising a combination of a specific base stock or mixture of base stocks and a friction reducing additive to improve fuel economy and fuel economy longevity of the automotive engine oil. The friction reducing additive is a specific partial polyol ester and may also include

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a specific saturated primary amide. The automotive engine is stated to include gasoline and heavy duty diesel. The examples disclose GMO in a particular composition.

[0012] US Patent Application 2006/183647 discloses lubricating compositions containing tartaric acid derivatives as fuel economy improvers and anti-wear agents in crankcase oils. The tartaric acid derivatives include tartrates, tartrimides and tartramides. The lubricating oils have low sulfur, phosphorus and ash content. Further disclosed is these use of the lubricant compositions as being useful in automobile and truck engines, two-cycle engines, aviation piston engines, marine and railroad diesel engines.

[0013] US Patent Application 2006/079413 discloses lubricant formulations using tartaric compounds in a low sulfur, low ash and low phosphorus lubricant lowering wear and friction and improving fuel economy. The disclosure further describes the use of the lubricants in automobile and truck engines, two-cycle engines, aviation piston engines, marine and railroad diesel engines. Also disclosed are combination of tartaric compounds with additional friction modifiers are selected from the group consisting of glycerol monooleates, oleyl amides, diethanol fatty amines and mixtures thereof.

[0014] SAE Special Publication SP-1550, "Topics in Lubricants, pp 225-231, Sasak et al., 2000, discloses development of high performance heavy-duty diesel engine oil to extend oil drain intervals by providing a 5W-30 fully synthetic oil containing molybdenum dithiocarbamate.

[0015] It is believed that molybdenum compounds ae uniquely suitable as friction modifiers for lubricants for high temperature engines. However, it is desirable to formulate lubricants which avoid the use of molybdenum compounds for a variety of reasons including cost and minimizing the discharge of heavy metals into the environment, as high temperature engines such as marine diesel engines are normally designed to consume the lubricating oil and discharge its combustion products.

[0016] The disclosed technology, therefore, provides a method for improving the fuel economy of a high temperature engine such as a marine diesel engine by supplying a lubricant which does not include a molybdenum compound but yet provides good lubricant performance.

[0017] The lubricating composition of the present invention is useful for an internal combustion engine, for example a diesel fueled engine, a gasoline fueled engine, a natural gas fueled engine or a mixed gasoline/alcohol fueled engine. In one embodiment the internal combustion engine is a 4-stroke and in

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another embodiment a 2-stroke engine. In one embodiment the engine has a power output of at least 1600 kilowatts. In one embodiment the diesel fueled engine is a marine diesel engine. In certain marine diesel engines, a lubricant is prepared specifically for and is supplied to the cylinder wall, that is the cylinder liner, in order to lubricate the interface of the piston and the cylinder wall, rather than being supplied to or from a crankcase. Since marine diesel engines typically are operated at relatively high temperatures, the cylinder liner may commonly be at a temperature of 150°C or greater during operation, e.g, 175°C to 300°C. For such lubricating conditions, specially adapted lubricants are desirable.

SUMMARY OF THE INVENTION

[0018] The disclosed technology provides, in one embodiment, a lubricant composition suitable for use in lubricating an engine operating above 150°C at the cylinder liner, comprising an oil of lubricating viscosity and 0.01 to 5 percent by weight of an organic friction modifier, said lubricant composition being substantially free from molybdenum compounds.

[0019] The invention also provides a method for lubricating an engine operating above 150°C at the cylinder liner, comprising supplying thereto the lubricant composition as described above and herein.

DETAILED DESCRIPTION OF THE INVENTION

[0020] Various preferred features and embodiments will be described below by way of non-limiting illustration.

[0021] The lubricant described herein contains an oil of lubricating viscosity. The oil of lubricating viscosity may have a SAE grade of SAE 30, SAE 40, SAE 50, or SAE 60. In one embodiment the oil of lubricating viscosity may be a SAE 50 oil. Typically a SAE 50 oil has a kinematic viscosity of 16.3 mm^2/s to 21.9 mm^2/s at 100°C.

[0022] The oil, also referred to as a base oil, 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. The five base oil groups are as follows:

Base Oil Category	Sulfur (%)		Saturates(%)	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, II, III or IV			

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[0023] Groups I, II and III are mineral oil base stocks. The oil of lubricating viscosity, then, can include natural or synthetic lubricating oils and mixtures thereof. Mixture of mineral oil and synthetic oils, particularly polyalphaolefin oils and polyester oils, are often used.

[0024] Natural oils include 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. Hydrotreated or hydrocracked oils are included within the scope of useful oils of lubricating viscosity.

[0025] Oils of lubricating viscosity derived from coal or shale are also useful. Synthetic lubricating oils include hydrocarbon oils and halosubstituted hydrocarbon oils such as polymerized and interpolymerized olefins and mixtures thereof, alkylbenzenes, polyphenyl, (e.g., biphenyls, terphenyls, and alkylated polyphenyls), alkylated diphenyl ethers and alkylated diphenyl sulfides and their derivatives, analogs and homologues thereof. Alkylene oxide polymers and interpolymers and derivatives thereof, and those where terminal hydroxyl groups have been modified by, for example, esterification or etherification, constitute other classes of known synthetic lubricating oils that can be used. Another suitable class of synthetic lubricating oils that can be used comprises the esters of dicarboxylic acids and those made from C_5 to C_{12} monocarboxylic acids and polyols or polyol ethers.

[0026] Other synthetic lubricating oils include liquid esters of phosphorus-containing acids, polymeric tetrahydrofurans, silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy-, or polyaryloxy-siloxane oils, and silicate oils.

[0027] Hydrotreated naphthenic oils are also known and can be used, as well as oils prepared by a Fischer-Tropsch gas-to-liquid synthetic procedure, including hydroisomerized Fischer-Tropsch waxes or other waxes.

[0028] 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 used in the compositions of the present invention. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. 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. Rerefined oils are obtained by processes similar to those used to obtain refined oils applied to refined oils which have been already used in

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service. Such rerefined oils often are additionally processed by techniques directed to removal of spent additives and oil breakdown products.

[0029] The lubricant compositions described herein will also contain an organic friction modifier. Friction modifiers in general are known to those skilled in the art. A useful list of friction modifiers is included in U.S. Pat. No. 4,792,410. A list of organic friction modifiers includes:

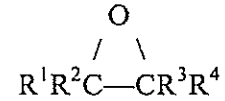
(i) fatty phosphites
(ii) fatty acid amides
(iii) fatty epoxides
(iv) borated fatty epoxides
(v) fatty amines
(vi) glycerol esters
(vii) borated glycerol esters
(viii) alkoxylated fatty amines
(ix) borated alkoxylated fatty amines
(x) metal salts of fatty acids (in some embodiments in amounts of at least 2 or 3%)
(xi) sulfurized olefins
(xii) fatty imidazolines
(xiii) condensation products of carboxylic acids and polyalkylene-polyamines
(xiv) metal salts of alkyl salicylates
(xv) amine salts of alkylphosphoric acids
(xvi) tartaric acid derivatives
(xvii) fatty acids
and mixtures thereof.

[0030] Representatives of each of these types of friction modifiers are known and are commercially available. For instance, (i) fatty phosphites are generally of the formula $(RO)_2PHO$. An exemplary dialkyl phosphite, as shown in the preceding formula, is typically present with a minor amount of monoalkyl phosphite of the formula (RO)(HO)PHO. In these structures, the term "R" is conventionally referred to as an alkyl group. It is, of course, possible that the alkyl is actually alkenyl and thus the terms "alkyl" and "alkylated," as used herein, will embrace other than saturated alkyl groups within the phosphite. The phosphite will normally have sufficient hydrocarbyl groups to render the phosphite substantially oleophilic. The hydrocarbyl groups may be substantially unbranched. Many suitable phosphites are available commercially and may be

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synthesized as described in U.S. Patent 4,752,416. The phosphite may contain 8 to 24 carbon atoms in each of R groups. The fatty phosphite may contain 12 to 22 carbon atoms in each of the fatty radicals, or 16 to 20 carbon atoms. In one embodiment the fatty phosphite can be formed from oleyl groups, thus having 18 carbon atoms in each fatty radical.

[0031] (iv) Borated fatty epoxides are known from Canadian Patent No. 1,188,704. These oil-soluble boron- containing compositions are prepared by reacting, at a temperature from 80°C to 250°C, boric acid or boron trioxide with at least one fatty epoxide having the formula



wherein each of R^1, R^2, R^3 and R^4 is hydrogen or an aliphatic radical, or any two thereof together with the epoxy carbon atom or atoms to which they are attached, form a cyclic radical. The fatty epoxide may contain at least 8 carbon atoms.

[0032] (iii) Non-borated fatty epoxides are also useful as friction modifiers.

[0033] Borated amines are generally known from U.S. Patent 4,622,158. Borated amine friction modifiers (including (ix) borated alkoxylated fatty amines) are conveniently prepared by the reaction of a boron compounds, as described above, with the corresponding amines. The amine can be a simple fatty amine or hydroxy containing tertiary amines. The borated amines can be prepared by adding the boron reactant, as described above, to an amine reactant and heating the resulting mixture at a 50° to 300°C, preferably 100°C to 250°C or 150°C to 230°C, with stirring. The reaction is continued until by-product water ceases to evolve from the reaction mixture indicating completion of the reaction.

[0034] Among the amines useful in preparing the borated amines are commercial alkoxylated fatty amines known by the trademark "ETHOMEEN" and available from Akzo Nobel. Representative examples of these ETHOMEEN™ materials is ETHOMEEN™ C/12 (bis[2-hydroxyethyl]-coco-amine); ETHOMEEN™ C/20 (polyoxyethylene[10]cocoamine); ETHOMEEN™ S/12 (bis[2-hydroxyethyl]soyamine); ETHOMEEN™ T/12 (bis[2-hydroxyethyl]-tallow-amine); ETHOMEEN™ T/15 (polyoxyethylene-[5]tallowamine); ETHOMEEN™ 0/12 (bis[2-hydroxyethyl]oleyl-amine); ETHOMEEN™ 18/12 (bis[2—hydroxyethyl]octadecylamine); and ETHOMEEN™ 18/25 (polyoxyethyl-ene[15]octadecylamine). Fatty amines and ethoxylated fatty amines are also described in U.S. Patent 4,741,848.

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[0035] The (viii) alkoxylated fatty amines, and (v) fatty amines themselves (such as oleylamine) are generally useful as friction modifiers. Such amines are commercially available.

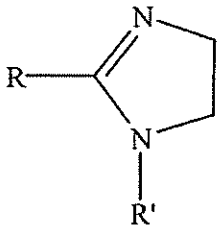
[0036] Both borated and unborated fatty acid esters of glycerol can be used as friction modifiers. The (vii) borated fatty acid esters of glycerol are prepared by borating a fatty acid ester of glycerol with boric acid with removal of the water of reaction. In certain embodiments, there is sufficient boron present such that each boron will react with from 1.5 to 2.5 hydroxyl groups present in the reaction mixture. The reaction may be carried out at a temperature in the range of 60°C to 135°C, in the absence or presence of any suitable organic solvent such as methanol, benzene, xylenes, toluene, or oil.

[0037] (vi) Fatty acid esters of glycerol themselves can be prepared by a variety of methods well known in the art. Many of these esters, such as glycerol monooleate and glycerol monotallowate, are manufactured on a commercial scale. The esters useful are oil-soluble and may be prepared from C8 to C22 fatty acids or mixtures thereof such as are found in natural products and as are described in greater detail below. Fatty acid monoesters of glycerol are commonly used, although, mixtures of mono- and diesters may be used. For example, commercial glycerol monooleate is believed to include about 60 $\pm$ 5 percent by weight of the chemical species "glycerol monooleate," along with 35 $\pm$ 5 percent glycerol dioleate, and less than about 5 percent trioleate and oleic acid. The amounts of such materials, as described herein, are the amounts of the commercial grade material.

[0038] Fatty acids (xvii) can be used as friction modifiers or they can be used in preparing the above glycerol esters; they can also be used in preparing their (x) metal salts (such as Ca, Mg or Na salts, any of which may also be excluded if, for instance, an ashless additive is desired), (ii) amides, and (xii) imidazolines, any of which can also be used as friction modifiers. Fatty acids include those containing 6 to 24 carbon atoms, such as 8 to 18. The acids can be branched or straight-chain, saturated or unsaturated. Suitable acids include 2-ethylhexanoic, decanoic, oleic, stearic, isostearic, palmitic, myristic, palmitoleic, linoleic, lauric, and linolenic acids, and the acids from the natural products tallow, palm oil, olive oil, peanut oil, corn oil, and Neat's foot oil. An example of a mixture of fatty acids is known as tall oil fatty acid. Fatty acids, such as C18 acids, may be supplied along with another component such as an overbased detergent. Fatty acids may be used in the preparation of certain overbased detergents.

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[0039] Suitable amides include those prepared by condensation with ammonia or with primary or secondary amines such as diethylamine and diethanolamine. Fatty imidazolines are the cyclic condensation product of an acid with a diamine or polyamine such as a polyethylenepolyamine. The imidazolines are generally represented by the structure



where R is an alkyl group and R′ is hydrogen or a hydrocarbyl group or a substituted hydrocarbyl group, including —$(CH_2CH_2NH)_n$— groups. In an embodiment the friction modifier is the condensation product of a C8 to C24 fatty acid with a polyalkylene polyamine, such as the product of isostearic acid with tetraethylenepentamine. The condensation products of carboxylic acids and polyalkyleneamines (xiii) may generally be imidazolines or amides.

[0040] Sulfurized olefins (xi) are well known commercial materials used as friction modifiers. A suitable sulfurized olefin is one which is prepared in accordance with the detailed teachings of U.S. Patents 4,957,651 and 4,959,168. Described therein is a cosulfurized mixture of 2 or more reactants selected from the group consisting of (1) at least one fatty acid ester of a polyhydric alcohol, (2) at least one fatty acid, (3) at least one olefin, and (4) at least one fatty acid ester of a monohydric alcohol. Reactant (3), the olefin component, comprises at least one olefin and may be an aliphatic olefin containing 4 to 40 carbon atoms. The cosulfurized mixture of two or more of the reactants is prepared by reacting the mixture of appropriate reactants with a source of sulfur.

[0041] Metal salts of alkyl salicylates (xiv) include calcium and other salts of long chain (e.g. C12 to C16) alkyl-substituted salicylic acids.

[0042] Amine salts of alkylphosphoric acids (xv) include salts of oleyl and other long chain esters of phosphoric acid, with amines as described below. Useful amines in this regard are tertiary-aliphatic primary amines, sold under the tradename Primene™.

[0043] These and other types of friction modifiers are described, for instance, in US Published Application 2006-0172899.

[0044] Certain friction modifiers which are suitable for the present invention include glycerol monooleate, which is representative of the glycerol esters

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(vi) described above; tartaric acid derivatives, described below;ethoxylated fatty amines, which are a species of the alkoxylated fatty amines described above (viii) and include, for example, ethoxylated cocoa amine (Ethomeen™. C/12 from Akzo Chemical), ethoxylated tallow amine (Ethomeen™. T12), ethoxylated hydrogenated tallow amine (Ethomeen™ 18/12), and borated ethoxylated fatty amines (e.g., a reaction product of 3 moles Ethomeen™. T-12 with 2 moles boric acid); and, and fatty amides as in (ii) above, such as oleylamide.

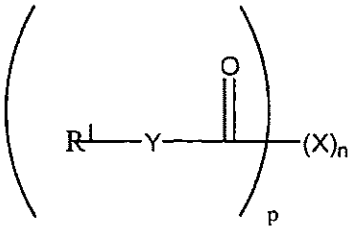
[0045] Tartaric acid derivatives are representative, more generally, of compound derived from hydroxycarboxylic acid, which may generally function as friction modifiers. Thus, in one embodiment the organic antiwear agent is derived from at least one of a hydroxy-carboxylic acid di-ester, a hydroxy-carboxylic acid di-amide, a hydroxy-carboxylic acid di-imide, a hydroxy-carboxylic acid ester-amide, a hydroxy-carboxylic acid ester-imide, and a hydroxy-carboxylic acid imide-amide. In one embodiment the ashless antiwear agent is derived from at least one of the group consisting of a hydroxy-carboxylic acid di-ester, a hydroxy-carboxylic acid di-amide, and a hydroxy-carboxylic acid ester-amide.

[0046] Examples of suitable a hydroxycarboxylic acids include citric acid, tartaric acid, malic acid (or hydroxy-succinic acid), lactic acid, glycolic acid, hydroxy-propionic acid, hydroxyglutaric acid, or mixtures thereof. In one embodiment ashless antiwear agent is derived from tartaric acid, citric acid, hydroxy-succinic acid, dihydroxy mono-acids, mono-hydroxy diacids, or mixtures thereof. In one embodiment the ashless antiwear agent includes a compound derived from tartaric acid. US Patent Application 2005/198894 discloses suitable hydroxycarboxylic acid compounds, and methods of preparing the same. Canadian Patent 1183125; US Patent Publication numbers 2006/0183647 and US-2006-0079413; US Patent Application number 60/867402; and British Patent 2 105 743 A, all disclose examples of suitable tartaric acid derivatives.

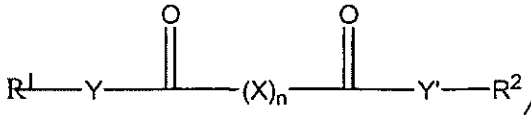
[0047] In one embodiment, di-esters, di-amides, ester-amide, or imide compounds are derived from a compound of Formula (1a) and/or (1b), below. A detailed description of methods for preparing suitable tartrimides (by reacting tartaric acid with a primary amine) is disclosed in US Patent 4,237,022. Examples of such tartrimides include those formed from condensation of tartaric acid with caproylamine, laurylamine, myristylamine, palmitylamine, stearylamine, myristoleylamine, palmitoleylamine, oleylamine, or linoleylamine or mixtures thereof. In one embodiment the ashless antiwear agent includes imides, di-esters, di-amides, and ester-amide derivatives of tartaric acid.

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[0048] In one embodiment the ashless antiwear agent is represented by a compound of Formula (1a) and/or (1b):



Formula (1a)



Formula (1b)

wherein

n is 0 to 10, 0 to 6, 0 to 4, 1 to 4, or 1 to 2;

p is 1 to 5, or 1 to 2, or 1;

Y and Y' are independently -O-, >NH, >NR^3; or alternatively a different cyclic structure (1c) comprising an imide group formed by a R^1-N< group between the two >C=O groups;

X is independently -CH_2-, >CHR^4 or >CR^4R^5, >$CHOR^6$, or >$C(CO_2R^6)_2$;

R^1 and R^2 are independently hydrocarbyl groups, typically containing 1 to 150, 4 to 30, or 6 to 20, or 10 to 20, or 11 to 18 carbon atoms;

R^3 is a hydrocarbyl group;

R^4 and R^5 are independently keto- groups, ester groups or hydrocarbyl groups; and

R^6 is independently hydrogen or a hydrocarbyl group, typically containing 1 to 150, or 4 to 30 carbon atoms.

[0049] In one embodiment the compound of Formula (1b) contains an imide group, which may be formed by taking together the Y and Y' groups and forming a R^1-N< group between two >C=O groups. In one embodiment the compound of Formula (1a) and/or (1b) has n, X, and R^1, R^2 and R^6 defined as follows: n is 1 to 2, X is >$CHOR^6$; and R^1, R^2 and R^6 are independently hydrocarbyl groups containing 4 to 30 carbon atoms. In one embodiment Y and Y' are both -O-. In one embodiment the compound of Formula (1a) and/or (1b) has n, X, Y, Y' and R^1, R^2 and R^6 defined as follows: n is 1 to 2, X is >$CHOR^6$; Y and Y' are both -O-, and R^1, R^2 and R^6 are independently hydrocarbyl groups containing 4 to 30 carbon atoms.

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[0050] The di-esters, di-amides, ester-amide, or imide compounds of Formula (1a) and/or (1b) and/or (1c) may be prepared by reacting a dicarboxylic acid (such as tartaric acid), with an amine or alcohol, optionally in the presence of a known esterification catalyst. The amine or alcohol typically has sufficient carbon atoms to fulfill the requirements of R^1 and/or R^2 as defined in Formula (1a) and/or (1b).

[0051] In one embodiment R^1 and R^2 are independently linear or branched hydrocarbyl groups. In one embodiment the hydrocarbyl groups are branched. In one embodiment the hydrocarbyl groups are linear. The R^1 and R^2 may be incorporated into Formula (1a) and/or (1b) by either an amine or an alcohol. The alcohol includes both monohydric alcohol and polyhydric alcohol. Examples of a suitable branched alcohol include 2-ethylhexanol, isotridecanol, Guerbet alcohols, or mixtures thereof. Examples of monohydric alcohols include methanol, ethanol, propanol, butanol, pentanol, hexanol, heptanol, octanol, nonanol, decanol, undecanol, dodecanol, tridecanol, tetradecanol, pentadecanol, hexadecanol, heptadecanol, octadecanol, nonadecanol, eicosanol, or mixtures thereof. In one embodiment the monohydric alcohol contains 5 to 20 carbon atoms. The alcohol includes either a monohydric alcohol or a polyhydric alcohol. Examples of suitable polyhydric alcohols include ethylene glycol, propylene glycol, 1,3-butanediol, 2,3-butanediol, 1,5-pentane diol, 1,6-hexane diol, glycerol, sorbitol, pentaerythritol, trimethylolpropane, starch, glucose, sucrose, methylglucoside, or mixtures thereof. In one embodiment the polyhydric alcohol is used in a mixture along with a monohydric alcohol. Typically, in such a combination the monohydric alcohol constitutes at least 60 mole percent, or at least 90 mole percent of the mixture.

[0052] Examples of esters include those prepared from condensation of tartaric acid with, e.g., long chain monohydric alcohols. These include a single alcohol, linear or branched, as well as mixtures of alcohols of various types. Examples of linear alcohols include those of 8-20 carbon atoms, such as 8-10, 8-12, 12-14, 12-16, and 14-18 carbon linear alcohols. Examples of branched alcohols include those of 8-20 carbon atoms such as 8 carbon atoms (e.g., 2-ethylhexanol) or 12-14 or 13 or 16 or 18 or 14-18 carbon branched alcohols. Thus esters may be derived from a mixture of all linear alcohols or all branched alcohols, or mixtures of linear and branched alcohols, e.g., mixtures of linear C8-14 alcohols with branched C8 alcohols, or linear C12-14 alcohols with branched C13 alcohols or linear C14-18 alcohols with branched C18 alcohols, as well as mixtures of C18 with C12 linear alcohols and mixtures of C13 with

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C8 branched alcohols, and other such combinations. The relative weight ratios of linear to branched alcohols or the ratios of one linear alcohol to another linear alcohol or one branched alcohol to another branched alcohol in any such combinations is not particularly restricted but may be, in some embodiments, 10~95:90~5 or 50~90:50~10, e.g., about 95:5 or 90:10 or 80:20 or 70:30 or 50:50 or 30:70.

[0053] In one embodiment the organic antiwear agent is derived from tartaric acid. The tartaric acid used for preparing the tartrates of the invention can be commercially available (for instance obtained from Sargent Welch), and it is likely to exist in one or more isomeric forms such as *d*-tartaric acid, *l*-tartaric acid, *d,l*-tartaric acid (racemic) or mesotartaric acid, often depending on the source (natural) or method of synthesis (e.g. from maleic acid). These derivatives can also be prepared from functional equivalents to the diacid readily apparent to those skilled in the art, such as esters, acid chlorides, or anhydrides.

[0054] When the compound of Formula (1a) and/or (1b) is derived from tartaric acid, resultant tartrates may be solid, semi-solid, or oil depending on the particular alcohol used in preparing the tartrate. For use as additives in oleaginous compositions including lubricating and fuel compositions the tartrates are advantageously soluble and/or stably dispersible in such oleaginous compositions. For example, compositions intended for use in oils are typically oil-soluble and/or stably dispersible in an oil in which they are to be used. The term "oil-soluble" as used in this specification and appended claims does not necessarily mean that all the compositions in question are miscible or soluble in all proportions in all oils. Rather, it is intended to mean that the composition is soluble in an oil (mineral, synthetic, etc.) in which it is intended to function to an extent which permits the solution to exhibit one or more of the desired properties. Similarly, it is not necessary that such "solutions" be true solutions in the strict physical or chemical sense. They may instead be micro-emulsions or colloidal dispersions which, for the purpose of this invention, exhibit properties sufficiently close to those of true solutions to be, for practical purposes, interchangeable with them within the context of this invention.

[0055] Also suitable for use as a friction modifier are vegetable oils such as, for instance, castor oil (a triglyceride based on a major component of ricinoleic acid, a hydroxy unsaturated acid), or sunflower oil.

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[0056] The amount of friction modifier present in the lubricants described herein may be 0.01 to 5 percent by weight, or 0.01 to 2% or 0.02 to 1.2% or 0.03 to 1%.

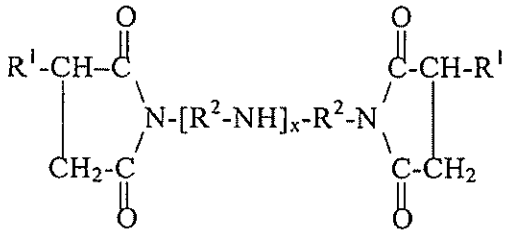
[0057] The compositions of the present invention may be substantially free or free from molybdenum compounds. Molybdenum compounds have been used as antioxidants, friction modifiers, and in various other functions, such as antiwear agents, in lubricant compositions. U.S. Pat. No. 4,285,822, for instance, discloses lubricating oil compositions containing a molybdenum and sulfur containing composition prepared by (1) combining a polar solvent, an acidic molybdenum compound and an oil-soluble basic nitrogen compound to form a molybdenum-containing complex and (2) contacting the complex with carbon disulfide to form the molybdenum and sulfur containing composition. The present lubricant formulations contain little or no molybdenum, for instance, less than 500, or less than 300 or less than 150 or less than 100 or less than 50 or less than 20 or less than 10 or less than 5 or less than 1 parts per million Mo by weight, or alternatively in amount of 0.1 to 50 parts per million or 1 to 5 parts per million. Alternatively expressed, the amount of molybdenum in the present lubricants may be less than an amount effective to provide significant antifriction activity.

[0058] The compositions of the present invention may also be free or substantially free from zinc compounds. Zinc compounds, such as zinc phosphates, zinc thiophosphates (in particular, zinc dialkyl diithiophosphates) and other zinc compounds such as zinc oleates are often used in lubricants as antiwear or antioxidant agents. The lubricants of the present invention may perform well even in the absence of these zinc compounds. Thus, the amount of zinc in the composition may be 0 to 1000 or 0 to 100, or 1 to 20, or less than 20, or less than 10, or less than 5 parts per million by weight.

[0059] The compositions as described herein may also contain a dispersant. Dispersants are well known in the field of lubricants and include primarily what is known as ashless dispersants and polymeric dispersants. Ashless dispersants are so-called because, as supplied, they do not contain metal and thus do not normally contribute to sulfated ash when added to a lubricant. However they may, of course, interact with ambient metals once they are added to a lubricant which includes metal-containing species. Ashless dispersants are characterized by a polar group attached to a relatively high molecular weight hydrocarbon chain. Typical ashless dispersants include N-substituted long

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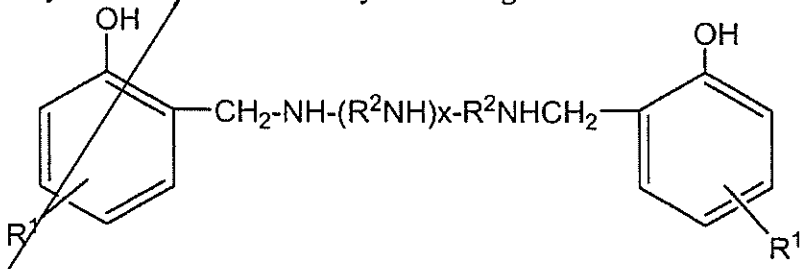
chain alkenyl succinimides, having a variety of chemical structures including typically



where each R^1 is independently an alkyl group, frequently a polyisobutylene group with a molecular weight of 500-5000, and R^2 are alkylene groups, commonly ethylene (C_2H_4) groups. Such molecules are commonly derived from reaction of an alkenyl acylating agent with a polyamine, and a wide variety of linkages between the two moieties is possible beside the simple imide structure shown above, including a variety of amides and quaternary ammonium salts. Also, a variety of modes of linkage of the R^1 groups onto the imide structure are possible, including various cyclic linkages. The ratio of the carbonyl groups of the acylating agent to the nitrogen atoms of the amine may be 1:0.5 to 1:3, and in other instances 1:1 to 1:2.75 or 1:1.5 to 1:2.5. Succinimide dispersants are more fully described in U.S. Patents 4,234,435 and 3,172,892.

[0060] Another class of ashless dispersant is high molecular weight esters. These materials are similar to the above-described succinimides except that they may be seen as having been prepared by reaction of a hydrocarbyl acylating agent and a polyhydric aliphatic alcohol such as glycerol, pentaerythritol, or sorbitol. Such materials are described in more detail in U.S. Patent 3,381,022.

[0061] Another class of ashless dispersant is Mannich disspersants. These are materials which are formed by the condensation of a higher molecular weight, alkyl substituted phenol, an alkylene polyamine, and an aldehyde such as formaldehyde. Such materials may have the general structure



(including a variety of isomers and the like) and are described in more detail in U.S. Patent 3,634,515.

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[0062] Other dispersants include polymeric dispersant additives, which are generally hydrocarbon-based polymers which contain polar functionality to impart dispersancy characteristics to the polymer.

[0063] Dispersants can also be post-treated by reaction with any of a variety of agents. Among these are urea, thiourea, dimercaptothiadiazoles, carbon disulfide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, nitriles, epoxides, boron compounds, and phosphorus compounds. References detailing such treatment are listed in U.S. Patent 4,654,403. Borated dispersants have been found to be useful in the present lubricants. Typically, the borated dispersant will contain 0.1% to 5%, or 0.5% to 4%, or 0.7% to 3% by weight boron. In one embodiment, the borated dispersant is a borated acylated amine, such as a borated succinimide dispersant. Borated dispersant are prepared by reaction of one or more dispersant with one or more boron compounds and are described in U.S. Pat. Nos. 3,000,916; 3,087,936; 3,254,025; 3,282,955; 3,313,727; 3,491,025; 3,533,945; 3,666,662 and 4,925,983.

[0064] The amount of dispersant or borated dispersant (or the combination of the two), if present in the present compositions, may be 0.1 or 0.2 to 5 weight percent, or 0.4 to 4 weight percent, or 0.5 to 3 weight percent, or 0.5 to 1.8 weight percent.

[0065] The present lubricant formulations may also contain one or more overbased detergents. Overbased materials, otherwise referred to as overbased or superbased salts, are generally homogeneous Newtonian systems characterized by a metal content in excess of that which would be present for neutralization according to the stoichiometry of the metal and the particular acidic organic compound reacted with the metal. The overbased materials are prepared by reacting an acidic material (typically an inorganic acid or lower carboxylic acid, such as carbon dioxide) with a mixture comprising an acidic organic compound, a reaction medium comprising at least one inert, organic solvent (e.g., mineral oil, naphtha, toluene, xylene) for said acidic organic material, a stoichiometric excess of a metal base, and a promoter such as a phenol or alcohol and optionally ammonia. The acidic organic material will normally have a sufficient number of carbon atoms, for instance, as a hydrocarbyl substituent, to provide a reasonable degree of solubility in oil. The amount of excess metal is commonly expressed in terms of metal ratio. The term "metal ratio" is the ratio of the total equivalents of the metal to the equivalents of the acidic organic compound. A neutral metal salt has a metal ratio of one. A salt having 4.5 times as much

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metal as present in a normal salt will have metal excess of 3.5 equivalents, or a ratio of 4.5.

[0066] Overbased detergents are often characterized by Total Base Number (TBN). TBN is the amount of strong acid (perchloric or hydrochloric) needed to neutralize all of the overbased material's basicity, expressed as potassium hydroxide equivalents (mg KOH per gram of sample). Since overbased detergents are commonly provided in a form which contains a certain amount of diluent oil, for example, 40-50% oil, the actual TBN value for such a detergent will depend on the amount of such diluent oil present, irrespective of the "inherent" basicity of the overbased material. For the purposes of the present invention, the TBN of an overbased detergent is to be recalculated to an oil-free basis. Thus, for instance, a detergent composition having an uncorrected TBN of 300 and 40% oil content could have a TBN (oil-free basis) of 500. Detergents which are useful in the present invention typically have a TBN (oil-free basis) of 100 to 800, and in one embodiment 150 to 750, and in another, 400 to 700. If multiple detergents are employed, the overall TBN of the detergent component (that is, an average of all the specific detergents together) will typically be in the above ranges.

[0067] The overall TBN of the composition, including oil, will be derived from the TBN contribution of the individual components, such as the dispersant, the detergent, and other basic materials. The overall TBN for lubricants used as marine diesel cylinder lubricants will typically be greater than 30, e.g., 31 to 100 or 35 to80 or 40 to 70. Other lubricants may have an overall TBN of at least 7 or at least 10, or sometimes even at least 20. The majority of the TBN is typically contributed by the overbased detergent component.

[0068] The metal compounds useful in making the basic metal salts are generally any Group 1 or Group 2 metal compounds (CAS version of the Periodic Table of the Elements). The Group 1 metals of the metal compound include Group 1a alkali metals such as sodium, potassium, and lithium, as well as Group 1b metals such as copper. The Group 2 metals of the metal base include the Group 2a alkaline earth metals such as magnesium, calcium, and barium, as well as the Group 2b metals such as zinc or cadmium.

[0069] Such overbased materials are well known to those skilled in the art. Patents describing techniques for making basic salts of sulfonic acids, carboxylic acids, (hydrocarbyl-substituted) phenols, phosphonic acids, and mixtures of any two or more of these include U.S. Patents 2,501,731; 2,616,905; 2,616,911;

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

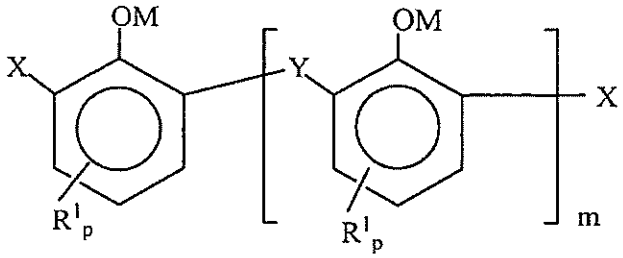
[0070] In one embodiment the lubricants of the present invention can contain an overbased sulfonate detergent. Suitable sulfonic acids include sulfonic and thiosulfonic acids. Sulfonic acids include the mono- or polynuclear aromatic or cycloaliphatic sulfonic acid compounds. Oil-soluble sulfonates may be represented by one of the following formulas: R^2-T-$(SO_3\text{-})_a$ and R^3-$(SO_3\text{-})_b$, where T is a cyclic nucleus such as typically benzene; R^2 is an aliphatic group such as alkyl, alkenyl, alkoxy, or alkoxyalkyl; (R^2)-T typically contains a total of at least 15 carbon atoms; and R^3 is an aliphatic hydrocarbyl group typically containing at least 15 carbon atoms. Examples of R^3 are alkyl, alkenyl, alkoxy-alkyl, and carboalkoxyalkyl groups. The R groups may be linear or branched or mixtures of linear and branched groups. The groups T, R^2, and R^3 may also contain other inorganic or organic substituents such as hydroxy, mercapto, halogen, nitro, amino, nitroso, sulfide, or disulfide. In the above formulas, a and b are at least 1.

[0071] Another overbased material which can be present is an overbased phenate detergent. The phenols useful in making phenate detergents can be represented by the formula $(R_1)_a$-Ar-$(OH)_b$, wherein R_1 is an aliphatic hydrocarbyl group of 4 to 400 carbon atoms, or 6 to 80 or 6 to 30 or 8 to 25 or 8 to 15 carbon atoms; Ar is an aromatic group (which can be a benzene group or another aromatic group such as naphthalene); a and b are independently numbers of at least one, the sum of a and b being up to the number of displaceable hydrogens on the aromatic nucleus or nuclei of Ar. In one embodiment, a and b are independently to 4, or 1 to 2. R_1 and a are typically such that there is an average of at least 8 aliphatic carbon atoms provided by the R_1 groups for each phenol compound. Phenate detergents are also sometimes provided as sulfur-bridged species.

[0072] In one embodiment, the overbased material is an overbased detergent selected from the group consisting of overbased salixarate detergents, overbased saligenin detergents, overbased salicylate detergents, and overbased glyoxylate detergents, and mixtures thereof. Overbased saligenin detergents are commonly overbased magnesium salts which are based on saligenin derivatives.

A general example of such a saligenin derivative can be represented by the formula

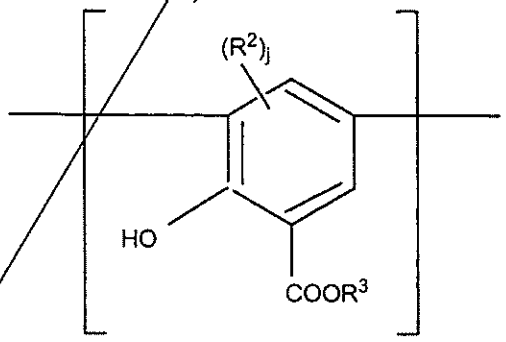
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wherein X comprises -CHO or -CH_2OH, Y comprises -CH_2- or -CH_2OCH_2-, and wherein such -CHO groups typically comprise at least 10 mole percent of the X and Y groups; M is hydrogen, ammonium, or a valence of a metal ion, R^1 is a hydrocarbyl group containing 1 to 60 carbon atoms, m is 0 to typically 10, and each p is independently 0, 1, 2, or 3, provided that at least one aromatic ring contains an R^1 substituent and that the total number of carbon atoms in all R^1 groups is at least 7. When m is 1 or greater, one of the X groups can be hydrogen. In one embodiment, M is a valence of a Mg ion or a mixture of Mg and hydrogen. Other metals include alkali metals such as lithium, sodium, or potassium; alkaline earth metals such as calcium or barium; and other metals such as copper, zinc, and tin. Saligenin detergents are disclosed in greater detail in U.S. Patent 6,310,009, with special reference to their methods of synthesis (Column 8 and Example 1) and preferred amounts of the various species of X and Y (Column 6).

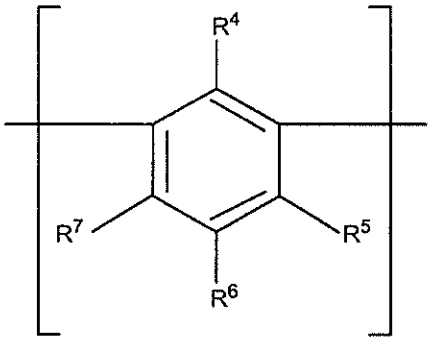
[0073] As used herein, the expression "represented by the formula" indicates that the formula presented is generally representative of the structure of the chemical in question. However, it is well known that minor variations can occur, including in particular positional isomerization, that is, location of the X, Y, and R groups at different position on the aromatic ring from those shown in the structure. The expression "represented by the formula" is expressly intended to encompass such variations.

[0074] Salixarate detergents are overbased materials that can be represented by a substantially linear compound comprising at least one unit of formula (I) or formula (II):



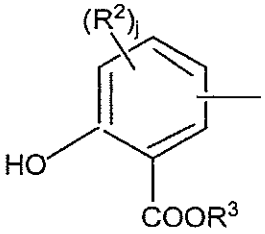
(I)

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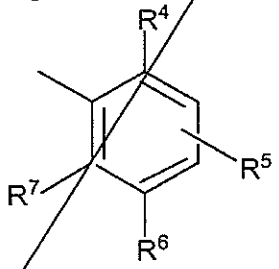


(II)

each end of the compound having a terminal group of formula (III) or (IV):



(III)

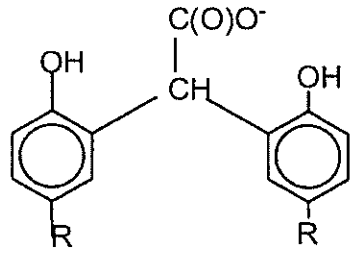


(IV)

such groups being linked by divalent bridging groups A, which may be the same or different for each linkage; wherein in formulas (I)-(IV) R^3 is hydrogen or a hydrocarbyl group; R^2 is hydroxyl or a hydrocarbyl group and j is 0, 1, or 2; R^6 is hydrogen, a hydrocarbyl group, or a hetero-substituted hydrocarbyl group; either R^4 is hydroxyl and R^5 and R^7 are independently either hydrogen, a hydrocarbyl group, or hetero-substituted hydrocarbyl group, or else R^5 and R^7 are both hydroxyl and R^4 is hydrogen, a hydrocarbyl group, or a hetero-substituted hydrocarbyl group; provided that at least one of R^4, R^5, R^6 and R^7 is hydrocarbyl containing at least 8 carbon atoms; and wherein the molecules on average contain at least one of unit (I) or (III) and at least one of unit (II) or (IV) and the ratio of the total number of units (I) and (III) to the total number of units of (II) and (IV) in the composition is about 0.1:1 to about 2:1. The divalent bridging group "A," which may be the same or different in each occurrence, includes -CH_2- (methylene bridge) and -CH_2OCH_2- (ether bridge), either of which may be derived from formaldehyde or a formaldehyde equivalent (e.g., paraform, formalin). Salixarate derivatives and methods of their preparation are described in greater detail in U.S. patent number 6,200,936 and PCT Publication WO 01/56968. It is believed that the salixarate derivatives have a predominantly linear, rather than macrocyclic, structure, although both structures are intended to be encompassed by the term "salixarate."

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[0075] Glyoxylate detergents are similar overbased materials which are based on an anionic group which, in one embodiment, may have the structure



wherein each R is independently an alkyl group containing at least 4, and preferably at least 8 carbon atoms, provided that the total number of carbon atoms in all such R groups is at least 12, preferably at least 16 or 24. Alternatively, each R can be an olefin polymer substituent. The acidic material upon from which the overbased glyoxylate detergent is prepared is the condensation product of a hydroxyaromatic material such as a hydrocarbyl-substituted phenol with a carboxylic reactant such as glyoxylic acid and other omega-oxoalkanoic acids. Overbased glyoxylic detergents and their methods of preparation are disclosed in greater detail in U.S. Patent 6,310,011 and references cited therein.

[0076] The overbased detergent can also be an overbased salicylate. The alkylsalicylate can be an alkali metal salt or an alkaline earth metal salt of an alkylsalicylic acid which can in turn be prepared from an alkylphenol by Kolbe-Schmitt reaction. The alkylphenol can be prepared by a reaction of α-olefin having, e.g., 8 to 30 carbon atoms (mean number) with phenol. Alternatively, calcium salicylate can be produced by direct neutralization of alkylphenol and subsequent carbonation. The salicylic acids may thus be hydrocarbyl-substituted salicylic acids, such as aliphatic hydrocarbon-substituted salicylic acids wherein each substituent contains an average of at least 8 carbon atoms per substituent and 1 to 3 substituents per molecule. The substituents can be polyalkene substituents, where polyalkenes include homopolymers and interpolymers of polymerizable olefin monomers of 2 to 16, or 2 to 6, or 2 to 4 carbon atoms. The olefins may be monoolefins such as ethylene, propylene, 1-butene, isobutene, and 1-octene; or a polyolefinic monomer, such as diolefinic monomer, such 1,3-butadiene and isoprene. In one embodiment, the hydrocarbyl substituent group or groups on the salicylic acid contains 7 to 300 carbon atoms and can be an alkyl group having a molecular weight of 150 to 2000. The polyalkenes and polyalkyl groups are prepared by conventional procedures, and substitution of such groups onto salicylic acid can be effected by known meth-

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ods. Overbased salicylate detergents and their methods of preparation are disclosed in U.S. Patents 4,719,023 and 3,372,116.

[0077] The detergent component may also be a mixture of detergents or so-called "hybrid detergents," also referred to as complex detergents or mixed substrate detergents. In one embodiment the hybrid may be an overbased phenate-salicylate detergent. Methods of preparing overbased phenate-salicylate detergents are disclosed in EP 123 6791 A1 and EP 123 6792 A1. In one embodiment the hybrid may be prepared by reacting, in the presence of a suspension and acidifying overbasing agent, an alkyl aromatic sulfonic acid and at least one alkyl phenol (such as alkyl phenol, aldehyde-coupled alkyl phenol, sulfurized alkyl phenol) and optionally alkyl salicylic acid. Preparation of such materials is also disclosed in WO97046643

[0078] The present lubricants may thus contain up to 20 percent by weight, (or 0.1 to 19 or 0.5 to 18 or 1 to17 or 0.1 to 10 or 0.5 to 7 or 1 to 5 percent by weight) of an overbased calcium alkylphenol sulfide detergent (of any of a number of degrees of overbasing, high or low TBN) or up to 20 percent by weight (or 0.1 to 17.5 or 0.1 to 17 or 0.5 to 15 or 1 to 17 or 0.5 to 15 or 2 to 12 or 6 to 10 percent by weight) of a relatively highly overbased linear alkyl sulfonate detergent, that is, having an oil-free TBN of 400-900, or mixtures of such materials. The total amount of the overbased detergents, in the formulations of the present invention, is typically at least 0.6 weight percent on an oil-free basis. In other embodiments, it can be present in amounts of 0.7 to 20 weight percent or 1 to 18 weight percent or 3 to 13 weight percent. In one embodiment the detergent component consists of a salicylate detergent (and no sulfonate). In another embodiment the detergent component consists of a sulfonate detergent (and no phenate).

[0079] The lubricants described herein may also contain one or more additional materials that are commonly used in formulating lubricants, especially marine diesel cylinder lubricants. Typically the other performance additives include metal deactivators, antioxidants, antiwear agents, corrosion inhibitors, antiscuffing agents, extreme pressure agents, foam inhibitors, demulsifiers, viscosity modifiers, pour point depressants and mixtures thereof. Typically, fully-formulated lubricating oil will contain one or more of these performance additives.

[0080] Antioxidant compounds are known and include for example, sulfurized olefins, alkylated diphenylamines (typically di-nonyl diphenylamine, octyl diphenylamine, di-octyl diphenylamine), hindered phenols, and mixtures

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thereof. Molybdenum compounds are also sometimes used as antioxidants, but, as stated above, Mo compounds are typically not included in the present compositions.

[0081] The hindered phenol antioxidant often contains a secondary butyl and/or a tertiary butyl group as a sterically hindering group. The phenol group is often further substituted with a hydrocarbyl group and/or a bridging group linking to a second aromatic group. Examples of suitable hindered phenol antioxidants include 2,6-di-tert-butylphenol, 4-methyl-2,6-di-tert-butylphenol, 4-ethyl-2,6-di-tert-butylphenol, 4-propyl-2,6-di-tert-butylphenol or 4-butyl-2,6-di-tert-butylphenol, or 4-dodecyl-2,6-di-tert-butylphenol. In one embodiment the hindered phenol antioxidant is an ester and may include, e.g., Irganox™ L-135 from Ciba. A more detailed description of suitable ester-containing hindered phenol antioxidant chemistry is found in US Patent 6,559,105.

[0082] Viscosity modifiers include hydrogenated copolymers of styrene and butadiene, ethylene-propylene copolymers, polyisobutenes, hydrogenated styrene-isoprene polymers, hydrogenated isoprene polymers, polymethacrylates, polyacrylates, polyalkyl styrenes, hydrogenated alkenyl aryl conjugated diene copolymers, polyolefins, esters of maleic anhydride olefin copolymers, and esters of maleic anhydride-styrene copolymers.

[0083] Examples of antiwear agents include boron-containing compounds such as borate esters or borated alcohols, phosphate esters, sulfurized olefins, sulfur-containing ashless anti-wear additives, metal dihydrocarbyldithiophosphates (such as zinc dialkyldithiophosphates, which, as mentioned above, may also be absent from the present formulations), thiocarbamate-containing compounds, such as thiocarbamate esters, alkylene-coupled thiocarbamates, and bis-(S-alkyldithiocarbamyl) disulfides. The antiwear agent may be present in ranges including 0 wt % to 15 wt %, or 0.1 wt % to 10 wt % or 1 wt % to 8 wt % of the lubricating composition.

[0084] The borate esters or borate alcohols may be substantially the same except the borate alcohol has at least one hydroxyl group that is not esterified. Therefore, as used herein the term "borate ester" is used to refer to either borate ester or borate alcohol. The borate esters or borate alcohols may have a formula $B(OR')_3$ or be a derivative thereof containing a >B-O-B< group, wherein R' may be hydrogen or a hydrocarbyl group, typically containing 1 to 40, or 1 to 20 carbon atoms on each R'. When R' is hydrogen, the boron-containing compound is a borate alcohol. When R' is hydrocarbyl, the boron-containing compound is a borate ester. The borate ester may be prepared by the reaction of a

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boron compound, such as boric acid, boron oxides, or boron halides, and at least one compound selected from epoxy compounds, halohydrin compounds, epihalohydrin compounds, alcohols and mixtures thereof. The alcohols include dihydric alcohols, trihydric alcohols or higher alcohols, with the proviso for one embodiment that hydroxyl groups are on adjacent, i.e., vicinal, carbon atoms. Some of the boron-containing compounds may also sere as friction modifiers, as described above.

[0085] Dithiocarbamate-containing compounds may be prepared by reacting a dithiocarbamate acid or salt with an unsaturated compound. The dithiocarbamate containing compounds may also be prepared by simultaneously reacting an amine, carbon disulfide and an unsaturated compound. Generally, the reaction occurs at a temperature of 25 °C to 125 °C. US Patents 4,758,362 and 4,997,969 describe dithiocarbamate compounds and methods of making them.

[0086] Examples of suitable olefins that may be sulfurized to form sulfurized olefins include propylene, butylene, isobutylene, pentene, hexane, heptene, octane, nonene, decene, undecene, dodecene, undecyl, tridecene, tetradecene, pentadecene, hexadecene, heptadecene, octadecene, octadecenene, nonodecene, eicosene or mixtures thereof. In one embodiment, hexadecene, heptadecene, octadecene, octadecenene, nonodecene, eicosene or mixtures thereof and their dimers, trimers and tetramers are especially useful olefins. Alternatively, the olefin may be a Diels-Alder adduct of a diene such as 1,3-butadiene and an unsaturated ester, such as, butylacrylate. Another class of sulfurized olefin includes fatty acids and their esters and mixtures with α-olefins. The fatty acids are often obtained from vegetable oil or animal oil and typically contain 4 to 22 carbon atoms.

[0087] Extreme Pressure (EP) agents include sulfur- and chlorosulfur-containing EP agents, chlorinated hydrocarbon EP agents and phosphorus EP agents. Examples of such EP agents include chlorinated wax; organic sulfides and polysulfides such as dibenzyldisulfide, bis–(chlorobenzyl) disulfide, dibutyl tetrasulfide, sulfurized methyl ester of oleic acid, sulfurized alkylphenol, sulfurized dipentene, sulfurized terpene, and sulfurized Diels-Alder adducts; phosphosulfurized hydrocarbons such as the reaction product of phosphorus sulfide with turpentine or methyl oleate; phosphorus esters such as the dihydrocarbon and trihydrocarbon phosphites, e.g., dibutyl phosphite, diheptyl phosphite, dicyclohexyl phosphite, pentylphenyl phosphite; dipentylphenyl phosphite, tridecyl phosphite, distearyl phosphite and polypropylene substituted phenol phosphite; metal thiocarbamates such as zinc dioctyldithiocarbamate and barium heptylphenol diacid; amine salts of alkyl and dialkylphosphoric acids,

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including, for example, the amine salt of the reaction product of a dialkyldithiophosphoric acid with propylene oxide; and mixtures thereof.

[0088] Other performance additives such as corrosion inhibitors include those described in paragraphs 5 to 8 of US Application 2005-038319 , octylamine octanoate, condensation products of dodecenyl succinic acid or anhydride and a fatty acid such as oleic acid with a polyamine. In one embodiment the corrosion inhibitors include the Synalox® corrosion inhibitor. The Synalox® corrosion inhibitor is typically a homopolymer or copolymer of propylene oxide. The Synalox® corrosion inhibitor is described in more detail in a product brochure with Form No. 118-01453-0702 AMS, published by The Dow Chemical Company. The product brochure is entitled "SYNALOX Lubricants, High-Performance Polyglycols for Demanding Applications."

[0089] Metal deactivators include derivatives of benzotriazoles (typically tolyltriazole), dimercaptothiadiazole derivatives, 1,2,4-triazoles, benzimidazoles, 2-alkyldithiobenzimidazoles, or 2-alkyldithiobenzothiazoles. Foam inhibitors include copolymers of ethyl acrylate and 2-ethylhexylacrylate and optionally vinyl acetate. Demulsifiers include trialkyl phosphates, polyethylene glycols, polyethylene oxides, polypropylene oxides and (ethylene oxide-propylene oxide) polymers. Pour point depressants include esters of maleic anhydride-styrene, polymethacrylates, polyacrylates or polyacrylamides.

[0090] The presently described lubricants may also contain titanium-containing additives such as titanium alkoxides or titanium-modified dispersants, as described in greater detail in, e.g., U.S. Application 2006-0217271.

[0091] As used herein, the term "hydrocarbyl substituent" or "hydrocarbyl group" is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group having a carbon atom directly attached to the remainder of the molecule and having predominantly hydrocarbon character. Examples of hydrocarbyl groups include:

hydrocarbon substituents, 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 a ring);

substituted hydrocarbon substituents, that is, substituents containing non-hydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbon nature of the substituent (e.g., halo (especially

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chloro and fluoro), hydroxy, alkoxy, mercapto, alkylmercapto, nitro, nitroso, and sulfoxy);

hetero substituents, that is, substituents which, while having a predominantly hydrocarbon character, in the context of this invention, contain atoms other than carbon in a ring or chain otherwise composed of carbon atoms. Heteroatoms include sulfur, oxygen, nitrogen, and encompass substituents as pyridyl, furyl, thienyl and imidazolyl. In general, no more than two, or 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.

[0092] It is known that some of the materials described above may interact in the final formulation, so that the components of the final formulation may be different from those that are initially added. For instance, metal ions (of, e.g., a detergent) can migrate to other acidic or anionic sites of other molecules. The products formed thereby, including the products formed upon employing the composition of the present invention in its intended use, may not be susceptible of easy description. Nevertheless, all such modifications and reaction products are included within the scope of the present invention; the present invention encompasses the composition prepared by admixing the components described above.

EXAMPLES

[0093] A "good" baseline lubricant formulation is prepared characteristic of a marine diesel cylinder lubricant. The lubricant contains, in an API Group I mineral oil:

12.5% of a mixture of overbased calcium benzenesulfonate and phenate detergents, imparting a total of about 69 TBN to the lubricant; and

0.67 weight percent of a borated succinimide dispersant.

It is noted that some commercial components may contain small amounts of other components such as stearic acid or dispersants, to aid in their manufacture.

[0094] The above lubricant is evaluated, in the absence and presence of various organic friction modifiers for coefficient of friction as a function of temperature. Evaluation was performed on a Cameron Plint™ test rig with a pin-on-plate geometry. Each lubricant is partially neutralized with sulfuric acid (3.5% acid) prior to testing. The lubricants are were subjected to a 100N load, while the temperature is raised from ambient to 300 °C. The friction coefficient, contact potential and specimen temperature are recorded every 10 seconds during a 2.5 hour test. Coefficients of friction for lubricants containing the

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various additives are reported in Table 1 as an average over various temperature ranges.

Table 1 – Coefficients of Friction

Ex.	Additive, %	50 - 100°C	100 - 150°C	150 - 200°C	200 - 250°C	250 - 300°C
1*	None: "good baseline"	0.095	0.089	0.076	0.064	0.054
2*	– comparative "poor baseline"	0.101	0.100	0.092	0.085	0.083
3*	Molybdenum dithiocarbamate, 0.5%	0.095	0.087	0.071	0.058	0.048
4	Tall oil fatty acid, 0.5%	0.097	0.084	0.066	0.053	0.046
5	Long chain tartaric esters, 0.5%	0.089	0.080	0.064	0.053	0.051
6	Glycerol monooleate, 0.5%	0.098	0.082	0.064	0.051	0.045
7	Oleylamide, 0.5%	0.097	0.084	0.068	0.054	0.047
8	Polyoxyethylene tallow-alkylamines, 0.5%	0.103	0.090	0.071	0.057	0.052
9	Castor oil, 0.5%	0.095	0.084	0.070	0.056	0.049
10	Long chain alkyl tartrimide, 0.5%	0.090	0.083	0.067	0.055	0.045

* A comparative or reference example

[0095] The results show that each of the tested organic friction modifiers provides significantly reduced friction to the lubricant formulation, especially at high temperatures of 150°C and above. At high temperatures, the organic, metal-free friction modifiers show performance equal to or better than that provided by molybdenum dithiocarbamate, a known metal-containing additive.

[0096] Example 11. The formulation of Example 6, containing glycerol monooleate, is repeated, except that the borated succinimide dispersant is replaced by an equal amount of a corresponding non-borated succinimide dispersant. The same friction test described above is performed, with the results shown below:

Ex.	Additives	50 - 100°C	100 - 150°C	150 - 200°C	200 - 250°C	250 - 300°C
6	GMO with borated dispersant	0.098	0.082	0.064	0.051	0.045
11	GMO with non-borated disp't.	0.100	0.084	0.065	0.054	0.050

[0097] The results show that the use of a borated dispersant can provide improved high temperature frictional performance in the subject lubricants, compared with the use of a non-borated dispersant.

[0098] Each of the documents referred to above is incorporated herein by reference. The mention of any document is not an admission that such document

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qualifies as prior art or constitutes the general knowledge of the skilled person in any jurisdiction. Except in the Examples, or where otherwise explicitly indicated, all numerical quantities in this description specifying amounts of materials, reaction conditions, molecular weights, number of carbon atoms, and the like, are to be understood as modified by the word "about." Unless otherwise indicated, each chemical or composition referred to herein should be interpreted as being a commercial grade material which may contain the isomers, by-products, derivatives, and other such materials which are normally understood to be present in the commercial grade. However, the amount of each chemical component is presented exclusive of any solvent or diluent oil, which may be customarily present in the commercial material, unless otherwise indicated. It is to be understood that the upper and lower amount, range, and ratio limits set forth herein may be independently combined. Similarly, the ranges and amounts for each element of the invention can be used together with ranges or amounts for any of the other elements. As used herein, the expression "consisting essentially of" permits the inclusion of substances that do not materially affect the basic and novel characteristics of the composition under consideration.

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Claims:

1. Use of a glycerol ester to reduce friction in lubricating a marine diesel engine operating above 150°C at the cylinder liner, comprising supplying to the cylinder liner thereof and not to or from a crankcase, a lubricant composition comprising an oil of lubricating viscosity and 0.01 to 5 percent by weight of said glycerol ester; said lubricant composition being substantially free from molybdenum compounds and substantially free from zinc compounds.

2. The use of claim 1 wherein the glycerol ester comprises glycerol monooleate.

3. The use of claim 1 or claim 2 wherein said lubricant further comprises 0.1 to 5 percent by weight of a borated dispersant.

4. The use of any one of claims 1 to 3, wherein said lubricant further comprises 0.1 to 17 percent by weight of an overbased calcium alkylphenol sulfide detergent.

5. The use of any one of claims 1 to 4, wherein said lubricant further comprises 0.5 to 15 percent by weight of an overbased linear alkyl sulfonate detergent having a total base number (TBN) of 400-900.

6. The use of any one of claims 1 to 5 wherein the total base number (TBN) of the lubricant is at least 35.

7. The use of any one of claims 1 to 6 wherein the engine is a two-stroke cycle engine.

TITLE

Marine Diesel Cylinder Lubricants for Improved Fuel Efficiency

BACKGROUND OF THE INVENTION

[0001] The disclosed technology relates to lubricants for internal combustion engines, and in particular marine diesel cylinder lubricants.

[0002] Improving fuel economy is of interest for the operation of nearly all engines from relatively small gasoline powered engines through large marine diesel engines. There are both economic and environmental advantages for improving fuel economy in the marine industry, the largest impact perhaps being from improvement in Marine Diesel Cylinder Lubricant (MDCL) technology, for instance, by improving the contact between the piston rings and cylinder liner in these engines. Particularly in the marine industry, much work has been done by original equipment manufacturers on improving fuel economy by engineering means.

[0003] In gasoline engines and smaller diesel engines, significant effort has been expended toward improving efficiency by means of reducing friction within the engine by modifying the lubricant. There are additional challenges, however, in attempting to apply such methods to lubricants for marine diesel engines because of the significantly higher operating temperatures of such engines, typically in excess of 150°C, e.g., 175-275°C in the area lubricated by a marine diesel cylinder lubricant (i.e., the cylinder liner), compared to the temperatures commonly encountered by lubricants in smaller engines, e.g., around 100°C or below. Natural gas-fueled engines (stationary engines) will also typically operate at high temperatures.

[0004] US Patent 4,683,069 discloses lubricating oil compositions containing 0.05 to 0.2 weight % of glycerol esters as fuel economy additives. The glycerol esters disclosed include GMO. The lubricating oil composition is suitable for either gasoline or diesel engines.

[0005] US Patent Application 2003/134758 discloses the use of an effective amount of one or more compounds capable of reducing friction coefficients under mixed lubrication or boundary lubrication conditions in a heavy duty diesel engine lubricating oil composition for improving the fuel economy of a heavy duty diesel engine. Example 1 contains glycerol monooleate.

[0006] US Patent Application 2003/134758 discloses heavy duty diesel engine lubricating oil compositions for improving the fuel economy. The treat

rate may range from 0.01 to 5.0 wt %, or preferably 0.15 to 0.5 wt %. Example 1 discloses a composition with glycerol monooleate in an amount of 0.3 mass %, while Example 2 contains as a friction reducer a trinuclear molybdenum dithiocarbamate.

[0007] US Patent 6,074,993 discloses a lubricating composition which exhibits improved fuel economy. The composition contains amongst other materials at least one organic oil-soluble friction modifier. Claim 12 discloses ethoxylated amine. The lubricating composition may be used in the formulation of crankcases oils. Heavy-duty diesel motor oils are mentioned as a possible crankcase oil.

[0008] US Patent Application 2007/0015672 discloses a drive in terms of fuel economy for gasoline and diesel engines which has resulted in increased levels of organic friction modifiers being used in lubricating oil compositions; unfortunately, there are compatibility issues between the friction modifiers and overbased detergents, such as overbased calcium sulphonates. The invention described therein is therefore concerned with improving the compatibility between friction modifiers and overbased detergents in lubricating oil compositions. Examples therein include the use of GMO and/or ethoxylated tallow amine.

[0009] US Patent 6,333,298 discloses a molybdenum-free lubricating oil composition exhibiting improved fuel economy and fuel economy retention properties by employing at least one friction modifier. Claim 8 specifies the friction modifier is an ethoxylated amine. The lubricating oil composition is suitable for heavy duty diesel engines.

[0010] US Patent 6,074,993 discloses a lubricating oil composition which exhibits improved fuel economy and wet clutch friction properties, said composition comprising: an oil of lubricating viscosity; at least one overbased calcium; at least one organic oil soluble friction modifier; and at least one zinc dihydrocarbyldithiophosphate compound, wherein said composition has a TBN of at least 3.6. Ethoxylated amines are disclosed in claim 12. The lubricating oil composition is suitable for crankcase lubricating oils (i.e., passenger car motor oils, heavy duty diesel motor oils, and passenger car diesel oils) for spark-ignited and compression-ignited engines.

[0011] US Patent Application 2006/276354 discloses lubricant compositions for use in automotive engine oils comprising a combination of a specific base stock or mixture of base stocks and a friction reducing additive to improve fuel economy and fuel economy longevity of the automotive engine oil. The friction reducing additive is a specific partial polyol ester and may also include a specif-

ic saturated primary amide. The automotive engine is stated to include gasoline and heavy duty diesel. The examples disclose GMO in a particular composition.

[0012] US Patent Application 2006/183647 discloses lubricating compositions containing tartaric acid derivatives as fuel economy improvers and anti-wear agents in crankcase oils. The tartaric acid derivatives include tartrates, tartrimides and tartramides. The lubricating oils have low sulfur, phosphorus and ash content. Further disclosed is these use of the lubricant compositions as being useful in automobile and truck engines, two-cycle engines, aviation piston engines, marine and railroad diesel engines.

[0013] US Patent Application 2006/079413 discloses lubricant formulations using tartaric compounds in a low sulfur, low ash and low phosphorus lubricant lowering wear and friction and improving fuel economy. The disclosure further describes the use of the lubricants in automobile and truck engines, two-cycle engines, aviation piston engines, marine and railroad diesel engines. Also disclosed are combination of tartaric compounds with additional friction modifiers are selected from the group consisting of glycerol monooleates, oleyl amides, diethanol fatty amines and mixtures thereof.

[0014] SAE Special Publication SP-1550, "Topics in Lubricants, pp 225-231, Sasak et al., 2000, discloses development of high performance heavy-duty diesel engine oil to extend oil drain intervals by providing a 5W-30 fully synthetic oil containing molybdenum dithiocarbamate.

[0015] It is believed that molybdenum compounds ae uniquely suitable as friction modifiers for lubricants for high temperature engines. However, it is desirable to formulate lubricants which avoid the use of molybdenum compounds for a variety of reasons including cost and minimizing the discharge of heavy metals into the environment, as high temperature engines such as marine diesel engines are normally designed to consume the lubricating oil and discharge its combustion products.

[0016] The disclosed technology, therefore, provides a method for improving the fuel economy of a high temperature engine such as a marine diesel engine by supplying a lubricant which does not include a molybdenum compound but yet provides good lubricant performance.

[0017] The lubricating compositions described therein are useful for an internal combustion engine, for example a diesel fueled engine, a gasoline fueled engine, a natural gas fueled engine or a mixed gasoline/alcohol fueled engine. In one embodiment the internal combustion engine is a 4-stroke and in another embodiment a 2-stroke engine. In one embodiment the engine has a

power output of at least 1600 kilowatts. In one embodiment the diesel fueled engine is a marine diesel engine. In certain marine diesel engines, a lubricant is prepared specifically for and is supplied to the cylinder wall, that is the cylinder liner, in order to lubricate the interface of the piston and the cylinder wall, rather than being supplied to or from a crankcase. Since marine diesel engines typically are operated at relatively high temperatures, the cylinder liner may commonly be at a temperature of 150°C or greater during operation, e.g, 175°C to 300°C. For such lubricating conditions, specially adapted lubricants are desirable.

SUMMARY OF THE INVENTION

[0018] The disclosed technology describes, in one embodiment, a lubricant composition suitable for use in lubricating an engine operating above 150°C at the cylinder liner, comprising an oil of lubricating viscosity and 0.01 to 5 percent by weight of an organic friction modifier, said lubricant composition being substantially free from molybdenum compounds.

[0019] The present invention is to the use of a glycerol ester as a friction modifier, the use comprising:

(a) supplying a lubricant composition to a cylinder liner of a marine diesel engine which is operating above 150°C at the cylinder liner;

(b) wherein the lubricant composition is not supplied to or from a crankcase; and

(c) wherein the lubricant composition comprises an oil of lubricating viscosity and 0.01 to 5 percent by weight of said glycerol ester, and is substantially free from molybdenum compounds and substantially free from zinc compounds;

wherein said glycerol ester reduces friction at the cylinder liner of the marine diesel engine.

DETAILED DESCRIPTION OF THE INVENTION

[0020] Various preferred features and embodiments will be described below by way of non-limiting illustration.

[0021] The lubricant described herein contains an oil of lubricating viscosity. The oil of lubricating viscosity may have a SAE grade of SAE 30, SAE 40, SAE 50, or SAE 60. In one embodiment the oil of lubricating viscosity may be a

SAE 50 oil. Typically a SAE 50 oil has a kinematic viscosity of 16.3 mm^2/s to 21.9 mm^2/s at 100°C.

[0022] The oil, also referred to as a base oil, 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. The five base oil groups are as follows:

Base Oil Category	Sulfur (%)		Saturates(%)	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, II, III or IV			

[0023] Groups I, II and III are mineral oil base stocks. The oil of lubricating viscosity, then, can include natural or synthetic lubricating oils and mixtures thereof. Mixture of mineral oil and synthetic oils, particularly polyalphaolefin oils and polyester oils, are often used.

[0024] Natural oils include 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. Hydrotreated or hydrocracked oils are included within the scope of useful oils of lubricating viscosity.

[0025] Oils of lubricating viscosity derived from coal or shale are also useful. Synthetic lubricating oils include hydrocarbon oils and halosubstituted hydrocarbon oils such as polymerized and interpolymerized olefins and mixtures thereof, alkylbenzenes, polyphenyl, (e.g., biphenyls, terphenyls, and alkylated polyphenyls), alkylated diphenyl ethers and alkylated diphenyl sulfides and their derivatives, analogs and homologues thereof. Alkylene oxide polymers and interpolymers and derivatives thereof, and those where terminal hydroxyl groups have been modified by, for example, esterification or etherification, constitute other classes of known synthetic lubricating oils that can be used. Another suitable class of synthetic lubricating oils that can be used comprises the esters of dicarboxylic acids and those made from C_5 to C_{12} monocarboxylic acids and polyols or polyol ethers.

[0026] Other synthetic lubricating oils include liquid esters of phosphorus-containing acids, polymeric tetrahydrofurans, silicon-based oils such as the poly-alkyl-, polyaryl-, polyalkoxy-, or polyaryloxy-siloxane oils, and silicate oils.

[0027] Hydrotreated naphthenic oils are also known and can be used, as well as oils prepared by a Fischer-Tropsch gas-to-liquid synthetic procedure, including hydroisomerized Fischer-Tropsch waxes or other waxes.

[0028] 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 used in the compositions described therein. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. 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. 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 often are additionally processed by techniques directed to removal of spent additives and oil breakdown products.

[0029] The lubricant compositions described herein will also contain a glycerol ester as a friction modifier.

[0030] Fatty acid esters of glycerol themselves can be prepared by a variety of methods well known in the art. Many of these esters, such as glycerol monooleate and glycerol monotallowate, are manufactured on a commercial scale. The esters useful are oil-soluble and may be prepared from C8 to C22 fatty acids or mixtures thereof such as are found in natural products and as are described in greater detail below. Fatty acid monoesters of glycerol are commonly used, although, mixtures of mono- and diesters may be used. For example, commercial glycerol monooleate is believed to include about 60 $\pm$ 5 percent by weight of the chemical species "glycerol monooleate," along with 35 $\pm$ 5 percent glycerol dioleate, and less than about 5 percent trioleate and oleic acid. The amounts of such materials, as described herein, are the amounts of the commercial grade material.

[0031] Fatty acids can be used in preparing the above glycerol esters; they can also be used in preparing their metal salts (such as Ca, Mg or Na salts, any of which may also be excluded if, for instance, an ashless additive is desired). Fatty acids include those containing 6 to 24 carbon atoms, such as 8 to 18. The acids can be branched or straight-chain, saturated or unsaturated. Suitable acids include 2-ethylhexanoic, decanoic, oleic, stearic, isostearic, palmitic, myristic, palmitoleic, linoleic, lauric, and linolenic acids, and the acids from the natural products tallow, palm oil, olive oil, peanut oil, corn oil, and Neat's foot oil. An example of a mixture of fatty acids is known as tall oil fatty acid. Fatty acids, such as C18 acids, may be supplied along with another component such as an

overbased detergent. Fatty acids may be used in the preparation of certain overbased detergents.

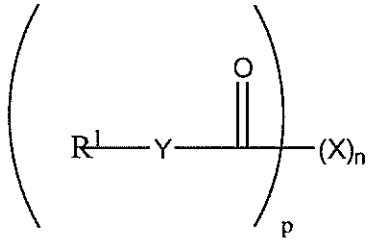
[0032] Friction modifiers which are suitable for the present invention include glycerol monooleate, which is representative of the glycerol esters described above.

[0033] Tartaric acid derivatives are representative, more generally, of compound derived from hydroxycarboxylic acid, which may generally function as an organic antiwear agent. Such an agent can be derived from at least one of a hydroxy-carboxylic acid di-ester, a hydroxy-carboxylic acid di-amide, a hydroxy-carboxylic acid di-imide, a hydroxy-carboxylic acid ester-amide, a hydroxy-carboxylic acid ester-imide, and a hydroxy-carboxylic acid imide-amide. In one embodiment the ashless antiwear agent is derived from at least one of the group consisting of a hydroxy-carboxylic acid di-ester, a hydroxy-carboxylic acid di-amide, and a hydroxy-carboxylic acid ester-amide.

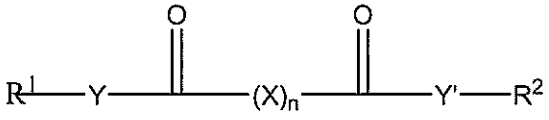
[0034] Examples of suitable a hydroxycarboxylic acids include citric acid, tartaric acid, malic acid (or hydroxy-succinic acid), lactic acid, glycolic acid, hydroxy-propionic acid, hydroxyglutaric acid, or mixtures thereof. In one embodiment ashless antiwear agent is derived from tartaric acid, citric acid, hydroxy-succinic acid, dihydroxy mono-acids, mono-hydroxy diacids, or mixtures thereof. In one embodiment the ashless antiwear agent includes a compound derived from tartaric acid. US Patent Application 2005/198894 discloses suitable hydroxycarboxylic acid compounds, and methods of preparing the same. Canadian Patent 1183125; US Patent Publication numbers 2006/0183647 and US-2006-0079413; US Patent Application number 60/867402; and British Patent 2 105 743 A, all disclose examples of suitable tartaric acid derivatives.

[0035] In one embodiment, di-esters, di-amides, ester-amide, or imide compounds are derived from a compound of Formula (1a) and/or (1b), below. A detailed description of methods for preparing suitable tartrimides (by reacting tartaric acid with a primary amine) is disclosed in US Patent 4,237,022. Examples of such tartrimides include those formed from condensation of tartaric acid with caproylamine, laurylamine, myristylamine, palmitylamine, stearylamine, myristoleylamine, palmitoleylamine, oleylamine, or linoleylamine or mixtures thereof. In one embodiment the ashless antiwear agent includes imides, di-esters, di-amides, and ester-amide derivatives of tartaric acid.

[0036] In one embodiment the ashless antiwear agent is represented by a compound of Formula (1a) and/or (1b):



Formula (1a)



Formula (1b)

wherein

n is 0 to 10, 0 to 6, 0 to 4, 1 to 4, or 1 to 2;

p is 1 to 5, or 1 to 2, or 1;

Y and Y' are independently -O-, >NH, >NR^3; or alternatively a different cyclic structure (1c) comprising an imide group formed by a R^1-N< group between the two >C=O groups;

X is independently -CH_2-, >CHR^4 or >CR^4R^5, >$CHOR^6$, or >$C(CO_2R^6)_2$;

R^1 and R^2 are independently hydrocarbyl groups, typically containing 1 to 150, 4 to 30, or 6 to 20, or 10 to 20, or 11 to 18 carbon atoms;

R^3 is a hydrocarbyl group;

R^4 and R^5 are independently keto- groups, ester groups or hydrocarbyl groups; and

R^6 is independently hydrogen or a hydrocarbyl group, typically containing 1 to 150, or 4 to 30 carbon atoms.

[0037] In one embodiment the compound of Formula (1b) contains an imide group, which may be formed by taking together the Y and Y' groups and forming a R^1-N< group between two >C=O groups. In one embodiment the compound of Formula (1a) and/or (1b) has n, X, and R^1, R^2 and R^6 defined as follows: n is 1 to 2, X is >$CHOR^6$; and R^1, R^2 and R^6 are independently hydrocarbyl groups containing 4 to 30 carbon atoms. In one embodiment Y and Y' are both -O-. In one embodiment the compound of Formula (1a) and/or (1b) has n, X, Y, Y' and R^1, R^2 and R^6 defined as follows: n is 1 to 2, X is >$CHOR^6$; Y and Y' are both -O-, and R^1, R^2 and R^6 are independently hydrocarbyl groups containing 4 to 30 carbon atoms.

[0038] The di-esters, di-amides, ester-amide, or imide compounds of Formula (1a) and/or (1b) and/or (1c) may be prepared by reacting a dicarboxylic acid

(such as tartaric acid), with an amine or alcohol, optionally in the presence of a known esterification catalyst. The amine or alcohol typically has sufficient carbon atoms to fulfill the requirements of R^1 and/or R^2 as defined in Formula (1a) and/or (1b).

[0039] In one embodiment R^1 and R^2 are independently linear or branched hydrocarbyl groups. In one embodiment the hydrocarbyl groups are branched. In one embodiment the hydrocarbyl groups are linear. The R^1 and R^2 may be incorporated into Formula (1a) and/or (1b) by either an amine or an alcohol. The alcohol includes both monohydric alcohol and polyhydric alcohol. Examples of a suitable branched alcohol include 2-ethylhexanol, isotridecanol, Guerbet alcohols, or mixtures thereof. Examples of monohydric alcohols include methanol, ethanol, propanol, butanol, pentanol, hexanol, heptanol, octanol, nonanol, decanol, undecanol, dodecanol, tridecanol, tetradecanol, pentadecanol, hexadecanol, heptadecanol, octadecanol, nonadecanol, eicosanol, or mixtures thereof. In one embodiment the monohydric alcohol contains 5 to 20 carbon atoms. The alcohol includes either a monohydric alcohol or a polyhydric alcohol. Examples of suitable polyhydric alcohols include ethylene glycol, propylene glycol, 1,3-butanediol, 2,3-butanediol, 1,5-pentane diol, 1,6-hexane diol, glycerol, sorbitol, pentaerythritol, trimethylolpropane, starch, glucose, sucrose, methylglucoside, or mixtures thereof. In one embodiment the polyhydric alcohol is used in a mixture along with a monohydric alcohol. Typically, in such a combination the monohydric alcohol constitutes at least 60 mole percent, or at least 90 mole percent of the mixture.

[0040] Examples of esters include those prepared from condensation of tartaric acid with, e.g., long chain monohydric alcohols. These include a single alcohol, linear or branched, as well as mixtures of alcohols of various types. Examples of linear alcohols include those of 8-20 carbon atoms, such as 8-10, 8-12, 12-14, 12-16, and 14-18 carbon linear alcohols. Examples of branched alcohols include those of 8-20 carbon atoms such as 8 carbon atoms (e.g., 2-ethylhexanol) or 12-14 or 13 or 16 or 18 or 14-18 carbon branched alcohols. Thus esters may be derived from a mixture of all linear alcohols or all branched alcohols, or mixtures of linear and branched alcohols, e.g., mixtures of linear C8-14 alcohols with branched C8 alcohols, or linear C12-14 alcohols with branched C13 alcohols or linear C14-18 alcohols with branched C18 alcohols, as well as mixtures of C18 with C12 linear alcohols and mixtures of C13 with C8 branched alcohols, and other such combinations. The relative weight ratios of linear to branched alcohols or the ratios of one linear alcohol to another linear

alcohol or one branched alcohol to another branched alcohol in any such combinations is not particularly restricted but may be, in some embodiments, 10~95:90~5 or 50~90:50~10, e.g., about 95:5 or 90:10 or 80:20 or 70:30 or 50:50 or 30:70.

[0041] In one embodiment the organic antiwear agent is derived from tartaric acid. The tartaric acid used for preparing the tartrates can be commercially available (for instance obtained from Sargent Welch), and it is likely to exist in one or more isomeric forms such as *d*-tartaric acid, *l*-tartaric acid, *d,l*-tartaric acid (racemic) or mesotartaric acid, often depending on the source (natural) or method of synthesis (e.g. from maleic acid). These derivatives can also be prepared from functional equivalents to the diacid readily apparent to those skilled in the art, such as esters, acid chlorides, or anhydrides.

[0042] When the compound of Formula (1a) and/or (1b) is derived from tartaric acid, resultant tartrates may be solid, semi-solid, or oil depending on the particular alcohol used in preparing the tartrate. For use as additives in oleaginous compositions including lubricating and fuel compositions the tartrates are advantageously soluble and/or stably dispersible in such oleaginous compositions. For example, compositions intended for use in oils are typically oil-soluble and/or stably dispersible in an oil in which they are to be used. The term "oil-soluble" as used in this specification and appended claims does not necessarily mean that all the compositions in question are miscible or soluble in all proportions in all oils. Rather, it is intended to mean that the composition is soluble in an oil (mineral, synthetic, etc.) in which it is intended to function to an extent which permits the solution to exhibit one or more of the desired properties. Similarly, it is not necessary that such "solutions" be true solutions in the strict physical or chemical sense. They may instead be micro-emulsions or colloidal dispersions which exhibit properties sufficiently close to those of true solutions to be, for practical purposes, interchangeable with them within the context of this invention.

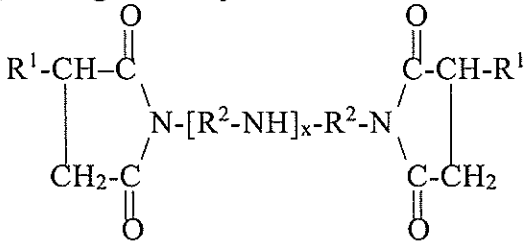
[0043] The amount of friction modifier present in the lubricants described herein may be 0.01 to 5 percent by weight, or 0.01 to 2% or 0.02 to 1.2% or 0.03 to 1%.

[0044] The compositions are substantially free or free from molybdenum compounds. Molybdenum compounds have been used as antioxidants, friction modifiers, and in various other functions, such as antiwear agents, in lubricant compositions. U.S. Pat. No. 4,285,822, for instance, discloses lubricating oil compositions containing a molybdenum and sulfur containing composition

prepared by (1) combining a polar solvent, an acidic molybdenum compound and an oil-soluble basic nitrogen compound to form a molybdenum-containing complex and (2) contacting the complex with carbon disulfide to form the molybdenum and sulfur containing composition. The present lubricant formulations contain little or no molybdenum, for instance, less than 500, or less than 300 or less than 150 or less than 100 or less than 50 or less than 20 or less than 10 or less than 5 or less than 1 parts per million Mo by weight, or alternatively in amount of 0.1 to 50 parts per million or 1 to 5 parts per million. Alternatively expressed, the amount of molybdenum in the present lubricants may be less than an amount effective to provide significant antifriction activity.

[0045] The compositions are also free or substantially free from zinc compounds. Zinc compounds, such as zinc phosphates, zinc thiophosphates (in particular, zinc dialkyl diithiophosphates) and other zinc compounds such as zinc oleates are often used in lubricants as antiwear or antioxidant agents. The lubricants may perform well even in the absence of these zinc compounds. Thus, the amount of zinc in the composition may be 0 to 1000 or 0 to 100, or 1 to 20, or less than 20, or less than 10, or less than 5 parts per million by weight.

[0046] The compositions as described herein may also contain a dispersant. Dispersants are well known in the field of lubricants and include primarily what is known as ashless dispersants and polymeric dispersants. Ashless dispersants are so-called because, as supplied, they do not contain metal and thus do not normally contribute to sulfated ash when added to a lubricant. However they may, of course, interact with ambient metals once they are added to a lubricant which includes metal-containing species. Ashless dispersants are characterized by a polar group attached to a relatively high molecular weight hydrocarbon chain. Typical ashless dispersants include N-substituted long chain alkenyl succinimides, having a variety of chemical structures including typically

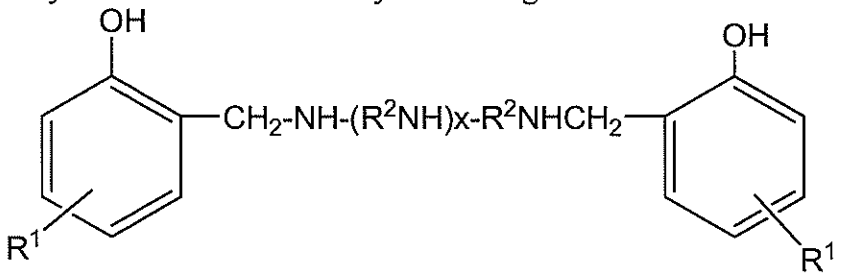


where each R^1 is independently an alkyl group, frequently a polyisobutylene group with a molecular weight of 500-5000, and R^2 are alkylene groups, commonly ethylene (C_2H_4) groups. Such molecules are commonly derived from reaction of an alkenyl acylating agent with a polyamine, and a wide variety of linkages between the two moieties is possible beside the simple imide structure

shown above, including a variety of amides and quaternary ammonium salts. Also, a variety of modes of linkage of the R^1 groups onto the imide structure are possible, including various cyclic linkages. The ratio of the carbonyl groups of the acylating agent to the nitrogen atoms of the amine may be 1:0.5 to 1:3, and in other instances 1:1 to 1:2.75 or 1:1.5 to 1:2.5. Succinimide dispersants are more fully described in U.S. Patents 4,234,435 and 3,172,892.

[0047] Another class of ashless dispersant is high molecular weight esters. These materials are similar to the above-described succinimides except that they may be seen as having been prepared by reaction of a hydrocarbyl acylating agent and a polyhydric aliphatic alcohol such as glycerol, pentaerythritol, or sorbitol. Such materials are described in more detail in U.S. Patent 3,381,022.

[0048] Another class of ashless dispersant is Mannich disspersants. These are materials which are formed by the condensation of a higher molecular weight, alkyl substituted phenol, an alkylene polyamine, and an aldehyde such as formaldehyde. Such materials may have the general structure



(including a variety of isomers and the like) and are described in more detail in U.S. Patent 3,634,515.

[0049] Other dispersants include polymeric dispersant additives, which are generally hydrocarbon-based polymers which contain polar functionality to impart dispersancy characteristics to the polymer.

[0050] Dispersants can also be post-treated by reaction with any of a variety of agents. Among these are urea, thiourea, dimercaptothiadiazoles, carbon disulfide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, nitriles, epoxides, boron compounds, and phosphorus compounds. References detailing such treatment are listed in U.S. Patent 4,654,403. Borated dispersants have been found to be useful in the present lubricants. Typically, the borated dispersant will contain 0.1% to 5%, or 0.5% to 4%, or 0.7% to 3% by weight boron. In one embodiment, the borated dispersant is a borated acylated amine, such as a borated succinimide dispersant. Borated dispersant are prepared by reaction of one or more dispersant with one or more boron compounds

and are described in U.S. Pat. Nos. 3,000,916; 3,087,936; 3,254,025; 3,282,955; 3,313,727; 3,491,025; 3,533,945; 3,666,662 and 4,925,983.

[0051] The amount of dispersant or borated dispersant (or the combination of the two), if present in the present compositions, may be 0.1 or 0.2 to 5 weight percent, or 0.4 to 4 weight percent, or 0.5 to 3 weight percent, or 0.5 to 1.8 weight percent.

[0052] The present lubricant formulations may also contain one or more overbased detergents. Overbased materials, otherwise referred to as overbased or superbased salts, are generally homogeneous Newtonian systems characterized by a metal content in excess of that which would be present for neutralization according to the stoichiometry of the metal and the particular acidic organic compound reacted with the metal. The overbased materials are prepared by reacting an acidic material (typically an inorganic acid or lower carboxylic acid, such as carbon dioxide) with a mixture comprising an acidic organic compound, a reaction medium comprising at least one inert, organic solvent (e.g., mineral oil, naphtha, toluene, xylene) for said acidic organic material, a stoichiometric excess of a metal base, and a promoter such as a phenol or alcohol and optionally ammonia. The acidic organic material will normally have a sufficient number of carbon atoms, for instance, as a hydrocarbyl substituent, to provide a reasonable degree of solubility in oil. The amount of excess metal is commonly expressed in terms of metal ratio. The term "metal ratio" is the ratio of the total equivalents of the metal to the equivalents of the acidic organic compound. A neutral metal salt has a metal ratio of one. A salt having 4.5 times as much metal as present in a normal salt will have metal excess of 3.5 equivalents, or a ratio of 4.5.

[0053] Overbased detergents are often characterized by Total Base Number (TBN). TBN is the amount of strong acid (perchloric or hydrochloric) needed to neutralize all of the overbased material's basicity, expressed as potassium hydroxide equivalents (mg KOH per gram of sample). Since overbased detergents are commonly provided in a form which contains a certain amount of diluent oil, for example, 40-50% oil, the actual TBN value for such a detergent will depend on the amount of such diluent oil present, irrespective of the "inherent" basicity of the overbased material. The TBN of an overbased detergent is to be recalculated to an oil-free basis. Thus, for instance, a detergent composition having an uncorrected TBN of 300 and 40% oil content could have a TBN (oil-free basis) of 500. Detergents which are useful typically have a TBN (oil-free basis) of 100 to 800, and in one embodiment 150 to 750, and in another,

400 to 700. If multiple detergents are employed, the overall TBN of the detergent component (that is, an average of all the specific detergents together) will typically be in the above ranges.

[0054] The overall TBN of the composition, including oil, will be derived from the TBN contribution of the individual components, such as the dispersant, the detergent, and other basic materials. The overall TBN for lubricants used as marine diesel cylinder lubricants will typically be greater than 30, e.g., 31 to 100 or 35 to80 or 40 to 70. Other lubricants may have an overall TBN of at least 7 or at least 10, or sometimes even at least 20. The majority of the TBN is typically contributed by the overbased detergent component.

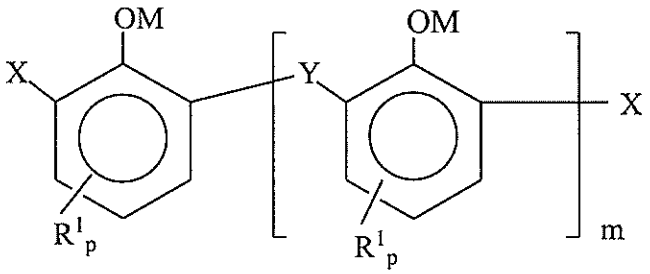
[0055] The metal compounds useful in making the basic metal salts are generally any Group 1 or Group 2 metal compounds (CAS version of the Periodic Table of the Elements). The Group 1 metals of the metal compound include Group 1a alkali metals such as sodium, potassium, and lithium, as well as Group 1b metals such as copper. The Group 2 metals of the metal base include the Group 2a alkaline earth metals such as magnesium, calcium, and barium, as well as the Group 2b metals such as zinc or cadmium.

[0056] Such overbased materials are well known to those skilled in the art. Patents describing techniques for making basic salts of sulfonic acids, carboxylic acids, (hydrocarbyl-substituted) phenols, phosphonic acids, and mixtures of any two or more of these include U.S. Patents 2,501,731; 2,616,905; 2,616,911; 2,616,925; 2,777,874; 3,256,186; 3,384,585; 3,365,396; 3,320,162; 3,318,809; 3,488,284; and 3,629,109.

[0057] In one embodiment the lubricants can contain an overbased sulfonate detergent. Suitable sulfonic acids include sulfonic and thiosulfonic acids. Sulfonic acids include the mono- or polynuclear aromatic or cycloaliphatic sulfonic acid compounds. Oil-soluble sulfonates may be represented by one of the following formulas: R^2-T-$(SO_3\text{-})_a$ and R^3-$(SO_3\text{-})_b$, where T is a cyclic nucleus such as typically benzene; R^2 is an aliphatic group such as alkyl, alkenyl, alkoxy, or alkoxyalkyl; (R^2)-T typically contains a total of at least 15 carbon atoms; and R^3 is an aliphatic hydrocarbyl group typically containing at least 15 carbon atoms. Examples of R^3 are alkyl, alkenyl, alkoxyalkyl, and carboalkoxyalkyl groups. The R groups may be linear or branched or mixtures of linear and branched groups. The groups T, R^2, and R^3 may also contain other inorganic or organic substituents such as hydroxy, mercapto, halogen, nitro, amino, nitroso, sulfide, or disulfide. In the above formulas, a and b are at least 1.

[0058] Another overbased material which can be present is an overbased phenate detergent. The phenols useful in making phenate detergents can be represented by the formula $(R_1)_a$-Ar-$(OH)_b$, wherein R_1 is an aliphatic hydrocarbyl group of 4 to 400 carbon atoms, or 6 to 80 or 6 to 30 or 8 to 25 or 8 to 15 carbon atoms; Ar is an aromatic group (which can be a benzene group or another aromatic group such as naphthalene); a and b are independently numbers of at least one, the sum of a and b being up to the number of displaceable hydrogens on the aromatic nucleus or nuclei of Ar. In one embodiment, a and b are independently to 4, or 1 to 2. R_1 and a are typically such that there is an average of at least 8 aliphatic carbon atoms provided by the R_1 groups for each phenol compound. Phenate detergents are also sometimes provided as sulfur-bridged species.

[0059] In one embodiment, the overbased material is an overbased detergent selected from the group consisting of overbased salixarate detergents, overbased saligenin detergents, overbased salicylate detergents, and overbased glyoxylate detergents, and mixtures thereof. Overbased saligenin detergents are commonly overbased magnesium salts which are based on saligenin derivatives. A general example of such a saligenin derivative can be represented by the formula

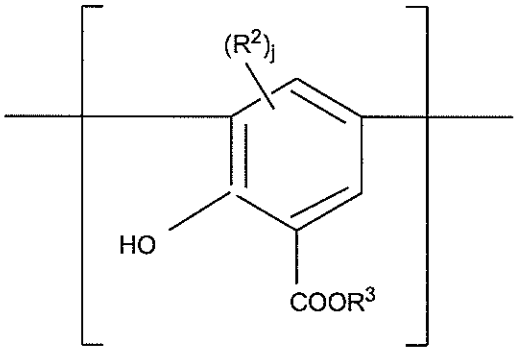


wherein X comprises -CHO or $-CH_2OH$, Y comprises $-CH_2-$ or $-CH_2OCH_2-$, and wherein such -CHO groups typically comprise at least 10 mole percent of the X and Y groups; M is hydrogen, ammonium, or a valence of a metal ion, R^1 is a hydrocarbyl group containing 1 to 60 carbon atoms, m is 0 to typically 10, and each p is independently 0, 1, 2, or 3, provided that at least one aromatic ring contains an R^1 substituent and that the total number of carbon atoms in all R^1 groups is at least 7. When m is 1 or greater, one of the X groups can be hydrogen. In one embodiment, M is a valence of a Mg ion or a mixture of Mg and hydrogen. Other metals include alkali metals such as lithium, sodium, or potassium; alkaline earth metals such as calcium or barium; and other metals such as copper, zinc, and tin. Saligenin detergents are disclosed in greater detail in U.S. Patent 6,310,009, with special reference to their methods of synthesis

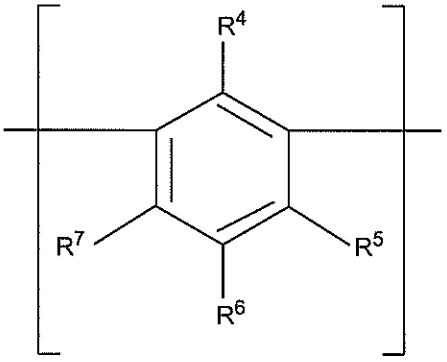
(Column 8 and Example 1) and preferred amounts of the various species of X and Y (Column 6).

[0060] As used herein, the expression "represented by the formula" indicates that the formula presented is generally representative of the structure of the chemical in question. However, it is well known that minor variations can occur, including in particular positional isomerization, that is, location of the X, Y, and R groups at different position on the aromatic ring from those shown in the structure. The expression "represented by the formula" is expressly intended to encompass such variations.

[0061] Salixarate detergents are overbased materials that can be represented by a substantially linear compound comprising at least one unit of formula (I) or formula (II):

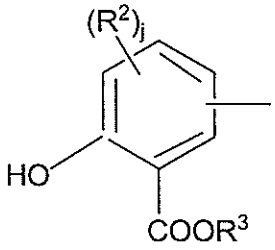


(I)

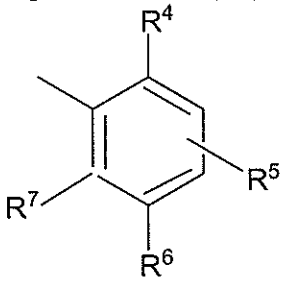


(II)

each end of the compound having a terminal group of formula (III) or (IV):



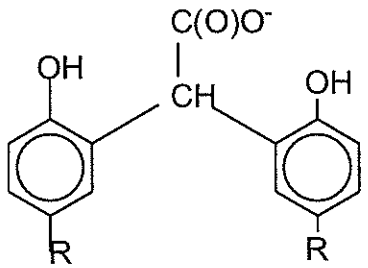
(III)



(IV)

such groups being linked by divalent bridging groups A, which may be the same or different for each linkage; wherein in formulas (I)-(IV) R^3 is hydrogen or a hydrocarbyl group; R^2 is hydroxyl or a hydrocarbyl group and j is 0, 1, or 2; R^6 is hydrogen, a hydrocarbyl group, or a hetero-substituted hydrocarbyl group; either R^4 is hydroxyl and R^5 and R^7 are independently either hydrogen, a hydrocarbyl group, or hetero-substituted hydrocarbyl group, or else R^5 and R^7 are both hydroxyl and R^4 is hydrogen, a hydrocarbyl group, or a hetero-substituted hydrocarbyl group; provided that at least one of R^4, R^5, R^6 and R^7 is hydrocarbyl containing at least 8 carbon atoms; and wherein the molecules on average contain at least one of unit (I) or (III) and at least one of unit (II) or (IV) and the ratio of the total number of units (I) and (III) to the total number of units of (II) and (IV) in the composition is about 0.1:1 to about 2:1. The divalent bridging group "A," which may be the same or different in each occurrence, includes -CH_2- (methylene bridge) and -CH_2OCH_2- (ether bridge), either of which may be derived from formaldehyde or a formaldehyde equivalent (e.g., paraform, formalin). Salixarate derivatives and methods of their preparation are described in greater detail in U.S. patent number 6,200,936 and PCT Publication WO 01/56968. It is believed that the salixarate derivatives have a predominantly linear, rather than macrocyclic, structure, although both structures are intended to be encompassed by the term "salixarate."

[0062] Glyoxylate detergents are similar overbased materials which are based on an anionic group which, in one embodiment, may have the structure



wherein each R is independently an alkyl group containing at least 4, and preferably at least 8 carbon atoms, provided that the total number of carbon atoms in all such R groups is at least 12, preferably at least 16 or 24. Alternatively, each R can be an olefin polymer substituent. The acidic material upon from which the overbased glyoxylate detergent is prepared is the condensation product of a hydroxyaromatic material such as a hydrocarbyl-substituted phenol with a carboxylic reactant such as glyoxylic acid and other omega-oxoalkanoic acids. Overbased glyoxylic detergents and their methods of preparation are disclosed in greater detail in U.S. Patent 6,310,011 and references cited therein.

[0063] The overbased detergent can also be an overbased salicylate. The alkylsalicylate can be an alkali metal salt or an alkaline earth metal salt of an alkylsalicylic acid which can in turn be prepared from an alkylphenol by Kolbe-Schmitt reaction. The alkylphenol can be prepared by a reaction of α-olefin having, e.g., 8 to 30 carbon atoms (mean number) with phenol. Alternatively, calcium salicylate can be produced by direct neutralization of alkylphenol and subsequent carbonation. The salicylic acids may thus be hydrocarbyl-substituted salicylic acids, such as aliphatic hydrocarbon-substituted salicylic acids wherein each substituent contains an average of at least 8 carbon atoms per substituent and 1 to 3 substituents per molecule. The substituents can be polyalkene substituents, where polyalkenes include homopolymers and inter-polymers of polymerizable olefin monomers of 2 to 16, or 2 to 6, or 2 to 4 carbon atoms. The olefins may be monoolefins such as ethylene, propylene, 1-butene, isobutene, and 1-octene; or a polyolefinic monomer, such as diolefinic monomer, such 1,3-butadiene and isoprene. In one embodiment, the hydro-carbyl substituent group or groups on the salicylic acid contains 7 to 300 carbon atoms and can be an alkyl group having a molecular weight of 150 to 2000. The polyalkenes and polyalkyl groups are prepared by conventional procedures, and substitution of such groups onto salicylic acid can be effected by known meth-ods. Overbased salicylate detergents and their methods of preparation are disclosed in U.S. Patents 4,719,023 and 3,372,116.

[0064] The detergent component may also be a mixture of detergents or so-called "hybrid detergents," also referred to as complex detergents or mixed substrate detergents. In one embodiment the hybrid may be an overbased phenate-salicylate detergent. Methods of preparing overbased phenate-salicylate detergents are disclosed in EP 123 6791 A1 and EP 123 6792 A1. In one embodiment the hybrid may be prepared by reacting, in the presence of a suspension and acidifying overbasing agent, an alkyl aromatic sulfonic acid and at least one alkyl phenol (such as alkyl phenol, aldehyde-coupled alkyl phenol, sulfurized alkyl phenol) and optionally alkyl salicylic acid. Preparation of such materials is also disclosed in WO97046643

[0065] The present lubricants may thus contain up to 20 percent by weight, (or 0.1 to 19 or 0.5 to 18 or 1 to17 or 0.1 to 10 or 0.5 to 7 or 1 to 5 percent by weight) of an overbased calcium alkylphenol sulfide detergent (of any of a number of degrees of overbasing, high or low TBN) or up to 20 percent by weight (or 0.1 to 17.5 or 0.1 to 17 or 0.5 to 15 or 1 to 17 or 0.5 to 15 or 2 to 12 or 6 to 10 percent by weight) of a relatively highly overbased linear alkyl

sulfonate detergent, that is, having an oil-free TBN of 400-900, or mixtures of such materials. The total amount of the overbased detergents, in the formulations, is typically at least 0.6 weight percent on an oil-free basis. In other embodiments, it can be present in amounts of 0.7 to 20 weight percent or 1 to 18 weight percent or 3 to 13 weight percent. In one embodiment the detergent component consists of a salicylate detergent (and no sulfonate). In another embodiment the detergent component consists of a sulfonate detergent (and no phenate).

[0066] The lubricants described herein may also contain one or more additional materials that are commonly used in formulating lubricants, especially marine diesel cylinder lubricants. Typically the other performance additives include metal deactivators, antioxidants, antiwear agents, corrosion inhibitors, antiscuffing agents, extreme pressure agents, foam inhibitors, demulsifiers, viscosity modifiers, pour point depressants and mixtures thereof. Typically, fully-formulated lubricating oil will contain one or more of these performance additives.

[0067] Antioxidant compounds are known and include for example, sulfurized olefins, alkylated diphenylamines (typically di-nonyl diphenylamine, octyl diphenylamine, di-octyl diphenylamine), hindered phenols, and mixtures thereof. Molybdenum compounds are also sometimes used as antioxidants, but, as stated above, Mo compounds are typically not included in the present compositions.

[0068] The hindered phenol antioxidant often contains a secondary butyl and/or a tertiary butyl group as a sterically hindering group. The phenol group is often further substituted with a hydrocarbyl group and/or a bridging group linking to a second aromatic group. Examples of suitable hindered phenol antioxidants include 2,6-di-tert-butylphenol, 4-methyl-2,6-di-tert-butylphenol, 4-ethyl-2,6-di-tert-butylphenol, 4-propyl-2,6-di-tert-butylphenol or 4-butyl-2,6-di-tert-butylphenol, or 4-dodecyl-2,6-di-tert-butylphenol. In one embodiment the hindered phenol antioxidant is an ester and may include, e.g., Irganox™ L-135 from Ciba. A more detailed description of suitable ester-containing hindered phenol antioxidant chemistry is found in US Patent 6,559,105.

[0069] Viscosity modifiers include hydrogenated copolymers of styrene and butadiene, ethylene-propylene copolymers, polyisobutenes, hydrogenated styrene-isoprene polymers, hydrogenated isoprene polymers, polymethacrylates, polyacrylates, polyalkyl styrenes, hydrogenated alkenyl aryl conjugated diene copolymers, polyolefins, esters of maleic anhydride olefin copolymers, and esters of maleic anhydride-styrene copolymers.

[0070] Examples of antiwear agents include boron-containing compounds such as borate esters or borated alcohols, phosphate esters, sulfurized olefins, sulfur-containing ashless anti-wear additives, metal dihydrocarbyldithiophosphates (such as zinc dialkyldithiophosphates, which, as mentioned above, may also be absent from the present formulations), thiocarbamate-containing compounds, such as thiocarbamate esters, alkylene-coupled thiocarbamates, and bis-(S-alkyldithiocarbamyl) disulfides. The antiwear agent may be present in ranges including 0 wt % to 15 wt %, or 0.1 wt % to 10 wt % or 1 wt % to 8 wt % of the lubricating composition.

[0071] The borate esters or borate alcohols may be substantially the same except the borate alcohol has at least one hydroxyl group that is not esterified. Therefore, as used herein the term "borate ester" is used to refer to either borate ester or borate alcohol. The borate esters or borate alcohols may have a formula $B(OR')_3$ or be a derivative thereof containing a >B-O-B< group, wherein R' may be hydrogen or a hydrocarbyl group, typically containing 1 to 40, or 1 to 20 carbon atoms on each R'. When R' is hydrogen, the boron-containing compound is a borate alcohol. When R' is hydrocarbyl, the boron-containing compound is a borate ester. The borate ester may be prepared by the reaction of a boron compound, such as boric acid, boron oxides, or boron halides, and at least one compound selected from epoxy compounds, halohydrin compounds, epihalohydrin compounds, alcohols and mixtures thereof. The alcohols include dihydric alcohols, trihydric alcohols or higher alcohols, with the proviso for one embodiment that hydroxyl groups are on adjacent, i.e., vicinal, carbon atoms. .

[0072] Dithiocarbamate-containing compounds may be prepared by reacting a dithiocarbamate acid or salt with an unsaturated compound. The dithiocarbamate containing compounds may also be prepared by simultaneously reacting an amine, carbon disulfide and an unsaturated compound. Generally, the reaction occurs at a temperature of 25 °C to 125 °C. US Patents 4,758,362 and 4,997,969 describe dithiocarbamate compounds and methods of making them.

[0073] Examples of suitable olefins that may be sulfurized to form sulfurized olefins include propylene, butylene, isobutylene, pentene, hexane, heptene, octane, nonene, decene, undecene, dodecene, undecyl, tridecene, tetradecene, pentadecene, hexadecene, heptadecene, octadecene, octadecenene, nonodecene, eicosene or mixtures thereof. In one embodiment, hexadecene, heptadecene, octadecene, octadecenene, nonodecene, eicosene or mixtures thereof and their dimers, trimers and tetramers are especially useful olefins. Alternatively, the olefin may be a Diels-Alder adduct of a diene such as 1,3-butadiene and an

unsaturated ester, such as, butylacrylate. Another class of sulfurized olefin includes fatty acids and their esters and mixtures with α-olefins. The fatty acids are often obtained from vegetable oil or animal oil and typically contain 4 to 22 carbon atoms.

[0074] Extreme Pressure (EP) agents include sulfur- and chlorosulfur-containing EP agents, chlorinated hydrocarbon EP agents and phosphorus EP agents. Examples of such EP agents include chlorinated wax; organic sulfides and polysulfides such as dibenzyldisulfide, bis–(chlorobenzyl) disulfide, dibutyl tetrasulfide, sulfurized methyl ester of oleic acid, sulfurized alkylphenol, sulfurized dipentene, sulfurized terpene, and sulfurized Diels-Alder adducts; phosphosulfurized hydrocarbons such as the reaction product of phosphorus sulfide with turpentine or methyl oleate; phosphorus esters such as the dihydrocarbon and trihydrocarbon phosphites, e.g., dibutyl phosphite, diheptyl phosphite, dicyclohexyl phosphite, pentylphenyl phosphite; dipentylphenyl phosphite, tridecyl phosphite, distearyl phosphite and polypropylene substituted phenol phosphite; metal thiocarbamates such as zinc dioctyldithiocarbamate and barium heptylphenol diacid; amine salts of alkyl and dialkylphosphoric acids, including, for example, the amine salt of the reaction product of a dialkyldithiophosphoric acid with propylene oxide; and mixtures thereof.

[0075] Other performance additives such as corrosion inhibitors include those described in paragraphs 5 to 8 of US Application 2005-038319 , octylamine octanoate, condensation products of dodecenyl succinic acid or anhydride and a fatty acid such as oleic acid with a polyamine. In one embodiment the corrosion inhibitors include the Synalox® corrosion inhibitor. The Synalox® corrosion inhibitor is typically a homopolymer or copolymer of propylene oxide. The Synalox® corrosion inhibitor is described in more detail in a product brochure with Form No. 118-01453-0702 AMS, published by The Dow Chemical Company. The product brochure is entitled "SYNALOX Lubricants, High-Performance Polyglycols for Demanding Applications."

[0076] Metal deactivators include derivatives of benzotriazoles (typically tolyltriazole), dimercaptothiadiazole derivatives, 1,2,4-triazoles, benzimidazoles, 2-alkyldithiobenzimidazoles, or 2-alkyldithiobenzothiazoles. Foam inhibitors include copolymers of ethyl acrylate and 2-ethylhexylacrylate and optionally vinyl acetate. Demulsifiers include trialkyl phosphates, polyethylene glycols, polyethylene oxides, polypropylene oxides and (ethylene oxide-propylene oxide) polymers. Pour point depressants include esters of maleic anhydride-styrene, polymethacrylates, polyacrylates or polyacrylamides.

[0077] The presently described lubricants may also contain titanium-containing additives such as titanium alkoxides or titanium-modified dispersants, as described in greater detail in, e.g., U.S. Application 2006-0217271.

[0078] As used herein, the term "hydrocarbyl substituent" or "hydrocarbyl group" is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group having a carbon atom directly attached to the remainder of the molecule and having predominantly hydrocarbon character. Examples of hydrocarbyl groups include:

hydrocarbon substituents, 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 a ring);

substituted hydrocarbon substituents, that is, substituents containing non-hydrocarbon groups which do not alter the predominantly hydrocarbon nature of the substituent (e.g., halo (especially chloro and fluoro), hydroxy, alkoxy, mercapto, alkylmercapto, nitro, nitroso, and sulfoxy);

hetero substituents, that is, substituents which, while having a predominantly hydrocarbon character contain atoms other than carbon in a ring or chain otherwise composed of carbon atoms. Heteroatoms include sulfur, oxygen, nitrogen, and encompass substituents as pyridyl, furyl, thienyl and imidazolyl. In general, no more than two, or 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.

[0079] It is known that some of the materials described above may interact in the final formulation, so that the components of the final formulation may be different from those that are initially added. For instance, metal ions (of, e.g., a detergent) can migrate to other acidic or anionic sites of other molecules. The products formed thereby, including the products formed upon employing the composition described in its intended use, may not be susceptible of easy description.

EXAMPLES

[0080] A "good" baseline lubricant formulation is prepared characteristic of a marine diesel cylinder lubricant. The lubricant contains, in an API Group I mineral oil:

12.5% of a mixture of overbased calcium benzenesulfonate and phenate detergents, imparting a total of about 69 TBN to the lubricant; and

0.67 weight percent of a borated succinimide dispersant.

It is noted that some commercial components may contain small amounts of other components such as stearic acid or dispersants, to aid in their manufacture.

[0081] The above lubricant is evaluated, in the absence and presence of various organic friction modifiers for coefficient of friction as a function of temperature. Evaluation was performed on a Cameron Plint™ test rig with a pin-on-plate geometry. Each lubricant is partially neutralized with sulfuric acid (3.5% acid) prior to testing. The lubricants are subjected to a 100N load, while the temperature is raised from ambient to 300 °C. The friction coefficient, contact potential and specimen temperature are recorded every 10 seconds during a 2.5 hour test. Coefficients of friction for lubricants containing the various additives are reported in Table 1 as an average over various temperature ranges.

Table 1 – Coefficients of Friction

Ex.	Additive, %	50 - 100°C	100 - 150°C	150 - 200°C	200 - 250°C	250 - 300°C
1*	None: "good baseline"	0.095	0.089	0.076	0.064	0.054
2*	– comparative "poor baseline"	0.101	0.100	0.092	0.085	0.083
3*	Molybdenum dithiocarbamate, 0.5%	0.095	0.087	0.071	0.058	0.048
4	Glycerol monooleate, 0.5%	0.098	0.082	0.064	0.051	0.045

* A comparative or reference example

[0082] The results show that the glycerol monooleate friction modifier provides significantly reduced friction to the lubricant formulation, especially at high temperatures of 150°C and above. At high temperatures, the glycerol monooleate friction modifier shows performance equal to or better than that provided by molybdenum dithiocarbamate, a known metal-containing additive.

[0083] Example 5. The formulation of Example 4, containing glycerol monooleate, is repeated, except that the borated succinimide dispersant is replaced by an equal amount of a corresponding non-borated succinimide dispersant. The same friction test described above is performed, with the results shown below:

Ex.	Additives	50 - 100°C	100 - 150°C	150 - 200°C	200 - 250°C	250 - 300°C
4	GMO with borated dispersant	0.098	0.082	0.064	0.051	0.045
5	GMO with non-borated disp't.	0.100	0.084	0.065	0.054	0.050

[0084] The results show that the use of a borated dispersant can provide improved high temperature frictional performance in the subject lubricants, compared with the use of a non-borated dispersant.

[0085] Each of the documents referred to above is incorporated herein by reference. The mention of any document is not an admission that such document qualifies as prior art or constitutes the general knowledge of the skilled person in any jurisdiction. Except in the Examples, or where otherwise explicitly indicated, all numerical quantities in this description specifying amounts of materials, reaction conditions, molecular weights, number of carbon atoms, and the like, are to be understood as modified by the word "about." Unless otherwise indicated, each chemical or composition referred to herein should be interpreted as being a commercial grade material which may contain the isomers, by-products, derivatives, and other such materials which are normally understood to be present in the commercial grade. However, the amount of each chemical component is presented exclusive of any solvent or diluent oil, which may be customarily present in the commercial material, unless otherwise indicated. It is to be understood that the upper and lower amount, range, and ratio limits set forth herein may be independently combined. Similarly, the ranges and amounts for each element of the invention can be used together with ranges or amounts for any of the other elements. As used herein, the expression "consisting essentially of" permits the inclusion of substances that do not materially affect the basic and novel characteristics of the composition under consideration.

Claims:

1. Use of a glycerol ester as a friction modifier, the use comprising:

(a) supplying a lubricant composition to a cylinder liner of a marine diesel engine which is operating above 150°C at the cylinder liner;

(b) wherein the lubricant composition is not supplied to or from a crankcase; and

(c) wherein the lubricant composition comprises an oil of lubricating viscosity and 0.01 to 5 percent by weight of said glycerol ester, and is substantially free from molybdenum compounds and substantially free from zinc compounds;

wherein said glycerol ester reduces friction at the cylinder liner of the marine diesel engine.

2. The use of claim 1 wherein the glycerol ester comprises glycerol monooleate.

3. The use of claim 1 or claim 2, wherein said lubricant further comprises 0.1 to 5 percent by weight of a borated dispersant.

4. The use of any one of claims 1 to 3, wherein said lubricant further comprises 0.1 to 17 percent by weight of an overbased calcium alkylphenol sulfide detergent.

5. The use of any one of claims 1 to 4, wherein said lubricant further comprises 0.5 to 15 percent by weight of an overbased linear alkyl sulfonate detergent having a total base number (TBN) of 400-900.

6. The use of any one of claims 1 to 5, wherein the total base number (TBN) of the lubricant is at least 35.

7. The use of any one of claims 1 to 6, wherein the engine is a two-stroke cycle engine.