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(54) Titre : LUBRIFIANT MOTEUR CONTENANT DES COMPOSES DE POLYETHER
(54) Title: ENGINE LUBRICANT CONTAINING POLYETHER COMPOUNDS

(57) **Abrégé/Abstract:**

The present invention relates to lubricant compositions for scooter engines and methods for reducing static friction between ferrous and non-ferrous surfaces as may be found in a wet clutch. The lubricant compositions contain polyether compounds in combination with one or more ash-free friction modifiers.

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(54) Title: ENGINE LUBRICANT CONTAINING POLYETHER COMPOUNDS

(57) Abstract: The present invention relates to lubricant compositions for scooter engines and methods for reducing static friction between ferrous and non-ferrous surfaces as may be found in a wet clutch. The lubricant compositions contain polyether compounds in combination with one or more ash-free friction modifiers.

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ENGINE LUBRICANT CONTAINING POLYETHER COMPOUNDS

BACKGROUND OF THE INVENTION

[0001] The present invention relates to lubricant compositions primarily, but not exclusively intended for 4-stroke, typically air-cooled scooter and motorcycle engines, that demonstrate reduced static clutch friction between ferrous and non-ferrous surfaces, such as conventionally found in a motorcycle wet clutch.

[0002] Conventionally, at least two approaches for reducing static clutch friction are known. First, lubricants may be formulated to have desired clutch friction properties that meet desired specifications. Second, lubricants may be modified with a booster package or concentrate of additives intended to adjust the clutch friction performance of the lubricant to the desired specification. Amongst additives commonly employed as booster additives to reduce clutch friction performance, are molybdenum compounds, such as molybdenum dithiocarbamate compounds. These compounds can be costly. Other additives used in boosting lubricants to reduce static clutch friction, such as certain phenol compounds, which are employed as solubilizers, are coming under increasing regulatory pressure. Accordingly, there is a need for cost-effective and functional additive components that may be employed in lubricants, including in booster packages for lubricants that will effectively reduce clutch friction, while not unduly harming other performance properties, such as fuel economy, cleanliness, dispersancy, wear and the like.

[0003] The disclosed technology, therefore, addresses the problem of providing lubricants and booster packages for lubricants that effectively reduce the static friction in a clutch having at least one ferrous and one non-ferrous clutch plate. Further the disclosed technology solves the problem of providing lubricants and booster packages for lubricants that both effectively reduce static friction, while maintaining or improving at least one of fuel economy, cleanliness and wear. This is accomplished by the surprising discovery that certain polyethers and polyetheramines, in effective treat rates, reduce static friction between the ferrous and non-ferrous surfaces in a clutch having at least one ferrous and one non-ferrous clutch plate. Moreover, a combination of polyethers and/or polyetheramines and ashless friction modifiers, in

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effective treat rates, provides reduced static friction while synergistically preserving fuel economy.

SUMMARY OF THE INVENTION

[0004] The present invention provides a lubricant composition comprising (a) an oil of lubricating viscosity, (b) a polyether compound, (c) an over-based detergent, (d) an ash-free friction modifier, (e) a dispersant, and (f) optionally, an antioxidant.

[0005] According to one embodiment, the polyether compound may comprise a polyetheramine.

[0006] According to still another embodiment, the ash-free friction modifier may be derived from an alpha-hydroxy carboxylic acid, such as a derivative of tartaric acid, citric acid, malic acid, lactic acid, glycolic acid, oligomers of said acids, or combinations thereof.

[0007] According to still another embodiment, the ash-free friction modifier may be an imide, ester, or amide of tartaric acid, and in one embodiment, may be a tartaric acid imide.

[0008] According to another embodiment the over-based detergent may comprise a metal containing detergent and wherein the metal is selected from the group consisting of sodium, magnesium and calcium.

[0009] According to another embodiment, the over-based detergent may be selected from the group consisting of sulfonates, phenates, salicylates, salixarates and mixtures thereof.

[0010] According to another embodiment, the detergent may comprise a calcium sulfonate detergent.

[0011] According to one embodiment, the lubricating composition the over-based detergent may be free or substantially free of phenates.

[0012] According to one embodiment, the lubricating composition may be free or substantially free of phenolic compounds, and in one embodiment, may be free or substantially free of alkyl phenolic compounds.

[0013] In one embodiment, the lubricating composition may comprise a molybdenum containing compound, and in an alternative embodiment, may be free or substantially free of a molybdenum containing compound.

[0014] In still another embodiment, a lubricating composition may comprise (a) a major amount of an oil of lubricating viscosity, (b) 0.05 to 3.0 wt.% (or 0.1 to 2.0 wt.% or 0.1 to 1.0

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wt.% or 0.2 to 0.8 wt.%) of a polyether compound, (c) 0.05 to 3.0 wt.% (or 0.1 to 2.0 wt.% or 0.1 to 1.0 wt.% or 0.2 to 0.8 wt.%) of an over-based detergent, (d) 0.05 to 2.0 wt.% (or 0.1 to 1.0 wt.% or 0.1 to 0.8 wt.% or 0.2 to 0.8 wt.%) of an ash-free friction modifier, and (e) 0.1 wt.% to 20 wt.%, (or 1.0 wt.% to 15 wt.%, or 1.5 wt.% to 10 wt.%, or 2 wt.% to 6 wt.%) of a dispersant.

[0015] In further embodiments, the present invention provides methods of lubricating a wet clutch by supplying to the wet clutch a lubricating composition as taught herein.

[0016] In another embodiment, the present invention provides methods of reducing static friction between a ferrous and non-ferrous surface in a wet clutch, wherein the wet clutch comprises at least one clutch plate having a non-ferrous surface and at least one clutch plate having a ferrous surface, the methods comprising supplying between the ferrous and non-ferrous clutch plate surfaces a lubricating composition as taught herein.

[0017] In another embodiment, the present invention provides methods of lubricating an engine comprising supplying to an engine a lubricating composition as taught herein.

[0018] In some embodiments, the engine may be a 4-stroke engine, and usefully an air-cooled engine, and typically an engine providing less than about 150, or 125 or 100 or 85 horsepower.

[0019] In one embodiment, the method of lubricating the engine comprises supplying a lubricant composition that does not lubricate a wet clutch.

[0020] According to another embodiment, there is provided an additive concentrate for top treating a lubricating composition, comprising (a) 2 to 35 wt.% (or 5 to 30 wt.% or 10 to 25 wt.% or 10 to 20 wt.%) of a polyether compound, (b) 2 to 25 wt.% (or 3 to 20 wt.% or 5 to 20 wt.% or 7 to 15 wt.%) of an ash-free friction modifier, and (c) 10 to 80 wt.% (or 10 to 75 wt.% or 30 to 75 wt.% or 40 wt.% to 70 wt.%) of a metal containing, over-based detergent.

[0021] According to yet another embodiment, there is provided a lubricant composition comprising (a) a major amount of an oil of lubricating viscosity, and (b) 0.5 to 5.0 wt.% (or 0.5 to 3.0 wt.% or 0.5 to 1.5 wt.%) of an additive concentrate provided herein.

[0022] The disclosed technology further provides lubricating compositions that provide reduced static friction while maintaining fuel economy.

[0023] In one embodiment, the lubricant has a static friction characteristic index (SFI) according to JASO T903:2011 MB specifications of less than 1.25 and in another embodiment, between 0.5 and 1.25.

DETAILED DESCRIPTION OF THE INVENTION

[0024] Various features and embodiments will be described below by way of non-limiting illustration.

[0025] The present invention provides, in one embodiment, a lubricant composition comprising (a) an oil of lubricating viscosity, (b) a polyether compound, (c) an over-based detergent, (d) an ash-free friction modifier, (e) a dispersant, and (f) optionally, an antioxidant.

Oil of Lubricating Viscosity

[0026] The lubricating composition comprises an oil of lubricating viscosity. Such oils include natural and synthetic oils, oil derived from hydrocracking, hydrogenation, and hydrofinishing, unrefined, refined and re-refined oils and mixtures thereof.

[0027] Unrefined oils are those obtained directly from a natural or synthetic source generally without (or with little) 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. Purification techniques are known in the art and include solvent extraction, secondary distillation, acid or base extraction, filtration, percolation and the like. Re-refined oils are also known as reclaimed or reprocessed oils, and are obtained by processes similar to those used to obtain refined oils and often are additionally processed by techniques directed to removal of spent additives and oil breakdown products.

[0028] Natural oils useful in making the inventive lubricants include animal oils, vegetable oils (e.g., castor oil,), 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 and oils derived from coal or shale or mixtures thereof.

[0029] Synthetic lubricating oils are useful and include hydrocarbon oils such as polymerized and interpolymerized olefins (e.g., polybutylenes, polypropylenes, propylene-isobutylene copolymers); poly(1-hexenes), poly(1-octenes), poly(1-decenes), and mixtures thereof; alkylbenzenes (e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di-(2-ethylhexyl)benzenes); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenyls); diphenyl alkanes, alkylated diphenyl alkanes, alkylated diphenyl ethers and alkylated diphenyl sulfides and the derivatives, analogs and homologs thereof or mixtures thereof.

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[0030] Other synthetic lubricating oils include polyol esters (such as Priolube®3970), diesters, liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, and the diethyl ester of decane phosphonic acid), or polymeric tetrahydrofurans. Synthetic oils may be produced by Fischer-Tropsch reactions and typically may be hydroisomerized Fischer-Tropsch hydrocarbons or waxes. In one embodiment oils may be prepared by a Fischer-Tropsch gas-to-liquid synthetic procedure as well as other gas-to-liquid oils.

[0031] Oils of lubricating viscosity may also be defined as specified in the American Petroleum Institute (API) Base Oil Interchangeability Guidelines. The five base oil groups are as follows: Group I (sulfur content >0.03 wt.%, and/or <90 wt.% saturates, viscosity index 80-120); Group II (sulfur content <0.03 wt.%, and >90 wt.% saturates, viscosity index 80-120); Group III (sulfur content <0.03 wt.%, and >90 wt.% saturates, viscosity index >120); Group IV (all polyalphaolefins (PAOs)); and Group V (all others not included in Groups I, II, III, or IV). The oil of lubricating viscosity may also be an API Group II+ base oil, which term refers to a Group II base oil having a viscosity index greater than or equal to 110 and less than 120, as described in SAE publication "Design Practice: Passenger Car Automatic Transmissions," 4th Edition, AE-29, 2012, page 12-9, as well as in US Pat. No. 8,216,448, column 1, line 57.

[0032] The oil of lubricating viscosity may be an API Group IV oil, or mixtures thereof, i.e., a polyalphaolefin. The polyalphaolefin may be prepared by metallocene catalyzed processes or from a non-metallocene process.

[0033] The oil of lubricating viscosity comprises an API Group I, Group II, Group III, Group IV, Group V oil or mixtures thereof. Often the oil of lubricating viscosity is an API Group I, Group II, Group II+, Group III, Group IV oil or mixtures thereof. Alternatively, the oil of lubricating viscosity is often an API Group II, Group II+, Group III or Group IV oil or mixtures thereof. Alternatively, the oil of lubricating viscosity is often an API Group II, Group II+, Group III oil or mixtures thereof.

[0034] The amount of the oil of lubricating viscosity present is typically the balance remaining after subtracting from 100 wt.% the sum of the amount of the additive as described herein above, and the other performance additives. Typically, the major part of the fully formulated lubricating compositions disclosed herein, that is, greater than 50 wt.% of the fully formulated lubricating compositions, will consist of one or more oils of lubricating viscosity. Typically, the lubricating

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composition of the disclosed technology comprises at least 60 wt.%, or at least 70 wt.%, or at least 80 wt.% or at least 90 wt.% of an oil of lubricating viscosity.

[0035] The lubricating composition may be in the form of a concentrate and/or a fully formulated lubricant. If the lubricating composition of the invention is in the form of a concentrate (which may be combined with additional oil to form, in whole or in part, a finished lubricant), the ratio of the of components of the invention to the oil of lubricating viscosity and/or to diluent oil include the ranges of 1:99 to 99:1 by weight, or 80:20 to 10:90 by weight.

[0036] In certain embodiments, the lubricating composition may contain synthetic ester base fluids. Synthetic esters may have a kinematic viscosity measured at 100 C of 2.5 mm²/s to 30 mm²/s. In one embodiment, the lubricating composition comprises less than 50 wt.% of a synthetic ester base fluid with a kinematic viscosity at 100 C of at least 5.5 mm²/s, or at least 6 mm²/s, or at least 8 mm²/s.

[0037] Synthetic esters of the present invention may comprise esters of a dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids and alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkyl malonic acids, and alkenyl malonic acids) with any of variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, and propylene glycol). Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid.

[0038] Esters useful as synthetic oils also include those made from C5 to C12 monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol, and tripentaerythritol. Esters can also be monoesters, such as are available under the trade name Priolube 1976™ (C18-alkyl--COO--C20 alkyl).

[0039] Synthetic ester base oils may be present in the lubricating composition of the invention in an amount less than 50 wt.% of the composition, or less than 40 wt.%, or less than 35 wt.%, or less than 28 wt.%, or less than 21 wt.%, or less than 17 wt.%, or less than 10 wt.%, or less than 5 wt.% of the composition. In one embodiment, the lubricating composition of the invention is free

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of, or substantially free of, a synthetic ester base fluid having a kinematic viscosity of at least 5.5 mm²/s at 100 C.

Polyether Compound

[0040] In the present technology, the lubricating composition comprises an oil of lubricating viscosity and a polyether compound. In one embodiment, the polyether compound may comprise a polyether amine or a blend of polyethers and polyetheramines.

[0041] The polyether compounds of the present invention may be represented by the Formula 1:



Formula 1

where R is a hydrogen or a linear, branched, or cyclic hydrocarbyl group of 1 to 32 (or 1 to 26 or 2 to 26 or 4 to 24 or 8 to 20 or 10 to 20 or 12 to 18) carbon atoms,

R¹ is selected from the group consisting of hydrogen, hydrocarbyl groups of 1 to 6 (or 1 to 4 or 1 to 2 or 1 or 2) carbon atoms, and mixtures thereof,

n is a number from 2 to about 50 (or 12 to 36 or 18 to 30 or 2 to 20), and

A is selected from the group consisting of hydrogen, R¹, —R⁷NR²R², C=OR⁸ and —NR³R³, where

each R² is independently hydrogen or a hydrocarbyl group of 1 to 24 (or 2 to 24 or 4 to 20 or 8 to 20 or 12 to 18 or 2 to 12) carbon atoms,

each R³ is independently hydrogen, a hydrocarbyl group of 1 to 24 (or 2 to 24 or 4 to 20 or 8 to 20 or 12 to 18 or 2 to 12) carbon atoms, or —[R⁴N(R⁵)]_pR⁶

R⁴ is C₂-C₁₀ alkylene,

R⁵ and R⁶ are independently hydrogen or a hydrocarbyl group of 1 to 6 (or 1 to 4 or 1 to 2 or 2 to 4),

R⁷ and R⁸ are independently hydrogen or a hydrocarbyl group of 1 to 6 (or 1 to 4 or 1 to 2 or 2 to 4 or 3) carbon atoms, and

p is a number from 1-7.

[0042] Useful polyetheramines can be prepared by condensing hydric compound such as an alcohol or alkylphenol with an alkylene oxide, mixture of alkylene oxides or with several alkylene oxides in sequential fashion in a 1:2-50 mole ratio of hydric compound to alkylene

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oxide, typically ethylene oxide, to form a polyether. U.S. Pat. No. 5,094,667 provides reaction conditions for preparing a polyether, the disclosure of which is incorporated herein by reference.

[0043] The alcohols can be linear or branched from 1 to 32 carbon atoms, or from 1 to 26 or 2 to 26 or 4 to 24 or 8 to 20 or 10 to 20 or 12 to 18 carbon atoms. The alkyl group of the alkylphenols may have a similar range of carbon atoms as the alcohols.

[0044] The alkylene oxides are preferably ethylene oxide, propylene oxide or butylene oxide. The number of alkylene oxide units in the polyether may be from 2 to 50, or 12 to 36 or 18 to 30 or 2 to 20.

[0045] In one particularly useful embodiment, the polyether compound may be a polyetheramine. The polyetheramines of the present invention may be as represented by Formula 1:

where R is a hydrogen or hydrocarbyl group of 1 to 32 (or 1 to 26 or 2 to 26 or 4 to 24 or 8 to 20 or 10 to 20 or 12 to 18) carbon atoms,

R¹ is selected from the group consisting of hydrogen, hydrocarbyl groups of 1 to 6 (or 1 to 4 or 1 to 2 or 1 or 2) carbon atoms, and mixtures thereof,

n is a number from 2 to about 50, and

A is selected from the group consisting of —R⁷NR²R² and —NR³R³, preferably —R⁷NR²R², where

each R² is independently hydrogen or a hydrocarbyl group of 1 to 24 (or 2 to 24 or 4 to 20 or 8 to 20 or 12 to 18 or 2 to 12) carbon atoms,

each R³ is independently hydrogen, a hydrocarbyl group of 1 to 24 (or 2 to 24 or 4 to 20 or 8 to 20 or 12 to 18 or 2 to 12) carbon atoms, or —[R⁴N(R⁵)]_pR⁶

where R⁴ is C₂-C₁₀ alkylene,

R⁵ and R⁶ are independently hydrogen or a hydrocarbyl group of 1 to 6 (or 1 to 4 or 1 to 2 or 2 to 4),

R⁷ and R⁸ are independently hydrogen or a hydrocarbyl group of 1 to 6 (or 1 to 4 or 1 to 2 or 2 to 4 or 3) carbon atoms, and

p is a number from 1-7.

[0046] Useful polyetheramines can be prepared by converting a polyetheramine, as described above, by amination with ammonia, an amine or a polyamine to form a polyetheramine of the

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type where A is $\text{—NR}^3\text{R}^3$. Published Patent Application EP310875 provides reaction conditions for the amination reaction, the disclosure of which is incorporated herein by reference.

Alternately, the polyether intermediate can also be converted to a polyetheramine of the type where A is $\text{—R}^7\text{NR}^2\text{R}^2$ by reaction with acrylonitrile followed by hydrogenation. U.S. Pat. No. 5,094,667 provides reaction conditions for the cyanoethylation and subsequent hydrogenation, the disclosure of which is incorporated herein by reference.

[0047] Polyetheramines according to Formula 1 where A is $\text{—R}^7\text{NH}_2$ are useful. Commercial examples of useful polyetheramines are the Techron® range from Chevron and the Jeffamine® range from Huntsman.

[0048] Where the polyether compound is part of a fully formulated lubricant composition, it may be present in an amount of about 0.05 to about 3.0 wt.% (or about 0.1 to about 2.0 wt.% or about 0.1 to about 1.0 wt.% or about 0.2 to about 0.8 wt.%, with respect to the lubricating composition. In another embodiment, however, the polyether compound may be a component of an additive concentrate comprising the polyether compound, an ash-free friction modifier and optionally, a detergent. In the additive concentrate, the polyether compound may be present (on an oil free basis) at about 2 to about 35 wt.% or about 5 to about 30 wt.% or about 10 to about 25 wt.% or about 10 to about 20 wt.%, with respect to the additive concentrate.

Ash-free Friction Modifier

[0049] The lubricant composition will also include at least one ash-free friction modifier. The friction modifier is a non-metal containing additive. A non-metal containing additive may also be referred to as an ashless (or ash-free) additive, since it will typically not produce any sulfated ash when subjected to the conditions of ASTM D 874. An additive is referred to as “non-metal containing” if it does not contribute metal content to the lubricant composition.

[0050] In certain embodiments, the friction modifier may be chosen from long chain fatty acid derivatives of amines, long chain fatty esters, or derivatives of long chain fatty epoxides; fatty imidazolines; amine salts of alkylphosphoric acids; and fatty esters, amides and/or imides of various hydroxy-carboxylic acids, such as tartaric acid, citric acid, malic acid, lactic acid, glycolic acid, and mandelic acid.

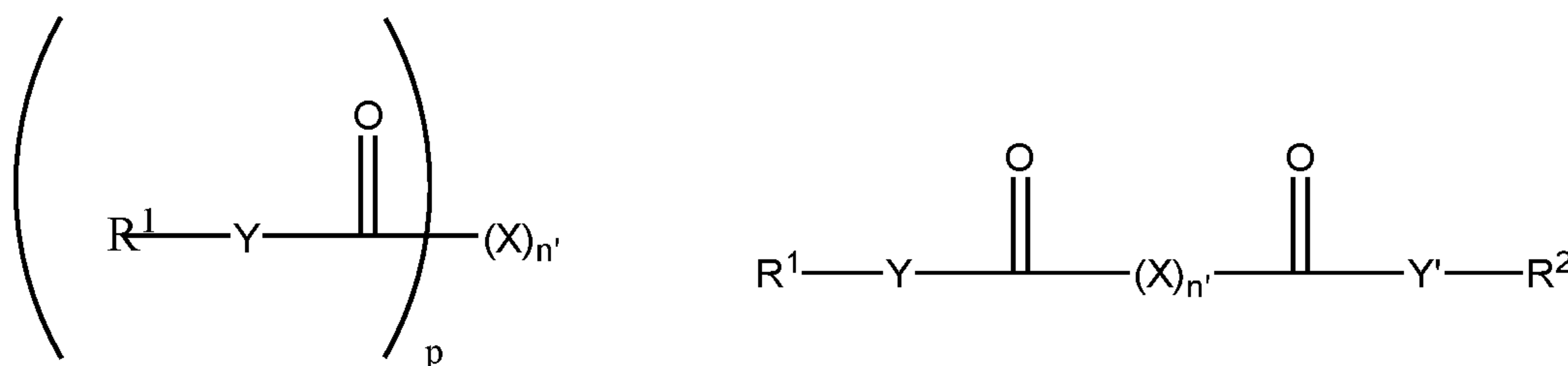
[0051] As used herein the term “fatty alkyl” or “fatty” in relation to friction modifiers means a carbon chain having 8 to 30 carbon atoms, typically a straight carbon chain.

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[0052] In one embodiment, ash-free friction modifier may comprise an amide, ester or imide derivative of a hydroxycarboxylic acid. Such materials and their syntheses are known from, for instance, PCT Publ. No. WO 2006/044411 and US Publ. No. 2009/067091. They have been employed in lubricants for their properties as thermal or oxidative stability, deposit control, and friction control.

[0053] Examples of suitable hydroxy-carboxylic acids include citric acid, tartaric acid, lactic acid, malic acid, glycolic acid, hydroxy-propionic acid, hydroxyglutaric acid, and mixtures thereof. Oligomers of such acids may also be employed (e.g., the self-condensate of glycolic acid by ester formation). In one embodiment, an amide, ester or imide derivative of a hydroxy-carboxylic acid may be derived from tartaric acid, citric acid, hydroxy-succinic acid, dihydroxy mono-acids, mono-hydroxy diacids, or mixtures thereof. In one embodiment, the amide, ester or imide derivative of a hydroxy-carboxylic acid includes a derivative (or compound derived from) tartaric acid or citric acid, or, in another embodiment, from tartaric acid.

[0054] In one embodiment the amide, ester or imide derivative of a hydroxy-carboxylic acid may be represented by Formula 2 (encompassing, 2a or 2b):



Formula 2a

or

Formula 2b

wherein n' is 0 to 10 for Formula 2b, and 1 to 10 for Formula 2a;

p is 1 to 5;

Y and Y' are independently $-O-$, $>NH$, $>NR_3$, or an imide group formed by taking together both Y and Y' groups in 2b or two Y groups in 1a and forming a $R^1-N<$ group between two $>C=O$ groups;

X is independently $-CH_2-$, $>CHR^4$, $>CR^4R^5$, $>CHOR^6$, $>C(OH)CO_2R^6$, $>C(CO_2R^6)_2$, $-CH_3$, $-CH_2R^4$ or CHR_4R^5 , $-CH_2OR^6$, $-CH(CO_2R^6)_2$, $\equiv C-R^6$ (where \equiv refers to three valences, and may only apply to Formula 1), or mixtures thereof, to fulfill the valence of

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Formula 2a and/or 2b (the compound of Formula 2a or 2b may have at least one X that is hydroxyl-containing (i.e., $>\text{CHOR}^6$, wherein R^6 is hydrogen);

R^1 and R^2 are independently hydrocarbyl groups, typically containing 1 to 150, or 4 to 30, or 8 to 15 carbon atoms;

R^3 is a hydrocarbyl group;

R^4 and R^5 are independently keto-containing groups (such as acyl groups), ester groups, hydrocarbyl groups, $-\text{OR}^6$, $-\text{CO}_2\text{R}^6$, or $-\text{OH}$ (typically not more than one $-\text{OH}$ when X is $>\text{CR}^4\text{R}^5$); and

R^6 is independently hydrogen or a hydrocarbyl group, typically containing 1 to 150, or 4 to 30, or 8 to 15 carbon atoms.

[0055] In one embodiment, the compound of Formula 2 contains an imide group, which may be formed by taking together the Y and Y' groups and forming a $\text{R}^1\text{-N}<$ group between two $>\text{C}=\text{O}$ groups. In one embodiment the compound of Formula (1) has m, n, X, and R^1 , R^2 and R^6 defined as follows: m is 0 or 1, n is 1 to 2, X is $>\text{CHOR}^6$, 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 2 has m, n, X, Y, Y' and R^1 , R^2 and R^6 defined as follows: m is 0 or 1, n is 1 to 2, X is $>\text{CHOR}^6$; Y and Y' are both -O-, and R^1 , R^2 and R^6 are independently hydrogen or hydrocarbyl groups containing 4 to 30 carbon atoms.

[0056] The di-esters, di-amides, ester-amide, ester-imide compounds of Formula 2 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. In the case of ester-imide compounds, it is necessary to have at least three carboxylic acid groups (such as provided by citric acid). The amine or alcohol which is reacted typically has sufficient carbon atoms to fulfill the requirements of R^1 and/or R^2 as defined in Formula 2.

[0057] In one embodiment R^1 and R^2 are independently linear or branched hydrocarbyl groups. In one embodiment they are branched; in another they are linear; or some may be branched and some linear. The R^1 and R^2 may be incorporated into Formula 2 by either an amine or an alcohol. The alcohol includes both monohydric alcohol and polyhydric alcohol. The carbon atoms of the alcohol may be linear chains, branched chains, or mixtures thereof.

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[0058] Examples of suitable alcohols include 2-ethylhexanol, isotridecanol, Guerbet alcohols, methanol, ethanol, propanol, butanol, pentanol, hexanol, heptanol, Ctanol, nonanol, decanol, undecanol, dodecanol, tridecanol, tetradecanol, pentadecanol, hexadecanol, heptadecanol, Ctadecanol, nonadecanol, eicosanol, ethylene glycol, propylene glycol, 1,3-butylene glycol, 2,3-butylene glycol, 1,5-pentane diol, 1,6-hexane diol, glycerol, sorbitol, pentaerythritol, trimethylolpropane, starch, glucose, sucrose, methylglucoside, or mixtures thereof. In one embodiment, a polyhydric alcohol is used in a mixture along with a monohydric alcohol; in such a combination the monohydric alcohol may constitute at least 60 or at least 90 mole% of the mixture.

[0059] If the acid employed is tartaric acid, it may be a commercially available material, and it may exist in one or more isomeric forms such as d-tartaric acid, l-tartaric acid, d,l-tartaric acid or a racemic mixture of d-tartaric acid and l-tartaric acid, or mesotartaric acid.

[0060] In certain embodiments, the hydroxycarboxylic acid derivative may comprise a tartramide such as a tartimide formed from a primary amine having 8 to 24 carbon atoms or 12 to 20 carbon atoms or 16 to 18 carbon atoms or mixtures thereof. In one embodiment, the tartramide is oleyl tartramide. In other embodiments, the hydroxycarboxylic acid derivative may comprise a tartrate ester such as a diester of tartaric acid and one or more alcohols having 8 to 24 carbon atoms or 8 to 18 carbon atoms or 12 to 14 carbon atoms. In one embodiment, the tartrate is the ester from mixed C12-C14 alcohols.

[0061] The amount of the ash-free friction modifier in a lubricant may be 0.05 to 3.0 wt.% or 0.05 to 2.0 wt.% (or 0.1 to 1.0 wt.% or 0.1 to 0.8 wt.% or 0.2 to 0.8 wt.%) with respect to the lubricant composition. The ash-free friction modifier may also be present in a concentrate as described above, where it may be present (on an oil free basis) at 2 to 25 wt.% or 3 to 20 wt.% or 5 to 20 wt.% or 7 to 10 wt.%) with respect to the additive concentrate. In a concentrate, the amount of material may be two to twenty times the above concentration amounts.

Detergents

[0062] In one embodiment, the invention provides a lubricating composition further comprising an over-based, metal-containing detergent. The metal of the metal-containing detergent may be zinc, sodium, calcium, barium, or magnesium. Typically, the metal of the metal-containing detergent may be sodium, calcium, or magnesium.

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[0063] The over-based, metal-containing detergent may be chosen from sulfonates, non-sulfur containing phenates, sulfur containing phenates, salixarates, salicylates, and mixtures thereof, or borated equivalents thereof. The over-based detergent may be borated with a borating agent such as boric acid.

[0064] The over-based, metal-containing detergent may also include “hybrid” detergents formed with mixed surfactant systems including phenate and/or sulfonate components, e.g., phenate/salicylates, sulfonate/phenates, sulfonate/salicylates, sulfonates/phenates/salicylates, as described; for example, in US Pat. Nos. 6,429,178, 6,429,179, 6,153,565 and 6,281,179. For example, a “hybrid sulfonate/phenate detergent is employed, the “hybrid detergent would be considered equivalent to amounts of distinct phenate and sulfonate detergents introducing like amounts of phenate and sulfonate soaps, respectively.

[0065] Typically, an over-based, metal-containing detergent may be a zinc, sodium, calcium or magnesium salt of a sulfonate, a phenate, sulfur containing phenate, salixarate or salicylate. Over-based sulfonates, salixarates, phenates and salicylates typically have a total base number of 120 to 700 TBN.

[0066] Typically, the over-based, metal-containing detergent may be a calcium or magnesium an over-based detergent.

[0067] In another embodiment, the lubricating composition comprises a calcium sulfonate over-based detergent, which may have a TBN of 120 to 700. The over-based sulfonate detergent may have a metal ratio of 12 to less than 20, or 12 to 18, or 20 to 30, or 22 to 25.

[0068] Over-based sulfonates typically have a total base number of 120 to 700, or 250 to 600, or 300 to 500 (on an oil free basis). Over-based detergents are known in the art. The sulfonate detergent may be a linear or branched alkylbenzene sulfonate detergent having a metal ratio of at least 8 as is described in paragraphs [0026] to [0037] of US Publ. No. 2005/065045 (granted as US Pat. No. 7,407,919). Linear alkyl benzenes may have the benzene ring attached anywhere on the linear chain, usually at the 2, 3 or 4 position, or mixtures thereof. Linear alkylbenzene sulfonate detergent may be particularly useful for assisting in improving fuel economy. In one embodiment, the alkylbenzene sulfonate detergent may be a branched alkylbenzene sulfonate, a linear alkylbenzene sulfonate, or mixtures thereof. In one embodiment, the lubricating composition may be free of linear alkylbenzene sulfonate detergent. In one embodiment, the

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sulfonate detergent may be a metal salt of one or more oil-soluble alkyl toluene sulfonate compounds as disclosed in paragraphs [0046] to [0053] of US Publ. No. 2008/0119378. The detergent, such as a branched alkylbenzenesulfonate detergent, may be present in the lubricating composition at 0.1 to 3 wt.%, or 0.25 to 1.5 wt.%, or 0.5 to 1.1 wt.%.

[0069] In one embodiment, the lubricating composition further comprises a “hybrid” detergent formed with mixed surfactant systems including phenate and/or sulfonate components, e.g., phenate/salicylates, sulfonate/phenates, sulfonate/salicylates, or sulfonates/phenates/salicylates.

[0070] Detergents may be present in an amount of 0.05 to 3.0 wt.% (or 0.1 to 2.0 wt.% or 0.1 to 1.0 wt.% or 0.2 to 0.8 wt.%) with respect to the fully formulated lubricant composition. The detergent may be present in the additive concentrate in an amount (on an oil free basis) of 10 to 80 wt.% (or 10 to 75 wt.% or 30 to 75 wt.% or 40 wt.% to 70 wt.%) with respect to the additive concentrate. In some embodiments, it may be useful to include the detergent to assist in solubilizing the ash-free friction modifier. In other embodiments, it may be useful to omit the detergent from the additive concentrate.

Other Performance Additives

[0071] A lubricating composition may be prepared by adding the product of the process described herein to an oil of lubricating viscosity, optionally in the presence of other performance additives (as described herein below).

[0072] The lubricating composition of the disclosed technology optionally comprises other performance additives. The other performance additives may include at least one of a molybdenum compound, a metal deactivators, viscosity modifiers, detergents, friction modifiers, antiwear agents, corrosion inhibitors, dispersants, extreme pressure agents, antioxidants, foam inhibitors, demulsifiers, pour point depressants, seal swelling agents (different from those of the invention) and mixtures thereof. Typically, fully-formulated lubricating oil will contain one or more of these performance additives.

[0073] The lubricant composition may also include molybdenum containing compounds, such as molybdenum containing dithiocarbamate compounds and nitrogen-containing molybdenum compounds, such as those described in U.S. Pat. No. 6,329,327; and organomolybdenum compounds made from the reaction of a molybdenum source, fatty oil, and a diamine as described in U.S. Pat. No. 6,914,037.

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[0074] The molybdenum compound may be present in the lubricant composition at 0.005 to 2 wt.% of the composition, or 0.01 to 1.3 wt.% of the composition, or even 0.02 to 1.0 wt.% of the composition. The molybdenum compound may provide the lubricant composition with 0 to 1000 ppm, or 5 to 1000 ppm, or 10 to 750 ppm 5 ppm to 300 ppm, or 20 ppm to 250 ppm of molybdenum. In some embodiments, however, the lubricant composition will be free or substantially free of molybdenum compounds.

[0075] The lubricating composition in a further embodiment may comprise an antioxidant, wherein the antioxidant comprises a phenolic or an aminic antioxidant or mixtures thereof. The antioxidants include diarylamines, alkylated diarylamines, hindered phenols, or mixtures thereof. When present, the antioxidant may be present at 0.1 wt.% to 3 wt.%, or 0.5 wt.% to 2.75 wt.%, or 1 wt.% to 2.5 wt.% of the lubricating composition.

[0076] The diarylamine or alkylated diarylamine may be a phenyl- α -naphthylamine (PANA), an alkylated diphenylamine, or an alkylated phenyl-naphthylamine, or mixtures thereof. The alkylated diphenylamine may include di-nonylated diphenylamine, nonyl diphenylamine, Cetyl diphenylamine, di-octylated diphenylamine, di-decylated diphenylamine, decyl diphenylamine and mixtures thereof. In one embodiment, the diphenylamine may include nonyl diphenylamine, dinonyl diphenylamine, Cetyl diphenylamine, dioctyl diphenylamine, or mixtures thereof. In another embodiment the alkylated diphenylamine may include nonyl diphenylamine, or dinonyl diphenylamine. The alkylated diarylamine may include Cetyl, di-octyl, nonyl, di-nonyl, decyl or di-decyl phenyl-naphthylamines.

[0077] The hindered phenol antioxidant often contains a secondary butyl and/or a tertiary butyl group as a sterically hindering group. The phenol group may be further substituted with a hydrocarbyl group (typically linear or branched alkyl) 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 may be 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 Pat. No. 6,559,105.

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[0078] The lubricating composition may in a further embodiment include a dispersant, or mixtures thereof. The dispersant may be a succinimide dispersant, a Mannich dispersant, a succinamide dispersant, a polyolefin succinic acid ester, amide, or ester-amide, or mixtures thereof. In one embodiment the dispersant may be present as a single dispersant. In one embodiment, the dispersant may be present as a mixture of two or three different dispersants, wherein at least one may be a succinimide dispersant.

[0079] The succinimide dispersant may be derived from an aliphatic polyamine, or mixtures thereof. The aliphatic polyamine may be aliphatic polyamine such as an ethylenepolyamine, a propylenepolyamine, a butylenepolyamine, or mixtures thereof. In one embodiment, the aliphatic polyamine may be ethylenepolyamine. In one embodiment, the aliphatic polyamine may be chosen from ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylene-hexamine, polyamine still bottoms, and mixtures thereof.

[0080] In one embodiment, the dispersant may be a polyolefin succinic acid ester, amide, or ester-amide. For instance, a polyolefin succinic acid ester may be a polyisobutylene succinic acid ester of pentaerythritol, or mixtures thereof. A polyolefin succinic acid ester-amide may be a polyisobutylene succinic acid reacted with an alcohol (such as pentaerythritol) and a polyamine as described above.

[0081] The dispersant may be an N-substituted long chain alkenyl succinimide. An example of an N-substituted long chain alkenyl succinimide is polyisobutylene succinimide. Typically, the polyisobutylene from which polyisobutylene succinic anhydride is derived has a number average molecular weight of 350 to 5000, or 550 to 3000 or 750 to 2500 g/mole. Succinimide dispersants and their preparation are disclosed, for instance in US Pat. Nos. 3,172,892, 3,219,666, 3,316,177, 3,340,281, 3,351,552, 3,381,022, 3,433,744, 3,444,170, 3,467,668, 3,501,405, 3,542,680, 3,576,743, 3,632,511, 4,234,435, 6,165,235, 7,238,650, Re 26,433 and EP Publication No. 0355895A.

[0082] The dispersants may also be post-treated by conventional methods by a reaction with any of a variety of agents. Among these are boron compounds (such as boric acid), urea, thiourea, dimercaptothiadiazoles, carbon disulfide, aldehydes, ketones, carboxylic acids such as terephthalic acid, hydrocarbon-substituted succinic anhydrides, maleic anhydride, nitriles, epoxides, and phosphorus compounds. In one embodiment, the post-treated dispersant is

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borated. In one embodiment, the post-treated dispersant is reacted with dimercapthiadiazoles. In one embodiment the post-treated dispersant is reacted with phosphoric or phosphorous acid. In one embodiment, the post-treated dispersant is reacted with terephthalic acid and boric acid (as described in US Publ. No. 2009/0054278).

[0083] The dispersant may be present at 0.1 wt.% to 20 wt.%, (or 1.0 wt.% to 15 wt.%, or 1.5 wt.% to 10 wt.%, or 2 wt.% to 6 wt.% or 1 to 3 wt.%) of the lubricating composition.

[0084] The succinimide dispersant may comprise a polyisobutylene succinimide, wherein the polyisobutylene from which polyisobutylene succinimide is derived has a number average molecular weight of 350 to 5000, or 750 to 2500 g/mole.

[0085] Another class of additives that may perform as antiwear agents as well as in other roles includes oil-soluble titanium compounds as disclosed in US Pat. No. 7,727,943 and US Publ. No. 2006/0014651. The oil-soluble titanium compounds may function as antiwear agents, friction modifiers, antioxidants, deposit control additives, or more than one of these functions. In one embodiment the oil soluble titanium compound is a titanium (IV) alkoxide. The titanium alkoxide is formed from a monohydric alcohol, a polyol or mixtures thereof. The monohydric alkoxides may have 2 to 16, or 3 to 10 carbon atoms. In one embodiment, the titanium alkoxide is titanium (IV) isopropoxide. In one embodiment, the titanium alkoxide is titanium (IV) 2 ethylhexoxide. In one embodiment, the titanium compound comprises the alkoxide of a vicinal 1,2-diol or polyol. In one embodiment, the 1,2-vicinal diol comprises a fatty acid mono-ester of glycerol, often the fatty acid is oleic acid.

[0086] In one embodiment, the oil soluble titanium compound is a titanium carboxylate. In a further embodiment the titanium (IV) carboxylate is titanium neodecanoate.

[0087] The lubricating composition may in one embodiment further include a phosphorus-containing antiwear agent. Typically the phosphorus-containing antiwear agent may be a zinc dialkyldithiophosphate, phosphite, phosphate, phosphonate, and ammonium phosphate salts, or mixtures thereof. Zinc dialkyldithiophosphates are known in the art. The antiwear agent, of whatever type, may be present at 0 wt.% to 3 wt.%, or 0.1 wt.% to 1.5 wt.%, or 0.5 wt.% to 0.9 wt.% of the lubricating composition.

[0088] Extreme Pressure (EP) agents may also be present. EP agents that are soluble in the oil include sulfur- and chlorosulfur-containing EP agents, dimercapthiadiazole or CS₂ derivatives

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of dispersants (typically succinimide dispersants), derivative of chlorinated hydrocarbon EP agents and phosphorus EP agents. Examples of such EP agents include chlorinated wax; sulfurized olefins (such as sulfurized isobutylene), a hydrocarbyl-substituted 2,5-dimercapto-1,3,4-thiadiazole, or oligomers thereof, organic sulfides and polysulfides such as dibenzyl disulfide, 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 or derivatives including, for example, the amine salt of a reaction product of a dialkyldithiophosphoric acid with propylene oxide and subsequently followed by a further reaction with P_2O_5 ; and mixtures thereof (as described in US Pat. No. 3,197,405). The amount of EP agent, if present, may be 0.001 to 5 wt.%, or 0.1 to 2 wt.%, or 0.2 to 1 wt.%.

[0089] Foam inhibitors that may be useful in the lubricant compositions of the disclosed technology include polysiloxanes, copolymers of ethyl acrylate and 2-ethylhexylacrylate and optionally vinyl acetate; demulsifiers including fluorinated polysiloxanes, trialkyl phosphates, polyethylene glycols, polyethylene oxides, polypropylene oxides and (ethylene oxide-propylene oxide) polymers. The amount of foam inhibitor, if present, may be 0.001 to 0.012 wt.% or to 0.004 wt.%, or 0.001 to 0.003 wt.%.

[0090] Viscosity improvers (also sometimes referred to as viscosity index improvers or viscosity modifiers) may be included in the compositions of this invention. Viscosity improvers are usually polymers, including polyisobutenes, polymethacrylates (PMA) and polymethacrylic acid esters, diene polymers, polyalkylstyrenes, esterified styrene-maleic anhydride copolymers, hydrogenated alkenylarene-conjugated diene copolymers and polyolefins also referred to as olefin copolymer or CP). PMA's are prepared from mixtures of methacrylate monomers having different alkyl groups. The alkyl groups may be either straight chain or branched chain groups containing from 1 to 18 carbon atoms. Most PMA's are viscosity modifiers as well as pour point

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depressants. In certain embodiments, the viscosity index improver is a polyolefin comprising ethylene and one or more higher olefin, such as propylene. Polymeric viscosity modifiers may be present in a lubricating composition from 0.1 to 10 wt.%, 0.3 to 5 wt.%, or 0.5 to 2.5 wt.%.

[0091] Pour point depressants that may be useful in the lubricant compositions of the disclosed technology include polyalphaolefins, esters of maleic anhydride-styrene copolymers, poly(meth)acrylates, polyacrylates or polyacrylamides. Pour point depressants may be present in a lubricating composition from 0.1 to 10 wt.%, 0.3 to 5 wt.%, or 0.5 to 2.5 wt.%.

[0092] Demulsifiers include trialkyl phosphates, and various polymers and copolymers of ethylene glycol, ethylene oxide, propylene oxide, or mixtures thereof.

[0093] Metal deactivators include derivatives of benzotriazoles (typically tolyltriazole), 1,2,4-triazoles, benzimidazoles, 2-alkyldithiobenzimidazoles or 2-alkyldithiobenzothiazoles. The metal deactivators may also be described as corrosion inhibitors.

[0094] Seal swell agents include sulfolene derivatives Exxon Necton-37™ (FN 1380) and Exxon Mineral Seal Oil™ (FN 3200).

[0095] Examples of suitable friction modifiers, other than the ash-free friction modifiers disclosed above may include long chain fatty acid derivatives of amines, fatty esters, or fatty epoxides; fatty imidazolines such as condensation products of carboxylic acids and polyalkylene-polyamines; amine salts of alkylphosphoric acids; fatty phosphonates; fatty phosphites; borated phospholipids, borated fatty epoxides; glycerol esters; borated glycerol esters; fatty amines; alkoxyated fatty amines; borated alkoxyated fatty amines; hydroxyl and polyhydroxy fatty amines including tertiary hydroxy fatty amines; hydroxy alkyl amides; metal salts of fatty acids; metal salts of alkyl salicylates; fatty oxazolines; fatty ethoxyated alcohols; condensation products of carboxylic acids and polyalkylene polyamines; or reaction products from fatty carboxylic acids with guanidine, aminoguanidine, urea, or thiourea and salts thereof.

[0096] Friction modifiers may also encompass materials such as sulfurized fatty compounds and olefins, sunflower oil or soybean oil monoester of a polyol and an aliphatic carboxylic acid.

[0097] In another embodiment, the friction modifier may be a long chain fatty acid ester. In another embodiment, the long chain fatty acid ester may be a mono-ester and in another embodiment the long chain fatty acid ester may be a triglyceride.

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[0098] The present technology discloses fully formulated lubricants as well as additive concentrates for top-treating lubricants. Where the additive concentrate comprises the polyether compound, ash-free friction modifier and optional detergent, the present technology contemplates that an existing lubricant may be top treated with 0.5 to 15 wt.% or 0.5 to 10 wt.% or 0.5 to 5.0 wt.% or 0.5 to 3.0 wt.% or 0.5 to 1.5 wt.% or 0.5 to 1.2 wt.% of the additive concentrate. By top treating the lubricant, the friction properties of the lubricant may be adjusted to render the treated lubricant suitable for use in a scooter engine, even where the pre-treated lubricant was suitable for use in a motorcycle having an engine and a wet clutch. It will also be understood that one or more of the aforementioned “other performance additives” may be present in the fully formulated lubricant or may be present in the additive concentrate, provided the effective treat rate of the polyether compound and ash-free friction modifier in the fully formulated lubricant does not fail to fall within the ranges taught herein.

[0099] A fully formulated lubricant composition in different embodiments may have a composition as disclosed in the following table:

Additive	Embodiments (wt.%)		
	A	B	C
Polyether compound	0.025 to 4	0.05 to 1.8	0.1 to 0.8
Ash-free Friction Modifier	0.01 to 6	0.05 to 4	0.1 to 2
Molybdenum Compound	0 to 2	0 to 1.2	0 to 0.6
(Borated) Dispersant	0 to 12	0.5 to 8	1 to 6
Over-based Detergent	0 to 9	0.5 to 8	1 to 5
Corrosion Inhibitor	0.05 to 2	0.1 to 1	0.2 to 0.5
Dispersant Viscosity Modifier	0 to 5	0 to 4	0.05 to 2
Antioxidant	0.1 to 13	0.1 to 10	0.5 to 5
Antiwear Agent	0.1 to 15	0.1 to 10	0.3 to 5
Viscosity Modifier	0 to 10	0.5 to 8	1 to 6
Any Other Performance Additive	0 to 10	0 to 8	0 to 6
Oil of Lubricating Viscosity	Major portion typically balance to 100%		

[0100] An additive concentrate in different embodiments may have a composition as disclosed in the following table:

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Additive	Embodiments (wt.%)		
	A	B	C
Polyether compound	5 to 80	15 to 50	20 to 40
Ash-free Friction Modifier	5 to 50	10 to 40	15 to 30
Over-based Detergent	0 to 90	10 to 75	30 to 70
Oil of Lubricating Viscosity	Balance to 100%; typically diluent oil in amount less than about 30%		

Industrial Application

[0101] The technology disclosed may include a method of lubricating one of a wet clutch or an internal combustion engine, comprising supplying to the wet clutch or the engine a lubricating composition comprising (a) an oil of lubricating viscosity, (b) a polyether compound, (c) an over-based detergent, (d) an ash-free friction modifier; (e) a dispersant and (f) optionally, an antioxidant.

[0102] The technology disclosed may include a method of lubricating an internal combustion engine comprising supplying to the engine a lubricating composition as described above.

[0103] The internal combustion engine may be a 4-stroke engine. The internal combustion engine may be fitted with an emission control system or a turbocharger. Examples of the emission control system include particulate filters, or systems employing selective catalytic reduction (SCR).

[0104] The internal combustion engine may be port fuel injected or direct injection. In one embodiment, the internal combustion engine is a gasoline direct injection (GDI) engine.

[0105] The technology disclosed may include a method of lubricating a wet clutch, wherein the wet clutch comprises at least one clutch plate having a non-ferrous surface and at least one clutch plate having a ferrous surface, comprising supplying to the wet clutch, and more particularly, supplying between the interface of the ferrous and non-ferrous surfaces, a lubricating composition as described herein.

[0106] The technology disclosed may include a method of reducing static friction between a ferrous and non-ferrous surface, such as may be found in a wet clutch having at least one clutch plate having a non-ferrous surface and at least one clutch plate having a ferrous surface, the method comprising supplying between the ferrous and non-ferrous clutch plate surfaces a lubricating composition as described herein.

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[0107] It is contemplated that the lubricant compositions of the present invention may be employed in a wet clutch, that is, where clutch plates which are immersed in a lubricant. Such clutches are well known and not extensively described herein, save that they typically contain a two or more plates. Plate materials may include steel (that is, a ferrous material), and non-ferrous materials, such as paper, ceramic, and carbon fiber. The present technology is particularly useful in reducing static friction between a steel plate and a carbon fiber or fiberglass plate. While the present invention may be taught in relation to reducing at least one of static friction and dynamic friction between a ferrous and non-ferrous surface exemplified in a wet clutch, it will be understood that the compositions of the present invention may be useful in reducing one of static or dynamic friction between ferrous and non-ferrous surfaces in other contexts.

[0108] The lubricating compositions of the present invention may have a total sulfated ash content of 1.2 wt.% or less. The sulfur content of the lubricating composition may be 1 wt.% or less, or 0.8 wt.% or less, or 0.5 wt.% or less, or 0.3 wt.% or less. In one embodiment, the sulfur content may be in the range of 0.001 wt.% to 0.5 wt.%, or 0.01 wt.% to 0.3 wt.%. The phosphorus content may be 0.2 wt.% or less, or 0.12 wt.% or less, or 0.1 wt.% or less, or 0.085 wt.% or less, or 0.08 wt.% or less, or even 0.06 wt.% or less, 0.055 wt.% or less, or 0.05 wt.% or less. In one embodiment, the phosphorus content may be 0.04 wt.% to 0.12 wt.%. In one embodiment, the phosphorus content may be 100 ppm to 1000 ppm, or 200 ppm to 600 ppm. The total sulfated ash content may be 0.3 wt.% to 1.2 wt.%, or 0.5 wt.% to 1.1 wt.% of the lubricating composition. In one embodiment, the sulfated ash content may be 0.5 wt.% to 1.1 wt.% of the lubricating composition.

[0109] In one embodiment, the lubricating composition may be characterized as having (i) a sulfur content of 0.5 wt.% or less, (ii) a phosphorus content of 0.15 wt.% or less, and (iii) a sulfated ash content of 0.5 wt.% to 1.5 wt.% or less.

[0110] The lubricating composition may be characterized as having at least one of (i) a sulfur content of 0.2 wt.% to 0.4 wt.% or less, (ii) a phosphorus content of 0.08 wt.% to 0.15 wt.%, and (iii) a sulfated ash content of 0.5 wt.% to 1.5 wt.% or less.

[0111] The lubricating composition may be characterized as having a sulfated ash content of 0.5 wt.% to 1.2 wt.%.

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[0112] As used herein TBN values are (total base number) measured by the methodology described in D4739 (buffer).

[0113] The lubricating composition may be characterized as having a total base number (TBN) content of at least 5 mg KOH/g. The lubricating composition may be characterized as having a total base number (TBN) content of 6 to 13 mg KOH/g, or 7 to 12 mg KOH/g. The lubricant may have a SAE viscosity grade of XW-Y, wherein X may be 0, 5, 10, or 15; and Y may be 16, 20, 30, 40, or 50 or a monograde viscosity of SAE 20, 30, 40, or SAE 50.

[0114] The internal combustion engine disclosed herein may have a steel surface on a cylinder bore, cylinder block, or piston ring.

[0115] The internal combustion engine may have a surface of steel, or an aluminum alloy, or an aluminum composite. The internal combustion engine may be an aluminum block engine where the internal surface of the cylinder bores has been thermally coated with iron, such as by a plasma transferred wire arc (PTWA) thermal spraying process. Thermally-coated iron surfaces may be subjected to conditioning to provide ultra-fine surfaces.

EXAMPLES

[0116] The following examples provide illustrations of the invention. These examples are non-exhaustive and are not intended to limit the scope of the invention.

[0117] A series of 10W-30 motorcycle lubricants are prepared as summarized in Table 1. The inventive oil examples 1 and 2 of the invention contain a polyethyleneamine, an over-based detergent, an ash-free friction modifier, and a dispersant, as well as several other conventional lubricant additives. The inventive oils are evaluated and compared to a similarly formulated oil without the polyetheramine (Comparative 1).

Table 1 – Lubricating Compositions

	Comparative 1	Example 1	Example 2
Mineral Oil	Balance to 100%	Balance to 100%	Balance to 100%
Viscosity Modifier	0.625	0.625	0.625
PMA Pour Depressant	0.120	0.120	0.120
Aminic Antioxidant	0.601	0.601	0.601
300 TBN Ca Sulfonate	0.087	0.087	0.087
400 TBN Ca Sulfonate	0.518	0.518	0.518
255 TBN Ca Phenate	0.150	0.093	0.093
Borated Succinimide Dispersant	0.100	0.100	0.100
Succinimide Dispersant	1.532	1.532	1.532
Secondary ZDP	0.758	0.758	0.758
Sulfurized Olefin	0.100	0.100	0.100
PDMS Anti-foam	0.010	0.010	0.010
Booster Composition			
Aminated polyether (PAG-24A)	-	0.500	0.200
300 TBN Ca Sulfonate	-	-	0.348
Oleyl Tartramide	-	-	0.120
Total¹	100.000	100.000	100.000

¹ All treat rates on an oil-free basis.

[0118] The lubricants are evaluated for balance of static and dynamic friction performance.

[0119] The industry-standard JASO T 903:2011 test utilizes a clutch pack consisting of several steel disks and fiber plates enclosed in a test head. The clutch pack operates in a temperature controlled oil bath. An electric motor is then used to rotate the fiber plates to 3,600 RPM while the steel disks are held static in the test head. During this motoring phase, there is no pressure applied to the clutch pack. Once speed and temperature set points are met, pressure is then applied to the clutch pack to cause lock up. This event is referred to as a dynamic engagement. A metal disc connected to the electric motor simulates vehicle inertia. During this dynamic engagement, parameters such as speed and torque are measured and are used to calculate the Dynamic Friction Characteristic Index (DFI) and Stop Time Index (STI). These are the first two parameters which are used to classify an engine oil's frictional performance. The third parameter is called the Static Friction Characteristic Index (SFI). For this evaluation, the same test rig is used, but now the evaluation begins with the pressure applied to the clutch to facilitate

lock up. A low speed (300 RPM), high torque motor is used to ‘break’ the clutch pack loose and cause slippage. Once again, torque, speed, and other parameters are measured and used to calculate SFI. For JASO T903:2011 MB specifications, SFI must fall between 0.5 and 1.25.

Table 2 – Friction Measurements

JASO T903:2011	Comparative 1	Example 1	Example 2
Dynamic FI (DFI)	2.12	1.73	1.95
Static FI (SFI)	2.14	1.07	1.13
Stop Time Index	2.11	1.77	1.94

[0120] As the results indicate, the inventive lubricant composition provides for desired reduction in static friction.

[0121] 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. The products formed thereby, including the products formed upon employing lubricant 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 lubricant composition prepared by admixing the components described above.

[0122] 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:

(i) 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);

(ii) 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 chloro and fluoro), hydroxy, alkoxy, mercapto, alkylmercapto, nitro, nitroso, and sulphoxy);

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(iii) hetero substituents, that is, substituents which, while having a predominantly hydrocarbon character, in the context of this invention, contain other than carbon in a ring or chain otherwise composed of carbon atoms; and

(iv) heteroatoms include sulphur, oxygen, nitrogen, and encompass substituents as pyridyl, furyl, thienyl and imidazolyl. In general, no more than two, preferably 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.

[0123] Each of the documents referred to above is incorporated herein by reference. 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 may be used together with ranges or amounts for any of the other elements.

[0124] As used herein the term “free of” defines the absence of a material and the term “substantially free of” defines an amount which is present as impurities, e.g., a trace amount or a non-effective amount.

[0125] While the invention has been explained in relation to its preferred embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.

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What is claimed:

1. A lubricant composition comprising:
 - a) an oil of lubricating viscosity,
 - b) a polyether compound,
 - c) an over-based detergent,
 - d) a dispersant,
 - e) optimally, an ash-free friction modifier, and
 - f) optionally, an antioxidant.

2. The lubricating composition of any of the previous claims, wherein the polyether is represented by the formula:



where R is a hydrogen or hydrocarbyl group of 1 to 32 (or 1 to 26 or 2 to 26 or 4 to 24 or or 8 to 20 or 10 to 20 or 12 to 18) carbon atoms,

R¹ is selected from the group consisting of hydrogen, hydrocarbyl groups of 1 to 6 (or 1 to 4 or 1 to 2 or 1 or 2) carbon atoms, and mixtures thereof,

n is a number from 2 to about 50 (or 12 to 36 or 18 to 30 or 2 to 20), and

A is selected from the group consisting of hydrogen, R¹, —R⁷NR²R², C=OR⁸ and —NR³R³, where

each R² is independently hydrogen or a hydrocarbyl group of 1 to 24 (or 2 to 24 or 4 to 20 or 8 to 20 or 12 to 18 or 2 to 12) carbon atoms,

each R³ is independently hydrogen, a hydrocarbyl group of 1 to 24 (or 2 to 24 or 4 to 20 or 8 to 20 or 12 to 18 or 2 to 12) carbon atoms, or —[R⁴N(R⁵)]_pR⁶ where R⁴ is C₂-C₁₀ alkylene,

R⁵ and R⁶ are independently hydrogen or a hydrocarbyl group of 1 to 6 (or 1 to 4 or 1 to 2 or 2 to 4),

R⁷ and R⁸ are independently hydrogen or a hydrocarbyl group of 1 to 6 (or 1 to 4 or 1 to 2 or 2 to 4) carbon atoms, and

p is a number from 1-7.

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3. The lubricating composition of any of the previous claims, wherein the polyether compound is a polyetheramine represented by the formula $\text{RO}[\text{CH}_2\text{CH}(\text{R}^1)\text{O}]_n\text{A}$, wherein:

R is a hydrocarbyl group of 2 to 26 (or 4 to 24 or 8 to 20 or 10 to 20 or 12 to 18) carbon atoms,

A is $\text{—R}^7\text{NR}^2\text{R}^2$,

each R^2 is independently hydrogen or a hydrocarbyl group of 1 to 24 (or 2 to 24 or 4 to 20 or 8 to 20 or 12 to 18 or 2 to 12),

R^7 is a hydrocarbyl group of 2 to 4 carbon atoms, and

n is 12 to 36 (or 18 to 30).

4. The lubricating composition of any of the previous claims, comprising the ash-free friction modifier and wherein the ash-free friction modifier is derived from an alpha-hydroxy carboxylic acid.

5. The lubricating composition of any of the previous claims, wherein the ash-free the friction modifier is present and is derived from an alpha-hydroxy carboxylic acid (typically, tartaric acid, citric acid, malic acid, lactic acid, glycolic acid, oligomers of said acids, or combinations thereof).

6. The lubricating composition of any of the previous claims, wherein the ash-free friction modifier is present and is an imide, ester, or amide of tartaric acid.

7. The lubricating composition of any of the previous claims, wherein the over-based detergent comprises a metal containing detergent.

8. The lubricating composition of any of the previous claims, wherein the over-based detergent comprises a metal containing detergent and wherein the metal is selected from the group consisting of sodium, magnesium and calcium.

9. The lubricating composition of any of the previous claims, wherein the over-based detergent comprises a metal containing detergent, wherein the metal is calcium.

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10. The lubricating composition of any of the previous claims, wherein the over-based detergent is selected from the group consisting of sulfonates, phenates, salicylates, salixarates and mixtures thereof.

11. The lubricating composition of any of the previous claims, wherein the over-based detergent is substantially free of phenates.

12. The lubricating composition of any of the previous claims, wherein the detergent comprises a calcium sulfonate detergent.

13. The lubricating composition of any of the previous claims wherein the dispersant is a succinimide dispersant.

14. The lubricating composition of any of the previous claims wherein the dispersant comprises a borated dispersant

15. The lubricating composition of any of the previous claims comprising an antioxidant.

16. The lubricating composition of any of the previous claims further comprising a molybdenum containing compound.

17. The lubricating composition of any of claims 1 through 15, wherein the composition is substantially free of a molybdenum containing compound.

18. The lubricating composition of any of the previous claims, wherein the composition is substantially free of phenolic compounds.

19. The lubricating composition of any of the previous claims, wherein the composition comprises:

- a) a major amount of an oil of lubricating viscosity,
- b) 0.05 to 3.0 wt.% (or 0.1 to 2.0 wt.% or 0.1 to 1.0 wt.% or 0.2 to 0.8 wt.%) of the polyether compound,

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c) 0.05 to 3.0 wt.% (or 0.1 to 2.0 wt.% or 0.1 to 1.0 wt.% or 0.2 to 0.8 wt.%) of the over-based detergent,

d) 0.05 to 2.0 wt.% (or 0.1 to 1.0 wt.% or 0.1 to 0.8 wt.% or 0.2 to 0.8 wt.%) of the ash-free friction modifier, and

e) 0.1 to 12 wt.% (or 0.5 to 8.0 wt.% or 1 to 6.0 wt.% or 1.5 to 6.0 wt.%) of the dispersant.

20. A method of lubricating a wet clutch comprising, supplying to the wet clutch a lubricating composition of any of the previous claims.

21. The method of claim 20, wherein the wet clutch comprises at least one clutch plate having a non-ferrous surface and at least one clutch plate having a ferrous surface.

22. A method of reducing static friction between a ferrous and non-ferrous surface in a wet clutch, wherein the wet clutch comprises at least one clutch plate having a non-ferrous surface and at least one clutch plate having a ferrous surface, the method comprising supplying between the ferrous and non-ferrous clutch plate surfaces a lubricating composition of any of the previous claims 1 through 19.

23. A method of lubricating an engine comprising supplying to engine a lubricating composition of any of claims 1 through 19.

24. The method of claim 23, wherein the engine a 4-stroke engine.

25. The method of any of previous claims 23 or 24, wherein the engine is an air-cooled engine.

26. The method of any of previous claims 23 through 25, wherein the lubricating composition does not lubricate a wet clutch.

27. An additive concentrate for top treating a lubricating composition, comprising on an oil-free basis:

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- a) 2 to 35 wt.% (or 5 to 30 wt.% or 10 to 25 wt.% or 10 to 20 wt.%) of a polyether compound,
- b) 2 to 25 wt.% (or 3 to 20 wt.% or 5 to 20 wt.% or 7 to 15 wt.%) of an ash-free friction modifier, and
- c) 10 to 80 wt.% (or 10 to 75 wt.% or 30 to 75 wt.% or 40 wt.% to 70 wt.%) of a metal containing, over-based detergent.

28. The additive concentrate of claim 27, wherein the polyether is represented by Formula 1:



Formula 1

where R is a hydrogen or hydrocarbyl group of 1 to 32 (or 1 to 26 or 2 to 26 or 4 to 24 or or 8 to 20 or 10 to 20 or 12 to 18) carbon atoms,

R¹ is selected from the group consisting of hydrogen, hydrocarbyl groups of 1 to 6 (or 1 to 4 or 1 to 2 or 1 or 2) carbon atoms, and mixtures thereof,

n is a number from 2 to about 50 (or 12 to 36 or 18 to 30 or 2 to 20), and

A is selected from the group consisting of hydrogen, R¹, —R⁷NR²R², C=OR⁸ and —NR³R³ where

each R² is independently hydrogen or a hydrocarbyl group of 1 to 24 (or 2 to 24 or 4 to 20 or 8 to 20 or 12 to 18 or 2 to 12) carbon atoms,

each R³ is independently hydrogen, a hydrocarbyl group of 1 to 24 (or 2 to 24 or 4 to 20 or 8 to 20 or 12 to 18 or 2 to 12) carbon atoms, or —[R⁴N(R⁵)]_pR⁶ where R⁴ is C₂-C₁₀ alkylene,

R⁵ and R⁶ are independently hydrogen or a hydrocarbyl group of 1 to 6 (or 1 to 4 or 1 to 2 or 2 to 4),

R⁷ and R⁸ are independently hydrogen or a hydrocarbyl group of 1 to 6 (or 1 to 4 or 1 to 2 or 2 to 4) carbon atoms, and

p is a number from 1-7.

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29. The additive concentrate of any of claims 27 and 28, wherein the polyether compound is a polyetheramine represented by the formula:



wherein A is $\text{—R}^7\text{NR}^2\text{R}^2$, and

each R^2 is independently hydrogen or a hydrocarbyl group of 1 to 24 (or 2 to 24 or 4 to 20 or 8 to 20 or 12 to 18 or 2 to 12).

30. The additive concentrate of any of claims 27 through 30, wherein the ash-free friction modifier is derived from an alpha-hydroxy carboxylic acid.

31. The additive concentrate of any of claims 27 through 30, wherein the ash-free the friction modifier is derived from tartaric acid, citric acid, malic acid, lactic acid, glycolic acid, oligomers of said acids, or combinations thereof.

32. The additive concentrate of any of claims 27 through 31, wherein the ash-free friction modifier is an imide, ester, or amide of tartaric acid.

33. A lubricant composition comprising:

- a) A major amount of an oil of lubricating viscosity, and
- b) 0.5 to 5.0 wt.% (or 0.5 to 3.0 wt.% or 0.5 to 1.5 wt.%) of the additive concentrate of any of claims 27 through 32.