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(54) **MIXTURES OF FRICTION MODIFIERS TO PROVIDE GOOD FRICTION PERFORMANCE TO TRANSMISSION FLUIDS**

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(57) **ABSTRACT**

Mixtures of friction modifiers provide excellent friction performance to transmission fluids, where the friction modifiers include an N-substituted oxalic acid bisamide or amide-ester containing at least two hydrocarbyl groups of 12 to 22 carbon atoms; and an amide or thioamide represented by $R^1R^2N—C(X)R^3$ where X is O or S, R^1 and R^2 are hydrocarbyl groups of at least 6 carbon atoms, and R^3 is hydroxyalkyl group of 1 to 6 carbon atoms or a condensate thereof.

MIXTURES OF FRICTION MODIFIERS TO PROVIDE GOOD FRICTION PERFORMANCE TO TRANSMISSION FLUIDS

BACKGROUND

[0001] The disclosed technology relates to additives and fluids for transmissions such as automatic transmission fluids.

[0002] In the automatic transmission marketplace, where there is rapid engineering change driven by the desire to reduce weight and increase transmission capacity, there is a desire for automatic transmission fluids that exhibit a high static coefficient of friction for improved clutch holding capacity. Continuously slipping torque converter clutches, for instance, impose exacting friction requirements on automatic transmission fluids (ATFs). The fluid must have a good friction versus sliding speed relationship, or an objectionable phenomenon called shudder will occur in the vehicle. Transmission shudder is a self-excited vibrational state commonly called "stick-slip" or "dynamic frictional vibration" generally occurring in slipping torque converter clutches. The friction characteristics of the fluid and material system, combined with the mechanical design and controls of the transmission, determine the susceptibility of the transmission to shudder. Plotting the measured coefficient of friction (μ) versus sliding speed (V), commonly called a μ-V curve, has been shown to correlate to transmission shudder. Both theory and experiments support the region of positive to slightly negative slope of this μ-V curve to correlate to good anti-shudder performance of transmission fluids. A fluid which allows the vehicle to operate without vibration or shudder is said to have good "anti-shudder" performance. The fluid should maintain those characteristics over its service lifetime. The longevity of the anti-shudder performance in the vehicle is commonly referred to as "anti-shudder durability." The variable speed friction tester (VSFT) measures the coefficient of friction with respect to sliding speed simulating the speeds, loads, and friction materials found in transmission clutches and correlates to the performance found in actual use. The procedures are well documented in the literature; see for example Society of Automotive Engineers publication #941883. It is also desirable to obtain good torque capacity in an automatic transmission with wet clutches by providing a lubricant with good frictional performance.

[0003] The combined requirements of high static coefficient of friction and durable positive slope are often incompatible with traditional ATF friction modifier technology which is extremely well described in the patent literature. Many of the commonly used friction modifiers result in a low static coefficient of friction and are not durable enough on positive slope to be of sufficient use.

[0004] U.S. Pat. No. 8,691,740, Vickerman et al., Apr. 8, 2014, discloses a composition suitable for use as a friction modifier for an automatic transmission, comprising an N-substituted oxalic acid bisamide or amide-ester containing at least two hydrocarbyl groups of 12 to 22 carbon atoms. Other, supplemental friction modifiers may also be present. Other materials that may also be present include antiwear agents such as, among others, various long-chain derivatives of hydroxy carboxylic acids, such as tartrates, tartramides, tartrimides, and citrates.

[0005] U.S. Pat. No. 8,148,306, Bartley et al., Apr. 3, 2012, discloses products of amines with hydroxy acid as friction modifiers suitable for automatic transmission fluids. An example is an amide or thioamide represented by the formula $R^1R^2N—C(X)R^3$ wherein X is O or S, R^1 and R^2 are each independently hydrocarbyl groups of at least 6 carbon atoms, and R^3 is a hydroxyalkyl group of 1 to 6 carbon atoms or a group formed by the condensation of said hydroxyalkyl group, through a hydroxyl group thereof, with an acylating agent.

[0006] U.S. Pat. No. 8,450,255, Sumiejski et al., May 28, 2013, discloses a friction modifier comprising at least two hydrocarbyl groups attached to a polar group or atom (e.g., a nitrogen atom), the friction modifier being (a) the reaction product of at least one carboxylic acid or equivalent with at least one aminoalcohol, (b) the reaction product of at least one carboxylic acid or equivalent with at least one polyamine, (c) an amide or thioamide represented by the formula $R^1R^2N—C(X)R^3$ wherein X is O or S, R^1 and R^2 are each independently hydrocarbyl groups of at least about 6 carbon atoms, and R^3 is a hydroxyalkyl group of 1 to about 6 carbon atoms or a group formed by the condensation of the hydroxyalkyl group, through a hydroxyl group thereof, with an acylating agent, (d) at least one tertiary amine containing two hydrocarbyl groups and a polyhydroxyl-containing alkyl group or a polyhydroxyl-containing alkoxyalkyl group, or (e) a mixture of two or more of (a), (b), (c) and (d).

SUMMARY

[0007] The disclosed technology provides a composition comprising: (a) an oil of lubricating viscosity; (b) 0.05 to 3.0 percent by weight (or 0.1 to 2 or 0.3 to 1 or about 0.7%) of an N-substituted oxalic acid bisamide or amide-ester containing at least two hydrocarbyl groups of about 12 to about 22 (or 12 to 20 or 12 to 18 or 12 to 16 or 12 to 14 or 14 to 20 or 14 to 18 or 14 to 16) carbon atoms carbon atoms; and (c) 0.05 to 3.0 percent by weight (or 0.1 to 2 or 0.3 to 1 or about 0.7%) of an amide or thioamide represented by the formula $R^1R^2N—C(X)R^3$ wherein X is O or S, R^1 and R^2 are each independently hydrocarbyl groups of at least 6 (or 8 to 24 or 10 to 18) carbon atoms, and R^3 is hydroxyalkyl group of 1 to 6 carbon atoms or a group formed by the condensation of said hydroxyalkyl group, through a hydroxyl group thereof, with an acylating agent.

[0008] In one embodiment the composition further comprises (d) 1 to 6 percent by weight (or 2 to 5.5 or 3 to 5 percent) of a dispersant component, comprising one or more succinimide dispersants, said dispersant component containing 0.05 to 1 percent by weight (or 0.1 to 0.5 or 0.2 to 0.4 percent) boron and having a TBN (oil free) of 40 to 90 (or 45 to 70 or 50 to 68).

[0009] It is desirable for an automatic transmission fluid to have a high quasi-static friction (described in greater detail below), ideally higher than the commonly attained value of about 0.092, without increasing the static friction (again described in greater detail below) to a value greater than about 0.135. Moreover, it is desired that these values be stable over time, that is, that they show minimal decrease in friction coefficient from the value at 500 test cycles extending out to 2500 or 10,000 cycles. The good performance should ideally persist over the range of transmission operating temperatures. Meeting these goals will help provide a fluid that has the properties of good torque capacity, anti-

shudder performance, and durability. The materials of the present invention will be suitable for meeting one or more of these objectives.

DETAILED DESCRIPTION OF THE INVENTION

[0010] Various features and embodiments will be described below by way of non-limiting illustration.

[0011] One component which is used in certain embodiments of the disclosed technology is 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.

[0012] Unrefined oils are those obtained directly from a natural or synthetic source generally without (or with little) further purification treatment.

[0013] 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.

[0014] 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.

[0015] 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.

[0016] 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; alkyl-benzenes (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.

[0017] 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.

[0018] 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", fourth Edition, AE-29, 2012, page 12-9, as well as in U.S. Pat. No. 8,216,448, column 1 line 57.

[0019] 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.

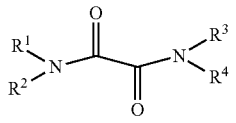
[0020] The oil of lubricating viscosity comprises an API Group I, Group II, Group III, Group IV, Group V oil or mixtures thereof.

[0021] 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.

[0022] 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.

[0023] 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.

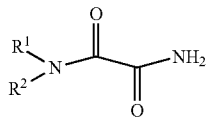
[0024] The present technology provides, as one component, an N-substituted oxalic acid bisamide or amide-ester containing at least two hydrocarbyl groups of 12 to 22 carbon atoms. In certain embodiments, the compound does not contain a primary amine group. (This may be absent in any of the embodiments whatever the detailed chemical nature, and in the presence or absence of other components.) This material is useful as a friction modifier, particularly for lubricating automatic transmissions. This component, as the bisamide, may be represented by the formula



[0025] In this structure at least two of the Rs are independently groups comprising a hydrocarbyl group of 1 to 22 carbon atoms and up to two of the R groups are hydrogen or a hydrocarbyl group of 10 or fewer carbon atoms. In other embodiments, one or more of the R groups may independently contain 12 to 20 or 12 to 18 or 12 to 16 or 12 to 14 or 14 to 20 or 14 to 18 or 14 to 16 carbon atoms. If there are two hydrocarbyl groups of 12 to 22 carbon atoms, they may be both on the same nitrogen or they may be on different nitrogen atoms; that is, either R^3 and R^4 or alternatively R^1 and R^4 may be hydrogen. The hydrocarbyl groups may be the same or different within a given molecule or within a mixture of molecules in the overall composition.

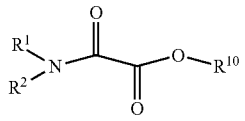
[0026] Since at least two of the groups R^1, R^2, R^3 and R^4 comprise a hydrocarbyl group of 12 to 22 carbon atoms, such groups may be such a hydrocarbyl group, for instance, an alkyl group of 12 to 22 carbon atoms. Alternatively, such groups may comprise such a hydrocarbyl group as a part of a larger structure. That is, such groups may have the general structure such as $R^5R^6N—R^9—$ where one or both of the R^5 and R^6 are hydrocarbyl groups of 12 to 22 carbons and optionally one of the R^5 and R^6 may be hydrogen or a shorter hydrocarbyl group. R^9 would be a hydrocarbylene linking group, such as methylene, ethylene, propylene, or butylene, and in some cases a 1-3-propylene group. In certain embodiments the alkyl groups of 12 to 22 carbon atoms may contain both linear and cyclic species, e.g., up to 20 percent cyclic species.

[0027] In some embodiments, therefore, the substituted oxalic acid bisamide may comprise a material of the structure about in which two of the groups R^1, R^2, R^4, and R^4 are independently alkyl groups of 12 to 22 carbon atoms. Such materials may have a structure such as



wherein each R^1 and R^2 is independently an alkyl group of, for example, 12 to 18 carbon atoms. Such a material may be obtained or obtainable by known methods such as the process of reacting a dialkylamine with an alkyl oxamate such as ethyl oxamate.

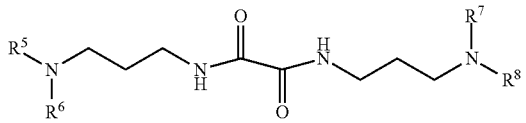
[0028] In another embodiment, the N-substituted oxalic acid bisamide or amide-ester comprises an amide-ester represented by the formula:



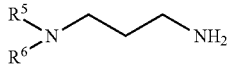
In this embodiment, each R^1 and R^2 may independently be a hydrocarbyl group of 12 to 22 carbon atoms, as defined elsewhere herein, and R^{10} may be a hydrocarbyl group of 1 to 22 carbon atoms. In certain embodiments, R^{10} is methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl, or t-butyl.

[0029] Long chain monoalkyl and dialkyl amines are commercially available. The hydrocarbyl group or groups of the amines may be described as long chain hydrocarbyl groups, by which is meant generally hydrocarbyl groups containing 12 to 22 carbon atoms. For monoalkyl amines, that is, primary amines, the hydrocarbyl group may comprise a mixture of individual groups on different molecules having a variety of carbon numbers falling generally within the range of 12 to 22 carbon atoms, although molecules with hydrocarbyl groups falling outside this range may also be present. If a mixture of hydrocarbyl groups is present, they may be primarily of even carbon number (e.g., 12, 14, 16, 18, 20, or 22) as is characteristic of groups derived from many naturally-occurring materials, or they may be a mixture of even and odd carbon numbers or, alternatively, an odd carbon number or a mixture of odd numbers. They may be branched, linear, or cyclic and may be saturated or unsaturated, or combinations thereof. In certain embodiments the hydrocarbyl groups may contain 16 to 18 carbon atoms, and sometimes predominantly 16 or predominantly 18. Specific examples include mixed "coco" groups, that is, cocoalkyl groups, from cocoamine (predominantly C12 and C14 amines) and mixed "tallow" groups, that is, tallowalkyl groups, from tallowamine (predominantly C16 and C18 groups), and isostearyl groups. The tallow groups may optionally be hydrogenated. Likewise, dialkyl amines, that is, secondary amine, are commercially available, which may have one long chain alkyl group as described above and one short chain alkyl group of 1 to 10 carbon atoms, or which may have two long chain alkyl groups. Examples of the latter include dicocoamine (available as Armeen 2C™), and ditallowamine. Others, such is isostearyl-coco amine may be synthesized generally as described for preparative example B below.

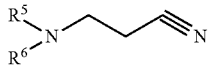
[0030] It is also contemplated that two or more of the groups R^1, R^2, R^3, and R^4 may be independently N-hydrocarbyl-substituted or di-substituted aminoalkyl groups wherein the hydrocarbyl substituent or substituents contain 12 to 22 carbon atoms and the alkyl moieties contain 1 to 4 carbon atoms. A formula representing this general structure may be represented by



wherein R^5 and R^7 are independently a hydrocarbyl group of about 12 to about 22 carbon atoms and R^6 and R^8 are independently hydrogen or a hydrocarbyl group of 1 to 22 carbon atoms, e.g., a hydrocarbyl group of 10 or fewer carbon atoms or a hydrocarbyl group of about 12 to about 22 carbon atoms. Diamines suitable for preparing such products include those in the "Duomeen" series, available from Akzo, having a general structure such as

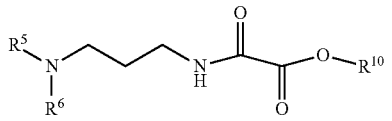


Such polyamines may be prepared by the addition of the monoamine R^3R^4NH to acrylonitrile, to prepare the alkyl nitrile amine,



followed by catalytic reduction of the nitrile group using, e.g., H_2 over Pd/C catalyst, to give the diamine.

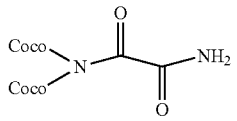
[0031] In a related embodiment, the N-substituted oxalic acid bisamide or amide-ester may comprise an amide-ester represented by the formula:



wherein R^5 and R^6 are independently hydrocarbyl groups of 12 to 22 carbon atoms as defined above and R^{10} may be a hydrocarbyl group of 1 to 22 carbon atoms, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl, or t-butyl.

[0032] Some specific examples of the materials for this component of the disclosed technology include those represented by the following structures:

(I)



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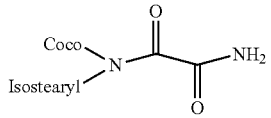

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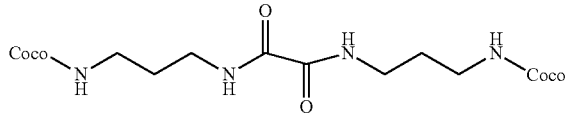

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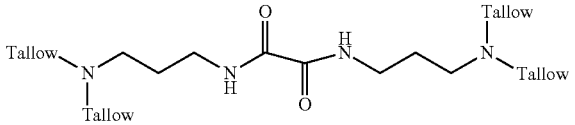

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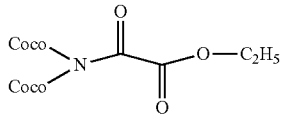

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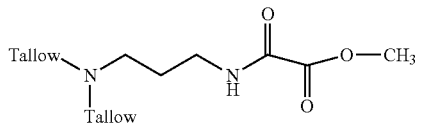


where coco and tallow are as defined above and isostearyl represents the carbon architecture of isostearic acid.

[0033] The bisamides disclosed herein may be prepared by known techniques such as reaction of the appropriate amine with oxalic acid or a reactive equivalent thereof, such as ethyl oxamide or dimethyl oxalate, as illustrated in the preparative examples of U.S. Pat. No. 8,691,740. The amide-esters may be prepared by reaction of the appropriate amine with a dialkyl oxalate, using a controlled amount of amine (approximating 1:1 molar ratio) or by reacting the amine with the half ester-half chloride (e.g., ethyl 2-chloro-2-oxo-acetate). Minor amounts of the amide-esters may be formed along with the preparation of the bisamides, and the relative amounts may be adjusted by known techniques.

[0034] The amount of the oxalic acid bisamide or amide ester in a fully formulated lubricant may be 0.05 to 3 percent by weight, or 0.1 to 2 percent or 0.3 to 1 percent or about 0.7 percent by weight.

[0035] Another component of the disclosed technology, component (c) is an amide or thioamide (at least one amide or thioamide) represented by the formula $R^1R^2N—C(X)R^3$ wherein X is O or S, R^1 and R^2 are each independently hydrocarbyl groups of at least about 6 (or 8 to 24 or 10 to 18) carbon atoms, and R^3 is hydroxyalkyl group of 1 to about 6 carbon atoms or a group formed by the condensation of said hydroxyalkyl group, through a hydroxyl group thereof, with an acylating agent. This component can be viewed as the condensation product of a secondary amine with a hydroxy acid or thioacid (described below), which can also serve as a friction modifier. The amine will contain substituent hydrocarbyl groups, for example, alkyl groups. The amine may be represented by the formula R^1R^2NH wherein R^1 and R^2 are each independently a hydrocarbyl group of at least 6 carbon atoms (e.g., 6 to 30 carbon atoms or 8 to 24 carbon atoms or 10 to 20 or 10 to 18 or 12 to 16). The R^1 and R^2 groups may be linear or branched, saturated or unsaturated, aliphatic, aromatic, or mixed aliphatic and aromatic. In certain embodiments they are alkyl groups and in particular linear alkyl groups. The R^1 and R^2 groups may be the same or different. A commercial example of a suitable amine is sold under the trade name Armeen 2C™, which is believed to have two C_{12} alkyl groups. In one embodiment the amine comprises di-cocoalkyl amine or homologous amines. Di-cocoalkyl amine (or di-cocoamine) is a secondary amine in which the two R groups in the above formula are predominantly C_{12} groups (although amounts of C_8 through C_{18} are generally also present), derived from coconut oil. In certain embodiments, one both of the groups R^1 and R^2 may be 2-ethylhexyl groups. In one embodiment, the amine moiety (or "substituted nitrogen moiety") $R^1R^2N—$ of the amide or thioamide comprises a (2-ethylhexyl)(hydrogenated tallow) amine moiety, where the "hydrogenated tallow" moiety is derived from tallow, having predominantly C_{18} groups. It is understood that commercially available dialkylamines will contain certain amounts of monoalkylamines and/or trialkylamines, and products formed from such commercial materials are contemplated to be within the scope of the present inventions (recognizing that any trialkylamine component would not be expected to be reactive to form an amide.)

[0036] The amide or thioamide of the present invention may be viewed as a condensation product of the above-described amine with a hydroxy acid or hydroxy thioacid or reactive equivalent thereof. In the instance where X is O, the amide is a derivative of a hydroxy acid which can be represented by the formula R^3COOH. In the hydroxy acid (or hydroxy thioacid, as the case may be) R^3 is a hydroxyalkyl group of 1 to 6 carbon atoms or a group formed by the condensation of such hydroxyalkyl group, through the hydroxyl group thereof, with an acylating agent (which may include a sulfur-containing acylating agent). That is, the —OH group on R^3 is itself potentially reactive and may condense with additional acidic materials or their reactive equivalents to form, e.g., esters. Thus, the hydroxy acid may be condensed, for instance, with one or more additional molecules of acid such as glycolic acid. An example of a

suitable hydroxy acid is glycolic acid, that is, hydroxyacetic acid, HO—CH_2—COOH. Glycolic acid is readily commercially available, either in substantially neat form or as a 70% solution in water. When R^3 contains more than 1 carbon atom, the hydroxy group may be on the 1 carbon (α) or on another carbon in the chain (e.g., β or ω). The carbon chain itself may be linear, branched, or cyclic.

[0037] The amount of component (c) in the compositions of the present invention can be 0.05 to 3.0 percent by weight of the finished fluid formulation. Alternative amounts include 0.1 percent to 2 percent, or 0.3 percent to 1 percent, or about 0.7 percent by weight. In a concentrate, the amounts will be proportionately higher.

[0038] Another component that may be present is a dispersant component, which may comprise either a single dispersant species or multiple dispersant species. The dispersant may be described as "other than a compound as described above" in the event that some of the compounds described above may exhibit some dispersant characteristics. Examples of "carboxylic dispersants," as an example, are described in many U.S. Patents including the following: U.S. Pat. Nos. 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, Re 26,433, and 6,165,235.

[0039] Succinimide dispersants, a species of carboxylic dispersants, are prepared by the reaction of a hydrocarbyl-substituted succinic anhydride (or reactive equivalent thereof, such as an acid, acid halide, or ester) with an amine, as described above. The hydrocarbyl substituent group generally contains an average of at least 8, or 20, or 30, or 35 up to 350, or to 200, or to 100 carbon atoms. In one embodiment, the hydrocarbyl group is derived from a polyalkene. Such a polyalkene can be characterized by an $\overline{M_n}$ (number average molecular weight, which may also be written as M_n) of at least 500. Generally, the polyalkene is characterized by an $\overline{M_n}$ of 500 or 700 or 800 or 900, up to 5000 or to 2500 or to 2000 or to 1500. In another embodiment $\overline{M_n}$ varies from 500 or 700 or 800, to 1200 or 1300. In one embodiment the polydispersity ($\overline{M_w}/\overline{M_n}$) is at least 1.5.

[0040] The polyalkenes include homopolymers and interpolymers of polymerizable olefin monomers of 2 to 16 or to 6, or 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 polymer is a homo-polymer. An example of a polymer is a polybutene. In one instance about 50% of the polybutene is derived from isobutylene. The polyalkenes can be prepared by conventional procedures.

[0041] In one embodiment, the succinic acylating agents are prepared by reacting a polyalkene with an excess of maleic anhydride to provide substituted succinic acylating agents wherein the number of succinic groups for each equivalent weight of substituent group is at least 1.3, e.g., 1.5, or 1.7, or 1.8. The maximum number of succinic groups per substituent group generally will not exceed 4.5, or 2.5, or 2.1, or 2.0. The preparation and use of substituted succinic acylating agents wherein the substituent is derived from such polyolefins are described in U.S. Pat. No. 4,234,435. The succinic acylating agents may be prepared either by a chlorine-assisted route or by a thermal ("ene") reaction. These synthetic routes are more fully described in U.S. Pat. No. 7,615,521, see columns 3-5.

[0042] The substituted succinic acylating agent can be reacted with an amine, including those amines described above and heavy amine products known as amine still bottoms. The amount of amine reacted with the acylating agent is typically an amount to provide a mole ratio of CO:N of 1:2 to 1:0.25, or 1:2 to 1:0.75 or 1:1.4 to 1:0.95. In another embodiment the CO:N ratio may be 1:0.2 to 1:0.3, and for this or any of the other ratios the resulting dispersant may be further treated with, e.g., dimercaptothiadiazole. If the amine is a primary amine, complete condensation to the imide can occur. Varying amounts of amide product, such as the amidic acid, may also be present. If the reaction is, rather, with an alcohol, the resulting dispersant will be an ester dispersant. If both amine and alcohol functionality are present, whether in separate molecules or in the same molecule (as in the above-described condensed amines), mixtures of amide, ester, and possibly imide functionality can be present. These are the so-called ester-amide dispersants.

[0043] "Amine dispersants" are reaction products of relatively high molecular weight aliphatic or alicyclic halides and amines, such as polyalkylene polyamines. Examples thereof are described in the following U.S. Pat. Nos. 3,275,554, 3,438,757, 3,454,555, and 3,565,804.

[0044] "Mannich dispersants" are the reaction products of alkyl phenols in which the alkyl group contains at least 30 carbon atoms with aldehydes (especially formaldehyde) and amines (especially polyalkylene polyamines). The materials described in the following U.S. Patents are illustrative: U.S. Pat. Nos. 3,036,003, 3,236,770, 3,414,347, 3,448,047, 3,461,172, 3,539,633, 3,586,629, 3,591,598, 3,634,515, 3,725,480, 3,726,882, and 3,980,569.

[0045] Post-treated dispersants may also be a part of the disclosed technology. They are generally obtained by reacting carboxylic, amine or Mannich dispersants with reagents such as urea, thiourea, carbon disulfide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, nitriles, epoxides, boron compounds such as boric acid (to give "borated dispersants"), phosphorus compounds such as phosphorus acids or anhydrides, or 2,5-dimercaptothiadiazole (DMTD). In certain embodiments one or more of the individual dispersants may be post-treated with boron or DMTD or with both boron and DMTD. Exemplary materials of these kinds are described in the following U.S. Pat. Nos. 3,200,107, 3,282,955, 3,367,943, 3,513,093, 3,639,242, 3,649,659, 3,442,808, 3,455,832, 3,579,450, 3,600,372, 3,702,757, and 3,708,422.

[0046] In one embodiment, the dispersant component will be present in an amount of 1 to 6 percent by weight of the lubricant formulation, or alternatively 2 to 5.5 or 3 to 5 percent. These amounts represent the total of the individual dispersants that may be present, if more than one species is present. In one embodiment, the dispersant component comprises one or more succinimide dispersants. In one embodiment, the succinimide dispersant or dispersants will be borated, that is, boron-containing or reacted with a boron species or borating agent, such that the dispersant component as a whole will contain 0.05 to 1 percent by weight boron, or alternatively, 0.1 to 0.7 percent or 0.2 to 0.6 percent. If multiple succinimide dispersants are present, the boron may be contained on or associated with one or more of the dispersants while one or more of the other dispersants will not be borated. (The form of the reaction or association of the boron with the dispersant species is not intended to be

limiting.) The TBN of the overall dispersant component, may be 40 to 100, or 40 to 95, or 40 to 90, or 45 to 70, or 50 to 68, as expressed on an oil-free basis. (TBN, or total base number, is the quantity of acid, expressed in milligrams of KOH per gram of sample, that is required to titrate a sample to the specified end point, and is defined in AS™ D-794.)

[0047] In one embodiment the dispersant component comprises a first borated succinimide dispersant component (that is, one more individual species) having a boron content of about 0.1 to about 1 percent by weight, or 0.3 to 0.8, or 0.5 to 0.7 percent by weight and a TBN, in certain embodiments, of 4 to 90 or 50 to 70. In this embodiment the dispersant component will also comprise a second dispersant component (one or more individual species) that is not borated or is borated to a lesser extent than that of the first dispersant component. The second succinimide dispersant component may thus have a boron content of less than 0.1 percent by weight, or less than 0.05 or 0.01 percent by weight, or may be free of boron. The TBN of the second succinimide dispersant component may be, in certain embodiments, 40 to 80 or 40 to 70 or 50 to 60.

[0048] In certain embodiments the dispersant component comprises more than one individual dispersant species, e.g., more than one individual succinimide dispersant species. One or more of these may be a succinimide dispersant that is reacted (or post-treated) with at least one of terephthalic acid, or an inorganic phosphorus compound, or a dimercaptothiadiazole compound. For example, in one embodiment there may be three individual succinimide dispersant species present: one may be treated with boron and terephthalic acid; a second may be treated with boron, terephthalic acid, and dimercaptothiadiazole, and the third may be treated with none of the post-treatment agents. Many such combinations of individual dispersants will be apparent to the person of skill in the art; such combinations may be selected such that the specified amounts of boron are met for the overall dispersant component.

[0049] Other additives may be present in the lubricants of the disclosed technology. One component frequently used is a viscosity modifier, also referred to as a viscosity improver. Viscosity modifiers (VM) and dispersant viscosity modifiers (DVM) are well known. Examples of VMs and DVMs may include polymethacrylates, polyacrylates, polyolefins, styrene-maleic ester copolymers, and similar polymeric substances including homopolymers, copolymers, and graft copolymers. The DVM may comprise a nitrogen-containing methacrylate polymer, for example, a nitrogen-containing methacrylate polymer derived from methyl methacrylate and dimethylaminopropylamine.

[0050] Examples of commercially available VMs, DVMs and their chemical types may include the following: polyisobutylenes (such as Indopol™ from BP Amoco or Parapol™ from ExxonMobil); olefin copolymers (such as Lubrizol™ 7060, 7065, and 7067 from Lubrizol and Lucant™ HC-2000L and HC-600 from Mitsui); hydrogenated styrene-diene copolymers (such as Shellvis™ 40 and 50, from Shell and LZ® 7308, and 7318 from Lubrizol); styrene/maleate copolymers, which are dispersant copolymers (such as LZ® 3702 and 3715 from Lubrizol); polymethacrylates, some of which have dispersant properties (such as those in the Viscoplex™ series from RohMax, the Hitec™ series from Afton, and LZ 7702™, LZ 7727™, LZ 7725™ and LZ 7720C™ from Lubrizol); olefin-graft-polymethacrylate polymers (such as Viscoplex™ 2-500 and 2-600 from RohMax); and hydrogenated polyisoprene star polymers (such as Shellvis™ 200 and 260, from Shell). Also included are Asteric™ polymers from Lubrizol (methacrylate polymers with radial or star architecture). Viscosity modifiers that may be used are described in U.S. Pat. Nos. 5,157,088, 5,256,752 and 5,395,539. The VMs and/or DVMs may be used in the functional fluid at a concentration of up to 20% by weight. Concentrations of 1 to 12%, or 3 to 10% by weight may be used.

[0051] Another component that may be used in the composition used in the present technology is a supplemental friction modifier. These friction modifiers are well known to those skilled in the art. A list of friction modifiers that may be used is included in U.S. Pat. Nos. 4,792,410, 5,395,539, 5,484,543 and 6,660,695. U.S. Pat. No. 5,110,488 discloses metal salts of fatty acids and especially zinc salts, useful as friction modifiers. A list of supplemental friction modifiers that may be used may include:

fatty phosphites	borated alkoxylated fatty amines
fatty acid amides	metal salts of fatty acids
fatty epoxides	sulfurized olefins
borated fatty epoxides	fatty imidazolines
fatty amines other than the fatty amines discussed above	condensation products of carboxylic acids and polyalkylene-polyamines
glycerol esters	metal salts of alkyl salicylates
borated glycerol esters	amine salts of alkylphosphoric acids
alkoxylated fatty amines	ethoxylated alcohols
oxazolines	imidazolines
hydroxyalkyl amides	polyhydroxy tertiary amines
and mixtures of two or more thereof.	

[0052] Representatives of each of these types of friction modifiers are known and are commercially available. For instance, fatty phosphites may be generally of the formula $(RO)_2PHO$ or (RO)(HO)PHO where R may be an alkyl or alkenyl group of sufficient length to impart oil solubility. Suitable phosphites are available commercially and may be synthesized as described in U.S. Pat. No. 4,752,416.

[0053] Borated fatty epoxides that may be used are disclosed in Canadian Patent No. 1,188,704. These oil-soluble boron-containing compositions may be prepared by reacting a boron source such as boric acid or boron trioxide with a fatty epoxide which may contain at least 8 carbon atoms. Non-borated fatty epoxides may also be useful as supplemental friction modifiers.

[0054] Borated amines that may be used are disclosed in U.S. Pat. No. 4,622,158. Borated amine friction modifiers (including borated alkoxylated fatty amines) may be prepared by the reaction of a boron compounds, as described above, with the corresponding amines, including simple fatty amines and hydroxy containing tertiary amines. The amines useful for preparing the borated amines may include commercial alkoxylated fatty amines known by the trademark "ETHOMEEN" and available from Akzo Nobel, such as bis[2-hydroxyethyl]-cocoamine, polyoxyethylene[10]cocoamine, bis[2-hydroxyethyl]-soyamine, bis[2-hydroxyethyl]-tallowamine, polyoxyethylene-[5]tallowamine, bis[2-hydroxyethyl]oleylamine, bis[2-hydroxyethyl] octadecylamine, and polyoxyethylene[15]-octadecylamine. Such amines are described in U.S. Pat. No. 4,741,848.

[0055] Alkoxylated fatty amines and fatty amines themselves (such as oleylamine) may be useful as friction modifiers. These amines are commercially available.

[0056] Both borated and unborated fatty acid esters of glycerol may be used as friction modifiers. Borated fatty acid esters of glycerol may be prepared by borating a fatty acid ester of glycerol with a boron source such as boric acid. Fatty acid esters of glycerol themselves may be prepared by a variety of methods well known in the art. Many of these esters, such as glycerol monooleate and glycerol tallowate, are manufactured on a commercial scale. Commercial glycerol monooleates may contain a mixture of 45% to 55% by weight monoester and 55% to 45% by weight diester.

[0057] Fatty acids may be used in preparing the above glycerol esters; they may also be used in preparing their metal salts, amides, and imidazolines, any of which may also be used as friction modifiers. The fatty acids may contain 6 to 24 carbon atoms, or 8 to 18 carbon atoms. A useful acid may be oleic acid.

[0058] The amides of fatty acids may be those prepared by condensation with ammonia or with primary or secondary amines such as diethylamine and diethanolamine. Fatty imidazolines may include the cyclic condensation product of an acid with a diamine or polyamine such as a polyethylenepolyamine. In one embodiment, the friction modifier may be the condensation product of a C8 to C24 fatty acid with a polyalkylene polyamine, for example, the product of isostearic acid with tetraethylenepentamine. The condensation products of carboxylic acids and polyalkyleneamines may be imidazolines or amides.

[0059] The fatty acid may also be present as its metal salt, e.g., a zinc salt. These zinc salts may be acidic, neutral, or basic (overbased). These salts may be prepared from the reaction of a zinc containing reagent with a carboxylic acid or salt thereof. A useful method of preparation of these salts is to react zinc oxide with a carboxylic acid. Useful carboxylic acids are those described hereinabove. Suitable carboxylic acids include those of the formula RCOOH where R is an aliphatic or alicyclic hydrocarbon radical. Among these are those wherein R is a fatty group, e.g., stearyl, oleyl, linoleyl, or palmityl. Also suitable are the zinc salts wherein zinc is present in a stoichiometric excess over the amount needed to prepare a neutral salt. Salts wherein the zinc is present from 1.1 to 1.8 times the stoichiometric amount, e.g., 1.3 to 1.6 times the stoichiometric amount of zinc, may be used. These zinc carboxylates are known in the art and are described in U.S. Pat. 3,367,869. Metal salts may also include calcium salts. Examples may include overbased calcium salts.

[0060] Sulfurized olefins are also 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. Pat. Nos. 4,957,651 and 4,959,168. Described therein is a cosulfurized mixture of 2 or more reactants selected from the group consisting of at least one fatty acid ester of a polyhydric alcohol, at least one fatty acid, at least one olefin, and at least one fatty acid ester of a monohydric alcohol. The olefin component may be an aliphatic olefin, which usually will contain 4 to 40 carbon atoms. Mixtures of these olefins are commercially available. The sulfurizing agents useful in the process of the present invention include elemental sulfur, hydrogen sulfide, sulfur halide plus sodium sulfide, and a mixture of hydrogen sulfide and sulfur or sulfur dioxide.

[0061] Metal salts of alkyl salicylates include calcium and other salts of long chain (e.g. C12 to C16) alkyl-substituted salicylic acids.

[0062] Amine salts of alkylphosphoric acids include salts of oleyl and other long chain esters of phosphoric acid, with amines such as tertiary-aliphatic primary amines, sold under the trade name Primene™.

[0063] The amount of the supplemental friction modifier, if it is present, may be 0.1 to 1.5 percent by weight of the lubricating composition, such as 0.2 to 1.0 or 0.25 to 0.75 percent. In some embodiments, however, the amount of the supplemental friction modifier is present at less than 0.2 percent or less than 0.1 percent by weight, for example, 0.01 to 0.1 percent.

[0064] The compositions of the present technology can also include a detergent. Detergents as used herein are metal salts of organic acids. The organic acid portion of the detergent may be a sulfonate, carboxylate, phenate, or salicylate. The metal portion of the detergent may be an alkali or alkaline earth metal. Suitable metals include sodium, calcium, potassium, and magnesium. Typically, the detergents are overbased, meaning that there is a stoichiometric excess of metal base over that needed to form the neutral metal salt.

[0065] Suitable overbased organic salts include the sulfonate salts having a substantially oleophilic character and which are formed from organic materials. Organic sulfonates are well known materials in the lubricant and detergent arts. The sulfonate compound should contain on average 10 to 40 carbon atoms, such as 12 to 36 carbon atoms or 14 to 32 carbon atoms on average. Similarly, the phenates, salicylates, and carboxylates have a substantially oleophilic character.

[0066] While the present invention allows for the carbon atoms to be either aromatic or in paraffinic configuration, in certain embodiments alkylated aromatics are employed. While naphthalene based materials may be employed, the aromatic of choice is the benzene moiety.

[0067] Suitable compositions thus include an overbased monosulfonated alkylated benzene such as a monoalkylated benzene. Typically, alkyl benzene fractions are obtained from still bottom sources and are mono- or di-alkylated. It is believed, in the present invention, that the mono-alkylated aromatics are superior to the dialkylated aromatics in overall properties.

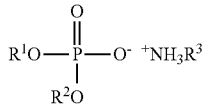
[0068] It is sometimes desired that a mixture of mono-alkylated aromatics (benzene) be utilized to obtain the mono-alkylated salt (benzene sulfonate) in the present invention. The mixtures wherein a substantial portion of the composition contains polymers of propylene as the source of the alkyl groups may assist in the solubility of the salt. The use of mono-functional (e.g., mono-sulfonated) materials avoids crosslinking of the molecules with less precipitation of the salt from the lubricant. It is also frequently desired to use an alkylated benzene prepared by alkylation with an α-olefin.

[0069] The salt may be "overbased." By overbasing, it is meant that a stoichiometric excess of the metal base be present over that required for the anion of the neutral salt. The excess metal from overbasing has the effect of neutralizing acids which may build up in the lubricant. Typically, the excess metal will be present over that which is required to neutralize the anion at in the ratio of up to 30:1, such as 5:1 to 18:1 on an equivalent basis. Overbased materials are often carbonated, that is, reacted with carbon dioxide, to aid in the acceptance of an equivalent excess of metal.

[0070] The amount of the overbased salt utilized in the composition is typically 0.025 to 3 weight percent on an oil free basis, such as 0.1 to 1.0 percent. In other embodiments, the final lubricating composition may contain no detergent or substantially no detergent or only a low amount of detergent. That is, for a calcium overbased detergent for instance, the amount may be such as to provide less than 250 parts per million calcium, e.g., 0 to 250 or 1 to 200 or 10 to 150 or 20 to 100 or 30 to 50 parts per million calcium, or less than any of the foregoing non-zero amounts. This is in contrast with more conventional formulations which may contain sufficient calcium detergent to provide 300 to 600 ppm calcium. The overbased salt usually has up to about 50% oil and has a TBN range of 10-800 or 10-600 on an oil free basis. Borated and non-borated overbased detergents are described in U.S. Pat. Nos. 5,403,501 and 4,792,410.

[0071] The compositions of the present invention can also include at least one phosphorus acid, phosphorus acid salt, phosphorus acid ester or derivative thereof including sulfur-containing analogs in the amount of 0.002-1.0 weight percent. The phosphorus acids, salts, esters or derivatives thereof include phosphoric acid, phosphorous acid, phosphorus acid esters or salts thereof, phosphites, phosphorus-containing amides, phosphorus-containing carboxylic acids or esters, phosphorus-containing ethers, and mixtures thereof.

[0072] In one embodiment, the phosphorus acid, ester or derivative can be an organic or inorganic phosphorus acid, phosphorus acid ester, phosphorus acid salt, or derivative thereof. The phosphorus acids include the phosphoric, phosphonic, phosphinic, and thiophosphoric acids including dithiophosphoric acid as well as the monothiophosphoric, thiophosphinic and thiophosphonic acids. One group of phosphorus compounds are alkylphosphoric acid mono alkyl primary amine salts as represented by the formula



where R^1, R^2, R^3 are alkyl or hydrocarbyl groups or one of R^1 and R^2 can be H. The materials can be a 1:1 mixture of dialkyl and monoalkyl phosphoric acid esters. Compounds of this type are described in U.S. Pat. No. 5,354,484.

[0073] Eighty-five percent phosphoric acid is a suitable material for addition to the fully-formulated compositions and can be included at a level of 0.01-0.3 weight percent based on the weight of the composition, such as 0.03 to 0.2 or to 0.1 percent.

[0074] Other phosphorus-containing materials that may be present include dialkylphosphites (sometimes referred to as dialkyl hydrogen phosphonates) such as dibutyl phosphite. Yet other phosphorus materials include phosphorylated hydroxy-substituted triesters of phosphorothioic acids and amine salts thereof, as well as sulfur-free hydroxy-substituted di-esters of phosphoric acid, sulfur-free phosphorylated hydroxy-substituted di- or tri-esters of phosphoric acid, and amine salts thereof. These materials are further described in U.S. patent application US 2008-0182770.

[0075] Other materials can optionally be included in the compositions of the present technology, provided that they are not incompatible with the afore-mentioned required components or specifications. Such materials include antioxidants (that is, oxidation inhibitors), including hindered phenolic antioxidants, secondary aromatic amine antioxidants such as dinonyldiphenylamine as well as such well-known variants as monononyldiphenylamine and diphenylamines with other alkyl substituents such as mono- or di-octyl, sulfurized phenolic antioxidants, oil-soluble copper compounds, phosphorus-containing antioxidants, and organic sulfides, disulfides, and polysulfides such as 2-hydroxyalkyl, alkyl thioethers or 1-t-dodecylthio-2-propanol or sulfurized 4-carbobutoxycyclohexene or other sulfurized olefins. Also included may be corrosion inhibitors such as tolyl triazole and dimercaptothiadiazole and oil-soluble derivatives of such materials. Other optional components include seal swell compositions, such as isodecyl sulfolane or phthalate esters, which are designed to keep seals pliable. Also permissible are pour point depressants, such as alkylnaphthalenes, polymethacrylates, vinyl acetate/fumarate or/maleate copolymers, and styrene/maleate copolymers. Other materials are anti-wear agents such as zinc dialkyldithiophosphates, tridecyl adipate, and various long-chain derivatives of hydroxy carboxylic acids, such as tartrates, tartramides, tartrimides, and citrates as described in US Application 2006-0183647. These optional materials are known to those skilled in the art, are generally commercially available, and are described in greater detail in published European Patent Application 761,805. Also included can be known materials such as corrosion inhibitors (e.g., tolyltriazole, dimercaptothiadiazoles), dyes, fluidizing agents, odor masking agents, and antifoam agents. Organic borate esters and organic borate salts can also be included.

[0076] The above components can be in the form of a fully-formulated lubricant or in the form of a concentrate within a smaller amount of lubricating oil. If they are present in a concentrate, their concentrations will generally be directly proportional to their concentrations in the more dilute form in the final blend.

[0077] 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:

[0078] 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);

[0079] 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 sulfoxy);

[0080] 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 encompass substituents as pyridyl, furyl, thienyl and imidazolyl. Heteroatoms include sulfur,

oxygen, and nitrogen. In general, no more than two, or no more than one, heteroatom will be present for every ten carbon atoms in the hydrocarbyl group; typically, there will be no heteroatoms in the hydrocarbyl group.

[0081] 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.

[0082] The amount of the phosphorus-containing compound or compounds in the compositions of the present invention may, in certain embodiments, be 0.01 to 2 percent by weight, alternatively, 0.02 to 1 or 0.05 to 0.5 percent by weight. Correspondingly, the total phosphorus content of the compositions may be, for instance 0.01 to 0.3 percent by weight or 0.003 or 0.03 to 0.20 percent by weight or 0.05 to 0.15 percent by weight, depending, of course, on the phosphorus content of the particular compounds that are selected. In certain embodiments, the formulations of the disclosed technology may contain, or may not contain, phosphorus in the form of a zinc dialkyldithiophosphate. In some embodiments there is less than 0.1 percent or 0.01 percent by weight of a zinc dialkyldithiophosphate. Such materials may be represented by the formula

$$[(R^8O)(R^9O)P(=S)—S—]_2—Zn$$

where R^8 and R^9 are independently hydrocarbyl groups such as alkyl, cycloalkyl, aralkyl or alkaryl groups having 3 to 20 carbon atoms, or 3 to 16 or 3 to 12 carbon atoms. They are typically prepared by the reaction of one or a mixture of alcohols R^8OH and R^9OH, which can be a mixture of a secondary alcohol and a primary alcohol, for instance, isopropanol and 4-methyl-2-pentanol, with phosphorus pentasulfide to give the acid, followed by neutralization with zinc oxide.

[0083] When the composition is in the form of a concentrate, the relative amounts of the various components will be proportionately increased, for instance, by a factor such as 10 (except for the oil of lubricating viscosity, which will be correspondingly decreased).

[0084] As used herein, the term "condensation product" is intended to encompass esters, amides, imides and other such materials that may be prepared by a condensation reaction of an acid or a reactive equivalent of an acid (e.g., an acid halide, anhydride, or ester) with an alcohol or amine, irrespective of whether a condensation reaction is actually performed to lead directly to the product. Thus, for example, a particular ester may be prepared by a transesterification reaction rather than directly by a condensation reaction. The resulting product is still considered a condensation product.

[0085] The amount of each chemical component described is presented exclusive of any solvent or diluent oil, which may be customarily present in the commercial material, that is, on an active chemical basis, unless otherwise indicated. However, 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.

[0086] 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, including aliphatic, alicyclic, and aromatic substituents; 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; and hetero substituents, that is, substituents which similarly have a predominantly hydrocarbon character but contain other than carbon in a ring or chain. A more detailed definition of the term "hydrocarbyl substituent" or "hydrocarbyl group" is found in paragraphs [0137] to [0141] of published application US 2010-0197536 .

[0087] 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.

[0088] The invention herein is useful for providing good friction performance to transmission fluids, which may be better understood with reference to the following examples.

EXAMPLES

[0089] The following formulations are prepared for testing:

[0090] A Starting Lubricant, representing a typical or conventional lubricant for an automatic transmission, is prepared containing the following (each of the components other than oil being presented on an oil-free basis, and all percentages being by weight):

[0091] Oil(s) of lubricating viscosity (in an amount to total 100%);

[0092] Polymethacrylate viscosity modifier, 3.4%

[0093] Pour point depressant, 0.2%

[0094] Antiwear agents: 0.28%, including dibutyl phosphite and di(long chain alkyl) phosphite

[0095] Succinimide dispersants: 4.28%, including borated succinimide dispersant(s) and dimercaptothiadiazole-treated dispersant(s)

[0096] Seal swell agent: 0.5%

[0097] Corrosion inhibitors: 0.06%

[0098] Antioxidants: 1.1%, including a hindered phenolic ester antioxidant and an aromatic amine antioxidant

[0099] Detergents: 0.18% overbased calcium sulfonate detergents (low and high TBN materials)

[0100] Conventional friction modifier package: 0.61%, including phosphoric acid (85%), borate ester, polyoxyethylene tallowalkylamine, hydroxyethyl heptadecenyl imidazoline, and a long chain hydroxyalkylamine

[0101] Small amounts of other conventional additives (including antifoam agents, dye and fragrance additive(s))

[0102] Example 1 also contains, within the Starting Lubricant, 0.70 percent by weight of the condensation product (amide) of dicocoamine and glycolic acid and 0.70 percent by weight of the bisamide formed by reaction of dimethyl oxalate with and N,N-di(C18 alkyl) propylene-1,3-diamine. (The C18 alkyl groups are characteristic of the structure of isostearic acid.)

Example 2

[0103] The same Starting Lubricant is used as for Example 1, except that the amount of the long chain hydroxyalkylamine is less by an amount of 0.01%, the antioxidant component further comprises 0.4% of a substituted hydrocarbyl sulfide, and the specific small amounts of the other conventional additives are slightly different. The formulation of Example 2 contains, within the modified Starting Lubricant, 0.70 percent by weight of the bisamide formed by reaction of dimethyl oxalate with and N,N-di(C18 alkyl) propylene-1,3-diamine. (The C18 alkyl groups are characteristic of the structure of isostearic acid.)

[0104] For Reference Examples B (138), C (129), and D (123), similar starting lubricants are used, which, however, differ in amounts and compositions of certain of the specific components and amounts, generally indicated as follows:

Reference Example B (138)

[0105] amount of antiwear component: 0.28%

[0106] amount of dispersant component: 3.71%

[0107] amount of antioxidant component: 1.5%

[0108] amount of detergent component: 0.29%

[0109] amount of conventional friction modifier component: 0.51%

Reference Example B (138) also contains 0.60 percent by weight of the bisamide formed by reaction of dimethyl oxalate with and N,N-di(C18 alkyl) propylene-1,3-diamine.

Reference Example C (129)

[0110] amount of antiwear component: 0.2%

[0111] amount of dispersant component: 3.77%

[0112] amount of corrosion inhibitor component: 0.11%

[0113] amount of antioxidant component: 1.5%

[0114] amount of detergent component: 0.23%

[0115] amount of conventional friction modifier component: 0.62%

Reference Example C (129) also contains 0.75% by weight of the condensation product (amide) of dicocoamine and glycolic acid.

Reference Example D (123)

[0116] amount of antiwear component: 0.2%

[0117] amount of dispersant component: 3.99%

[0118] amount of corrosion inhibitor component: 0.12%

[0119] amount of antioxidant component: 1.5%

[0120] amount of detergent component: 0.10%

[0121] amount of conventional friction modifier component: 0.57%

Reference Example D (123) also contains 0.66 percent by weight of the condensation product (amide) of dicocoamine and glycolic acid.

[0122] The formulations thus prepared are subjected to a friction test involving repeated engagement and disengagement of lubricated steel clutch plates with paper-based friction disks. The testing is conducted on an SAE No. 2 Universal Wet Friction Material Test Machine or on an equivalent machine according to GK or DKA specifications. The values of measurements are reported at 500, 2500, and 10,000 disengagement cycles.

[0123] All measurements are made with a lubricant formulation maintained at 100° C. A first measurement is the "quasi-static" coefficient of friction. For this measurement, at a hot condition, the clutch is broken away immediately after the shift with 10 r.p.m to reach 270° C. steel plate temperature. The quasi-static friction coefficient is measured 0.5 seconds after breakaway has started and the slip speed has stabilized. A second measurement is for "static" coefficient of friction, which condition is defined as the coefficient of friction immediately after disengagement of the clutch plates, the plates moving at a relative rate of 10 r.p.m. Similarly, dynamic coefficients of friction are reported at 90%, 50%, and 10% slip speeds as the clutch engages.

[0124] Results from the testing is shown in the Table below. For each entry, the relevant coefficients of friction are reported, in turn, at 500 cycles (start of test), 2500 cycles (middle of test), and 10,000 cycles (end of test):

	μ-quasi-static	μ-static	μ-90%	μ-50%	μ-10%
Ex. 1-both f.m.s	0.106	0.128	0.136	0.135	0.136
(start)	0.103	0.131	0.129	0.127	0.131
(oxalic bisamide	0.108	0.123	0.130	0.129	0.134
(middle)					
and amide (c))					
(end)					
Ex. 2-both f.m.s	0.109	0.136	0.139	0.137	0.143
(start)	0.102	0.134	0.135	0.128	0.132
(oxalic bisamide	0.107	0.128	0.132	0.132	0.135
(middle)					
and amide (c))					
(end)					
Ref. Ex. B(138)-	0.108	0.160	0.129	0.127	0.133
(start)	0.102	0.157	0.126	0.120	0.126
(with oxalic	0.099	0.161	0.125	0.115	0.120
(middle)					
bisamide)					
(end)					
Ref. Ex. C(129)-	0.105	0.154	0.131	0.126	0.130
(start)	0.098	0.158	0.129	0.120	0.125
(with amide (c))	0.097	0.158	0.129	0.119	0.122
(middle)					
(end)					
Ref. Ex. D(123)-	0.103	0.133	0.130	0.132	0.131
(start)	0.100	0.134	0.128	0.127	0.129
(with amide (c))	0.094	0.107	0.110	0.125	0.125
(middle)					
(end)					

[0125] The results show that the inventive examples, containing both the oxalic bisamide and the amide of component (c), exhibit superior friction performance properties that remain relatively stable from 500 to 10,000 cycles in the test. The quasi-static coefficient of friction is a high, stable value of 1.02-1.09. The static coefficient of friction is a stable value that does not substantially exceed 0.135.

[0126] Each of the documents referred to above is incorporated herein by reference, including any prior applications, whether or not specifically listed above, from which priority is claimed. 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 optionally modified by the word "about." 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.

[0127] As used herein, the transitional term "comprising," which is synonymous with "including," "containing," or "characterized by," is inclusive or open-ended and does not exclude additional, un-recited elements or method steps. However, in each recitation of "comprising" herein, it is intended that the term also encompass, as alternative embodiments, the phrases "consisting essentially of" and "consisting of," where "consisting of" excludes any element or step not specified and "consisting essentially of" permits the inclusion of additional un-recited elements or steps that do not materially affect the essential or basic and novel characteristics of the composition or method under consideration. The expression "consisting of" or "consisting essentially of," when applied to one element of a claim, is intended to restrict all species of the type represented by that element, notwithstanding the presence of "comprising" elsewhere in the claim.

[0128] While certain representative embodiments and details have been shown for the purpose of illustrating the subject invention, it will be apparent to those skilled in this art that various changes and modifications can be made therein without departing from the scope of the subject invention. In this regard, the scope of the invention is to be limited only by the following claims. In certain jurisdictions, recitation of one or more of narrower values for a numerical range or recitation of a narrower selection of elements from a broader list means that such recitations represent preferred embodiments.

1. A composition comprising:

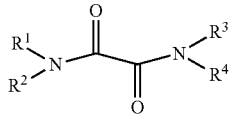
(a) an oil of lubricating viscosity;

(b) about 0.05 to about 3.0 percent by weight of an N-substituted oxalic acid bisamide or amide-ester containing at least two hydrocarbyl groups of about 12 to about 22 carbon atoms; and

(c) about 0.05 to about 3.0 percent by weight of an amide or thioamide represented by the formula R^1R^2N—C(X)R^3 wherein X is O or S, R^1 and R^2 are each independently hydrocarbyl groups of at least about 6 to 24 carbon atoms, and R^3 is hydroxyalkyl group of 1 to about 6 carbon atoms or a group formed by the condensation of said hydroxyalkyl group, through a hydroxyl group thereof, with an acylating agent.

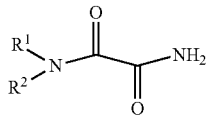
2. The composition of claim **1** further comprising (d) about 1 to about 6 percent by weight of a dispersant component, comprising one or more succinimide dispersants, said dispersant component containing about 0.05 to about 1 percent by weight boron and having a TBN (oil free) of about 40 to about 100.

3. The composition of claim **1** wherein the N-substituted oxalic acid bisamide or amide ester comprises a bisamide represented by the formula:



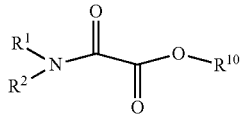
wherein at least two of R^1, R^2, R^3, and R^4 are independently groups comprising a hydrocarbyl group of about 12 to about 22 carbon atoms and up to two of said groups R^1, R^2, R^3, and R^4 are independently hydrogen or a hydrocarbyl group of 10 or fewer carbon atoms.

4. The composition of claim **1** wherein the N-substituted oxalic acid bisamide or amide ester comprises a bisamide represented by the formula



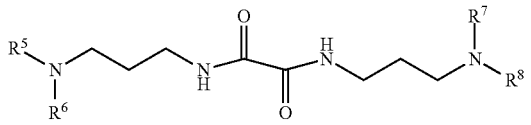
wherein each R^1 and R^2 is independently an alkyl group of about 12 to about 18 carbon atoms.

5. The composition of claim **1** wherein the N-substituted oxalic acid bisamide or amide-ester comprises an amide-ester represented by the formula:



wherein R^1 and R^2 are independently hydrocarbyl groups of about 12 to about 22 carbon atoms and R^{10} is a hydrocarbyl group of 1 to about 22 carbon atoms.

6. The composition of claim **1** wherein (b) the N-substituted oxalic acid bisamide or amide ester comprises a bisamide represented by the formula



wherein each of R^5 and R^7 is independently a hydrocarbyl group of about 12 to about 22 carbon atoms and each of R^6 and R^8 is independently hydrogen or a hydrocarbyl group of 1 to about 22 carbon atoms.

7. The composition of claim **1** wherein in (c), the amide or thioamide, each of R^1 and R^2 is independently a 2-ethylhexyl group or a group of about 10 to about 18 carbon atoms.

8. The composition of claim **1** wherein in (c), the amide or thioamide, is an amide.

9. The composition of claim **1** wherein (c), the amide or thioamide, comprises a substituted nitrogen moiety, R^1R^2N—, comprising a di-cocoalkylamine moiety or a (2-ethylhexyl)(hydrogenated tallow)amine moiety and a carboxy moiety, —C(O)R^3, comprising a glycolic moiety.

10. The composition of claim **2** wherein (d), the dispersant component, comprises a first borated succinimide dispersant component having a boron content of about 0.1 to about 1 percent by weight and a TBN (oil-free) of about 50 to about 100; and a second succinimide dispersant component having a boron content of less than about 0.1 percent by weight and a TBN (oil-free) of about 40 to about 80.

11. The composition of claim **10** wherein the second succinimide dispersant component is boron-free.

12. The composition of claim **2** wherein (d,) the dispersant component, comprises at least one succinimide dispersant that is reacted with at least one of terephthalic acid or an inorganic phosphorus compound or a dimercaptothiadiazole compound.

13. The composition of claim **1** further comprising at least one of detergents, antioxidants, corrosion inhibitors, seal swell agents, anti-wear agents, organic borate esters, organic borate salts, anti-foam agents, viscosity improvers, or friction modifiers other than those of component (b) or component (c).

14. A composition prepared by admixing the components of claim **1**.

15. A method for lubricating a device with a lubricated clutch comprising supplying thereto the composition of claim **1**.

16. The method of claim **15** wherein the device comprises an automatic transmission.

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