(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
14 January 2010 (14.01.2010)

PCT

(10) International Publication Number
WO 2010/005921 A1

(51) International Patent Classification:
C10L 1/18 (2006.01) ***C10L 10/08*** (2006.01)
C10L 1/22 (2006.01)

(21) International Application Number: PCT/US2009/049739

(22) International Filing Date: 7 July 2009 (07.07.2009)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/079,533 10 July 2008 (10.07.2008) US

(71) Applicant *(for all designated States except US)*: **THE LUBRIZOL CORPORATION** [US/US]; 29400 Lakeland Blvd., Wickliffe, OH 44092-2298 (US).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **VILARDO, Jonathan, S.** [US/US]; 29400 Lakeland Blvd., Wickliffe, OH 44092-2298 (US). **MOSIER, Patrick, E.** [US/US]; 29400 Lakeland Blvd., Wickliffe, OH 44092-2298 (US).

(74) Agents: HILKER, Christopher, D. et al.; The Lubrizol Corporation, Patent Dept./052A, 29400 Lakeland Blvd., Wickliffe, OH 44092-2298 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

Published:

— *with international search report (Art. 21(3))*

(54) Title: CARBOXYLIC ACID DERIVATIVES AS FRICTION MODIFIERS IN FUELS

(57) Abstract: The present invention provides an additive composition and a fuel composition for use in internal combustion engines, where the compositions comprise a friction modifier which is the condensation product of (i) certain carboxylic acids and (ii) a mixture comprising a branched alcohol or branched amine having 1 to about 150 carbon atoms, or combinations thereof wherein the fuel composition improves the fuel economy of the engine in which it is used and where the fuel additive composition has improved low temperature storage stability compared to compositions containing other fatty acid-derived friction modifiers.

TITLE

CARBOXYLIC ACID DERIVATIVES AS FRICTION MODIFIERS IN FUELS

BACKGROUND OF THE INVENTION

[0001] The present invention relates to fuel additive compositions and fuel compositions as well as a method for fueling an internal combustion engine, providing reduced friction inside the engine and so improved fuel economy while also providing improved low temperature stability characteristics and handling properties of the fuel additive compositions.

[0002] Fuel additives comprised of fatty acids and their derivatives are generally known to effectively improve fuel economy by reducing internal friction losses in an engine. However, due to the fatty and sometimes waxy nature of fatty acids and their derivatives, concentrated additive packages containing such materials tend to have poor low temperature storage stability. This poor low temperature storage stability is seen in the formation of solids, sediments and/or thick gels in the additive packages containing these materials. This low temperature storage stability results in poor handling characteristics of packages containing these additives, especially in northern and/or cooler climates where the packages may be regularly exposed to cooler temperatures.

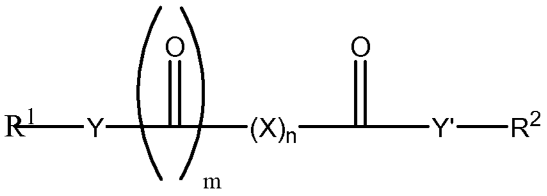
[0003] U.S. Patent 4,237,022, Barrer, December 2, 1980, discloses tartrimides useful as additives in lubricants and fuels for effective reduction in squeal and friction as well as improvement in fuel economy.

[0004] U.S. Patent 4,326,972, Chamberlin, April 27, 1982, discloses lubricant compositions for improving fuel economy of internal combustion engines. The composition includes a specific sulfurized composition (based on an ester of a carboxylic acid) and a basic alkali metal sulfonate. Additional ingredients may include at least one oil and/or fuel-dispersible detergent or dispersant, a viscosity improving agent, and a specific salt of a phosphorus acid.

[0005] The present invention solves these problems by providing an alternative type of friction modifier using derivatives of certain carboxylic acids. These alternative friction modifiers provide the same or better fuel economy improving performance while also exhibiting improved low temperature stability of the additive compositions in which they are used, eliminating the handling the problems seen with other fatty acid and fatty acid-derived friction modifiers.

SUMMARY OF THE INVENTION

[0006] In one embodiment the present invention provides an additive composition for use in an internal combustion engine, comprising: (a) a friction modifier represented by Formula I; and further comprising (b) and optional solvent; and (c) one or more optional additional performance additives;

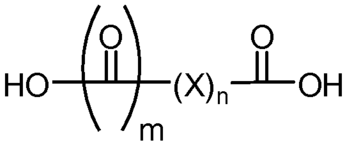


$$R^1-Y-\left(\overset{O}{\overset{\|}{C}}\right)_m-(X)_n-\overset{O}{\overset{\|}{C}}-Y'-R^2$$

Formula I

wherein: Y and Y' are independently -O-, >NH, >NR^3, or an imide group formed by taking together both Y and Y' groups and forming a R^1-N< group between two >C=O groups; X is independently -Z-O-Z'-, >CH$_2$, >CHR^4, >CR^{4}R^5, >C(OH)(CO$_2$R^2), >C(CO$_2$R^2)$_2$, >CHOR^6, or >CHCO$_2$R^2; Z and Z' are independently >CH$_2$, >CHR^4, >CR^{4}R^5, >C(OH)(CO$_2$R^2), or >CHOR^6; n is 0 to 10, or 1 to 8, or 1 to 6, or 2 to 6, or 2 to 4, with the proviso that when n=1, X is not >CH$_2$, and when n=2, both X's are not simultaneously >CH$_2$; m is 0 or 1; R^1 is independently hydrogen or a hydrocarbyl group, typically containing 1 to 150, 4 to 30, or 6 to 20, or 10 to 20, or 11 to 18, or 8 to 10 carbon atoms, with the proviso that when R^1 is hydrogen, m is 0, and n is more than or equal to 1; R^2 is a hydrocarbyl group, typically containing 1 to 150, 4 to 30, or 6 to 20, or 10 to 20, or 11 to 18, or 8 to 10 carbon atoms; R^3, R^4 and R^5 are independently hydrocarbyl groups, hydroxyl-containing groups, or carboxyl-containing groups; and R^6 is hydrogen or a hydrocarbyl group, typically containing 1 to 150, or 4 to 30 carbon atoms. In one set of embodiments the hydrocarbyl groups used for R1 and R2 contain at least some portion of branched hydrocarbyl groups.

[0007] In one set of embodiments of present invention, component (a), the friction modifier is a condensation product of (a)(i), a material represented by formula II and (a)(ii), a mixture comprising a branched alcohol or branched amine having 1 to about 150 carbon atoms, or combinations thereof;



Formula II

wherein each X is independently -Z-O-Z-, >CH_2, >CR^1R^2, >C(OH)(CO_2R^2), or >$CHOR^2$; and wherein each Z is independently >CH_2, >CR^1R^2, >C(OH)(CO_2R^2), or >$CHOR^2$; m is 0 or 1; n is 1 to 10, with the proviso that when n=1, X is not >CH_2, and when n=2, both X's are not >CH_2; and each R^1 and R^2 are independently hydrogen or a hydrocarbyl group.

[0008] In one embodiment, within formula II, the X is >$CHOR^2$ and n is 2. In another embodiment, within formula II, (X)n is -CH_2-C(OH)(CO_2R^2)-CH_2-. In another embodiment, the m in formula II is 1. In yet other embodiments, component (a)(i) is tartaric acid, citric acid, derivatives of either acid, or combinations thereof.

[0009] In one set of embodiments, alone or in combination with any of the embodiments described above, component (a)(ii) comprises a mixture of one or more branched alcohols or amines. In one embodiment, the mixture comprises one or more branched alcohols where the alcohols contain from 6 to 16 carbon atoms. In another embodiment, the mixture comprises branched amines containing 6 to 16 carbon atoms.

[0010] In another set of embodiments, alone or in combination with any of the embodiments described above, component (a)(ii) is made up of a mixture of one or more branched alcohols or amines where the overall mixture is at least 25 percent by weight branched, in that at least 25 percent by weight of the alcohols and/or amines making up the mixture have a branched structure.

[0011] The invention also provides a fuel composition comprising the fuel additive composition described herein. The invention also provides a method of operating an internal combustion engine, comprising supplying to said engine a fuel composition comprising any of the compositions described herein.

DETAILED DESCRIPTION OF THE INVENTION

[0012] Various preferred features and embodiments will be described below by way of non-limiting illustration.

Field of the Invention

[0013] The present invention involves a fuel additive composition, a fuel composition and a method for fueling an internal combustion engine, where the fuel additive includes a friction modifier (which may also be referred to as an antiwear agent) derived from the reaction of certain carboxylic acids and a mixture comprising one or more branched alcohols and/or branched amines having 1 to about 150 carbon atoms. The fuel additive composition of the invention shows improved low temperature stability characteristic, thereby reducing additive handling issues. The additive composition may also be used in fuel compositions to provide reduced friction inside the engine and so improved fuel economy.

The Additive Compositions

[0014] The additive composition of the present invention comprises the friction modifier described herein and, in some embodiments, may further comprise a solvent and/or one or more additional performance additives.

[0015] The solvents suitable for use in the present invention include hydrocarbon solvents that provide for the additive composition's compatibility and/or homogeneity and to facilitate their handling and transfer and may include a fuel as described below. The solvent can be an aliphatic hydrocarbon, an aromatic hydrocarbon, an oxygen-containing composition, or a mixture thereof. In some embodiments the flash point of the solvent is generally about 25°C or higher. In some embodiments the hydrocarbon solvent is an aromatic naphtha having a flash point above 62°C or an aromatic naphtha having a flash point of 40°C or a kerosene with a 16% aromatic content having a flash point above 62°C.

[0016] Aliphatic hydrocarbons include various naphtha and kerosene boiling point fractions that have a majority of aliphatic components. Aromatic hydrocarbons include benzene, toluene, xylenes and various naphtha and kerosene boiling point fractions that have a majority of aromatic components. Alcohols are usually aliphatic alcohols having about 2 to 10 carbon atoms and include ethanol, 1-propanol, isopropyl alcohol, 1-butanol, isobutyl alcohol, amyl alcohol, and 2-methyl-1-butanol.

[0017] The oxygen containing composition can include an alcohol, a ketone, an ester of a carboxylic acid, a glycol and/or a polyglycol, or a mixture thereof. The solvent in an embodiment of the invention will be substantially free of to free of sulphur having a sulphur content in several instances that is below 50 ppm, 25 ppm, below 18 ppm, below 10 ppm, below 8 ppm, below 4 ppm, or below 2 ppm. The solvent can be present in the additive concentrate composition at 0 to 99 percent by weight, and in other instances at 3 to 80 percent by weight, or 10 to 70 percent by weight. The friction modifier of the present invention and the additional performance additives taken separately or in combination can be present in the additive concentrate composition at 0.01 to 100 percent by weight, and in other instances can be present at 0.01 to 95 percent by weight, at 0.01 to 90 percent by weight, or at 0.1 to 80 percent by weight.

[0018] As allowed for by the ranges above, in one embodiment, the additive concentrate may comprise the friction modifier of the present invention and be substantially free of any additional solvent. In these embodiments the additive concentrate containing the friction modifier of the present invention is neat, in that it does not contain any additional solvent added to improve the material handling characteristics of the concentrate, such as its viscosity.

[0019] In several embodiments of the invention the fuel composition, fuel additive concentrate, and/or the friction modifier itself are substantially free of or free of at least one member selected from the group consisting of sulphur, phosphorus, sulfated ash, and combinations thereof, and in other embodiments the fuel composition contains less than 50 ppm, 20 ppm, less than 15 ppm, less than 10 ppm, or less than 1 ppm of any one or all of these members.

[0020] In an embodiment of the invention the additive concentrate composition or fuel composition containing the friction modifier of the present invention can be prepared by admixing or mixing the components of the composition at ambient to elevated temperatures usually up to 60°C until the composition is homogeneous.

[0021] The additional performance additives which may be included in the additive compositions of the present invention are described below.

The Fuel

[0022] The fuel composition of the present invention comprises the friction modifier described above and a liquid fuel and is useful in fueling an internal combustion engine. Fuel may also be a component on the additive compositions described above.

[0023] The fuel is normally a liquid at ambient conditions e.g., room temperature (20 to 30°C). The liquid fuel can be a hydrocarbon fuel, a non-hydrocarbon fuel, or a mixture thereof. The hydrocarbon fuel can be a petroleum distillate to include a gasoline as defined by ASTM specification D4814 or a diesel fuel as defined by ASTM specification D975. In an embodiment of the invention the liquid fuel is a gasoline, and in one embodiment the liquid fuel is a a nonleaded gasoline. In another embodiment of this invention the liquid fuel is a diesel fuel. The hydrocarbon fuel can be a hydrocarbon prepared by a gas to liquid process to include for example hydrocarbons prepared by a process such as the Fischer-Tropsch process. The non-hydrocarbon fuel can be an oxygen containing composition, often referred to as an oxygenate, which includes an alcohol, an ether, a ketone, an ester of a carboxylic acid, a nitroalkane, or a mixture thereof. The non-hydrocarbon fuel can include for example methanol, ethanol, methyl t-butyl ether, methyl ethyl ketone, transesterified oils and/or fats from plants and animals such as rapeseed methyl ester and soybean methyl ester, and nitromethane. Mixtures of hydrocarbon and non-hydrocarbon fuels can include for example gasoline and methanol and/or ethanol, diesel fuel and ethanol, and diesel fuel and a transesterified plant oil such as rapeseed methyl ester and other bio-derived fuels. In an embodiment of the invention the liquid fuel is an emulsion of water in a hydrocarbon fuel, a non-hydrocarbon fuel, or a mixture thereof. In several embodiments of this invention the liquid fuel can have a sulphur content on a weight basis that is 5000 ppm or less, 1000 ppm or less, 300 ppm or less, 200 ppm or less, 30 ppm or less, or 10 ppm or less. The liquid fuel of the invention is present in a fuel composition in a major amount that is generally greater than 95% by weight, and in other embodiments is present at greater than 97% by weight, greater than 99.5% by weight, or greater than 99.9% by weight.

The Friction Modifier

[0024] The friction modifier of the present invention may be represented by Formula I, as shown above. The friction modifier may also be used as an antioxidant, a rust and/or corrosion inhibitor, an antiwear agent, a demulsifier, or some combination thereof.

[0025] In one embodiment the compound of Formula I contains an imide group. The imide group is typically formed by taking together the Y and Y' groups and forming a R^1-N< group between two >C=O groups.

[0026] In one embodiment the compound of Formula I 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 >CHOR^6, and R^1, R^2 and R^6 are independently hydrocarbyl groups containing 4 to 30 carbon atoms.

[0027] In one embodiment, within Formula I, Y and Y' are both -O-.

[0028] In one embodiment the compound of Formula I 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 >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.

[0029] In one embodiment the friction modifier includes imides, di-esters, di-amides, di-imides, ester-amides, ester-imides, or imide-amides. In one embodiment the friction modifier includes imides, di-esters, di-amides, or ester-amides.

[0030] The di-esters, di-amides, ester-amide, ester-imide compounds of Formula I 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 citric acid). In the case of a di-imide, it is necessary to have at least four carboxylic acid groups. The amine or alcohol typically has sufficient carbon atoms to fulfill the requirements of R^1 and/or R^2 as defined in Formula I.

[0031] In one embodiment R^1 and R^2 are independently linear or branched hydrocarbyl groups. In one embodiment the hydrocarbyl groups are branched. In one embodiment the hydrocarbyl groups are linear. The R^1 and R^2 may be incorporated into Formula I 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.

[0032] Examples of a suitable branched alcohol include 2-ethylhexanol, isotridecanol, Guerbet alcohols, or mixtures thereof.

[0033] Examples of a monohydric alcohol include methanol, ethanol, propanol, butanol, pentanol, hexanol, heptanol, octanol, nonanol, decanol, undecanol, dodecanol, tridecanol, tetradecanol, pentadecanol, hexadecanol, heptadecanol, octadecanol, nonadecanol, eicosanol, or mixtures thereof. In one embodiment the monohydric alcohol contains 5 to 20 carbon atoms.

[0034] The alcohol includes either a monohydric alcohol or a polyhydric alcohol. Examples of a suitable polyhydric alcohol include 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 the polyhydric alcohol is used in a mixture along with a monohydric alcohol. Typically, in such a combination the monohydric alcohol constitutes at least 60 mole percent, or at least 90 mole percent of the mixture.

[0035] In one embodiment the friction modifier is derived from tartaric acid. The tartaric acid used for preparing the tartrates of the invention can be commercially available, and it is likely to exist in one or more isomeric forms such as d-tartaric acid, l-tartaric acid, d,l-tartaric acid or mesotartaric acid, often depending on the source (natural) or method of synthesis (from maleic acid). For example a racemic mixture of d-tartaric acid and l-tartaric acid is obtained from a catalysed oxidation of maleic acid with hydrogen peroxide (with tungstic acid catalyst). These derivatives can also be prepared from functional equivalents to the diacid readily apparent to those skilled in the art, such as esters, acid chlorides, or anhydrides.

[0036] In one embodiment the friction modifier includes a compound derived from a hydroxycarboxylic acid. In one embodiment the friction modifier is derived from at least one of hydroxy-polycarboxylic acid di-ester, a hydroxy-polycarboxylic acid di-amide, a hydroxy-polycarboxylic acid di-imide, a hydroxy-polycarboxylic acid ester-amide, a hydroxy-polycarboxylic acid ester-imide, and a hydroxy-polycarboxylic acid imide-amide. In one embodiment the friction modifier is derived from at least one of the group consisting of a hydroxy-polycarboxylic acid di-ester, a hydroxy-polycarboxylic acid di-amide, and a hydroxy-polycarboxylic acid ester-amide.

[0037] Examples of a suitable a hydroxycarboxylic acid include citric acid, tartaric acid, lactic acid, glycolic acid, hydroxy-propionic acid, hydroxyglutaric acid, or mixtures thereof. In one embodiment friction modifier is derived from tartaric acid, citric acid, hydroxy-succinic acid, dihydroxy mono-acids, mono-hydroxy diacids, or mixtures thereof. In one embodiment the friction modifier includes a compound derived from tartaric acid or citric acid. In one embodiment the friction modifier includes a compound derived from tartaric acid. In one embodiment the compound of Formula (1) is not a citrate.

[0038] US Patent Application 2005/198894 discloses suitable hydroxycarboxylic acid compounds, and methods of preparing the same. Canadian Patent 1183125; US Patent Publication numbers 2006/0183647 and US-2006-0079413; US Patent Application number 60/867402; and British Patent 2 105 743 A, all disclose examples of suitable tartaric acid derivatives. In one embodiment the di-esters, di-amides, di-imides, ester-amide, ester-imide, imide-amide compounds are derived from a compound of Formula I. In one embodiment the di-esters, di-amides, ester-amide, compounds are derived from a compound of Formula I. A detailed description of methods for preparing suitable tartrimides (by reacting tartaric acid with a primary amine) is disclosed in US Patent 4,237,022. In one embodiment the friction modifier includes imide, di-esters, di-amides, ester-amide derivatives of tartaric acid.

[0039] Examples of a suitable citric acid derivative include trialkyl citrates or borated trialkyl citrates. Suitable examples include triethyl citrate, tripentyl citrate with ethyl dipentyl citrate, borated triethyl citrate, tributyl citrate, triethyl citrate transesterified with 1,2-propandiol, triethyl O-acetyl citrate, triethyl citrate octadecyl succinate, or mixtures thereof. A more detailed description of suitable citrates is disclosed in WO 2005/087904 and U.S. Patent 5,338,470. Other suitable citrates include 2-ethylhexyl citrate, dodecyl citrate, or mixtures thereof.

[0040] The friction modifier of the invention, typically a tartrate, may also function as a rust and/or corrosion inhibitor, an antiwear agent, and/or a demulsifier.

[0041] In one embodiment the friction modifier is not borated.

[0042] In some embodiments the friction modifier, as represented by formula I, is the condensation product derived from the reaction of component (a)(i), which is made up of certain carboxylic acids, and component (a)(ii), a mixture comprising one or more branched alcohols or branched amines where the alcohols and/or amine each contain from 1 to about 150 carbon atoms. This condensation product acts as a friction modifier and/or antiwear agent in the fuel compositions of the present invention.

[0043] The friction modifier of the present invention may be prepared conveniently by reacting one or more of the carboxylic acids described either above or below with one or more of the branched alcohols and/or branched amines described either above or below by a well-known condensation process. In one embodiment components (a)(i) and (a)(ii) are reacted in a 1:0.5-2 molar ratio wherein the ratio represents moles of reactive carboxylic acid functional groups in (a)(i) to moles of active hydroxyl groups in (a)(ii). In another embodiment the ratio is a 1:0.5-1 molar ratio, and in some embodiments, the ratio is a 1:1 molar ratio.

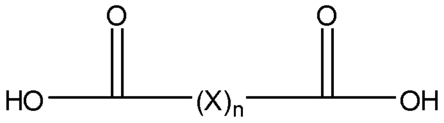
[0044] The friction modifiers of the present invention can be solids, semi-solids, or liquids (oils) depending on the particular alcohol(s) and/or amine(s) used in preparing them. For use as additives in oleaginous compositions including lubricating and fuel compositions the friction modifiers are advantageously soluble and/or stably dispersible in such oleaginous compositions. Thus, for example, compositions intended for use in fuels are typically fuel-soluble and/or stably dispersible in a fuel in which they are to be used. The term "fuel-soluble" as used in this specification and appended claims does not necessarily mean that all the compositions in question are miscible or soluble in all proportions in all fuels. Rather, it is intended to mean that the composition is soluble in a fuel (hydrocarbon, non-hydrocarbon, mixtures, etc) in which it is intended to function to an extent which permits the solution to exhibit one or more of the desired properties. Similarly, it is not necessary that such "solutions" be true solutions in the strict physical or chemical sense. They may instead be microemulsions or colloidal dispersions which, for the purpose of this invention, exhibit properties sufficiently close to those of true solutions to be, for practical purposes, interchangeable with them within the context of this invention.

[0045] As previously indicated, the friction modifiers of this invention are useful as additives for fuels, in which they may function not only as friction modifiers but also as rust and/or corrosion inhibitors, antiwear agents, and/or demulsifiers. The friction modifier of the present invention can be present in fuel compositions at 1 to 10,000 ppm (where ppm is calculated on a weight:weight basis). In additional embodiments, the friction modifier is present in fuel compositions in ranges with lower limits of 1, 3, 5, 10, 50, 100, 150 and 200 ppm and upper limits of 10,000, 7,500, 5,000, and 2,500 where any upper limit may be combined with any lower limit to provide a range friction modifier present in the fuel compositions.

The Carboxylic Acids

[0046] Component (a)(i) is made up of one or more carboxylic acids where the acid is described by Formula II shown above.

[0047] In one embodiment, which may each be used alone or in combination with one or more of the embodiments described above and below, the m in formula II is 1, such that the acid used in the invention is a dicarboxylic acid. In these embodiments, component (a)(i) is made up of one or more dicarboxylic acids where the acid is described by the following formula:



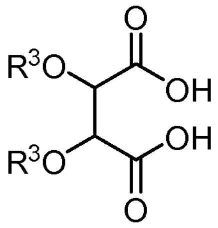
$$HO-C(=O)-(X)_n-C(=O)-OH$$

Formula IIa

wherein each X is independently -Z-O-Z-, >CH_2, >CR^1R^2, >C(OH)(CO_2R^2), or >$CHOR^2$; and wherein each Z is independently >CH_2, >CR^1R^2, >C(OH)(CO_2R^2), or >$CHOR^2$; m is 0 or 1; n is 1 to 10, with the proviso that when n=1, X is not >CH_2, and when n=2, both X's are not >CH_2; and each R^1 and R^2 are independently hydrogen or a hydrocarbyl groups.

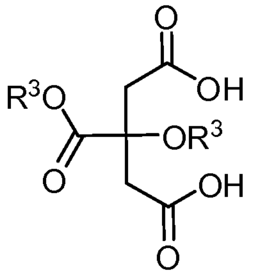
[0048] In set one embodiments, which may each be used alone or in combination with one or more of the embodiments described above and below, the X in formula I and/or formula Ia is >$CHOR^2$ and n is 2. In other embodiments of this set, $(X)_n$ in formula I and/or formula Ia is -CH_2-C(OH)(CO_2R^2)-CH_2-. In yet other embodiments, component (a)(i) is tartaric acid, citric acid, derivatives and/or functional equivalents of either acid, or combinations thereof.

[0049] In another set of embodiments component (a)(i) is represented by either Formula III:



Formula III

wherein each R^3 is independently H, or a hydrocarbyl group, or wherein the R^3 groups together form a ring; or Formula IV:



Formula IV

wherein each R^3 is independently H, or a hydrocarbyl group; or combinations thereof.

[0050] When the acid used in the present invention includes tartaric acid, the acid can be the commercially available type (obtained from Sargent Welch), and it is likely to exist in one or more isomeric forms such as *d*-tartaric acid, *l*-tartaric acid, d,l-tartaric acid, or mesotartaric acid, often depending on the source (natural) or method of synthesis (e.g. from maleic acid). These derivatives can also be prepared from functional equivalents to the diacid readily apparent to those skilled in the art, such as esters, acid chlorides, anhydrides, etc. Similar characteristics apply to the citric acid and other acids which may be used in the present invention, including but not limited to the fact that isomers may be present in the acid source and that functional equivalents of the acids may be used.

<u>The Alcohols and/or Amines</u>

[0051] Component (a)(ii) is made up of one or more branched alcohols, one or more branched amines, or combinations thereof. The alcohols and amines suitable for use in the invention are branched as opposed to linear in structure. In one embodiment all, or substantially all, of the alcohols and/or amines that make up component (a)(ii) are branched. It is understood that industrial sources of some alcohols and amines contain ranges of structures and configurations and that while, for example, an alcohol source may be identified as a branched structure, the source may contain some small amount of linear alcohols and even small amounts of linear and branched alcohols other than the primary identify given.

[0052] In another set of embodiments, alone or in combination with any of the other embodiments described above and below, the alcohols and/or amines that make up component (a)(ii) are ≥25 or >25 percent by weight branched in structure, or are ≥50 or >50 percent by weight branched in structure, or are ≥75 or >75 percent by weight branched in structure, or are ≥90 or >90 percent by weight branched in structure. In yet another embodiment, component (a)(ii) is more than 95 percent by weight branched.

[0053] The amines suitable for use in the invention may have the formula RR'NH wherein R and R' each independently represent H or a branched hydrocarbon-based radical of from 1 to 150, or from 1 to 30 or from 6 to 16, or from 6 to 150, or from 8 to 150 carbon atoms. In another embodiment, R and R' each independently represent H or a branched hydrocarbon-based radical of from 1 to 75, or from 1 to 15 or from 3 to 8, or from 3 to 75, or from 4 to 75 carbon atoms with the proviso that the total number of carbon atoms in R and R' combined is from 1 to 150, or from 1 to 30, or from 8 to 16, or from 6 to 150, or from 8 to 150 carbon atoms. In one embodiment the total number of carbon atoms in R and R' combined is from 6 to 16. The amines may be branched at any point in the chain of each hydrocarbon-based radical and the branching may be of any length.

[0054] Other amines may be employed either alone or in combination with the amines described above wherein the amines are characterized by the ranges of the number of carbon atoms present in the amine, where the ranges have a lower carbon number of 2, 3, 4, 6, 10, or 12 carbon atoms and an upper carbon number of 120, 80, 48, 24, 20, 18, or 16 carbon atoms. In one embodiment, each of the groups R and R' has 8 to 30 carbon atoms. In one embodiment, the sum of carbon atoms in R and R' is at least 8. The substituent R and R' may also be -R''OR''' in which R'' is a divalent alkylene radical of 2 to 6 carbon atoms and R''' is a hydrocarbyl radical of 5 to 150 or to 148 or to 146 or to 144 carbon atoms.

[0055] In one set of embodiments of the present invention, alone or in combination with any of the other embodiments described both above and below, the amines suitable for the present invention include those represented by the formula RR'NH wherein R and R' represent H or a hydrocarbyl radical of 1 to 150 carbon atoms provided that the sum of the carbon atoms in R and R' is at least 6. In one embodiment R or R' contain 6 to 16 carbons and in another embodiment from 8 to 13 carbon atoms, and in yet another embodiment 8 carbon atoms

[0056] The alcohols useful for preparing the friction modifier are branched alcohols and similarly contain from 1 to 150, or from 1 to 30 or from 6 to 16, or from 6 to 150, or from 8 to 150 carbon atoms. In one set of embodiments, the alcohols may contain the same ranges of total number of carbon atoms as described above for the amines. The alcohols may be branched at any point in the chain and the branching may be of any length.

[0057] In one embodiments, which may be used alone or in combination with any of the other embodiments described above and below, component (a)(ii) contains one or more alcohols selected from the following group: 2-methyl-1-pentanol, 2-ethylhexanol, 2-octanol, isooctyl alcohol, isotridecyl alcohol, or combinations thereof.

[0058] In one set of embodiments, the specific alcohols described above are used in combination with dicarboxylic acids, wherein the dicarboxylic acids are tartaric acid, citric acid or combinations thereof.

[0059] Other alcohols may be employed either alone or in combination with the alcohols described above. The alcohols suitable for use in the present invention contain from 6 to 150 carbon atoms and in some embodiments from 6 to 16 carbon atoms. In other embodiments the alcohols used in the present invention contain from 8 to 150 carbon atoms or from 8 to 16 carbon atoms. In still other embodiments the alcohols contain 8 to 10 carbon atoms or 8 carbon atoms.

[0060] In another embodiment the alcohols are characterized by the ranges of the number of carbon atoms present in the alcohol, where the ranges have a lower carbon number of 2, 3, 4, 6, 8, 10, or 13 carbon atoms and an upper carbon number of 120, 80, 48, 24, 20, 18, 16, or 13 carbon atoms.

[0061] In one set of embodiments, alone or in combination with any of the other embodiments described above and below, component (a)(ii) includes one or more branches alcohols and/or amines wherein the branching occurs in the number two position. In another embodiment of this set, the alcohols and/or amines are iso structured. In yet another embodiment of this set, the alcohols and/or amines contain at least one branched group where the branched group is a methyl group or an ethyl group. In still another embodiment, the alcohols and/or amines contain one branched group where the branched group is a methyl group or an ethyl group.

[0062] In some embodiments of the present invention the alcohols and/or amines that make up component (a)(ii) are ≥25 or >25 percent by weight branched in structure and contain from 6 or 8 to 13 carbon atoms. In other embodiments the alcohols are ≥50 or >50 percent by weight branched in structure and contain either from 6 or 8 to 13 carbon atoms. In still other embodiments the alcohols are >95 percent by weight branched in structure and contain either from 6 or 8 to 13 carbon atoms.

Additional Performance Additives

[0063] The additive compositions and fuel compositions of the present invention can further comprise one or more additional performance additives. Additional performance additives can be added to a fuel composition depending on several factors to include the type of internal combustion engine and the type of fuel being used in that engine, the quality of the fuel, and the service conditions under which the engine is being operated. The additional performance additives can include an antioxidant such as a hindered phenol or derivative thereof and/or a diarylamine or derivative thereof, a corrosion inhibitor such as an alkenylsuccinic acid, and/or a detergent/dispersant additive such as a polyetheramine or nitrogen containing detergent, including but not limited to PIB amine dispersants, quaternary salt dispersants, and succinimide dispersants. The additional performance additives may also include a cold flow improver such as an esterified copolymer of maleic anhydride and styrene and/or a copolymer of ethylene and vinyl acetate, a foam inhibitor such as a silicone fluid, a demulsifier such as a polyalkoxylated alcohol, a lubricity agent such as a fatty carboxylic acid, a metal deactivator such as an aromatic triazole or derivative thereof, a valve seat recession additive such as an alkali metal sulfosuccinate salt, a biocide, an antistatic agent, a deicer, a fluidizer such as a mineral oil and/or a poly(alpha-olefin) and/or a polyether, and a combustion improver such as an octane or cetane improver.

[0064] The additional performance additives can each be added directly to a additive and/or fuel compositions of the present invention, but they are generally added together in an additive concentrate composition to a fuel composition with the friction modifier of the present invention. The additive concentrate composition is described in more detail above.

Industrial Application

[0065] In one embodiment the invention is useful for a liquid fuel and/or for an internal combustion engine, including either compression ignition engines or spark ignited engines. The internal combustion engine includes 2-stroke or 4-stroke engines fuelled with gasoline, diesel, a natural gas, a mixed gasoline/alcohol or any of the fuels described in the sections above. The compression ignition engines include both light duty and heavy duty diesel engines. The spark ignited engines include direct injection gasoline engines.

[0066] In other embodiments the invention is useful in additive compositions in that the friction modifier described above provides improve low temperature storage stability and so improved handling properties for the friction modifier itself and additive compositions and/or concentrates containing the friction modifier.

[0067] In still other embodiments the additive compositions of the present invention may be used in a lubricating composition such that the additives are present in the lubricating system of the engine. The additives may also enter the combustion chamber of the engine during operation of the engine by the transfer of small amounts of the additive containing lubricating composition to the combustion chamber due to a phenomenon referred to as “blow by” where the lubricating composition, and in this case the additive composition, pass around the piston heads inside the cylinder, moving from the lubricating system of the engine into the combustion chamber.

[0068] As used herein, the term "hydrocarbyl substituent" or "hydrocarbyl group" is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group having a carbon atom directly attached to the remainder of the molecule and having predominantly hydrocarbon character. Examples of hydrocarbyl groups include: hydrocarbon substituents, that is, aliphatic (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl, cycloalkenyl) substituents, and aromatic-, aliphatic-, and alicyclic-substituted aromatic substituents, as well as cyclic substituents wherein the ring is completed through another portion of the molecule (e.g., two substituents together form a ring); substituted hydrocarbon substituents, that is, substituents containing non-hydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbon nature of the substituent (e.g., halo (especially chloro and fluoro), hydroxy, alkoxy, mercapto, alkylmercapto, nitro, nitroso, and sulfoxy); hetero substituents, that is, substituents which, while having a predominantly hydrocarbon character, in the context of this invention, contain other than carbon in a ring or chain otherwise composed of carbon atoms. Heteroatoms include sulfur, oxygen, nitrogen, and encompass substituents as pyridyl, furyl, thienyl and imidazolyl. In general, no more than two, 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.

[0069] It is known that some of the materials described above may interact in the final formulation, so that the components of the final formulation may be different from those that are initially added. For instance, metal ions (of, e.g., a detergent) can migrate to other acidic or anionic sites of other molecules. The products formed thereby, including the products formed upon employing the composition of the present invention in its intended use, may not be susceptible of easy description. Nevertheless, all such modifications and reaction products are included within the scope of the present invention; the present invention encompasses the composition prepared by admixing the components described above.

EXAMPLES

[0070] The invention will be further illustrated by the following examples, which sets forth particularly advantageous embodiments. While the examples are provided to illustrate the present invention, they are not intended to limit it.

[0071] Samples of friction modifiers, including the friction modifiers of the present invention are tested to evaluate their low temperature storage stability characteristics. Samples of the friction modifiers are tested neat, with no other components present in the sample, and in blends, where the friction modifiers are mixed with one or more solvents to give results representative of a fuel concentrate or fuel composition containing the friction modifiers. In the test, sample bottles are filled approximately 2/3 full with sample materials, typically requiring about 50 ml for each test sample. Each sample is stored for four weeks at three different temperatures, with a separate sample set prepared for each temperature tested. The neat samples and the blend samples are rated after 3 weeks and 4 weeks of storage. In this testing, one set of neat samples is stored at 0°C and one set at -18°C, while one set of blend samples is stored at 0°C, one set at -8°C, and one set at -18°C. The table below summarizes the examples:

Table 1 – Formulation of Neat Examples:

Example ID	Friction Modifier		
	Acid – (a)(i)	Alcohol – (a)(ii)	Product – (a)
Comp 1	citric acid	ethanol	linear (triethyl) C2 citrate
Comp 2	citric acid	butanol	linear (tributyl) C3 citrate
Comp 3	tartaric acid	ALFOL 8-10	linear C8-C10 tartrate
Comp 4	tartaric acid	ALFOL 12-14	linear C12-14 tartrate
Comp 5	citric acid	ALFOL 12-14	linear C12-14 citrate
Comp 6	tartaric acid	NEODOL 45	linear C14-15 tartrate
Comp 7	tartaric acid	ALFOL 12-18	linear C12-18 tartrate
Comp 8	tartaric acid	oleyl alcohol	linear C18 tartrate
Comp 9	tartaric acid	ISOFOL 32	linear C32 tartrate
1	tartaric acid	isobutyl alcohol	branched C4 tartrate
2	tartaric acid	2-methyl-1-butanol	branched C5 tartrate
3	tartaric acid	2-methyl-1-pentanol	branched C6 tartrate
4	tartaric acid	2-octanol	branched C8 tartrate
5	tartaric acid	2-ethyl hexanol	branched C8 tartrate
6	tartaric acid	isotridecyl alcohol	branched C13 tartrate
7	citric acid	isotridecyl alcohol	branched C13 citrate
8	tartaric acid	ALFOL 8-10 : isooctyl alcohol (50:50)	mixed C8-C10 tartrate
9	tartaric acid	ALFOL 12-14 : isotridecyl alcohol (50:50)	mixed C12-14 tartrate

Table 2 – Formulation of Blend Examples:

Example ID	Blend Components and Formulation		
	Friction Modifier	Solvent(s)	Formulation in PBW[1]
Comp 1B	Comp 1	Xylene:Isobutanol:Amyl Alcohol	30:35:17.5:17.5
Comp 2B	Comp 2	Xylene:Isobutanol:Amyl Alcohol	30:35:17.5:17.5
Comp 3B	Comp 3	Xylene:Isobutanol:Amyl Alcohol	30:35:17.5:17.5
Comp 4B	Comp 4	Xylene:Isobutanol:Amyl Alcohol	30:35:17.5:17.5
Comp 5B	Comp 5	Xylene:Isobutanol:Amyl Alcohol	30:35:17.5:17.5
Comp 6B	Comp 6	Xylene:Isobutanol:Amyl Alcohol	30:35:17.5:17.5
Comp 7B	Comp 7	Xylene:Isobutanol:Amyl Alcohol	30:35:17.5:17.5
Comp 8B	Comp 8	Xylene:Isobutanol:Amyl Alcohol	30:35:17.5:17.5
Comp 9B	Comp 9	Xylene:Isobutanol:Amyl Alcohol	30:35:17.5:17.5
1B	Example 1	Petroleum Naptha Solvent	50:50
2B	Example 2	Petroleum Naptha Solvent	50:50
3B-1	Example 3	Petroleum Naptha Solvent	50:50
3B-2	Example 3	Xylene:Isobutanol:Amyl Alcohol	30:35:17.5:17.5
4B	Example 4	Xylene:Isobutanol:Amyl Alcohol	30:35:17.5:17.5
5B-1	Example 5	Petroleum Naptha Solvent	75:25
5B-2	Example 5	Xylene:Isobutanol:Amyl Alcohol	30:35:17.5:17.5
6B	Example 6	Xylene:Isobutanol:Amyl Alcohol	30:35:17.5:17.5
7B	Example 7	Xylene:Isobutanol:Amyl Alcohol	30:35:17.5:17.5
8B	Example 8	Xylene:Isobutanol:Amyl Alcohol	30:35:17.5:17.5
9B	Example 9	Xylene:Isobutanol:Amyl Alcohol	30:35:17.5:17.5

1 – PBW of each blend examples is given in the following order: FM, solvent 1, solvent 2, if any, and so on. As an example, Comp 1B, with a formulation shown as 30:35:17.5:17.5 is 30 pbw friction modifier, 35 pbw xylene, 17.5 pbw isobutanol and 17.5 pbw amyl alcohol.

[0072] When the samples are evaluated at 3 weeks and 4 weeks, each sample is rated for its clarity, the presence of any sediment, and the presence of any gel. Other observations on the sample are also taken. Abbreviations are used in the rating process and results are reported in the following order: Clarity / Sediment / Gel / Special Cases. If one or more category above is left blank, then it is to be understood that nothing was observed under that category. The table below summarizes the rating abbreviations used in the testing, with the various ratings given in each category from good to bad and/or better to worse, with the caveat that no rating in the sediment, gel or special case categories, meaning no sediment, gel or special case is present, is preferred.

Table 3 – Low Temperature Stability Rating Abbreviations: (OK TO PUBLISH?)

Clarity Rating Abbreviations

Abbrev	Short Meaning	Operational Definition
C	Clear	Light filament clearly seen, no distortion of filament and no diffraction of light
SLZ	Slightly Hazy	Distortion of light filament. Not sharp view of light filament. Fuzzy.
Z	Hazy	Light filament barely visible. Sometimes not visible. Lack of transparency.
O	Opaque	Lacks translucency, no light passes through

Sediment Rating Abbreviations

Abbrev	Short Meaning	Operational Definition
T	Trace sediment	No visible sediment until bottle tilted, <50% of bottom covered
L	Light sediment	Thin layer of film of sediment covering 50-100% of bottom
M	Medium sediment	Layer of sediment <1/16”
H	Heavy sediment	Any amount of sediment >1/16”

Gel Rating Abbreviations

Abbrev	Short Meaning	Operational Definition
TG	Trace Gel	Less than 10 globules
LG	Light Gel	Covers 1-10% of inside surface
MG	Medium Gel	Covers 11-49% of inside surface
HG	Heavy Gel	Covers 50-100% of inside surface

Special Case Abbreviations

Abbrev	Short Meaning	Operational Definition
F	Flocculent	Snowflake-like appearances in blend
N	Suspension	Wispy appearances suspended in blend. No connection to side or top of blend.
Q	Separation	Distinct appearance of 2 or more different phases.
X	Crystals	Light can be observed being diffracted in prism fashion. Various shapes and sizes of crystals may be observed.
S	Solid	No flow of sample after held horizontally for 3 seconds

[0073] In accordance with the description and ratings provided above, the best possible rating a sample could receive is “C” meaning the sample is clear and there is no sediment, gel or special case present.

[0074] These rating abbreviations and definitions were used to evaluate each sample after 3 weeks and 4 weeks of storage at their respective temperatures. The tables below summarize the results of the low temperature stability testing:

Table 4 – Evaluations of Neat Samples at 3 and 4 Weeks

Example ID	Sample Evaluations at 3 Weeks		Sample Evaluations at 4 Weeks	
	At 0°C	At -18°C	At 0°C	At -18°C
Comp 1	*pending*	*pending*	*pending*	*pending*
Comp 2	*pending*	*pending*	*pending*	*pending*
Comp 3*	O/S/Q & O/S	O/S/Q & O/S	O/S/Q & O/S	O/S/Q & O/S
Comp 4	Z/S	Z/S	Z/S	Z/S
Comp 5	O/S	O/S	O/S	O/S
Comp 6	O/S	O/S	O/S	O/S
Comp 7	O/S	O/S	O/S	O/S
Comp 8	O/S	O/S	O/S	O/S
Comp 9	O/S	O/S	O/S	O/S
1	*Not Tested*	*Not Tested*	*Not Tested*	*Not Tested*
2	Z/L/F	Z/L	Z/L/F	Z/L
3*	Z/T & Z/T	Z/T & Z/T	Z/T & Z/T	Z/T & Z/T
4	C	C/S	C	C/S
5*	C/T & C/T	C & C	C/T & C/T	C & C
6	C	C/S	C	C/S
7	*Not Tested*	Z	*Not Tested*	Z
8	Z/S	Z/S	Z/S	Z/S
9	O/S/Q & Z/S	O/S & Z/S	O/S & Z/S	O/S & Z/S

*Comparative Example 3, Example 3 and Example 5 were repeated, where the repeat samples have the exact same formulations and in these cases both sets of results are reported.

Table 5 – Evaluations of Blend Samples at 3 and 4 Weeks

Example ID	Sample Evaluations at 3 Weeks			Sample Evaluations at 4 Weeks		
	At 0°C	At -8°C	At -18°C	At 0°C	At -8°C	At -18°C
Comp 1B	*pending*	*pending*	*pending*	*pending*	*pending*	*pending*
Comp 2B	*pending*	*pending*	*pending*	*pending*	*pending*	*pending*
Comp 3B*	C/T & C/T	S/L/Z & C/T	O/S & C/H/S	C/T & C/T/TG	S/L/Z & C/T	O/S & C/H/S
Comp 4B	O/S	O/S	O/S	O/S	O/S	O/S
Comp 5B	O/S	O/S	O/S	O/S	O/S	O/S
Comp 6B	O/S	O/S	O/S	O/S	O/S	O/S
Comp 7B	O/S	O/S	O/S	O/S	O/S	O/S
Comp 8B	O/H	O/S/Q	O/S	O/S	O/S/Q	O/S
Comp 9B	Z/H/Q	O/S	O/S	Z/H/Q	O/S	O/S
1B	Z/S	*Not Tested*	*Not Tested*	Z/S	*Not Tested*	*Not Tested*
2B	*Not Tested*	*Not Tested*	C/T/F	*Not Tested*	*Not Tested*	C/T/F
3B-1	*Not Tested*	*Not Tested*	SLZ/T/F	*Not Tested*	*Not Tested*	SLZ/T/F
3B-2	C/T/N	SLZ/T/N	SLZ/T/N	C/T/N	C/T/N	SLZ/T/N
4B	C/T	C/T	C/T	C/T	C/T	C/T
5B-1	C/L	C/L	C/L	C/L	C/L	C/L
5B-2	C/T	C/T	C/T	C/T	C/T	C/T
6B	C/T	C/T	C/T	C/T/TG	C/T/TG	C/T/TG
7B	SLZ/T/N	SLZ/T/N	SLZ/L/N/F	C/T/N	C/T/N/F	SLZ/L/N/F
8B	C/T	C/T	C/T	C/T	C/T	C/T
9B*	O/F/S & Z/H/Q/F	O/S & Z/H/S	O/S & SLZ/H/S	O/S & SLZ/H/Q/F	O/S & Z/S	O/S & SLZ/H/S

*Comparative Example 3B and Example 9B were repeated and in these cases both sets of results are reported.

[0075] The data above shows that neat samples and blend samples containing the friction modifiers of the present invention possess improved low temperature stability, as examples containing the present invention have results more consistently showing clear samples with little or no sediment, gel and/or special cases compared to friction modifiers outside the scope of the invention.

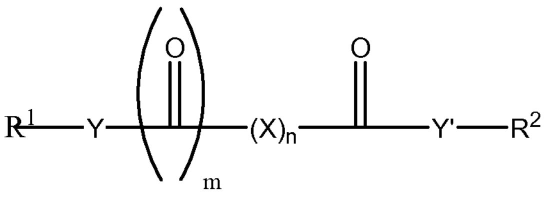
[0076] Each of the documents referred to above is incorporated herein by reference. Except in the Examples, or where otherwise explicitly indicated, all numerical quantities in this description specifying amounts of materials, reaction conditions, molecular weights, number of carbon atoms, and the like, 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, which may be customarily present in the commercial material, unless otherwise indicated. It is to be understood that the upper and lower amount, range, and ratio limits set forth herein may be independently combined. Similarly, the ranges and amounts for each element of the invention can be used together with ranges or amounts for any of the other elements. As used herein, the expression "consisting essentially of" permits the inclusion of substances that do not materially affect the basic and novel characteristics of the composition under consideration.

[0077] In addition, all the embodiments described above have been contemplated as to their use, both alone and in combination, with all of the other embodiments described above, and these combinations are considered to be part of the present invention. The specific embodiments of amines and alcohols described above have been contemplated in combination with the specific embodiments of the carboxylic acids useful in the present invention.

3623-01-WO

What we claim:

1. A fuel additive composition comprising:
(a) an ashless friction modifier represented by Formula I;
(b) an optional solvent; and
(c) one or more optional additional performance additives;



$$R^1-Y-\left(\overset{O}{\overset{\|}{C}}\right)_m-(X)_n-\overset{O}{\overset{\|}{C}}-Y'-R^2$$

Formula I

wherein:

Y and Y' are independently -O-, >NH, >NR^3, or an imide group formed by taking together both Y and Y' groups and forming a R^1-N< group between two >C=O groups;

X is independently -Z-O-Z'-, >CH$_2$, >CHR^4, >CR^{4}R^5, >C(OH)(CO$_2$R^2), >C(CO$_2$R^2)$_2$, >CHOR^6, or >CHCO$_2$R^2.

Z and Z' are independently >CH$_2$, >CHR^4, >CR^{4}R^5, >C(OH)(CO$_2$R^2), or >CHOR^6;

n is 0 to 10, or 1 to 8, or 1 to 6, or 2 to 6, or 2 to 4, with the provisos that when n is 1, X is not >CH$_2$, and when n is 2, both X's are not simultaneously >CH$_2$;

m is 0 or 1;

R^1 is independently hydrogen or a hydrocarbyl group, typically containing 1 to 150, 4 to 30, or 6 to 20, or 10 to 20, or 11 to 18, or 8 to 10 carbon atoms, with the proviso that when R^1 is hydrogen, m is 0, and n is more than or equal to 1;

R^2 is a hydrocarbyl group, typically containing 1 to 150, 4 to 30, or 6 to 20, or 10 to 20, or 11 to 18, or 8 to 10 carbon atoms;

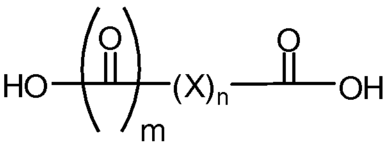
R^3, R^4 and R^5 are independently hydrocarbyl groups, hydroxyl-containing hydrocarbyl groups, or carboxyl-containing hydrocarbyl groups; and

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

2. The additive composition of claim 1, wherein the friction modifier of Formula I is derived from at least one of a hydroxy-polycarboxylic acid di-ester, a hydroxy-polycarboxylic acid di-amide, a hydroxy-polycarboxylic acid di-imide, a hydroxy-polycarboxylic acid ester-amide, a hydroxy-polycarboxylic acid ester-imide, and a hydroxy-polycarboxylic acid imide-amide.

3. The additive composition of claim 1, wherein Formula I defines m as 0 or 1, n as 1 to 2, X is >$CHOR^6$, and R^1, R^2 and R^6 are independently hydrogen or hydrocarbyl groups containing 4 to 30 carbon atoms.

4. The additive composition of claim 1 wherein component (a) is the condensation product of (i) a material represented by Formula II and (ii) a mixture comprising a branched alcohol or branched amine having 1 to about 150 carbon atoms, or combinations thereof;



Formula II

wherein

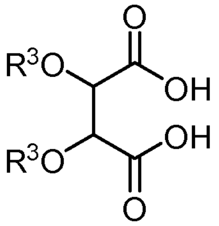
each X is independently -Z-O-Z-, >CH_2, >CR^1R^2, >$C(OH)(CO_2R^2)$, or >$CHOR^2$; and wherein each Z is independently >CH_2, >CR^1R^2, >$C(OH)(CO_2R^2)$, or >$CHOR^2$;

m is 0 or 1; n is 1 to 10, with the proviso that when n=1, X is not >CH_2, and when n=2, both X's are not >CH_2; and

each R^1 and R^2 are independently hydrogen or a hydrocarbyl groups.

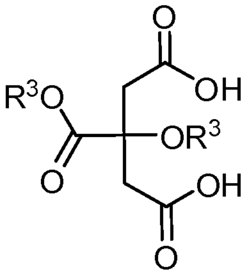
5. The additive composition of claim 4 wherein X in Formula II is >CHOR^2, m is 1, and n is 2 or wherein $(X)_n$ in Formula II is -CH$_2$-C(OH)(CO$_2$R^2)-CH$_2$- and m is 1.

6. The additive composition of claim 4 wherein component (a)(i) is represented by Formula III, Formula IV, or a combination thereof:



Formula III

wherein each R^3 is independently H, or a hydrocarbyl group, or wherein the R^3 groups together form a ring;



Formula IV

wherein each R^3 is independently H, or a hydrocarbyl group.

7. The additive composition of claim 4 wherein component (a)(ii) comprises a mixture of one or more branched alcohols or branched amines, or combinations thereof wherein the branched alcohols or branched amines contain from 6 to 16 carbon atoms.

8. The additive composition of claim 4 wherein at least 25 percent by weight of component (a)(ii) are branched alcohols, branched amines or combinations thereof.

9. The additive composition of claim 4 wherein the component (a)(ii) comprises alcohols selected from the group consisting of: 2-methyl-1-pentanol,

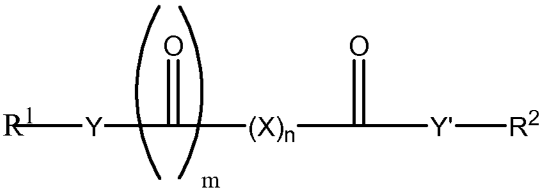
2-ethylhexanol, 2-octanol, isooctyl alcohol, isotridecyl alcohol, or combinations thereof.

10. The additive composition of claim 1, wherein component (a) is present in an amount of about 1 ppm to about 10000 ppm.

11. A fuel composition suitable for use in an internal combustion engine, comprising:

(a) an friction modifier represented by Formula I; and

(b) a fuel:



Formula I

wherein:

Y and Y' are independently -O-, >NH, >NR^3, or an imide group formed by taking together both Y and Y' groups and forming a R^1-N< group between two >C=O groups;

X is independently -Z-O-Z'-, >CH$_2$, >CHR^4, >CR^{4}R^5, >C(OH)(CO$_2$R^2), >C(CO$_2$R^2)$_2$, >CHOR^6, or >CHCO$_2$R^2.

Z and Z' are independently >CH$_2$, >CHR^4, >CR^{4}R^5, >C(OH)(CO$_2$R^2), or >CHOR^6;

n is 0 to 10, or 1 to 8, or 1 to 6, or 2 to 6, or 2 to 4, with the provisos that when n is 1, X is not >CH$_2$, and when n is 2, both X's are not simultaneously >CH$_2$;

m is 0 or 1;

R^1 is independently hydrogen or a hydrocarbyl group, typically containing 1 to 150, 4 to 30, or 6 to 20, or 10 to 20, or 11 to 18, or 8 to 10 carbon atoms, with the proviso that when R^1 is hydrogen, m is 0, and n is more than or equal to 1;

R^2 is a hydrocarbyl group, typically containing 1 to 150, 4 to 30, or 6 to 20, or 10 to 20, or 11 to 18, or 8 to 10 carbon atoms;

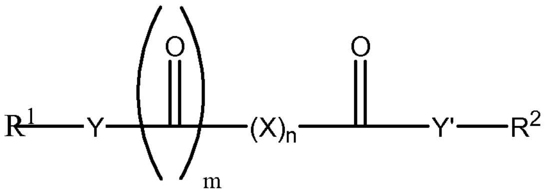
R^3, R^4 and R^5 are independently hydrocarbyl groups, hydroxyl-containing hydrocarbyl groups, or carboxyl-containing hydrocarbyl groups; and

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

12. A method of operating an internal combustion engine, comprising supplying to said engine a fuel composition comprising:

(a) a friction modifier represented by Formula I; and

(b) a fuel;



$$R^1-Y-\left(\overset{O}{\overset{\|}{C}}\right)_m-(X)_n-\overset{O}{\overset{\|}{C}}-Y'-R^2$$

Formula I

wherein:

Y and Y’ are independently -O-, >NH, $>NR^3$, or an imide group formed by taking together both Y and Y’ groups and forming a R^1-N< group between two >C=O groups;

X is independently -Z-O-Z’-, $>CH_2$, $>CHR^4$, $>CR^4R^5$, $>C(OH)(CO_2R^2)$, $>C(CO_2R^2)_2$, $>CHOR^6$, or $>CHCO_2R^2$.

Z and Z’ are independently $>CH_2$, $>CHR^4$, $>CR^4R^5$, $>C(OH)(CO_2R^2)$, or $>CHOR^6$;

n is 0 to 10, or 1 to 8, or 1 to 6, or 2 to 6, or 2 to 4, with the provisos that when n is 1, X is not $>CH_2$, and when n is 2, both X’s are not simultaneously $>CH_2$;

m is 0 or 1;

R^1 is independently hydrogen or a hydrocarbyl group, typically containing 1 to 150, 4 to 30, or 6 to 20, or 10 to 20, or 11 to 18, or 8 to 10 carbon atoms, with the proviso that when R^1 is hydrogen, m is 0, and n is more than or equal to 1;

R^2 is a hydrocarbyl group, typically containing 1 to 150, 4 to 30, or 6 to 20, or 10 to 20, or 11 to 18, or 8 to 10 carbon atoms;

R^3, R^4 and R^5 are independently hydrocarbyl groups, hydroxyl-containing hydrocarbyl groups, or carboxyl-containing hydrocarbyl groups; and

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

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2009/049739

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10L1/18 C10L1/22 C10L10/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10L C10M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 338 470 A (HIEBERT JOHN [US] ET AL) 16 August 1994 (1994-08-16) column 1, line 53 - line 61; examples 1-5; tables 1,2	1,2, 10-12
X	US 2005/198894 A1 (MIGDAL CYRIL A [US] ET AL) 15 September 2005 (2005-09-15) paragraph [0003]; example 17	1-6,8, 10-12
X	US 4 446 038 A (SCHLICHT RAYMOND C [US] ET AL) 1 May 1984 (1984-05-01) claims 10,12; table 1	1,2,10
X	US 2006/183647 A1 (KOCSIS JODY [US] ET AL) 17 August 2006 (2006-08-17) paragraphs [0027], [0031], [0036]	1-9,11, 12
	-/--	

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed
- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search 26 August 2009	Date of mailing of the international search report 03/09/2009
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Fax: (+31–70) 340–3016	Authorized officer Klaes, Daphne

1

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2009/049739

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO 2008/147701 A (LUBRIZOL CORP [US]; DAVIES MARK [GB]; MCATEE RODNEY J [GB]) 4 December 2008 (2008-12-04) paragraphs [0020], [0026]; claim 4; example 1	1-9
P,X	WO 2008/147704 A (LUBRIZOL CORP [US]; MOSIER PATRICK E [US]; KOCSIS JODY [US]; DAVIES MA) 4 December 2008 (2008-12-04) paragraph [0049]; claim 1; example 1	1-9

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2009/049739

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5338470 A	16-08-1994	NONE	
US 2005198894 A1	15-09-2005	EP 1740679 A2	10-01-2007
		JP 2007528440 T	11-10-2007
		WO 2005087904 A2	22-09-2005
US 4446038 A	01-05-1984	NONE	
US 2006183647 A1	17-08-2006	CA 2637238 A1	16-08-2007
		CN 101379169 A	04-03-2009
		EP 1991645 A2	19-11-2008
		JP 2009526097 T	16-07-2009
		WO 2007092724 A2	16-08-2007
WO 2008147701 A	04-12-2008	NONE	
WO 2008147704 A	04-12-2008	NONE	