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(54) **STABILIZED BLENDS CONTAINING FRICTION MODIFIERS**

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(57) **ABSTRACT**

The present invention relates to functional fluid compositions containing friction modifiers, and specifically stable compositions containing friction modifiers with limited solubility in and/or limited compatibility with the functional fluids with which they are used. In particular the present invention deals with functional fluids used in internal combustion engines, such as engine oils, and friction modifiers that contain one or more amide functional groups, where the friction modifier is present in the functional fluid composition at levels that would otherwise cause the composition to be unstable and/or hazy.

STABILIZED BLENDS CONTAINING FRICTION MODIFIERS

CROSS REFERENCE TO RELATED APPLICATION

[0001] This application is a continuation application of U.S. application Ser. No. 13/512,395 filed on Jul. 17, 2012, which claims priority to PCT Application Serial No. PCT/US2010/056916 filed on Nov. 17, 2010, which claims the benefit of Provisional Application Ser. No. 61/264,875 filed on Nov. 30, 2009. These applications are incorporated in their entirety herein by reference.

BACKGROUND OF THE INVENTION

[0002] The present invention relates to functional fluid compositions containing friction modifiers, and specifically stable compositions containing friction modifiers with limited solubility in and/or limited compatibility with the functional fluids with which they are used.

[0003] Friction modifiers and their importance to various types of functional fluids are known. However, many friction modifiers may only be used in limited ways due to solubility and/or compatibility issues with the functional fluids in which they are used. Many friction modifiers, and specifically those derived from hydroxy-carboxylic acids, have limited solubility in functional fluids, such as engine oils and gear oils. These friction modifiers, when used at levels above their solubility and/or compatibility limits, may fall out of the functional fluid composition over time and/or cause the composition to appear hazy or cloudy.

[0004] These are serious issues in the manufacturing and blending processes of the fluids as well as in the field. For example, a functional fluid additive manufacturer would sell a homogeneous additive package of performance chemicals, which may then be added to a base oil to give a final lubricant, which in turn is sold in tanks, drums, cans and plastic containers for final delivery of the lubricant to the equipment to be lubricated. To maintain assurance of performance of the final lubricant, or any other functional fluid, in the equipment in which it is used, the concentrate and the lubricant must remain homogeneous throughout these steps. In other words, all of the additives present must be compatible with each of the various materials it comes into contact with and/or finds itself, from the additive package to the concentrate to the final fluid. This stringent standard greatly limits the choices of and available treatment levels for many additives, including the friction modifiers discussed herein. These friction modifiers could provide improved performance to a functional fluid but not widely used and/or are not used at the optimal level because the additive does not meet the solubility and/or compatibility requirements discussed above.

[0005] In the field, functional fluid compositions that drop out one or more components over time may not perform properly unless they are well-mixed before use, or may be removed by filters associated with the equipment in which the functional fluid is used. The haziness and/or cloudiness of a functional fluid, which may be measured as the fluid's turbidity, is often seen as a sign the composition is not stable, or may be in an early stage of separation and/or component drop out. Such conditions are not desired in functional fluid compositions, for both performance and aesthetic related reasons. This reality has created constraints on the use of various friction modifiers, such as effective maximum treat rates.

[0006] Without these solubility and/or compatibility limitations on the use of these friction modifiers, greater performance and equipment protection might be achievable, including for example extended life of a lubricant or a lubricated piece of equipment such as engines, automatic transmissions, gear assemblies and the like. Improved fuel economy and viscosity stability might be achievable as well. Greater performance may even be achievable with lesser amounts of chemical as well as greater amounts, depending on the selection of the more effective, but otherwise not suitable chemicals from a compatibility or solubility standpoint when delivered in a conventional manner.

[0007] There is a need for functional fluid compositions that contain higher amounts of friction modifiers while still remaining stable and/or clear. There is particularly a need for functional fluid compositions, such as engine oil compositions, that contain friction modifiers derived from a hydroxy-carboxylic acid, at levels that would otherwise cause the composition to be unstable and/or hazy, as described above. The compositions and methods of the present invention overcome these constraints and thus allow the use of these friction modifiers at levels not otherwise possible while still maintaining the stability and/or clarity of the functional fluid composition.

SUMMARY OF THE INVENTION

[0008] Functional fluid compositions have been discovered that may contain high amounts of friction modifiers, and particularly friction modifiers with limited solubility in and/or compatibility with the functional fluid compositions in which they are used, allowing for the use of higher amounts of such friction modifiers in these functional fluid compositions, while maintaining the stability, clarity, and/or compatibility of the overall composition.

[0009] The present invention provides a composition that includes: (a) a medium, which may include a solvent, a functional fluid, or combinations thereof; and (b) a friction modifier component that is not fully soluble in the medium; and (c) a stabilizing component that is soluble in (a) and that interacts with (b) such that (b)'s solubility in (a) is improved, or perhaps more accurately, (b)'s solubility in the combination of (a) and (b) is improved over (b)'s solubility in (a). Components (b) and (c) may be present in component (a) in the form of dispersed particles having an average diameter of less than 10 microns.

[0010] In some embodiments component (b), the friction modifier, includes a compound containing one or more amide functional groups and component (c), the stabilizing component, includes: (i) an overbased detergent with a metal to substrate ratio of greater than 3:1, including borated versions; (ii) an alkyl imidazoline; (iii) a hydrocarbyl phosphoric acid or acid ester, a hydrocarbyl thiophosphoric acid or acid ester, a hydrocarbyl dithiophosphoric acid or acid ester, an amine salt of one or more of these acids and acids esters, or combinations thereof; (iv) an alkylbenzene sulfonate or derivatives thereof; or combinations thereof

[0011] In some embodiments the compositions of the present invention result in an improvement in the turbidity of the composition, as defined by a lower Jackson Turbidity Unit (JTU) and/or Nephelometric Turbidity Unit (NTU) value compared to the same composition that does not

contain (c), the stabilizing component. In some embodiments the compositions of the present invention have a maximum JTU and/or NTU value of 100.

[0012] The present invention also provides for a process of preparing a clear and stable composition, as described herein, said method including the steps of: (I) adding components (b) and (c) to component (a); and (II) mixing the components so that particles of components (b) and (c) have an average diameter of less than 10 microns.

DETAILED DESCRIPTION OF THE INVENTION

[0013] Various preferred features and embodiments will be described below by way of non-limiting illustration.

[0014] The present invention provides compositions and methods that allow for the use of certain friction modifiers in functional fluid compositions that could not otherwise be used, and/or could not be used at the levels allowed for by the present invention, without resulting in unstable, unclear, and/or hazy compositions.

[0015] The types of functional fluids in and with which the compositions and methods of the present invention may be used can include: gear oils, transmission oils, hydraulic fluids, engine oils, two cycle oils, metalworking fluid, fuels and the like. In one embodiment the functional fluid is engine oil. In another embodiment the functional fluid is gear oil. In another embodiment the functional fluid is a transmission fluid. In another embodiment the functional fluid is a hydraulic fluid. In another embodiment the functional fluid is a fuel.

[0016] In some embodiments the present invention does not include the use of a delivery device, for example a device that acts to contain the friction modifier and contact it with the functional fluid with which it is to be added. In some embodiments the present invention does not included the use of either a gel composition or a solid composition, where such compositions slow release one or more components into a functional fluid. Rather the present invention provides a means for incorporating friction modifiers into functional fluids, by use of a combination of components, which result in a functional fluid with the high level of friction modifier while still being stable, clear and/or non-hazy.

[0017] In some embodiments the present invention provides a composition that is more stable, clearer, and/or less hazy than a composition that is identical except for it missing one or more components. In some embodiments the missing component is the stabilizing component. In other embodiments the compositions of the present invention have a lower turbidity compared to compositions that are identical except for them missing the stabilizing component of the present invention. In some of these embodiments, the compositions' turbidity is expressed as a JTU and/or NTU value. In other embodiments the compositions of the present invention have a maximum JTU and/or NTU value of 100, of 90 or even of 80.

[0018] JTU and NTU values may be measured US EPA method 180.1. JTU and NTU values may also be measured without any further dilution in Jackson Turbidity Units (JTU's) by using a Monitek Model 151 Turbidimeter.

The Medium

[0019] The compositions of the present invention include a medium. The medium may be a solvent, a functional fluid, an additive concentrate, or combinations thereof.

[0020] Suitable solvents include aliphatic hydrocarbons, aromatic hydrocarbons, oxygen containing compositions, or mixtures thereof. 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. Suitable solvents also include oils of lubricating viscosity, naphtha, toluene, xylene, or combinations thereof. The oil of lubricating viscosity can comprise natural oils, synthetic oils, or mixtures thereof. The oil of lubricating viscosity can be an API (American Petroleum Institute) Group II, III, IV, V base oil or mixture thereof. Examples of commercially available aliphatic hydrocarbon solvents or diluents, to include oils of lubricating viscosity, are Pilot™ 140 and Pilot™ 299 and Pilot™ 900 available from Petrochem Carless, Petro-Canada™ 100N, Nexbase™, Yubase™, and 4 to 6 cSt poly(alpha-olefins).

[0021] Suitable functional fluids include any of the functional fluids listed above, including mixtures of such fluids. In many embodiments the functional fluids, or other materials used as the medium, contain additional additives in addition to components (b) and (c) described in detail below. These additional additives are described in greater detail below.

[0022] In one embodiment of the invention the medium and/or the overall composition is 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 20 ppm, less than 15 ppm, less than 10 ppm, or less than 1 ppm of at least one member selected from the group consisting of sulphur, phosphorus, sulfated ash, and combinations thereof.

[0023] In one embodiment, the medium and the stabilizing component may be similar materials. That is a material of the same type may perform the functions of both components. For example when the invention is in the form of a concentrate the medium present may act as a stabilizing component and vice versa. This concentrate may then be added to a functional fluid as a top treat and/or additive package, resulting in a stable and homogeneous functional fluid which would otherwise be cloudy or incompatible in the absence of stabilizer component/medium material.

The Friction Modifier

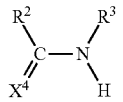
[0024] The compositions of the present invention include a friction modifier component. The friction modifier component may include a least one friction modifier that is not fully soluble and/or compatible in the medium and/or functional fluid in which it is to be used. By not fully soluble and/or compatible, it is meant that the friction modifier does not stay dissolved and/or suspended in the fluid to which it is added, causes the fluid to appear hazy and/or cloudy, have sediments, or any combination thereof. In some embodiments, the friction modifier causes the fluid in which it is used to have an NTU and/or JTU value above 80, 90 or even 100. In some embodiments this fluid is a functional fluid composition such as a finished lubricant or an additive concentrate.

[0025] In some embodiments the friction modifier of the present invention is soluble and/or compatible with a fluid at low concentrations, but becomes less than soluble and/or compatible at higher concentrations. In some embodiments friction modifiers suitable for use in the present invention are not fully soluble and/or compatible, as defined above,

when present in a fluid at concentrations of or more than 0.1, 0.15, 0.2, 0.3, 0.5, or 1.0 percent by weight.

[0026] In some embodiments the friction modifier of the present invention comprises a compound containing one or more amide functional groups. Suitable friction modifiers include compounds represented by Formula (I):

Formula I



wherein: X^4 is an oxygen atom or a sulfur atom; and each R^2 and R^3 is independently a hydrogen or a hydrocarbyl group. Examples of suitable friction modifiers include oleyl amide, stearyl amide, or combinations thereof.

[0027] Fatty acid amides have been discussed in detail in U.S. Pat. No. 4,280,916. Suitable amides are C_8-C_{24} aliphatic monocarboxylic amides and are well known. Reacting the fatty acid based compound with ammonia or an amine produces the fatty amide. The fatty acids and amides derived there from may be either saturated or unsaturated. Important fatty acids include lauric acid (C_{12}), palmitic acid (C_{16}), and steric acid (C_{18}). Other important unsaturated fatty acids include oleic, linoleic and linolenic acids, all of which are C_{18}. In one embodiment, the fatty amides of the instant invention are those derived from the C_{18} unsaturated fatty acids.

[0028] The fatty amines and the diethoxylated long chain amines such as N,N-bis-(2-hydroxyethyl)-tallowamine themselves are generally useful as friction modifier components of this invention. Both types of amines are commercially available. Fatty amines and ethoxylated fatty amines are described in greater detail in U.S. Pat. No. 4,741,848.

[0029] The friction modifier may be present in the compositions of the present invention at levels of at least 0.05, 0.1, 0.15, 0.2, 0.3, 0.5 or even 1.0 percent by weight. The friction modifier may be present at less than 10, 7.5, 5, or even 4 or 3 percent by weight.

[0030] The compositions of the present invention, and specifically the friction modifier component, may optionally include one or more additional friction modifiers. These additional friction modifiers may or may not have the solubility and/or compatibility issues of the friction modifiers described above. These additional friction modifiers may include esters of polyols such as glycerol monooleates, as well as there borated derivatives; fatty phosphites; borated fatty epoxides; sulfurized olefins; compounds derived from a hydroxy-carboxylic acid such as oleyl tartrimide, stearyl tartrimide, and 2-ethylhexyl tartrate; and mixtures thereof.

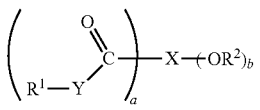
[0031] Esters of polyols include fatty acid esters of glycerol. These can be prepared by a variety of methods well known in the art. Many of these esters, such as glycerol monooleate and glycerol mono-tallowate, are manufactured on a commercial scale. The esters useful for this invention are oil-soluble and are preferably prepared from C_8 to C_{22} fatty acids or mixtures thereof such as are found in natural products. The fatty acid may be saturated or unsaturated. Certain compounds found in acids from natural sources may include licanic acid which contains one keto group. Useful C_8 to C_{22} fatty acids are those of the formula R—COOH wherein R is alkyl or alkenyl.

[0032] The fatty acid monoester of glycerol is useful. Mixtures of mono and diesters may be used. Mixtures of mono- and diester can contain at least about 40% of the monoester. Mixtures of mono- and diesters of glycerol containing from about 40% to about 60% by weight of the monoester can be used. For example, commercial glycerol monooleate containing a mixture of from 45% to 55% by weight monoester and from 55% to 45% diester can be used.

[0033] Useful fatty acids for making these fatty acid esters include oleic, stearic, isostearic, palmitic, myristic, palmitoleic, linoleic, lauric, linolenic, and eleostearic, and the acids from the natural products tallow, palm oil, olive oil, peanut oil.

[0034] Friction modifiers derived from a hydroxy-carboxylic acid may be formed by the reaction of the acid with an alcohol and/or an amine. Suitable hydroxy-carboxylic acid include those represented by Formula II:

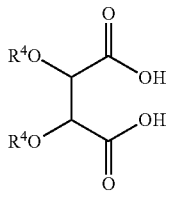
Formula II



wherein: a and b may be independently integers of 1 to 5, or 1 to 2; X may be an aliphatic or alicyclic group, or an aliphatic or alicyclic group containing an oxygen atom in the carbon chain, or a substituted group of the foregoing types, said group containing up to 6 carbon atoms and having a+b available points of attachment; each Y may be independently —O—, >NH, or >NR^3 or two Y's together representing the nitrogen of an imide structure R^1—N< formed between two carbonyl groups; and each R^1 and R^3 may be independently hydrogen or a hydrocarbyl group, provided that at least one R^1 and R^3 group may be a hydrocarbyl group; each R^2 may be independently hydrogen, a hydrocarbyl group or an acyl group, further provided that at least one —OR^2 group is located on a carbon atom within X that is α or β to at least one of the —C(O)—Y—R^1 groups.

[0035] In one embodiment the acid is represented by Formula III.

Formula III



wherein each R^4 is independently H or a hydrocarbyl group, or wherein the R^4 groups together form a ring. In one embodiment the friction modifier is borated. In another embodiment the friction modifier is not borated.

[0036] In any of the embodiments above, the hydroxy-carboxylic acid may be tartaric acid, citric acid, or combinations thereof, and may also be a reactive equivalent of such acids (including esters, acid halides, or anhydrides). The resulting friction modifiers may include imide, di-ester,

di-amide, or ester-amide derivatives of tartaric acid, citric acid, or mixtures thereof. In one embodiment the derivative of hydroxycarboxylic acid includes an imide, a di-ester, a di-amide, or an ester-amide derivative of tartaric acid.

[0037] The amines used in the preparation of the friction modifier may have the formula RR'NH wherein R and R' each independently represent H, a hydrocarbon-based radical of 1 or 8 to 30 or 150 carbon atoms, that is, 1 to 150 or 8 to 30 or 1 to 30 or 8 to 150 atoms. Amines having a range of carbon atoms with a lower limit of 2, 3, 4, 6, 10, or 12 carbon atoms and an upper limit of 120, 80, 48, 24, 20, 18, or 16 carbon atoms may also be used. In one embodiment, each of the groups R and R' has 8 or 6 to 30 or 12 carbon atoms. In one embodiment, the sum of carbon atoms in R and R' is at least 8. R and R' may be linear or branched. In one embodiment R and R' are linear and have at leas 12 carbons. In such embodiments the groups may include some unsaturation.

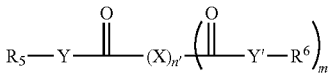
[0038] The alcohols useful for preparing the friction modifier will similarly contain 1 or 8 to 30 or 150 carbon atoms. Alcohols having a range of carbon atoms from a lower limit of 2, 3, 4, 6, 10, or 12 carbon atoms and an upper limit of 120, 80, 48, 24, 20, 18, or 16 carbon atoms may also be used. In certain embodiments the number of carbon atoms in the alcohol-derived group may be 8 to 24, 10 to 18, 12 to 16, or 13 carbon atoms.

[0039] The alcohols and amines may be linear or branched, and, if branched, the branching may occur at any point in the chain and the branching may be of any length. In some embodiments the alcohols and/or amines used include branched compounds, and in still other embodiments, the alcohols and amines used are at least 50%, 75% or even 80% branched.

[0040] In some embodiments, the alcohol and/or amine used includes branched C_{6-18} or C_{8-18} alcohols, branched C_{12-16} alcohols, 2-ethylhexanol, isotridecyl alcohol, linear C_{6-18} or C_{8-18} alcohols, linear C_{12-16} alcohols, or combinations thereof.

[0041] In one embodiment the hydroxy-acid derived friction modifier can be represented by a compound of Formula IV.

Formula IV



wherein: n' is 0 to 10; p is 1 to 5; Y and Y' are independently —O—, >NH, >NR^7, or an imide group formed by the linking of the Y and Y' groups forming a R^1—N< group between two >C═O groups; R^5 and R^6 are independently hydrocarbyl groups, typically containing 1, 4 or 6 to 150, 30 or 24 carbon atoms; m is 0 or 1, and X is independently —CH_2—, >CHR^8 or >CR^{8}R^9, >CHOR^{10}, or >C(CO_2R^{10})$_2$, —CH_3, —CH_2R^8 or —CHR^{8}R^9, —CH_2OR^{10}, or —CH(CO_2R^{10})$_2$, or mixtures thereof wherein: R^7 is a hydrocarbyl group; R^8 and R^9 are independently keto-containing groups (such as acyl groups), ester groups or hydrocarbyl groups; and R^{10} is independently hydrogen or a hydrocarbyl group, typically containing 1 to 150 carbon atoms.

[0042] In some embodiments the compounds represent by Formula IV have at least one X that is hydroxyl-containing (e.g., >CHOR^{10}, wherein R^{10} is hydrogen). When X is hydroxyl-containing, the compound may be derived from hydroxy-carboxylic acids such as tartaric acid, citric acid, or mixtures thereof. In one embodiment the compound is derived from citric acid and R^5 and R^6 contain at least 6 or 8 carbon atoms up to 150, or 6 or 8 to 30 or 24 carbon atoms. In one embodiment the compound is derived from tartaric acid and R^5 and R^6 contain 4 or 6 to 30 or 24 carbon atoms. When X is not hydroxyl-containing, the compound may be derived from malonic acid, oxalic acid, chlorophenyl malonic acid, reactive equivalents thereof such as esters, or mixtures thereof.

[0043] In some embodiments the compositions of the present invention do not include any of these optional friction modifiers and in other embodiments, one or more of any of the optional friction modifiers listed herein are not present in the compositions of the present invention.

[0044] In other embodiments an additional friction modifier is present, and that friction modifier is derived from a hydroxy-acid. In other embodiments the additional friction modifier is oleyl tartrimide, stearyl tartrimide, 2-ethylhexyl tartrimide, or combinations thereof.

[0045] The additional friction modifier may be present in the compositions of the present invention at levels of at least 0.05, 0.1, 0.15, 0.2, 0.3, 0.5 or even 1.0 percent by weight. The additional friction modifier may be present at less than 10, 7.5, 5, or even 4 or 3 percent by weight.

The Stabilizing Component

[0046] The compositions of the present invention include a stabilizing component. The stabilizing component of the present invention is soluble in medium and that interacts with the friction modifier such that its solubility in the medium and/or overall composition is improved. This may be accomplished by an association of the stabilizing component and the friction modifier, resulting in suspended particles of the associated molecules, which remain suspended, dispersed and/or dissolved in the medium and/or overall composition to an extent greater than obtained by the friction modifier alone.

[0047] The stabilizing component of the present invention is an additive that, when combined with the friction modifier in the medium, results in an improvement in the turbidity of the composition, compared to the same composition that does not contain the stabilizing component.

[0048] The stabilizing component may include: (i) an overbased detergent with a metal to substrate ratio of greater than 3:1, including borated versions thereof; (ii) an alkyl imidazoline; (iii) a hydrocarbyl phosphoric acid or acid ester, a hydrocarbyl thiophosphoric acid or acid ester, a hydrocarbyl dithiophosphoric acid or acid ester, an amine salt of one or more of these acids and acids esters, or combinations thereof; (iv) an alkylbenzene sulfonate or derivatives thereof; or combinations thereof.

The Overbased Detergent.

[0049] The stabilizing component may include an overbased detergent. Suitable detergents have a metal to substrate ratio of greater than 3:1. Overbased materials, also referred to as overbased or superbased salts, are generally single phase, homogeneous Newtonian systems characterized by an amount of excess metal that which would be necessary for neutralization according to the stoichiometry of the metal and the particular acidic organic compound

reacted with the metal. The amount of excess metal is commonly expressed in terms of "substrate to metal ratio" which is the ratio of the total equivalents of the metal to the equivalents of the substrate. A more detailed description of the term metal ratio is provided in "Chemistry and Technology of Lubricants", Second Edition, Edited by R. M. Mortier and S. T. Orszulik, pages 85 and 86, 1997.

[0050] The basicity of overbased materials is generally expressed in terms of a total base number (TBN). A TBN is the amount of acid (perchloric or hydrochloric) needed to neutralize all of the overbased material's basicity. The amount of acid is expressed as potassium hydroxide (mg KOH per gram of sample). TBN is determined by titration of overbased material with 0.1 Normal hydrochloric acid solution using bromophenol blue as an indicator. The equivalents of an overbased material are determined by the following equation: equivalent weight=(56,100/TBN). The overbased materials of the present invention generally have a total base number of at least 100 or 200 or 250 or 255 and generally less than 450 or no more than 400.

[0051] Overbased maybe prepared by reacting an acidic material (typically an inorganic acid or lower carboxylic acid, for example carbon dioxide) with a mixture comprising an acidic organic compound, a reaction medium comprising at least one inert, organic solvent (mineral oil, naphtha, toluene, xylene, etc.) for said acidic organic material, a stoichiometric excess of a metal base, and a promoter. Useful acidic organic compounds include carboxylic acids, sulfonic acids, phosphorus-containing acids, phenols (including alkylated phenols) or mixtures of two or more thereof. In some embodiments the acidic organic compounds are sulfonic acids or phenols. Throughout this specification, any reference to acids, such as carboxylic or sulfonic acids, is intended to include the acid-producing derivatives thereof such as anhydrides, lower alkyl esters, acyl halides, lactones and mixtures thereof, unless otherwise specifically stated.

[0052] Suitable overbased detergents include overbased calcium sulfonates, which are derived from sulfonic acids. Suitable acids include sulfonic and thiosulfonic acids, and salts thereof, and also include mono or polynuclear aromatic or cycloaliphatic compounds. The oil-soluble sulfonates can be represented for the most part by one of the following formulae: R_2-T-$(SO_3^+)_a$ and R_3—$(SO_3^-)_b$, wherein T is a cyclic nucleus such as benzene, toluene, naphthalene, anthracene, diphenyl oxide, diphenyl sulfide, petroleum naphthenes, or combinations thereof; R_2 is an aliphatic group such as alkyl, alkenyl, alkoxy, alkoxyalkyl, or combinations thereof; (R_2)+T contains a total of at least 15 carbon atoms; and R_3 is an aliphatic hydrocarbyl group containing at least 15 carbon atoms. R_3 may be an alkyl, alkenyl, alkoxyalkyl, or carboalkoxyalkyl group. In one embodiment, the sulfonic acids have a substituent (R_2 or R_3) derived from one of the above-described polyalkenes, and in some embodiments may be derived from PIB, as described above.

[0053] The production of sulfonates from detergent manufactured by-products by reaction with, e.g., SO_3, is well known to those skilled in the art. See, for example, the article "Sulfonates" in Kirk-Othmer "Encyclopedia of Chemical Technology", Second Edition, Vol. 19, pp. 291 et seq. published by John Wiley & Sons, N.Y. (1969).

[0054] The metal compounds useful in making the basic metal salts are generally any Group 1 or Group 2 metal compounds. In some embodiments the metal used is sodium or potassium, or even sodium. In other embodiments the metals of the metal base include the Group 2a alkaline earth metals such as magnesium, calcium, and barium, as well as the Group 2b metals such as zinc. In some embodiments the Group 2 metals are magnesium, calcium, barium, or zinc, and in some embodiments magnesium or calcium, or even calcium. The metal compounds may be delivered as metal salts. The anionic portion of the salt can be hydroxide, oxide, carbonate, borate, and/or nitrate.

[0055] An acidic material may be used to accomplish the formation of the overbased detergent. The acidic material may be a liquid such as formic acid, acetic acid, nitric acid, and/or sulfuric acid. Acetic acid is particularly useful. Inorganic acidic materials may also be used such as HCl, SO_2, SO_3, CO_2, and H_2S. In some embodiments the material used is CO_2, often used in combination with acetic acid. An acidic gas may be employed to accomplish the formation of the overbased detergent, such as carbon dioxide or sulfur dioxide.

[0056] A promoter is a chemical employed to facilitate the incorporation of metal into the basic metal compositions. A particularly comprehensive discussion of suitable promoters is found in U.S. Pat. Nos. 2,777,874, 2,695,910, and 2,616,904. These include the alcoholic and phenolic promoters. The alcoholic promoters include the alkanols of 1 to 12 carbon atoms such as methanol, ethanol, amyl alcohol, octanol, isopropanol, and mixtures of these and the like. Phenolic promoters include a variety of hydroxy-substituted benzenes and naphthalenes. Mixtures of various promoters are sometimes used.

[0057] The overbased salt may also be a borated complex. Borated complexes of this type can be prepared by heating the basic metal salt with boric acid at about 50-100° C., the number of equivalents of boric acid being roughly equal to the number of equivalents of metal in the salt. U.S. Pat. No. 3,929,650 discloses such borated complexes and their preparation.

[0058] Suitable overbased detergents also include those derived from phenol and alkylated phenols, which may be referred to as phenates, for example calcium phenate sulfides. The phenate may be a sulphur-containing phenate, a methylene-bridged phenate, or mixtures thereof. In one embodiment the phenate is sulphur-containing/coupled phenate. Such materials are described in U.S. Pat. No. 6,551,965 and EP Publications EP 1903093 A, EP 0601721 A, EP 0271262B2 and EP 0273588 B2.

[0059] Suitable phenate detergents may be formed by reacting an alkylphenol, an alkaline earth metal base and sulfur, typically carried out in the presence of a promoter solvent to form a sulfurized metal phenate. The alkylphenols useful in the present invention are of the formula $R(C_6H_4)OH$ where R is a straight chain or branched chain alkyl group having from 8 to 40 or from 10 to 30 carbons, and the moiety (C_6H_4) is a benzene ring. Examples of suitable alkyl groups include octyl, decyl, dodecyl, tetradecyl, and hexadecyl groups

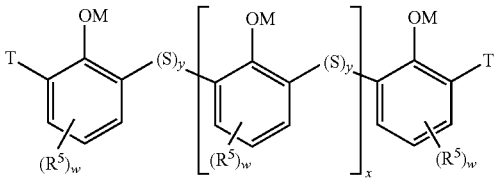
[0060] The alkaline earth metal base can be any of those described above and in some embodiments are calcium and/or magnesium. Examples include calcium oxide, calcium hydroxide, barium oxide, barium hydroxide, magnesium oxide, and the like. Calcium hydroxide, also called hydrated lime, is most commonly used. The promoter solvent, also called a mutual solvent, can be any stable organic

liquid which has appreciable solubility for the alkaline earth metal base, the alkylphenol, and the sulfurized metal phenate intermediate. Suitable solvents include glycols and glycol monoethers such as ethylene glycol, 1,4-butane diol, and derivatives of ethylene glycol, such as monomethyl ether, monoethyl ether, etc. In one embodiment the solvent is one or more vicinal glycols and in another embodiment the solvent includes ethylene glycol. The sulfur used in the reaction may be elemental sulfur, in the form of molten sulfur.

[0061] In some embodiments the phenate detergent is prepared in the presence of a co-surfactant. Suitable co-surfactants include low base alkylbenzene sulfonates, hydrocarbyl substituted acylating agents such as polyisobutenyl succinic anhydrides (PIBSA), and succinimide dispersants such as polyisobutenyl succinimides. Suitable sulfonates include sulfonic acid salts having a molecular weight preferably of more than 400 obtained by sulfonating alkylbenzenes derived from olefins or polymers of C2-C4 olefins of chain length C15-C80 and alkaline earth metals such as calcium, barium, magnesium etc. Suitable co-surfactants include and/or may be derived from PIMA, which may itself be derived from 300 to 5000, or 500 to 3000, or 800 to 1600 number average molecular weight polyisobutylene.

[0062] As noted above, these phenate detergents are overbased by reacting them with carbon dioxide gas in the presence of additional alkaline earth meal base, typically in the presence of a promoter solvent. In one embodiment, the phenate sulfide detergents of the composition can be represented by Formula (V):

Formula V



wherein the number of sulphur atoms y can be in the range from 1 to 8, 6 or 4; R^5 can be hydrogen or hydrocarbyl groups; T is hydrogen or an $(S)_y$ linkage terminating in hydrogen, an ion or a non-phenolic hydrocarbyl group; w can be an integer from 0 to 4; and M is hydrogen, a valence of a metal ion, an ammonium ion and mixtures thereof.

[0063] When M is an equivalent of a metal ion, the metal can be monovalent, divalent, trivalent or mixtures of such metals. When monovalent, the metal M can be an alkali metal, such as lithium, sodium, potassium or combinations thereof. When divalent, the metal M can be an alkaline earth metal, such as magnesium, calcium, barium or mixtures of such metals. When trivalent, the metal M can be aluminum. In one embodiment the metal is an alkaline earth metal and in another embodiment the metal is calcium.

[0064] The monomeric units of the above combine in such a way with itself x number of times to form oligomers of hydrocarbyl phenol. Oligomers are described as dimers, trimers, tetramers, pentamers and hexamers when x is equal to 0, 1, 2, 3, and 4. Typically the number of oligomers represented by x can be in the range from 0, 1 to 10, 9, 8, 6, 5 or even 2. Typically an oligomer is present in significant quantities if concentrations are above 0.1, 1 or even 2 percent by weight. Typically an oligomer is present in trace amounts if concentrations are less than 0.1 percent by weight. Generally for at least 50 percent of the molecules, x is 2 or higher. In some embodiments the overall sulfur-containing phenate detergent contains less than 20 percent by weight dimeric structures.

[0065] In the structure above each R^5 can be hydrogen or a hydrocarbyl group containing from 4, 6, 8 or 9 to 80, 45, 30 or 20 carbon atoms, or 14 carbon atoms. The number of R^5 substituents (w) other than hydrogen on each aromatic ring can be in the range from 0 or 1 to 4, 3 or 2, or be just 1. Where two or more hydrocarbyl groups are present they may be the same or different and the minimum total number of carbon atoms present in the hydrocarbyl substituents on all the rings, to ensure oil solubility, can be 8 or 9. The preferred components include 4-alkylated phenols containing alkyl groups with the number of carbon atoms between 9 and 14, for example 9, 10, 11, 12, 13, 14 and mixtures thereof. The 4-alkylated phenols typically contain sulphur at position 2. The phenate detergent represented by the structure above may also be overbased using an alkaline earth metal base, such as calcium hydroxide.

[0066] In some embodiments the phenate detergent used in the present invention is an overbased sulfurized alkaline earth metal hydrocarbyl phenate, which may optionally be modified by the incorporation of at least one carboxylic acid having the formula: R—CH(R^1)—COOH where R is a C_{10} to C_{24} straight chain alkyl group and R^1 is hydrogen, or an anhydride or ester thereof. Such overbased phenates may be prepared by reacting: (i) a non-overbased sulfurized alkaline earth metal hydrocarbyl phenate as described above, (ii) an alkaline earth metal base which may be added as a whole or in increments, (iii) either a polyhydric alcohol having from 2 to 4 carbon atoms, a di- or tri-(C_2 to C_4) glycol, an alkylene glycol alkyl ether or a polyalkylene glycol alkyl ether, (iv) a lubricating oil present as a diluent, (v) carbon dioxide added subsequent to each addition of component (ii), and optionally (vi) at least one carboxylic acid as defined above.

[0067] Component (ii) may be any of the earth metal based described above and in some embodiments is calcium hydroxide.

[0068] Component (iii) may suitably be either a dihydric alcohol, for example ethylene glycol or propylene glycol, or a trihydric alcohol, for example glycerol. The di- or tri-(C_2 to C_4) glycol may suitably be either diethylene glycol or triethylene glycol. The alkylene glycol alkyl ether or polyalkylene glycol alkyl ether may suitably be of the formula: $R(OR^1)_xOR^2$ where R is a C_1 to C_6 alkyl group, R^1 is an alkylene group, R^2 is hydrogen or C_1 to C_6 alkyl and x is an integer in the range from 1 to 6. Suitable examples include the monomethyl or dimethyl ethers of ethyleneglycol, diethylene glycol, triethylene glycol or tetraethylene glycol. A particularly suitable solvent is methyl digol. Mixtures of glycols and glycol ethers may also be employed. In some embodiments the glycol or glycol ether is used in combination with an inorganic halide. In one embodiment, component (c) is either ethylene glycol or methyl digol, the latter in combination with ammonium chloride and acetic acid.

[0069] In some embodiments, component (vi), the carboxylic acid used to modify the phenate has an R group that is an unbranched alkyl group, which may contain from 10 to 24 or 18 to 24 carbon atoms. Examples of suitable saturated carboxylic acids include capric acid, lauric acid, myristic

acid, palmitic acid, stearic acid, arachidic acid, behenic acid and lignoceric acid. Mixtures of acids may also be employed. Instead of, or in addition to, the carboxylic acid, there may be used the acid anhydride or the ester derivatives of the acid, preferably the acid anhydride. In one embodiment the acid used is stearic acid.

[0070] In some embodiments sulfur, additional to that already present in component (i), may be added to the reaction. The reaction may be carried out in the presence of a catalyst. Suitable catalysts include hydrogen chloride, calcium chloride, ammonium chloride, aluminum chloride and zinc chloride.

[0071] In one embodiment, the overbased detergent of the present invention is any one or more of the following: an overbased detergent derived from an alkylated phenol, which itself may be derived from conventional PIB; a calcium sulfonate overbased detergent derived from a sulfonic acid, which itself may be derived from conventional PIB, and optionally borated versions thereof. In some embodiments the detergents have a TBN of at least 200, 250 or 290. In other embodiments the calcium sulfonates of the present invention have a TBN of at least 270 or 280. In any such embodiments the TBN of the overbased detergent may be less than 500, 450 or even no more than 400.

[0072] In some embodiments the overbased detergents used in the stabilizing component of the present invention may include one or more of the overbased sulfonates described above having a TBN of at least 200 or 280. The detergents may also include any of the overbased phenate detergents described above having a TBN of at least 30, 50, 120, or at least 200 or 250.

The Alkyl Imidazoline.

[0073] In some embodiments the stabilizing component includes an alkyl imidazoline. Such materials may be derived from the reaction of a carboxylic acid and an amine, including an alkylene polyamine.

[0074] In some embodiments the alkyl imidazoline may also include a reaction product of a hydrocarbyl-substituted succinic acylating agent and a polyamine. Such materials are described in U.S. Pat. No. 4,234,435. However, in some embodiments the alkyl imidazolines of the present invention do not include additives derived from hydrocarbyl-substituted succinic acylating agents.

[0075] In other embodiments the alkyl imidazoline the condensation product of a fatty hydrocarbyl monocarboxylic acylating agent, such as a fatty acid, with a polyamine.

[0076] The hydrocarbyl portion of the fatty hydrocarbyl monocarboxylic acylating agent can be an aliphatic group. The aliphatic group can be linear, branched, or a mixture thereof. The aliphatic group can be saturated, unsaturated, or a mixture thereof. The aliphatic group can have 1 to 50 carbon atoms, in another instance 2 to 30 carbon atoms, and in a further instance 4 to 22 carbon atoms, preferably 8, 10, or 12, to 20 carbon atoms. If the fatty hydrocarbyl moncarboxylic acylating agent is an aliphatic carboxylic acid, it may be seen as comprising a carboxy group (COOH) and an aliphatic group. Thus, the total number of carbon atoms in the carboxylic acid can be from 2, 3, 5, 9 or 13 up to 51, 31, 23, 11, or 21. The monocarboxylic acylating agent can be a monocarboxylic acid or a reactive equivalent thereof, such as an anhydride, an ester, or an acid halide such as stearoyl chloride. Useful monocarboxylic acylating agents are available commercially from numerous suppliers and include tall oil fatty acids, oleic acid, stearic acid and isostearic acid. In some embodiment the fatty acids contain 12 to 24 carbon atoms, and in some embodiment 18 carbon atoms, such as stearic acid, isostearic acid, and combinations thereof.

[0077] A polyamine is an amine having two or more amine groups where a first amine group is a primary amine group and a second amine group is a primary or secondary amine group. The reaction product of the carboxylic acid and the polyamine can contain, in greater or lesser amounts depending on reaction conditions, a heterocyclic reaction product such as 2-imidazoline reaction products as well as amide condensation products. The polyamine can have 2 to 30 carbon atoms and in some embodiments includes alkylenediamines, N-alkyl alkylenediamines, and polyalkylenepolyamines. Useful polyamines include ethylenediamine, 1,2-diaminopropane, N-methylethylenediamine, N-tallow (C_{16}-C_{18})-1,3-propylenediamine, N-oleyl-1,3-propylenediamine, polyethylenepolyamines such as diethylenetriamine and tri ethylenetetramine and tetraethylenepentamine and polyethylenepolyamine bottoms.

[0078] In another embodiment of the invention the monocarboxylic acylating agent and the polyamine are respectively a C_4 to C_{22} fatty carboxylic acid and an alkylenediamine or a polyalkylenepolyamine, and in a further embodiment the fatty carboxylic acid is isostearic acid and the polyamine is a polyethylenepolyamine such as tetraethylenepentamine.

The Phosphorus Containing Additive.

[0079] The stabilizing component may also include a phosphorus containing additive, such as a hydrocarbyl phosphate, a hydrocarbyl thiophosphate, a di-hydrocarbyl dithiophosphate, or combinations thereof, as well as amine salts of one or more such materials. Such additives are generally prepared by reacting one or more phosphorus acids, such as a phosphoric or thiophosphoric acid, including dithiophosphoric acid, with an unsaturated amide, such as an acrylamide, and also include amine salts of full or partial esters of phosphoric or thiophosphoric acids.

[0080] Phosphorus-containing acids suitable for use in preparing the stabilizing component of the present invention include phosphorus acid esters prepared by reacting one or more phosphorus acids or anhydrides with an alcohol. The alcohol used may contain up to about 30, 24, 12 or even 3 carbon atoms. The phosphorus acid or anhydride may be an inorganic phosphorus reagent, such as phosphorus pentoxide, phosphorus trioxide, phosphorus tetraoxide, phosphorus acid, phosphorus halide, lower phosphorus esters, or a phosphorus sulfide, including phosphorus pentasulfide. In some embodiments the phosphorus acid is phosphorus pentoxide, phosphorus pentasulfide, phosphorus trichloride, or combinations thereof. The phosphorus acid ester may be a mono- or diester of phosphoric acid or mixtures thereof.

[0081] Examples of commercially available alcohols include Alfol 810 (a mixture of primarily straight chain, primary alcohols having from 8 to 10 carbon atoms); Alfol 1218 (a mixture of synthetic, primary, straight-chain alcohols containing 12 to 18 carbon atoms); Alfol 20+ alcohols (mixtures of C_{18}-C_{28} primary alcohols having mostly Cm); and Alfol 22+ alcohols (C_{18}-C_{28} primary alcohols containing primarily C_{22} alcohols).

[0082] In another embodiment, the phosphorus-containing acid is a thiophosphorus acid ester and may be a mono- or dithiophosphorus acid ester. Thiophosphorus acid esters are

also referred to as thiophosphoric acids. The thiophosphorus acid ester may be prepared by reacting a phosphorus sulfide, such as those described above, with any of the alcohols described above. Monothiophosphoric acid esters, or monothiophosphates, may be prepared by the reaction of a sulfur source, such as elemental sulfur, with a dihydrocarbyl phosphite. The sulfur source may also be an organosufide, such as a sulfur coupled olefin or dithiophosphate. Monothiophosphates may also be formed in the lubricant blend by adding a dihydrocarbyl phosphite to a lubricating composition containing a sulfur source, such as a sulfurized olefin.

[0083] Dithiophosphoric acids, or phosphorodithioic acids, may be reacted with an epoxide or a glycol and further reacted with a phosphorus acid, anhydride, or lower ester. The epoxide may be an aliphatic epoxide or a styrene oxide, such as ethylene oxide, propylene oxide, butene oxide, octene oxide, dodecene oxide, and styrene oxide. In one embodiment propylene oxide is used. The glycols may be aliphatic glycols having from for 2 to 12, 6 or 3 carbon atoms. The materials may be reacted with P_2O_5 and then salted with an amine.

[0084] The acidic phosphoric acid esters described above may be reacted with ammonia or an amine compound to form an ammonium salt. The salts may be formed separately and then the salt of the phosphorus acid ester may be added to the lubricating composition. Alternately, the salts may also be formed in situ when the acidic phosphorus acid ester is blended with other components to form a fully formulated lubricating composition.

[0085] Suitable amines include monoamines and polyamines, including those described above. The amines may be primary amines, secondary amines or tertiary amines. Useful monoamines may contain from 1 to 24, 14 or 8 carbon atoms, including methylamine, ethylamine, propylamine, butylamine, octylamine, and dodecylamine, dimethylamine, diethylamine, dipropylamine, dibutylamine, methyl butylamine, ethyl hexylamine, trimethylamine, tributylamine, methyl diethylamine, ethyl dibutylamine and the like.

[0086] In one embodiment, the amine may be a fatty (C_{4-30}) amine that include but are not limited to n-hexylamine, n-octylamine, n-decylamine, n-dodecylamine, n-tetradecylamine, n-hexadecylamine, n-octadecylamine, oleylamine and the like. Some examples are commercially available fatty amines such as "Armeen" amines (products available from Armak Chemicals, Chicago, Ill.), such as Armak's Armeen-C, Armeen-O, Armeen-OL, Armeen-T, Armeen-HT, Armeen S and Armeen SD, wherein the letter designation relates to the fatty group, such as cocoa, oleyl, tallow, or soya groups.

[0087] A useful amine is a C12-14 branched tertiary alkyl primary amine supplied by Rohm and Haas under the trade name Primene 81R. In one embodiment, the stabilizing component is an amine salt of a mixture of phosphoric acids and esters and/or an amine salt of a mixture of dithiophosphoric acids and esters, where the mixtures are salted with Primene 81R or a similar amine or mixture of amines.

[0088] The preparation of these phosphorus containing additives, including the amine salts of the acids and esters described above, is discussed in greater detail in U.S. Pat. No. 6,617,287.

[0089] In one embodiment the phosphorus containing additive of the present invention is one or more of the following: a mixture of phosphoric acids, such as hydrocarbyl phosphates, hydrocarbyl thiophosphates, hydrocarbyl dithiophosphates, and combinations thereof including dihydrocarbyl versions thereof; an amine salt of a mixture of such phosphoric acids and/or full or partial esters thereof; (viii) an amine salt of a mixture of such dithiophosphoric acids and/or full or partial esters.

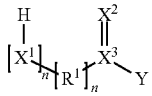
The Alkylbenzene Sulfonate.

[0090] The sulfonic acids described above as suitable for preparing the overbased detergents, may also be used themselves as stabilizing agents. In one embodiment the stabilizing agent includes sulfonic and thiosulfonic acids, and salts thereof, and also include mono or polynuclear aromatic or cycloaliphatic compounds. Such sulfonates are typically oil-soluble sulfonates and in some embodiments are represented by one of the following formulae: R_2-T-$(SO_3^-)_a$ and R_3—$(SO_3^-)_b$, wherein T is a cyclic nucleus such as benzene, toluene, naphthalene, anthracene, diphenyl oxide, diphenyl sulfide, petroleum naphthenes, or combinations thereof; R_2 is an aliphatic group such as alkyl, alkenyl, alkoxy, alkoxyalkyl, or combinations thereof; (R_2)+T contains a total of at least 15 carbon atoms; and R_3 is an aliphatic hydrocarbyl group containing at least 15 carbon atoms. R_3 may be an alkyl, alkenyl, alkoxyalkyl, or carboalkoxyalkyl group. In one embodiment, the sulfonic acids have a substituent (R_2 or R_3) derived from one of the above-described polyalkenes, and in some embodiments may be derived from PIB, as described above. In one embodiment the stabilizing agent of the present invention includes an alkyl benzene sulfonic acid where the alkyl group is derived from PIB.

[0091] The production of sulfonates from detergent manufactured by-products by reaction with, e.g., SO_3, is well known to those skilled in the art. See, for example, the article "Sulfonates" in Kirk-Othmer "Encyclopedia of Chemical Technology", Second Edition, Vol. 19, pp. 291 et seq. published by John Wiley & Sons, N.Y. (1969).

[0092] In some embodiments the stabilizing component of the present invention includes a compound that may be represented by Formula VI.

Formula VI



wherein: X^1 is an oxygen atom, a sulfur atom a hydrocarbylene group or —NR^2; X^2 is an oxygen atom or a sulfur atom; X^3 is =$P(OR^2)$<, or =S(O)<; and Y is —R^2, or —OR^2; each R^1 is a hydrocarbylene group; each R^2 is independently a hydrocarbyl group or —H; and each n is independently 0 or 1. In some embodiments the stabilizing component of the present invention includes a salted version of one or more of the compound described above. In any of the embodiments described above, X^2 of Formula VI may also be a hydrocarbyl group and X^3 may be =C< where the hydrocarbyl group of X^2 may be attached to the carbon atom of X^3 by either a double bond as shown in the formula or but a single bond. In still other embodiments, X^2 of Formula VI is a hydrocarbyl group and X^3 is =C< while the n for the $[R^1]$ group is 0. Various stabilizing components, including many of those described above, fall under this formula and/or at least one of its described embodiments.

[0093] In some embodiments the stabilizing components include compounds that comprise two anchor points and a solubilizing element. An anchor point may be an electron donor, such as an H bond acceptor, and/or an electron acceptor, such as an H bond donor. In some embodiments the two anchor points are in close proximity to one another within the molecule of the compound in the stabilizing component. For example the anchor point may be within 10, 8, 6 or even 4 carbon atoms of one another. In some embodiments the anchor points are within 2 carbon atoms of one another or even connected to adjacent carbon atoms. The solubilizing element may be a hydrocarbyl group long enough to provide the compound some level of solubility in the medium. The solubilizing element may also be a micelle to which the compound is attached, thus holding it in the medium. Many of the stabilizing components described above meet these requirements, as do various amide and acid compounds that fit Formula VI above.

INDUSTRIAL APPLICATION

[0094] The present invention includes a process of preparing a composition that includes combining: (a) a medium comprising a solvent, a functional fluid, or combinations thereof; (b) a friction modifier component that is not fully soluble in the medium; and (c) a stabilizing component that is soluble in (a) and that interacts with (b) such that (b)'s solubility in (a) is improved. The processes of the present invention involve adding components (b) and (c) to component (a) and mixing the components so that particles of components (b) and (c) have an average diameter of less than 10 microns. The processes of the present invention results in a mixture that is clear and/or stable in that the friction modifier does not drop out of solution, does not make the mixture appear cloudy or hazy, stays suspended, dispersed and/or dissolved in the mixture, or combinations thereof, or that at least shows improvement in one or more of these areas when compared to an identical composition that does not contain the stabilizing component.

[0095] While not wishing to be bound by theory, it is believed that in at least some embodiments the compositions of the present invention improve the stability and/or compatibility of the friction modifier component in the overall composition due to the friction modifier component being solubilized in a complex with the solubilizer.

[0096] In some embodiments the processes of the present invention result in a mixture with an improved clarity, as defined by a lower JTU and/or NTU value, compared to the same composition that does not contain the stabilizing component.

[0097] As noted above, components (b) and (c) may be present in component (a) in the form of dispersed particles having an average diameter of less than 10 microns. In some embodiments the particles have an average diameter of less than 10, 5 or 3 microns. In other embodiments, the particles have an average diameter of from 0.01, 0.02, 0.03 or 0.09 to 10, 6, 5 or 3 microns. In some embodiments 80% of the particles meet one or more of the size limitations described above. In other embodiments 90%, 95%, 99% or even 100% of the particles meet the size limits. The means by which the particles are formed is not overly limited, and may include the mixing of components (a), (b) and (c) using conventional equipment and/or techniques.

[0098] In some embodiments the compositions of the present invention and/or the compositions that result from the processes of the present invention include both finished functional fluids and additive concentrates. Finished functional fluids are fluids that are ready for use. Additive concentrates are compositions that may contain all of the additives required for a finished fluid, but in concentrated form. This makes shipment and handling easier. At the appropriate time, the additive concentrate may be blended with a fluid, solvent, or similar diluent, as well as additional additives, to produce a finished functional fluid that is ready for use.

[0099] When referring to finished functional fluids, the compositions involved with the present invention may include: from 1, 3 or 10 to 99, 80 or 70 percent by weight of component (a), the medium; from 0.1, 0.2, 0.3, 0.5 or 1.0 to 10, 7.5, 5, 4 or 3 percent by weight of component (b), the friction modifier; and from 0.1, 0.2, 0.3, 0.5 or 2.0 to 20, 10, 8, 5, 4 or 2 percent by weight of component (c), the stabilizing component.

[0100] When referring to additive concentrates, the compositions involved with the present invention may include: from 0.1, 1, 3 or 10 to 90, 60, 50, 30, or 20 percent by weight of component (a), the medium; from 0.1, 0.5, 1, 5 or 8 to 60, 30, 20 or 10 percent by weight of component (b), the friction modifier; and from 0.1, 0.2, 0.3, 0.5 or 2.0 to 20, 10, 8, 5, 4 or 2 percent by weight of component (c), the stabilizing component. As noted above in some embodiments the medium and the stabilizing component may be the same material, in which case the duel functioning material may be present in any of the ranges provided above for either component (a) or (c).

[0101] In some embodiments the compositions of the present invention are formed by mixing components (b) and (c) into component (a) such that component (b) forms small particles within component (a) and component (c) acts to stabilize these particles. In some embodiments component (c) and component (b) form mixed particles in component (a). In some embodiments some or all of the particles formed are within the sizes described above. In other embodiments, some or even all of the particles are larger than those described above.

[0102] In some embodiments the components of the present invention are mixed by conventional means. The amount of mixing required varies from composition to composition and is that sufficient to produce the particles of the desired size and/or stability. In some embodiments the mixing may be accomplished by milling the components and in still other embodiments the mixing may be accomplished by milling the components at low temperature.

[0103] In one such embodiment, a friction modifier may be mixed into oil in the presence stabilizing component, such as a succinimide dispersant, for example polyisobutylene succinimide. The mixing may be in the form of a milling process using conventional milling equipment and techniques. However, in some embodiments the milling is completed at low temperatures, in some embodiments from at less than 30 degrees C. and in other embodiments from −10, 0 or 5 to 30, 25 or 20 degrees C. The low temperature milling may be achieved by cooled milling equipment, pre-cooled components, adding a chilling agent such as dry ice (solid carbon dioxide) to the components during milling, or a combination thereof. The resulting compositions in some embodiments may be described as stable dispersions and in other embodiments may be described as solubilized

solutions, or even combinations thereof, where the main difference between such embodiments may be the size of the particles involved.

[0104] In other embodiments the compositions of present invention are not formed by milling or any other high-energy input methods, but rather are formed with simple mixing and very little mechanical energy input.

[0105] In some embodiments the functional fluid with which the compositions of the invention are used is a fuel. The fuel compositions of the present invention comprise the stabilized compositions described above and a liquid fuel, and is useful in fueling an internal combustion engine or an open flame burner. These compositions may also contain one or more additional additives described herein. In some embodiments, the fuels suitable for use in the present invention include any commercially available fuel, and in some embodiments any commercially available diesel fuel and/or biofuel.

[0106] The description that follows of the types of fuels suitable for use in the present invention refer to the fuel that may be present in the additive containing compositions of the present invention as well as the fuel and/or fuel additive concentrate compositions to which the additive containing compositions may be added.

[0107] Fuels suitable for use in the present invention are not overly limited. Generally, suitable fuels are normally liquid at ambient conditions e.g., room temperature (20 to 30° C.) or are normally liquid at operating conditions. The fuel can be a hydrocarbon fuel, non-hydrocarbon fuel, or mixture thereof.

[0108] The hydrocarbon fuel can be a petroleum distillate, including a gasoline as defined by ASTM specification D4814, or a diesel fuel, as defined by ASTM specification D975. In one embodiment the liquid fuel is a gasoline, and in another embodiment the liquid fuel is a non-leaded gasoline. In another embodiment 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. In some embodiments, the fuel used in the present invention is a diesel fuel, a biodiesel fuel, or combinations thereof.

[0109] Suitable fuels also include heavier fuel oils, such as number 5 and number 6 fuel oils, which are also referred to as residual fuel oils, heavy fuel oils, and/or furnace fuel oils. Such fuels may be used alone or mixed with other, typically lighter, fuels to form mixtures with lower viscosities. Bunker fuels are also included, which are generally used in marine engines. These types of fuels have high viscosities and may be solids at ambient conditions, but are liquid when heated and supplied to the engine or burner it is fueling.

[0110] The non-hydrocarbon fuel can be an oxygen containing composition, often referred to as an oxygenate, which includes alcohols, ethers, ketones, esters of a carboxylic acids, nitroalkanes, or mixtures thereof. Non-hydrocarbon fuels can include 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.

[0111] 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 one embodiment the liquid fuel is an emulsion of water in a hydrocarbon fuel, a non-hydrocarbon fuel, or a mixture thereof.

[0112] In several embodiments of this invention the liquid fuel can have a sulphur content on a weight basis that is 50,000 ppm or less, 5000 ppm or less, 1000 ppm or less, 350 ppm or less, 100 ppm or less, 50 ppm or less, or 15 ppm or less.

[0113] 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, greater than 99.9% by weight, or greater than 99.99% by weight.

[0114] The compositions described above may also include one or more additional additives. Such additives include oxidation inhibitors and antioxidants, friction modifiers antiwear agents, corrosion inhibitors, or viscosity modifiers, as well as dispersant and detergents different from those described above. These additional additives may be present in the medium, particularly when the medium includes a functional fluid. When present, these additional additives may represent from 0, 0.1, 0.5 or 1 to 2, 5, 10 or 15 percent of the overall composition, when considering a finished fluid, and from 0, 0.5, 1 or 2 to 4, 10, 20 or 40 percent of the overall composition, when considering an additive concentrate.

[0115] As allowed for by the ranges above, in one embodiment, the additive concentrate may comprise the additives of the present invention and be substantially free of any additional solvent. In these embodiments the additive concentrate containing the additives 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.

[0116] As used herein, the terms hydrocarbyl and/or hydrocarbylene substituent and/or group are used in their ordinary sense, which is well-known to those skilled in the art. Specifically, each refers to a group having a carbon atom directly attached to the remainder of the molecule and having predominantly hydrocarbon character. Examples 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.

[0117] 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. In addition the acylating agents and/or substituted hydrocarbon additives of the present invention may form salts or other complexes and/or derivatives, when interacting with other components of the compositions in which they are used. 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.

[0118] As allowed for by the ranges above, in one embodiment, the additive concentrate may comprise the additives of the present invention and be substantially free of any additional solvent. In these embodiments the additive concentrate containing the additives 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.

[0119] Unless otherwise indicates all percent values and ppm values herein are weight percent values and/or calculated on a weight basis.

EXAMPLES

[0120] 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

Example Set 1

[0121] A sample set is prepared by mixing various levels of a stabilizing component with friction modifier component known to have compatibility issues into a lubricating composition. The samples are prepared by adding a specified amount of friction modifier to a set of lubricating composition samples and then adding specified, increasing amounts of stabilizing component to each sample. After the addition the mixtures are heated to 100 degrees C. and stirred until clear. Each sample is then cooled and stored at room temperature. Each sample is then checked at 1 hour, 1 day, 3 days and 1 week after the being placed in storage to check for cloudiness, haziness and/or drop out of the friction modifier. The amount of stabilizing component required to stabilize the set amount of friction modifier component in the lubricating composition (that is, the minimum amount of stabilizing component required to provide a clear lubricating composition after one week of storage) is recorded. The steps are then repeated at another friction modifier component concentration level.

[0122] The lubricating composition used in this sample set is a fully formulated 0W20 GF-5 engine oil composition. The composition is clear when 0 wt % of the friction modifier component is present. The friction modifier used in these samples contains an amide functional group and is formed by the reaction of a carboxylic acid and ammonia or an amine. The stabilizing components used in these samples include: a 300 TBN calcium sulfonate overbased detergent (Inventive Example 1-1); an alkylbenzene sulfonic acid derived from PIB (Inventive Example 1-2); an amine salt of a mixture of phosphoric and/or acids dithiophosphoric and esters (Inventive Example 1-3); an alkyl imidazoline derived from a fatty mono-carboxylic acid and a polyamine (Inventive Example 1-4); a borated 300 TBN calcium sulfonate overbased detergent (Inventive Example 1-5); a non-borated polyisobutenyl succinimide dispersant derived from a polyisobutenyl succinic anhydride derived from PIB and a polyamine (Comparative Example 1-6).

[0123] The table below summarizes the results of the example set.

TABLE 1

Results from Example Set 1.

Example (Stabilizer Used)	Wt % Friction Modifier Present	Min wt % of Stabilizer Required for Clarity
Ex 1-1	0.25 wt %	1.2 wt %
	0.50 wt %	2.4 wt %
	1.0 wt %	7.9 wt %
Ex 1-2	0.25 wt %	0.13 wt %
	0.50 wt %	0.25 wt %
	1.0 wt %	1.0 wt %
Ex 1-3	0.25 wt %	0.5 wt %
	0.50 wt %	1.0 wt %
	1.0 wt %	3.0 wt %
Ex 14	0.25 wt %	1.0 wt %
	0.50 wt %	2.0 wt %
	1.0 wt %	5.0 wt %
Ex 1-5	0.25 wt %	0.25 wt %
	0.50 wt %	0.5 wt %
	1.0 wt %	5.0wt %
Comparative Ex 1-6	0.25 wt %	5.0 wt %
	0.50 wt %	10.0 wt %

[0124] The results show that the stabilizing components of the present invention result in compositions that have good stability. Further, the results show that the stabilizing components of the present invention perform surprisingly better than a non-borated polyisobutenyl succinimide dispersant derived from a polyisobutenyl succinic anhydride derived from PIB and a polyamine, as the inventive examples are required at much lower treat rates to provide a stable blend compared to the comparative example.

[0125] 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."

[0126] 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.

We claim:

1. A composition comprising:

(a) a medium comprising a solvent, a functional fluid, or combinations thereof;

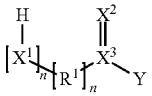
(b) from about 1.0 to about 5 percent by weight of a friction modifier component comprising oleyl amide, stearyl amide, or combinations thereof and is not fully soluble in the medium;

(c) from about 1 to about 8 percent by weight of a stabilizing component that is soluble in (a) and that interacts with (b) such that (b)'s solubility in (a) is improved;

wherein components (b) and (c) are present in component (a) in the form of dispersed particles having an average diameter of less than 10 microns.

2. The composition of claim **1** wherein component (c), the stabilizing component, comprises: (i) an overbased detergent with a metal to substrate ratio of greater than 3:1 wherein the overbased detergent is optionally borated; (ii) an alkyl imidazoline; (iii) a hydrocarbyl phosphoric acid or acid ester, a hydrocarbyl thiophosphoric acid or acid ester, a hydrocarbyl dithiophosphoric acid or acid ester, an amine salt of one or more of these acids and acids esters, or combinations thereof; (iv) an alkylbenzene sulfonate or derivatives thereof; or combinations thereof.

3. The composition of claim **2** wherein component (c), the stabilizing component, comprises a compound represented by the formula:



or a slated version thereof, wherein: X^1 is an oxygen atom, a sulfur atom, a hydrocarbylene group, or —$N(R^2)$—; R^1 is a hydrocarbylene group; X^2 is an oxygen atom or a sulfur atom or a hydrocarbyl group; X^3 is =C<, =$P(OR^2)$<, or =S(O)<; Y is —R^2, or —OR^2; each R^2 is independently a hydrocarbyl group or —H; and each n is independently 0 or 1.

4. The composition of claim **2** wherein (c), the stabilizing agent, comprises: (i) an overbased phenate detergent with a metal to substrate ratio of greater than 3:1; (ii) an alkyl imidazoline; (iii) a hydrocarbyl dithiophosphoric acid, (iv) a amine salt of a phosphoric acid ester; (v) an alkylbenzene-sulfonate or derivatives thereof, or combinations thereof.

5. The composition of claim **2** wherein the overbased detergent is an overbased phenate with a TBN of at least 200.

6. The composition of claim **2** wherein the alkyl imidazoline is derived from a fatty acid and an alkylene polyamine.

7. The composition of claim **1** wherein the turbidity of the overall composition is improved, as defined by a lower JTU and/or NTU value compared to the same composition that does not contain (c), the stabilizing component.

8. A process of preparing a clear and stable composition comprising:

(a) a medium comprising a solvent, a functional fluid, or combinations thereof;

(b) from about 1.0 to about 5 percent by weight of a friction modifier component comprising oleyl amide, stearyl amide, or combinations thereof and is not fully soluble in the medium; and

(c) from about 1 to about 8 percent by weight of a stabilizing component that is soluble in (a) and that interacts with (b) such that (b)'s solubility in (a) is improved;

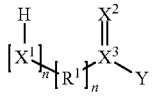
said method comprising the steps of:

I. adding components (b) and (c) to component (a); and

II. mixing the components so that particles of components (b) and (c) have an average diameter of less than 10 microns.

9. The process of claim **8**, wherein component (c), the stabilizing component, comprises: (i) an overbased detergent with a metal to substrate ratio of greater than 3:1 wherein the overbased detergent is optionally borated; (ii) an alkyl imidazoline; (iii) a hydrocarbyl phosphoric acid or acid ester, a hydrocarbyl thiophosphoric acid or acid ester, a hydrocarbyl dithiophosphoric acid or acid ester, an amine salt of one or more of these acids and acids esters, or combinations thereof; (iv) an alkylbenzene sulfonate or derivatives thereof; or combinations thereof.

10. The process of claim **9**, wherein component (c), the stabilizing component, comprises a compound represented by the formula:



or a slated version thereof, wherein: X^1 is an oxygen atom, a sulfur atom, a hydrocarbylene group, or —$N(R^2)$—; R^1 is a hydrocarbylene group; X^2 is an oxygen atom or a sulfur atom or a hydrocarbyl group; X^3 is =C<, =$P(OR^2)$<, or =S(O)<; Y is —R^2, or —OR^2; each R^2 is independently a hydrocarbyl group or —H; and each n is independently 0 or 1.

11. The process of claim **9**, wherein (c), the stabilizing agent, comprises: (i) an overbased phenate detergent with a metal to substrate ratio of greater than 3:1; (ii) an alkyl imidazoline; (iii) a hydrocarbyl dithiophosphoric acid, (iv) a amine salt of a phosphoric acid ester; (v) an alkylbenzene-sulfonate or derivatives thereof, or combinations thereof.

12. The process of claim **9**, wherein the overbased detergent is an overbased phenate with a TBN of at least 200.

13. The process of claim **9**, wherein the alkyl imidazoline is derived from a fatty acid and an alkylene polyamine.

14. The process of claim **8**, wherein the turbidity of the overall composition is improved, as defined by a lower JTU and/or NTU value compared to the same composition that does not contain (c), the stabilizing component.

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