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(54) **Lubricating oil additive concentrates**

(57) Lubricant additive concentrates containing an admixture of at least one basic metal complex and at least one surface active agent having at least one hydroxyl or amino group, in which the metal basic metal

complex is preblended with a polyalkenyl acylating agent prior to admixture with the surface active agent.

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Description**FIELD OF THE INVENTION**

5 **[0001]** The invention is directed to lubricating oil additive concentrates useful in the formulation of lubricating oil compositions. More specifically, the present invention is directed to lubricating oil additive concentrates containing at least a basic metal complex and a surface active agent having at least one hydroxyl or amino group.

BACKGROUND OF THE INVENTION

10 **[0002]** Lubricating oil compositions for use in crankcase engine oils comprise a major amount of base stock oil and minor amounts of additives that improve the performance and increase the useful life of the lubricant. Crankcase lubricating oil compositions conventionally contain basic metal complexes, which act as detergents and acid neutralizers, surface active agents containing at least one hydroxyl or amino group, which function as organic friction modifiers that are effective in improving fuel economy, and optionally, polyalkenyl acylating agents, which can act as compatibilizers and/or emulsifiers that ameliorate unwanted interactions between additives. In the face of increased demands for improved fuel economy, and further demands for reductions in the amounts of metal (ash) contained in the lubricant, formulators have used ever-increasing amounts of organic friction modifiers.

15 **[0003]** Lubricating oil additives are commonly provided to lubricant formulators in the form of 10 to 80 mass %, e.g., 20 to 80 mass % active ingredient (AI) concentrates, which are then dissolved in major amounts of oil of lubricating viscosity to provide a fully formulated lubricant. The concentrates are commonly diluted in 3 to 100, e.g., 5 to 40 parts by weight of oil of lubricating viscosity, per part by weight of the additive concentrate. As noted above, certain lubricating oil additives are known to interact with others in concentrates. One such known interaction occurs between organic friction modifiers and overbased metal detergents. Specifically, the organic friction modifiers have been found to adversely affect the complex of the metal detergents, causing the formation of sediment in the concentrate upon storage. The presence of a polyalkenyl acylating agent has been found to regulate this unwanted interaction. However, as the amount of the organic friction modifier increases to the levels now required, the effect of the polyalkenyl acylating agent has become insufficient.

25 **[0004]** As lubricating oil quality standards have become more stringent, the required amount of organic friction has increased, and the presence of even minor amounts of sediment in additive concentrates has become unacceptable to lubricant formulators. Therefore, it would be advantageous to be able to provide additive concentrates containing over-based metal detergents and high levels of organic friction modifiers, in which the components do not interact to form sediment.

SUMMARY OF THE INVENTION

35 **[0005]** The present invention is directed to lubricant additive concentrates comprising an admixture of at least one basic metal complex and at least one surface active agent having at least one hydroxyl or amino group, in which the basic metal complex is preblended with a polyalkenyl acylating agent prior to admixture with the surface active agent.

40 **[0006]** Other and further objects, advantages and features of the present invention will be understood by reference to the following specification.

DETAILED DESCRIPTION OF THE INVENTION

45 **[0007]** Surface active agents useful in the practice of the invention, also hereinafter referred to as organic friction modifiers, include oil-soluble compounds containing at least one polar group selected from hydroxyl and amine groups, which compounds are capable of reducing friction under hydrodynamic and mixed hydrodynamic/boundary layer conditions. Examples of such materials include glycerol esters of higher fatty acids, for example, glycerol mono-oleate; esters of long chain polycarboxylic acids with diols, for example, the butane diol ester of a dimerized unsaturated fatty acid; oxazoline compounds; and alkoxyated alkyl-substituted mono-amines, diamines and alkyl ether amines, for example, ethoxylated tallow amine and ethoxylated tallow ether amine. Particularly preferred surface active agents include glycerol oleates, particularly glycerol monooleate, and ethoxylated amines, particularly ethoxylated tallow amine. Because adverse interactions are more severe when elevated levels of surface active agent are present in the concentrate, in a preferred embodiment, the concentrate of the present invention contains at least 3 wt. %, preferably at least 5 wt. %, of surface active agent, based on the total weight of the additive concentrate. In alternative terms, concentrates that contain the surface active agent in an amount sufficient to provide a formulated lubricant with at least 0.5 wt. % of surface active agent after dilution are preferred.

55 **[0008]** Basic metal complexes useful in the context of the invention function as both detergents to reduce or remove

deposits and as acid neutralizers or rust inhibitors, thereby reducing wear and corrosion and extending engine life. Detergents generally comprise a polar head with a long hydrophobic tail. The polar head comprises a metal salt of an acidic organic compound. The salts may contain a substantially stoichiometric amount of the metal in which case they are usually described as normal or neutral salts, and would typically have a total base number or TBN (as can be measured by ASTM D2896) of from 0 to 80. A large amount of a metal base may be incorporated by reacting excess metal compound (e.g., an oxide or hydroxide) with an acidic gas (e.g., carbon dioxide). The resulting overbased detergent comprises neutralized detergent as the outer layer of a metal base (e.g. carbonate) micelle. Such overbased detergents may have a TBN of 150 or greater, and typically will have a TBN of from 250 to 450 or more.

[0009] Detergents that may be used include oil-soluble neutral and overbased sulfonates, phenates, sulfurized phenates, thiophosphonates, salicylates, and naphthenates and other oil-soluble carboxylates of a metal, particularly the alkali or alkaline earth metals, e.g., barium, sodium, potassium, lithium, calcium, and magnesium. The most commonly used metals are calcium and magnesium, which may both be present in detergents used in a lubricant, and mixtures of calcium and/or magnesium with sodium. Particularly convenient metal detergents are neutral and overbased calcium sulfonates having TBN of from 20 to 450, neutral and overbased calcium phenates and sulfurized phenates having TBN of from 50 to 450 and neutral and overbased magnesium or calcium salicylates having a TBN of from 20 to 450. Combinations of detergents, whether overbased or neutral or both, may be used.

[0010] Sulfonates may be prepared from sulfonic acids which are typically obtained by the sulfonation of alkyl substituted aromatic hydrocarbons such as those obtained from the fractionation of petroleum or by the alkylation of aromatic hydrocarbons. Examples included those obtained by alkylating benzene, toluene, xylene, naphthalene, diphenyl or their halogen derivatives such as chlorobenzene, chlorotoluene and chloronaphthalene. The alkylation may be carried out in the presence of a catalyst with alkylating agents having from about 3 to more than 70 carbon atoms. The alkaryl sulfonates usually contain from about 9 to about 80 or more carbon atoms, preferably from about 16 to about 60 carbon atoms per alkyl substituted aromatic moiety.

[0011] The oil soluble sulfonates or alkaryl sulfonic acids may be neutralized with oxides, hydroxides, alkoxides, carbonates, carboxylate, sulfides, hydrosulfides, nitrates, borates and ethers of the metal. The amount of metal compound is chosen having regard to the desired TBN of the final product but typically ranges from about 100 to 220 wt. % (preferably at least 125 wt. %) of that stoichiometrically required.

[0012] Metal salts of phenols and sulfurized phenols are prepared by reaction with an appropriate metal compound such as an oxide or hydroxide and neutral or overbased products may be obtained by methods well known in the art. Sulfurized phenols may be prepared by reacting a phenol with sulfur or a sulfur containing compound such as hydrogen sulfide, sulfur monohalide or sulfur dihalide, to form products which are generally mixtures of compounds in which 2 or more phenols are bridged by sulfur containing bridges.

[0013] Carboxylate detergents, e.g., salicylates, can be prepared by reacting an aromatic carboxylic acid with an appropriate metal compound such as an oxide or hydroxide and neutral or overbased products may be obtained by methods well known in the art. The aromatic moiety of the aromatic carboxylic acid can contain heteroatoms, such as nitrogen and oxygen. Preferably, the moiety contains only carbon atoms; more preferably the moiety contains six or more carbon atoms; for example benzene is a preferred moiety. The aromatic carboxylic acid may contain one or more aromatic moieties, such as one or more benzene rings, either fused or connected via alkylene bridges. The carboxylic moiety may be attached directly or indirectly to the aromatic moiety. Preferably the carboxylic acid group is attached directly to a carbon atom on the aromatic moiety, such as a carbon atom on the benzene ring. More preferably, the aromatic moiety also contains a second functional group, such as a hydroxy group or a sulfonate group, which can be attached directly or indirectly to a carbon atom on the aromatic moiety.

[0014] Preferred examples of aromatic carboxylic acids are salicylic acids and sulfurized derivatives thereof, such as hydrocarbyl substituted salicylic acid and derivatives thereof. Processes for sulfurizing, for example a hydrocarbyl - substituted salicylic acid, are known to those skilled in the art. Salicylic acids are typically prepared by carboxylation, for example, by the Kolbe - Schmitt process, of phenoxides, and in that case, will generally be obtained, normally in a diluent, in admixture with uncarboxylated phenol.

[0015] Preferred substituents in oil - soluble salicylic acids are alkyl substituents. In alkyl - substituted salicylic acids, the alkyl groups advantageously contain 5 to 100, preferably 9 to 30, especially 14 to 20, carbon atoms. Where there is more than one alkyl group, the average number of carbon atoms in all of the alkyl groups is preferably at least 9 to ensure adequate oil solubility.

[0016] Detergents generally useful in the formulation of lubricating oil compositions also include "hybrid" detergents formed with mixed surfactant systems, e.g., phenate/salicylates, sulfonate/phenates, sulfonate/salicylates, and sulfonate/phenate/salicylates, as described, for example, in pending U.S. Patent Application Nos. 09/180,435 and 09/180,436 and U.S. Patent Nos. 6,153,565 and 6,281,179.

[0017] Interaction with surface active agents in lubricating additive concentrates is particularly severe when the metal of the metal complex is calcium. Further, the interaction with the surface active agent is more pronounced in concentrates containing sulfonate detergents and complex detergents containing sulfonate surfactant. Therefore, in a preferred em-

bodiment, the basic metal complex is calcium overbased detergent or overbased sulfonate or sulfonate-containing complex detergent, more preferably overbased calcium sulfonate or sulfonate-containing complex detergent.

[0018] Polyalkenyl acylating agents useful in the practice of the invention include polyalkenyl substituted olefinic mono- and dicarboxylic acid and anhydride producing materials. Preferred polyalkenyl moieties are derived from α -olefin homopolymers, α -olefin copolymers, and ethylene- α -olefin copolymers. The α -olefin homo- and copolymers are respectively polymers of one and of at least two C_3 to C_{12} α -olefin(s) having the formula $CH_2=CHR'$, wherein R' is a straight or branched chain alkyl radical comprising 1 to 10 carbon atoms. The unsaturated ethylene- α -olefin copolymers are polymers of ethylene and at least one α -olefin of the above formula. The α -olefins employed in the foregoing homo- and copolymers are more preferably selected from the C_3 to C_6 α -olefins of the above formula, R' being a straight or branched chain alkyl of from 1 to 4 carbon atoms. Accordingly, useful α -olefin monomers and comonomers include, for example, propene, butene-1, hexene-1, octene-1, 4-methylpentene-1, decene-1, dodecene-1, and mixtures thereof (e.g., mixtures of propene and butene-1). Exemplary of such polymers are propene homopolymers, butene-1 homopolymers, ethylene-propene copolymers and the like. A preferred class of polymers are those derived from ethylene and the C_3 and C_4 α -olefins of the above formula; i.e., polyethylene, polypropene, polybutene-1, and copolymers of ethylene and propene, ethylene and butene-1, butene-1 and propene, and ethylene and propene and butene-1.

[0019] The polyalkenyl moieties from which the polyalkenyl acylating agent is derived can have a number average molecular weight in the range of from about 100 to 4000, preferably from about 450 to 2500, and more preferably from about 750 to 1500. Number average molecular weight (M_n) can be determined by several known techniques such as gel permeation chromatography ("GPC"), vapor phase osmometry, proton NMR and carbon-13 NMR. Particularly preferred polyalkenes are polyisobutenes and polybutenes having a number average molecular weight (M_n) of from about 450 to about 2500, more preferably from about 750 to 1500.

[0020] Mono- and dicarboxylic acid or anhydride producing materials, i.e., acid, anhydride, or acid ester materials from which the polyalkenyl acylating agents may be derived include (i) monounsaturated C_4 to C_{10} dicarboxylic acid wherein (a) the carboxyl groups are vicinyl, (i.e., located on adjacent carbon atoms) and (b) at least one, preferably both, of said adjacent carbon atoms are part of said mono unsaturation; (ii) derivatives of (i) such as anhydrides or C_1 to C_5 alcohol derived mono- or diesters of (i); (iii) monounsaturated C_3 to C_{10} monocarboxylic acid wherein the carbon-carbon double bond is conjugated with the carboxyl group, i.e., of the structure $-C=C-CO-$; and (iv) derivatives of (iii) such as C_1 to C_5 alcohol derived mono- or diesters of (iii). Mixtures of compounds (i) to (iv) may also be used. Upon reaction with the backbone, the monounsaturation of the reactant mono- or dicarboxylic acid or anhydride material becomes saturated. Thus, for example, maleic anhydride becomes backbone-substituted succinic anhydride, and acrylic acid becomes backbone-substituted propionic acid. Exemplary of such monounsaturated carboxylic reactants are fumaric acid, itaconic acid, maleic acid, maleic anhydride, chloromaleic acid, chloromaleic anhydride, acrylic acid, methacrylic acid, crotonic acid, cinnamic acid, and lower alkyl (e.g., C_1 to C_4 alkyl) acid esters of the foregoing, e.g., methyl maleate, ethyl fumarate, and methyl fumarate. A particularly preferred mono- or dicarboxylic acid or anhydride material is maleic anhydride and the preferred polyalkenyl acylating agent is polyisobutenyl succinic anhydride (PIBSA).

[0021] The polyalkenyl acylating agent and basic metal complex are premixed prior to contact with the surface active agent containing at least one hydroxyl or amino group. Preferably, the basic metal complex is premixed with the polyalkenyl acylating agent at an elevated temperature, such as from about 20 to about 250°C, preferably from about 50 to about 150°C, more preferably from about 75 to about 125°C, for a period of time, such as from about 0.25 to 24 hours, preferably from about 1 to 10 hours, more preferably from about 2 to 5 hours.

[0022] The basic metal complex and polyalkenyl acylating agent may be premixed in a wt. % ratio of basic metal complex to polyalkenyl acylating agent of from about 30:1 to about 1:30, preferably from about 20:1 to about 0.5:1, such as from about 20:1 to about 1:1, more preferably from about 10:1 to about 4:1.

[0023] The premixed polyalkenyl acylating agent and basic metal complex can be added to a concentrate containing additives including the hydroxyl or amino group-containing surface active agent. Alternatively, the premixed polyalkenyl acylating agent and basic metal complex or polyalkenyl acylated agent-treated basic metal complex, may be used to form a concentrate containing additives excluding the hydroxyl or amino group-containing-surface active agent, to which the surface active agent is subsequently introduced.

[0024] The concentrates of the invention are preferably prepared at an elevated temperature, i.e. above ambient temperature. Such concentrates may be prepared at a temperature of at least 50°C such as at least 80°C, preferably at least 90°C, more preferably at least 100°C. Although energy is saved at low temperatures, practical considerations dictate the most convenient temperature that can be used. Thus, where any additive is used that is solid at ambient temperature, it is usually more convenient to raise the temperature to a temperature at which the additive flows, rather than dissolving it in oil prior to addition to the other additives. Temperatures of 100°C or more can be employed if any additive is more conveniently handled at such temperatures. Consideration must be given to the time for which it is held at the mixing temperature and its stability under such temperatures and time conditions.

[0025] In order for the concentrate to be oleaginous, the additives may be in solution in an oleaginous carrier or such a carrier may be provided separately or both. Examples of suitable carriers are oils of lubricating viscosity, such as

described in detail hereinafter, and aliphatic, naphthenic and aromatic hydrocarbons.

[0026] The components are advantageously held at the mixing temperature for a time sufficient to achieve a homogeneous mixture thereof. This can usually be accomplished within one half hour, particularly when the temperature of mixing exceeds 80°C.

[0027] The concentrates of the invention can be incorporated into a lubricating oil composition in any convenient way. Thus, they can be added directly to an oil of lubricating viscosity by dispersing or dissolving them in the oil at the desired concentrations of the dispersant and detergent, respectively. Such blending can occur at ambient temperature or elevated temperatures. Alternatively, the composite can be blended with a suitable oil-soluble solvent and base oil to form a further concentrate which is then blended with an oil of lubricating viscosity to obtain the final lubricating oil composition. Such concentrate will typically contain (on an active ingredient (A.I.) basis) from about 0.5 wt. % to about 20 wt. %, preferably from about 1 wt. % to about 15 wt. %, more preferably from about 3 wt. % to about 10 wt. %, of the surface active agent containing at least one hydroxyl or amino group, and from 3 to 45 wt. %, preferably from 5 to 30 wt. %, more preferably from about 7.5 wt. % to about 25 wt. % of the premixed polyalkenyl acylating agent and basic metal complex, based on the concentrate weight; the remainder of the concentrate comprising diluent (preferably no more than 90 wt. %, such as not more than 80 wt. %) oil and, optionally, other additives.

[0028] The oil of lubricating viscosity, useful for making concentrates of the invention or for making lubricating oil compositions therefrom, may be selected from natural (vegetable, animal or mineral) and synthetic lubricating oils and mixtures thereof. It may range in viscosity from light distillate mineral oils to heavy lubricating oils such as gas engine oil, mineral lubricating oil, motor vehicle oil, and heavy duty diesel oil. Generally, the viscosity of the oil ranges from 2 centistokes to 30 centistokes, especially 5 centistokes to 20 centistokes, at 100°C.

[0029] Natural oils include animal oils and vegetable oils (e.g., castor oil, lard oil); liquid petroleum oils and hydro-refined, solvent-treated or acid-treated mineral oils of the paraffinic, naphthenic and mixed paraffinic-naphthenic types. Oils of lubricating viscosity derived from coal or shale also serve as useful base oils.

[0030] Synthetic lubricating oils include hydrocarbon oils and halo-substituted hydrocarbon oils such as polymerized and interpolymerized olefins (e.g., polybutylenes, polypropylenes, propylene-isobutylene copolymers, chlorinated polybutylenes, poly(1-hexenes), poly(1-octenes), poly(1-decenes)); alkylbenzenes (e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di(2-ethylhexyl)benzenes); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenols); and alkylated diphenyl ethers and alkylated diphenyl sulfides and derivative, analogs and homologs thereof.

[0031] Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc., constitute another class of known synthetic lubricating oils. These are exemplified by polyoxyalkylene polymers prepared by polymerization of ethylene oxide or propylene oxide, and the alkyl and aryl ethers of polyoxyalkylene polymers (e.g., methyl-polyiso-propylene glycol ether having a molecular weight of 1000 or diphenyl ether of poly-ethylene glycol having a molecular weight of 1000 to 1500); and mono- and polycarboxylic esters thereof, for example, the acetic acid esters, mixed C₃-C₈ fatty acid esters and C₁₃ Oxo acid diester of tetraethylene glycol.

[0032] Another suitable class of synthetic lubricating oils comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids and alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkylmalonic acids, alkenyl malonic acids) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol). Examples of such esters include dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid.

[0033] Esters useful as synthetic oils also include those made from C₅ to C₁₂ monocarboxylic acids and polyols and polyol esters such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol and tripentaerythritol.

[0034] Silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy- or polyaryloxysilicone oils and silicate oils comprise another useful class of synthetic lubricants; such oils include tetraethyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl)silicate, tetra-(4-methyl-2-ethylhexyl)silicate, tetra-(p-tert-butyl-phenyl) silicate, hexa-(4-methyl-2-ethylhexyl)disiloxane, poly(methyl)siloxanes and poly(methylphenyl)siloxanes. Other synthetic lubricating oils include liquid esters of phosphorous-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, diethyl ester of decylphosphonic acid) and polymeric tetrahydrofurans.

[0035] The oil of lubricating viscosity may comprise a Group I, Group II, Group III, Group IV or Group V oil or blends of the aforementioned oils. The oil of lubricating viscosity may also comprise a blend of a Group I oil and one or more of Group II, Group III, Group IV or Group V oil.

[0036] Definitions for the oils as used herein are the same as those found in the American Petroleum Institute (API) publication "Engine Oil Licensing and Certification System", Industry Services Department, Fourteenth Edition, December 1996, Addendum 1, December 1998. Said publication categorizes oils as follows:

- a) Group I oils contain less than 90 percent saturates and/or greater than 0.03 percent sulfur and have a viscosity index greater than or equal to 80 and less than 120 using the test methods specified in Table 1.
- b) Group II oils contain greater than or equal to 90 percent saturates and less than or equal to 0.03 percent sulfur and have a viscosity index greater than or equal to 80 and less than 120 using the test methods specified in Table 1. Although not a separate Group recognized by the API, Group II oils having a viscosity index greater than about 110 are often referred to as "Group II+" oils.
- c) Group III oils contain greater than or equal to 90 percent saturates and less than or equal to 0.03 percent sulfur and have a viscosity index greater than or equal to 120 using the test methods specified in Table 1.
- d) Group IV oils are polyalphaolefins (PAO).
- e) Group V oils are all other base stocks not included in Group I, II, III, or IV.

Table 1

Property	Test Method
Saturates	ASTM D2007
Viscosity Index	ASTM D2270
Sulfur	ASTM D4294

[0037] The oil of lubricating viscosity preferably has a saturate content of at least 65%, more preferably at least 75%, such as at least 85%. Most preferably, the oil of lubricating viscosity has a saturate content of greater than 90%. Preferably, the oil of lubricating viscosity has a sulfur content of less than 1%, preferably less than 0.6%, more preferably less than 0.3%, by mass, such as 0 to 0.3% by mass.

[0038] Preferably the volatility of the oil of lubricating viscosity, as measured by the Noack test (ASTM D5880), is less than or equal to about 40%, such as less than or equal to about 35%, preferably less than or equal to about 32%, such as less than or equal to about 28%, more preferably less than or equal to about 16%. Preferably, the viscosity index (VI) of the oil of lubricating viscosity is at least 85, preferably at least 100, most preferably from about 105 to 140.

[0039] In addition to the mixed basic metal complex/polyalkenyl acylating agent and organic friction modifier, a concentrate, and fully formulated lubricants formed therefrom, can contain a number of other performance improving additives selected from ashless dispersants, antiwear agents, oxidation inhibitors or antioxidants, metal-containing friction modifiers and fuel economy agents, antifoamants and corrosion inhibitors, including additional amounts of metal detergent and polyalkenyl acylating agent (independent of the premixed polyalkenyl acylating agent and basic metal complex). Conventionally, when formulating a lubricant, the additives will be provided to the formulator in one or more, preferably a single concentrated additive package, oftentimes referred to as a DI (dispersant-inhibitor) package and a VI improver and/or VI improver and LOFI, will be provided in a second package.

[0040] Ashless dispersants maintain in suspension oil insolubles resulting from oxidation of the oil during wear or combustion. They are particularly advantageous for preventing the precipitation of sludge and the formation of varnish, particularly in gasoline engines.

[0041] Dihydrocarbyl dithiophosphate metal salts are frequently used as antiwear and antioxidant agents. The metal may be an alkali or alkaline earth metal, or aluminum, lead, tin, molybdenum, manganese, nickel or copper. The zinc salts are most commonly used in lubricating oil and may be prepared in accordance with known techniques by first forming a dihydrocarbyl dithiophosphoric acid (DDPA), usually by reaction of one or more alcohol or a phenol with P_2S_5 and then neutralizing the formed DDPA with a zinc compound. For example, a dithiophosphoric acid may be made by reacting mixtures of primary and secondary alcohols. Alternatively, multiple dithiophosphoric acids can be prepared where the hydrocarbyl groups on one are entirely secondary in character and the hydrocarbyl groups on the others are entirely primary in character. To make the zinc salt, any basic or neutral zinc compound could be used but the oxides, hydroxides and carbonates are most generally employed. Commercial additives frequently contain an excess of zinc due to the use of an excess of the basic zinc compound in the neutralization reaction.

[0042] Oxidation inhibitors or antioxidants reduce the tendency of mineral oils to deteriorate in service. Oxidative deterioration can be evidenced by sludge in the lubricant, varnish-like deposits on the metal surfaces, and by viscosity growth. Such oxidation inhibitors include hindered phenols, alkaline earth metal salts of alkylphenolthioesters having preferably C_5 to C_{12} alkyl side chains, calcium nonylphenol sulfide, oil soluble phenates and sulfurized phenates, phosphosulfurized or sulfurized hydrocarbons, phosphorous esters, metal thiocarbamates, oil soluble copper compounds as described in U.S. Patent No. 4,867,890, and molybdenum-containing compounds and aromatic amines.

[0043] Known metal-containing friction modifiers include oil-soluble organo-molybdenum compounds. Such organo-molybdenum friction modifiers also provide antioxidant and antiwear credits to a lubricating oil composition. As an

example of such oil soluble organo-molybdenum compounds, there may be mentioned the dithiocarbamates, dithiophosphates, dithiophosphinates, xanthates, thioxanthates, sulfides, and the like, and mixtures thereof. Particularly preferred are molybdenum dithiocarbamates, dialkyldithiophosphates, alkyl xanthates and alkylthioxanthates.

[0044] Foam control can be provided by an antifoamant of the polysiloxane type, for example, silicone oil or polydimethyl siloxane.

[0045] Some of the above-mentioned additives can provide a multiplicity of effects; thus for example, a single additive may act as a dispersant-oxidation inhibitor. This approach is well known and need not be further elaborated herein.

[0046] Representative effective amounts of such additional additives, when used in fully formulated crankcase lubricants, are listed below in Table 2:

Table 2

ADDITIVE	Mass % (Broad)	Mass % (Preferred)
Ashless Dispersant	0.1-20	1-8
Metal Detergents	0.1-15	0.2-9
Corrosion Inhibitor	0-5	0-1.5
Metal Dihydrocarbyl Dithiophosphate	0.1 - 6	0.1-4
Antioxidant	0-5	0.01-2
Pour Point Depressant	0.01 - 5	0.01 - 1.5
Antifoaming Agent	0 - 5	0.001 - 0.15
Supplemental Antiwear Agents	0-1.0	0-0.5
Friction Modifier	0-5	0-1.5
Basestock	Balance	Balance

[0047] This invention will be further understood by reference to the following examples, wherein all parts are parts by weight (Al), unless otherwise noted and which include preferred embodiments of the invention.

EXAMPLES

[0048] A calcium sulfonate detergent having a TBN of 300 (55 wt. % Al) was treated with polyisobutenyl succinic anhydride (PIBSA), (PIB M_n of 950; 72 wt. % A.I.), for 3 hours, at a temperature of 100°C, in the amounts shown in Table 3:

Table 3

Det. No.	1	2	3
CaSulf Det.	1.60	1.60	1.60
PIBSA	0.072	0.14	0.28
Wt. %	1.672	1.74	1.88

[0049] Concentrates were formed using the above-described premixed PIBSA/detergents, or 1.60 wt. % of the analogous untreated detergent (Det. 4) and other additives normally provided in a concentrated dispersant inhibitor (DI) package, in the manner described below:

Dispersant	1.744	1.744	1.744	1.744	1.744	1.744	1.744
Antifoamant	0.0005	0.0005	0.0005	0.0005	0.0005	0.0005	0.0005
Diluent	3.01	3.01	3.01	3.01	3.01	3.01	3.01
blend for 0.5 hours @ 100° C and add							

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Det. 4	1.60				1.60	1.60	1.60
Det. 1		1.70					
Det. 2			1.80				
Det. 3				2.00			
blend for 3 hours @ 100° C and add							

Antioxidant	1.30	1.30	1.30	1.30	1.30	1.30	1.30
Mo-based Antiwear	0.0045	0.0045	0.0045	0.0045	0.0045	0.0045	0.0045
PIBSA					0.072	0.14	0.28
Diluent	0.0055	0.0055	0.0055	0.0055	0.0335	0.0655	0.1255
blend for 1 hour @ 70° C and add							

ZDDP	0.705	0.705	0.705	0.705	0.705	0.705	0.705
Glycerol Monooleate	0.60	0.60	0.60	0.60	0.60	0.60	0.60
Diluent	0.235	0.235	0.235	0.235	0.235	0.235	0.235
and blend for 1 hour @ 60° C.							

Conc. ID	A	B	C	D	E	F	G
Treat Rate*	9.30	9.40	9.50	9.70	9.40	9.50	9.70
Inv./Comp	Comp.	Inv.	Inv.	Inv.	Comp.	Comp.	Comp.
*recommended amount of concentrate blended with basestock to provide formulated lubricant							

[0050] Each of the above additive concentrates was then subjected to a storage stability test in which the concentrates were stored for a number of weeks @ 60°C with periodic measuring of the amount of sediment formed. A concentrate package failed the stability test at the time the amount of sediment measured was greater than 0.05 wt. %, based on the total weight of the concentrate. The results are provided in Table 4:

Table 4

Conc. ID	A	B	C	D	E	F	G
Week #							
1	Pass	Pass	Pass	Pass	Pass	Pass	Pass
2	Pass	Pass	Pass	Pass	Pass	Pass	Pass
3	Pass	Pass	Pass	Pass	Pass	Pass	Pass
4	Fail	Pass	Pass	Pass	Fail	Fail	Pass
5	Fail	Pass	Pass	Pass	Fail	Fail	Fail
6	Fail	Fail	Pass	Pass	Fail	Fail	Fail
7	Fail	Fail	Pass	Pass	Fail	Fail	Fail
8	Fail	Fail	Pass	Pass	Fail	Fail	Fail

Table continued

Conc. ID	A	B	C	D	E	F	G
Week #							
9	Fail	Fail	Pass	Pass	Fail	Fail	Fail
10	Fail	Fail	Pass	Pass	Fail	Fail	Fail
11	Fail	Fail	Pass	Pass	Fail	Fail	Fail
12	Fail	Fail	Pass	Pass	Fail	Fail	Fail
13	Fail	Fail	Pass	Pass	Fail	Fail	Fail

[0051] The data demonstrate that the use of a detergent treated with even a low level of PIBSA (Inventive Conc. B) increased the period for which the concentrate containing the high level of GMO remained stable from 3 weeks to 5 weeks (a 66% improvement) compared to the concentrate formed with the untreated detergent (Comparative Conc. A). Increasing the amount of PIBSA with which the detergent was treated further led to outstanding stability and Inventive Conc. C and D remained stable after 13 weeks of storage. A comparison between the Inventive Concentrates (B, C and D) and corresponding Comparative Concentrates (E, F and G), demonstrates that the presence of PIBSA has far less of an effect on concentrate stability when the PIBSA is added as a separate component.

[0052] The disclosures of all patents, articles and other materials described herein are hereby incorporated, in their entirety, into this specification by reference. A description of a composition comprising, consisting of, or consisting essentially of multiple specified components, as presented herein and in the appended claims, should be construed to also encompass compositions made by admixing said multiple specified components. The principles, preferred embodiments and modes of operation of the present invention have been described in the foregoing specification. What applicants submit is their invention, however, is not to be construed as limited to the particular embodiments disclosed, since the disclosed embodiments are regarded as illustrative rather than limiting. Changes may be made by those skilled in the art without departing from the spirit of the invention.

Claims

1. A lubricating oil additive concentrate comprising oil of lubricating viscosity, a basic metal complex, a polyalkenyl acylating agent, and a surface active agent containing at least one hydroxyl or amino group, wherein said basic metal complex is premixed with said polyalkenyl acylating agent prior to incorporation into said concentrate.
2. A concentrate, as claimed in claim 1, wherein said basic metal complex is an overbased metal detergent.
3. A concentrate, as claimed in claim 2, wherein said overbased metal detergent is selected from the group consisting of overbased calcium sulfonates, overbased magnesium sulfonates, overbased calcium phenates, overbased magnesium phenates, overbased calcium carboxylates, overbased magnesium carboxylates, overbased calcium hybrid detergents containing surfactant systems comprising at least two of sulfonate, phenate and carboxylate surfactant, overbased magnesium hybrid detergents containing surfactant systems comprising at least two of sulfonate, phenate and carboxylate surfactant, and mixtures thereof.
4. A concentrate, as claimed in claim 2, wherein said overbased metal detergent is an overbased calcium detergent.
5. A concentrate, as claimed in claim 2, wherein said overbased metal detergent is an overbased metal sulfonate detergent, or an overbased metal hybrid detergent containing a surfactant system comprising sulfonate surfactant and at least one other surfactants.
6. A concentrate, as claimed in claim 2, wherein said overbased metal detergent is an overbased calcium sulfonate detergent, or an overbased calcium hybrid detergent containing a surfactant system comprising sulfonate surfactant and at least one other surfactants.
7. A concentrate, as claimed in any one of the preceding claims, wherein said polyalkenyl acylating agent is a polyalkenyl substituted mono- or dicarboxylic acid or anhydride producing material.

8. A concentrate, as claimed in claim 7, wherein said polyalkenyl substituted mono- or dicarboxylic acid or anhydride producing material is polyisobutenyl succinic anhydride.
- 5 9. A concentrate, as claimed in claim 8, wherein said polyisobutenyl succinic anhydride is derived from polyisobutene having a number average molecular weight of from about 100 to about 4000.
- 10 10. A concentrate, as claimed in any one of the preceding claims, wherein said surface active agent is selected from the group consisting of glycerol esters of higher fatty acids; esters of long chain polycarboxylic acids with diols; oxazoline compounds; alkoxyated alkyl-substituted mono-amines, diamines and alkyl ether amines; and mixtures thereof.
- 11 11. A concentrate, as claimed in claim 10, wherein said surface active agent is selected from the group consisting of glycerol oleates; ethoxylated amines; and mixtures thereof.
- 15 12. A concentrate, as claimed in claim 11, wherein said surface active agent is selected from the group consisting of glycerol mono oleate; ethoxylated tallow amine; and mixtures thereof.
- 20 13. A concentrate, as claimed in any one of the preceding claims, wherein said basic metal complex and said polyalkenyl acylating agent are premixed in a weight ratio (basic metal complex to polyalkenyl acylating agent) of from about 30:1 to about 1:30.
- 25 14. A concentrate, as claimed in any one of the preceding claims, wherein said basic metal complex and said polyalkenyl acylating agent are premixed at a temperature of from about 20°C to about 250°C, for from about 0.25 to 24 hours.
- 30 15. A concentrate, as claimed in any one of the preceding claims, containing from about 3 wt. % to about 45 wt. % of the premixed basic metal complex and polyalkenyl acylating agent; and from about 0.5 wt. % to about 20 wt. % of said surface active agent containing at least one hydroxyl or amino group; and no more than 90 wt. % oil of lubricating viscosity; all wt. % being based on the total weight of said concentrate.
- 35 16. A concentrate, as claimed in claim 15, further comprising at least one other additive selected from the group consisting of dispersant, antioxidants and antiwear agents.
17. A concentrate, as claimed in claim 16, further comprising at least one other component selected from the group consisting of neutral and overbased metal detergents which have not been premixed with a polyalkenyl acylating agent; and polyalkenyl acylating agent which has not been premixed with overbased metal detergent.
- 40 18. A lubricating oil additive concentrate comprising:
oil of lubricating viscosity;
a premix of an overbased metal detergent selected from the group consisting of overbased calcium sulfonate detergent; overbased calcium hybrid detergent containing a surfactant system comprising sulfonate surfactant and at least one other surfactants; and mixtures thereof; and polyisobutenyl succinic anhydride; and a surface active agent selected from the group consisting of glycerol oleates; ethoxylated amines.
- 45 19. A concentrate as claimed in claim 18, wherein said overbased metal detergent and said polyisobutenyl succinic anhydride are premixed in a weight ratio (overbased metal detergent and said polyisobutenyl succinic anhydride) of from about 10:1 to about 4:1.
- 50 20. A concentrate, as claimed in claim 18 or 19, wherein said overbased metal detergent and said polyisobutenyl succinic anhydride are premixed at a temperature of from about 50°C to about 150°C, for from about 1 to 10 hours.
- 55 21. A concentrate, as claimed in claim 18, containing from about 5 wt. % to about 30 wt. % of the premixed overbased metal detergent and polyisobutenyl succinic anhydride; and from about 3 wt. % to about 10 wt. % of said surface active agent; and no more than 90 wt. % oil of lubricating viscosity; all wt. % being based on the total weight of said concentrate.
22. A concentrate, as claimed in any one of claims 18 to 21, further comprising at least one other additive selected from the group consisting of dispersant, antioxidants and antiwear agents.

23. A concentrate, as claimed in any one of claims 18 to 22, further comprising at least one other component selected from the group consisting of neutral and overbased metal detergents which have not been premixed with a polyalkenyl acylating agent; and polyalkenyl acylating agent which has not been premixed with overbased metal detergent.

5 24. A method of forming a stable additive concentrate comprising at least 0.5 wt. % of a surface active agent selected from the group consisting of glycerol oleates; ethoxylated amines and mixtures thereof and at least 3.0 wt. % of an overbased metal detergent, and no more than 90 wt. % of oil of lubricating viscosity which method comprises
10 premixing said overbased metal detergent with a polyalkenyl acylating agent in a weight ratio (overbased metal detergent to polyalkenyl acylating agent) of from about 30:1 to about 1:30, to provide a premix; and admixing at least said premix, said surface active agent and said oil of lubricating viscosity, wherein all wt. % being based on the total weight of said concentrate.



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 05 27 0032

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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Place of search Munich		Date of completion of the search 15 November 2005	Examiner Dötterl, E
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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**ANNEX TO THE EUROPEAN SEARCH REPORT
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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
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