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(54) USE OF LUBRICATING OIL COMPOSITION

(57) The invention provides the use of an overbased metal detergent in which two or more different surfactant groups, one being a hydrocarbyl-substituted hydroxybenzoate and another being a sulfonate group, are incorporated therein during its overbasing, and which has been manufactured in the presence of at least one amide-or ester-based co-surfactant, said use being as an additive in a motor vehicle lubricating oil composition to provide lubricant frictional benefits, exemplified by improved high frequency reciprocating rig performance thereof, and/or improved stability of the overbased detergent in the composition in comparison with an analogous lubricating oil compositions made by admixing said overbased metal detergent and said at least one amide-or ester-based co-surfactant.

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Description

FIELD OF THE INVENTION

[0001] This invention relates to stable hybrid detergents incorporating organic friction modifier surfactants and their use to provide lubricants with improved fuel economy performance.

BACKGROUND OF THE INVENTION

[0002] There is much interest in improving the fuel economy of gasoline and diesel engines and, for this reason, organic friction modifiers may be included in lubricating oil compositions (or 'lubricants') for such engines.

[0003] A problem with use of organic friction modifiers is that they may be poorly compatible with overbased calcium sulfonate detergents commonly used in lubricants. See EP-A-1710 294.

[0004] EP-A-2045 314 ('314) partly addresses the problem by incorporating an organic friction modifier, as a co-surfactant, into an overbased metal sulfonate detergent during manufacture of the detergent. The data in '314 show that compatibility, measured by a stability test, is improved when an overbased calcium sulfonate detergent is manufactured in the presence of an amine-based friction modifier. However, '314 observes that improvements in stability are not observed when the friction modifier is ester- or amide-based. '314 mentions, in the text, that the detergent may contain a further surfactant group, additional to sulfonate, and be in the form of a hybrid. An example is given of an overbased calcium salt of surfactants sulfonic acid and salicylic acid. '314 therefore teaches that ester- and amide-based friction modifiers do not give rise to stability improvements when incorporated into such hybrids.

[0005] US-B-7,935,664 (EP-A-2045313) describes use of amine- or ester-based friction modifiers, incorporated into overbased metal hydrocarbyl-substituted hydroxybenzoate detergents during manufacture, to improve stability. It mentions, in its general description but not in its examples, the possibility of using sulfonic acid as a further surfactant group, additional to a hydroxybenzoic acid surfactant. However, the above teaching of '314 teaches away from using a sulfonic acid in this way to improve stability.

SUMMARY OF THE INVENTION

[0006] The above problem is met by incorporating an ester- and/or amide-based friction modifier, as a co-surfactant, into a complex (or hybrid) calcium hydrocarbyl-substituted sulfonate and hydrocarbyl-substituted hydroxybenzoate detergent during its manufacture. The product, when blended into a lubricant, is stable and found to exhibit lubricant frictional benefits as exemplified by improved high frequency reciprocating rig performance.

[0007] Thus, in a first aspect, the invention provides a method of providing lubricant frictional benefits, exemplified by improved high frequency reciprocating rig performance, in a motor vehicle lubricating oil composition comprising the steps of

(i) making a stable overbased complex/hybrid calcium detergent incorporating hydrocarbyl-substituted hydroxybenzoate and hydrocarbyl-substituted sulfonate surfactant groups; and
(ii) blending the detergent, with other additive components, into the lubricating oil composition,

wherein at least one amide- or ester-based co-surfactant is incorporated into the detergent in step (i) and not as another additive component in step(ii).

[0008] In a second aspect, the invention provides the use of an overbased metal detergent in which two or more different surfactant groups, one being a hydrocarbyl-substituted hydroxybenzoate and another being a sulfonate group, are incorporated therein during its overbasing, and which has been manufactured in the presence of at least one amide- or ester-based co-surfactant, said use being as an additive in a motor vehicle lubricating oil composition to provide lubricant frictional benefits, exemplified by improved high frequency reciprocating rig performance thereof, and/or improved stability of the overbased detergent in the composition in comparison with an analogous lubricating oil composition made by admixing said overbased metal detergent and said at least one amide- or ester-based co-surfactant.

DETAILED DESCRIPTION OF THE INVENTION

Definitions

[0009] In this specification, the following words and expressions, if and when used, have the meanings ascribed below:

"active ingredient" or "(a.i.)" refers to additive material that is not diluent or solvent;

"comprising" or any cognate word specifies the presence of stated features, steps, or integers or components, but does not preclude the presence or addition of one or more other features, steps, integers, components or groups thereof. The expressions "consists of' or "consists essentially of' or cognates may be embraced within "comprises" or cognates, wherein "consists essentially of" permits inclusion of substances not materially affecting the characteristics of the composition to which it applies;

"hydrocarbyl" means a chemical group of a compound that normally contains only hydrogen and carbon atoms and that is bonded to the remainder of the compound directly via a carbon atom but that may contain hetero atoms provided that they do not detract from the essentially hydrocarbyl nature of the group;

"metal ratio" in relation to a detergent is the ratio of total base to total soap, i.e. based on metal content;

"oil-soluble" or "oil-dispersible", or cognate terms, do not necessarily indicate that the compounds or additives are soluble, dissolvable, miscible, or are capable of being suspended in the oil in all proportions. These do mean, however, that they are, for example, soluble or stably dispersible in oil to an extent sufficient to exert their intended effect in the environment in which the oil is employed. Moreover, the additional incorporation of other additives may also permit incorporation of higher levels of a particular additive, if desired;

"major amount" means in excess of 50 mass % of a composition;

"minor amount" means 50 mass % or less of a composition;

"TBN" means total base number as measured by ASTM D2896 in units of mg KOHg^{-1};

"phosphorus content" is measured by ASTM D5185;

"sulfur content" is measured by ASTM D2622; and

"sulfated ash content" is measured by ASTM D874.

[0010] Also, it will be understood that various components used, essential as well as optimal and customary, may react under conditions of formulation, storage or use and that the invention also provides the product obtainable or obtained as a result of any such reaction.

[0011] Further, it is understood that any upper and lower quantity, range and ratio limits set forth herein may be independently combined.

[0012] Furthermore, the constituents of this invention may be isolated or be present within a mixture and remain within the scope of the invention.

HYBRID/COMPLEX METAL DETERGENT

[0013] As indicated, the detergent comprises hydroxybenzoic acid and sulfonic acid as surfactant groups. The detergent is obtained or obtainable by manufacturing the hybrid material where said two different surfactant groups are incorporated during the overbasing process.

[0014] The metal may be an alkali metal or an alkaline earth metal, but is preferably calcium or magnesium, more preferably calcium.

[0015] Detergents that may be used in all aspects of the present invention include oil-soluble neutral and overbased hybrid/complex detergents that are hydrocarbyl substituted on the sulfonic acid and hydroxybenzoic acid co-surfactants.

[0016] Sulfonic acids, as the organic acid, may be obtained by sulfonating hydrocarbyl-substituted, especially alkyl-substituted, aromatic hydrocarbons such as those obtained from fractionating petroleum by distillation and/or extraction, or by alkylating aromatic hydrocarbons. Examples include those obtained by alkylating benzene, toluene, xylene, naphthalene, biphenyl or their halogen derivatives, for example chlorobenzene, chlorotoluene or chloronaphthalene. Aromatic hydrocarbons may be alkylated with alkylating agents having 3 to 100 carbon atoms in the presence of a catalyst. Examples of alkylating agent include haloparaffins, olefins obtained by dehydrogenating paraffins, and polyolefins such as polymers of ethylene, propylene, and/or butene. Alkylaryl sulfonic acids usually contain from 7 to 100 or more, preferably 16 to 80, or 12 to 40, carbon atoms per alkyl-substituted aromatic moiety, depending on their source. When neutralising alkylaryl sulfonic acids to obtain sulfonates, the reaction mixture used may also include hydrocarbon solvents and/or diluent oils, as well as promoters and viscosity-control agents. Such procedures may be described in the art.

[0017] Another type of sulfonic acid that may be used is an alkylphenol sulfonic acid, which may be sulfurised. When the sulfonic acid is an alkyl sulfonic acid, the alkyl group may contain 9 to 100, advantageously 12 to 80, especially 16 to 60, carbon atoms.

[0018] The hydroxybenzoic acid, when used as the organic acid, may be a hydrocarbyl-substituted hydroxybenzoic acid where hydrocarbyl includes alkyl or alkenyl. The hydrocarbyl group may be in the ortho, meta or para position with respect to the hydroxyl group; there may be more than one hydrocarbyl group attached to the benzene ring. Such hydrocarbyl groups are preferably alkyl (branched or, more preferably straight-chain) when they advantageously contain 5 to 100, preferably 9 to 30, especially 14 to 24, carbon atoms. The hydroxybenzoic acid is preferably a salicylic acid.

[0019] Hydroxybenzoic acids are typically prepared, as may be described in the art, by carboxylating phenoxides using the Kolbe-Schmitt process when they are generally obtained (normally in a diluent) in admixture with uncarboxylated phenol. The acids may be sulfurised or non-sulfurised, and may be chemically modified and/or contain additional substituents.

[0020] The detergent, may be synthesized with a wide mole/mole ratio range of hydroxybenezoade to sulfonate; preferably it is in the range of 1:1 to 4:1.

[0021] The detergent may typically have a metal ratio, as defined herein, in the range of 3:1 to 7:1.

[0022] Particular examples of hybrid materials may include, for example, some of those described in WO-A-97/46643; WO-A-97/46644; WO-A-97/46645; WO-A-46646; and WO-A-97/46647.

[0023] The ester- or amide-based co-surfactant may be added with the other surfactants at the beginning of synthesis, before neutralization and overbasing , and between neutralization and overbasing. They may be provided at levels of up to 20% or higher with respect to the total mass of the hybrid system. The ester-based friction modifier is preferably selected from partially esterified aliphatic polyhydric alcohols having from two to 30 carbon atoms and containing from two to six hydroxyl groups, wherein at least one free hydroxyl group remains. Preferably, at least one hydroxyl group should be on a terminal carbon atom, but it may be removed from the terminal carbon atom by as many as three or four carbon atoms. The partial ester alcohols may be derivatives of, for example, alkylene glycols (especially ethylene and propylene glycol), glycerol, erythritol, pentaerythritol, and the various isomeric pentitols and hexitols, such as mannitol, sorbitol, etc.

[0024] To the polyhydric alcoholic portion of the molecule there is preferably attached a predominantly hydrocarbon portion containing a number of carbon atoms sufficient to give the molecule a total minimum carbon content of about 12, and preferably 15 to 46 carbon atoms. This hydrocarbon portion is generally attached to the alcoholic portion through an ester linkage which may be formed between a hydroxyl radical of the polyhydric alcohol on the one hand, and an acid radical of the hydrocarbon portion on the other. It is also possible for the ester linkage to be inverted, that is to say for it to be formed between an acid radical attached to the polyhydric alcohol on the one hand and a hydroxyl radical attached to the hydrocarbon on the other.

[0025] It is desirable that the hydroxyl radicals and ester linkages of the polyhydric alcohol portion of the ester should be as close together as possible, preferably at least two hydroxyl radicals being separated from each other by not more than three directly connected atoms, and more preferably being attached to vicinal carbon atoms. It is advantageous if several polar groups are attached to directly connected carbon atoms.

[0026] The hydrocarbon portion of the ester should preferably have at least five and more preferably between about 10 and 40 carbon atoms, and be in the form of a branched- or straight- chain aliphatic or a cycloaliphatic (e.g. naphthenic) radical. The acid group of the hydrocarbon portion (if there is one) is preferably a carboxylic acid group. The acid may be, for example, caprylic, oleic, stearic, lauric, linoleic, linolenic or ricinoleic acid etc.

[0027] Specially preferred partial esters are sorbitan mono-oleate and sorbitan monolaurate, and in particular glycerol mono- and di- oleate, and mixtures thereof.

[0028] Amide-based friction modifiers include amine-derived esters such as tallow ester of triethanolamine or tallow ester of 2,2'-(methylimino)bis(ethanol), ethoxylated ether propyl amines, ethoxylated tallow amine, dihydroxyethyl isodecyloxypropyl amine, tallow alkyl dimethyl amine, oleylamine, N,N-dimethyl oleylamine & octadecyl dimethylamine.

LUBRICATING OIL COMPOSITIONS

[0029] Lubricating oil compositions of the invention may be those suitable for use as passenger car motor oils and conventionally comprise a major amount of oil of lubricating viscosity and minor amounts of performance-enhancing additives, including ash-containing detergents. Examples of suitable detergent additives in the invention include, but are not limited to, one or more mixed calcium and magnesium overbased salicylates or sulfonates.

[0030] The oil of lubricating viscosity (sometimes referred to as "base stock" or "base oil") is the primary liquid constituent of a lubricant, into which additives and possibly other oils are blended, for example to produce a final lubricant (or lubricant composition). A base oil, which is useful for making concentrates as well as for making lubricating oil compositions therefrom, may be selected from natural (vegetable, animal or mineral) and synthetic lubricating oils and mixtures thereof.

[0031] Definitions for the base stocks and base oils in this invention 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, which categorizes base stocks as follows:

a) Group I base stocks contain less than 90 percent saturates and/or greater than 0.03 percent sulphur and have a viscosity index greater than or equal to 80 and less than 120 using the test methods specified in Table E-1.

b) Group II base stocks contain greater than or equal to 90 percent saturates and less than or equal to 0.03 percent sulphur and have a viscosity index greater than or equal to 80 and less than 120 using the test methods specified in Table E-1.

c) Group III base stocks contain greater than or equal to 90 percent saturates and less than or equal to 0.03 percent sulphur and have a viscosity index greater than or equal to 120 using the test methods specified in Table E-1.

d) Group IV base stocks are polyalphaolefins (PAO).

e) Group V base stocks include all other base stocks not included in Group I, II, III, or IV.

[0032] Typically, the base stock will have a viscosity preferably of 3-12, more preferably 4-10, most preferably 4.5-8, mm^2/s at 100°C.

Table E-1: Analytical Methods for Base Stock

Property	Test Method
Saturates	ASTM D 2007
Viscosity Index	ASTM D 2270
Sulphur	ASTM D 2622
	ASTM D 4294
	ASTM D 4927
	ASTM D 3120

[0033] Preferably, the oil of lubricating viscosity comprises greater than or equal to 10, more preferably greater than or equal to 20, even more preferably greater than or equal to 25, even more preferably greater than or equal to 30, even more preferably greater than or equal to 40, even more preferably greater than or equal to 45, mass % of a Group II or Group III base stock, based on the total mass of the oil of lubricating viscosity. Even more preferably, the oil of lubricating viscosity comprises greater than 50, preferably greater than or equal to 60, more preferably greater than or equal to 70, even more preferably greater than or equal to 80, even more preferably greater than or equal to 90, mass % of a Group II or Group III base stock, based on the total mass of the oil of lubricating viscosity. Most preferably, the oil of lubricating viscosity consists essentially of a Group II and/or Group III base stock. In some embodiments the oil of lubricating viscosity consists solely of Group II and/or Group III base stock. In the latter case it is acknowledged that additives included in the lubricating oil composition may comprise a carrier oil which is not a Group II or Group III base stock.

[0034] Other oils of lubricating viscosity that may be included in the lubricating oil composition are detailed as follows:

Natural oils include animal and vegetable oils (e.g. castor and lard oil), liquid petroleum oils and hydrorefined, solvent-treated mineral lubricating oils of the paraffinic, naphthenic and mixed paraffinic-naphthenic types. Oils of lubricating viscosity derived from coal or shale are also useful base oils.

Synthetic lubricating oils include 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); polyphenols (e.g. biphenyls, terphenyls, alkylated polyphenols); and alkylated diphenyl ethers and alkylated diphenyl sulfides and the derivatives, analogues and homologues thereof.

[0035] Another suitable class of synthetic lubricating oil 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, sebasic 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). Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebacic acid with two moles oftetraethylene glycol and two moles of 2-ethylhexanoic acid.

[0036] Esters useful as synthetic oils also include those made from C_5 to C_{12} monocarboxylic acids and polyols, and polyol ethers such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol and tripentaerythritol.

[0037] Unrefined, refined and re-refined oils can be used in the compositions of the present invention. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. For example, a shale oil obtained directly from retorting operations, a petroleum oil obtained directly from distillation or ester oil obtained directly from an esterification process and used without further treatment would be unrefined oil. Refined oils are similar to the unrefined oils except they have been further treated in one or more purification steps to improve one or more properties. Many such purification techniques, such as distillation, solvent extraction, acid or base extraction, filtration and percolation, are known to those skilled in the art. Re-refined oils are obtained by processes similar to those used to obtain refined oils applied to refined oils that have been already used in service. Such re-refined oils are also known as reclaimed or reprocessed oils and often are additionally processed by techniques for treating spent additive and oil breakdown products.

[0038] Other examples of base oil are gas-to-liquid ("GTL") base oils, i.e. the base oil may be an oil derived from Fischer-Tropsch synthesised hydrocarbons made from synthesis gas containing H_2 and CO using a Fischer-Tropsch catalyst. These hydrocarbons typically require further processing in order to be useful as a base oil. For example, they may, by methods known in the art, be hydroisomerized; hydrocracked and hydroisomerized; dewaxed; or hydroisomerized and dewaxed.

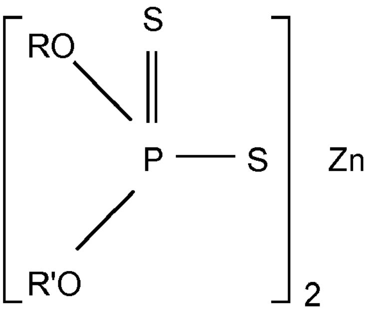
[0039] The oil of lubricating viscosity may also comprise a Group I, Group IV or Group V base stocks or base oil blends of the aforementioned base stocks.

CO-ADDITIVES

[0040] The lubricating oil compositions of all aspects of the present invention may further comprise a phosphorus-containing compound.

[0041] Suitable phosphorus-containing compounds include dihydrocarbyl dithiophosphate metal salts, which are frequently used as antiwear and antioxidant agents. The metal is preferably zinc, but 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 in amounts of 0.1 to 10, preferably 0.2 to 2 mass %, based upon the total weight of the lubricating oil composition. They 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] The preferred zinc dihydrocarbyl dithiophosphates are oil soluble salts of dihydrocarbyl dithiophosphoric acids and may be represented by the following formula:



wherein R and R' may be the same or different hydrocarbyl radicals containing from 1 to 18, preferably 2 to 12, carbon atoms and including radicals such as alkyl, alkenyl, aryl, arylalkyl, alkaryl and cycloaliphatic radicals. Particularly preferred as R and R' groups are alkyl groups of 2 to 8 carbon atoms. Thus, the radicals may, for example, be ethyl, n-propyl, i-propyl, n-butyl, i-butyl, sec-butyl, amyl, n-hexyl, i-hexyl, n-octyl, decyl, dodecyl, octadecyl, 2-ethylhexyl, phenyl, butylphenyl, cyclohexyl, methylcyclopentyl, propenyl, butenyl. In order to obtain oil solubility, the total number of carbon atoms (i.e. R and R') in the dithiophosphoric acid will generally be 5 or greater. The zinc dihydrocarbyl dithiophosphate (ZDDP) can therefore comprise zinc dialkyl dithiophosphates. Lubricating oil compositions of the present invention suitably may have a phosphorus content of no greater than about 0.08 mass % (800 ppm). Preferably, in the practice of the present invention, ZDDP is used in an amount close or equal to the maximum amount allowed, preferably in an amount that provides a phosphorus content within 100 ppm of the maximum allowable amount of phosphorus. Thus, lubricating oil compositions useful in the practice of the present invention preferably contain ZDDP or other zinc-phosphorus compounds, in an amount introducing from 0.01 to 0.08 mass % of phosphorus, such as from 0.04 to 0.08 mass % of phosphorus, preferably, from 0.05 to 0.08 mass % of phosphorus, based on the total mass of the lubricating oil composition.

[0043] 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 or esters, phosphorous esters, metal thiocarbamates, oil soluble copper compounds as described in U.S. Patent No. 4,867,890, and molybdenum-containing compounds.

[0044] Aromatic amines having at least two aromatic groups attached directly to the nitrogen constitute another class of compounds that is frequently used for antioxidancy. Typical oil-soluble aromatic amines having at least two aromatic groups attached directly to one amine nitrogen contain from 6 to 16 carbon atoms. The amines may contain more than two aromatic groups. Compounds having a total of at least three aromatic groups in which two aromatic groups are linked by a covalent bond or by an atom or group (e.g., an oxygen or sulfur atom, or a -CO-, - SO_2- or alkylene group) and two are directly attached to one amine nitrogen are also considered aromatic amines having at least two aromatic groups attached directly to the nitrogen. The aromatic rings are typically substituted by one or more substituents selected from alkyl, cycloalkyl, alkoxy, aryloxy, acyl, acylamino, hydroxy, and nitro groups. The amount of any such oil soluble aromatic amines having at least two aromatic groups attached directly to one amine nitrogen should preferably not exceed 0.4 mass %.

[0045] A dispersant is an additive whose primary function is to hold solid and liquid contaminations in suspension, thereby passivating them and reducing engine deposits at the same time as reducing sludge depositions. For example, a dispersant maintains in suspension oil-insoluble substances that result from oxidation during use of the lubricant, thus preventing sludge flocculation and precipitation or deposition on metal parts of the engine.

[0046] Dispersants in this invention are preferably "ashless", as mentioned above, being non-metallic organic materials that form substantially no ash on combustion, in contrast to metal-containing and hence ash-forming materials. They comprise a long hydrocarbon chain with a polar head, the polarity being derived from inclusion of e.g. an O, P, or N atom. The hydrocarbon is an oleophilic group that confers oil-solubility, having, for example 40 to 500 carbon atoms. Thus, ashless dispersants may comprise an oil-soluble polymeric backbone.

[0047] A preferred class of olefin polymers is constituted by polybutenes, specifically polyisobutenes (PIB) or poly-n-butenes, such as may be prepared by polymerization of a C_4 refinery stream.

[0048] Dispersants include, for example, derivatives of long chain hydrocarbon-substituted carboxylic acids, examples being derivatives of high molecular weight hydrocarbyl-substituted succinic acid. A noteworthy group of dispersants is constituted by hydrocarbon-substituted succinimides, made, for example, by reacting the above acids (or derivatives) with a nitrogen-containing compound, advantageously a polyalkylene polyamine, such as a polyethylene polyamine. Particularly preferred are the reaction products of polyalkylene polyamines with alkenyl succinic anhydrides, such as described in US-A-3,202,678; -3,154,560; -3,172,892; -3,024,195; -3,024,237, -3,219,666; and -3,216,936, that may be post-treated to improve their properties, such as borated (as described in US-A-3,087,936 and -3,254,025), fluorinated or oxylated. For example, boration may be accomplished by treating an acyl nitrogen-containing dispersant with a boron compound selected from boron oxide, boron halides, boron acids and esters of boron acids.

[0049] Preferably, the dispersant, if present, is a succinimide dispersant derived from a polyisobutene of number average molecular weight in the range of 1000 to 3000, preferably 1500 to 2500, and of moderate functionality. The succinimide is preferably derived from highly reactive polyisobutene.

[0050] Another example of dispersant type that may be used is a linked aromatic compound such as described in EP-A-2 090 642.

[0051] Additional additives may be incorporated into the compositions of the invention to enable particular performance requirements to be met. Examples of additives which may be included in the lubricating oil compositions of the present invention are metal rust inhibitors, viscosity index improvers, corrosion inhibitors, oxidation inhibitors, friction modifiers, anti-foaming agents, anti-wear agents and pour point depressants. Some are discussed in further detail below.

[0052] Friction modifiers and fuel economy agents that are compatible with the other ingredients of the final oil may also be included. Examples of such materials include glyceryl monoesters of higher fatty acids, for example, glyceryl 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 alkoxylated alkyl-substituted mono-amines, diamines and alkyl ether amines, for example, ethoxylated tallow amine and ethoxylated tallow ether amine.

[0053] Other known friction modifiers comprise oil-soluble organo-molybdenum compounds. Such organo-molybdenum friction modifiers also provide antioxidant and antiwear credits to a lubricating oil composition. Examples of such oil soluble organo-molybdenum compounds include dithiocarbamates, dithiophosphates, dithiophosphinates, xanthates, thioxanthates, sulfides, and the like, and mixtures thereof. Particularly preferred are molybdenum dithiocarbamates, dialkyldithiophosphates, alkyl xanthates and alkylthioxanthates.

[0054] Additionally, the molybdenum compound may be an acidic molybdenum compound. These compounds will react with a basic nitrogen compound as measured by ASTM test D-664 or D-2896 titration procedure and are typically hexavalent. Included are molybdic acid, ammonium molybdate, sodium molybdate, potassium molybdate, and other alkaline metal molybdates and other molybdenum salts, e.g., hydrogen sodium molybdate, $MoOCl_4$, MoO_2Br_2, $Mo_2O_3Cl_6$ molybdenum trioxide or similar acidic molybdenum compounds.

[0055] Among the molybdenum compounds useful in the compositions of this invention are organo-molybdenum compounds of the formula

$$Mo(ROCS_2)_4$$

and

$$Mo(RSCS_2)_4$$

wherein R is an organo group selected from the group consisting of alkyl, aryl, aralkyl and alkoxyalkyl, generally of from 1 to 30 carbon atoms, and preferably 2 to 12 carbon atoms and most preferably alkyl of 2 to 12 carbon atoms. Especially preferred are the dialkyldithiocarbamates of molybdenum.

[0056] Another group of organo-molybdenum compounds useful in the lubricating compositions of this invention are trinuclear molybdenum compounds, especially those of the formula $Mo_3S_kL_nQ_z$ and mixtures thereof wherein the L are independently selected ligands having organo groups with a sufficient number of carbon atoms to render the compound soluble or dispersible in the oil, n is from 1 to 4, k varies from 4 through 7, Q is selected from the group of neutral electron donating compounds such as water, amines, alcohols, phosphines, and ethers, and z ranges from 0 to 5 and includes non-stoichiometric values. At least 21 total carbon atoms should be present among all the ligand organo groups, such as at least 25, at least 30, or at least 35, carbon atoms.

[0057] Lubricating oil compositions useful in all aspects of the present invention preferably contain at least 10 ppm, at least 30 ppm, at least 40 ppm and more preferably at least 50 ppm molybdenum. Suitably, lubricating oil compositions useful in all aspects of the present invention contain no more than 1000 ppm, no more than 750 ppm or no more than 500 ppm of molybdenum. Lubricating oil compositions useful in all aspects of the present invention preferably contain from 10 to 1000, such as 30 to 750 or 40 to 500, ppm of molybdenum (measured as atoms of molybdenum).

[0058] The viscosity index of the base stock is increased, or improved, by incorporating therein certain polymeric materials that function as viscosity modifiers (VM) or viscosity index improvers (VII). Generally, polymeric materials useful as viscosity modifiers are those having number average molecular weights (Mn) of from 5,000 to 250,000, preferably from 15,000 to 200,000, more preferably from 20,000 to 150,000. These viscosity modifiers can be grafted with grafting materials such as, for example, maleic anhydride, and the grafted material can be reacted with, for example, amines, amides, nitrogen-containing heterocyclic compounds or alcohol, to form multifunctional viscosity modifiers (dispersant-viscosity modifiers). Polymer molecular weight, specifically $\overline{M}_n$, can be determined by various known techniques. One convenient method is gel permeation chromatography (GPC), which additionally provides molecular weight distribution information (see W. W. Yau, J. J. Kirkland and D. D. Bly, "Modern Size Exclusion Liquid Chromatography", John Wiley and Sons, New York, 1979). Another useful method for determining molecular weight, particularly for lower molecular weight polymers, is vapor pressure osmometry (see, e.g., ASTM D3592).

[0059] As used herein in connection with polymer block composition, "predominantly" means that the specified monomer or monomer type that is the principle component in that polymer block is present in an amount of at least 85% by weight of the block.

[0060] Polymers prepared with diolefins will contain ethylenic unsaturation, and such polymers are preferably hydrogenated. When the polymer is hydrogenated, the hydrogenation may be accomplished using any of the techniques known in the prior art. For example, the hydrogenation may be accomplished such that both ethylenic and aromatic unsaturation is converted (saturated) using methods such as those taught, for example, in U.S. Pat. Nos. 3,113,986 and 3,700,633 or the hydrogenation may be accomplished selectively such that a significant portion of the ethylenic unsaturation is converted while little or no aromatic unsaturation is converted as taught, for example, in U.S. Pat. Nos. 3,634,595; 3,670,054; 3,700,633 and Re 27,145. Any of these methods can also be used to hydrogenate polymers containing only ethylenic unsaturation and which are free of aromatic unsaturation.

[0061] The block copolymers may include mixtures of linear diblock polymers as disclosed above, having different molecular weights and/or different vinyl aromatic contents as well as mixtures of linear block copolymers having different molecular weights and/or different vinyl aromatic contents. The use of two or more different polymers may be preferred to a single polymer depending on the rheological properties the product is intended to impart when used to produce formulated engine oil. Examples of commercially available styrene/hydrogenated isoprene linear diblock copolymers include Infineum SV140™, Infineum SV150™ and Infineum SV160™, available from Infineum USA L.P. and Infineum UK Ltd.; Lubrizol® 7318, available from The Lubrizol Corporation; and Septon 1001™ and Septon 1020™, available from Septon Company of America (Kuraray Group). Suitable styrene/1, 3-butadiene hydrogenated block copolymers are sold under the tradename Glissoviscal™ by BASF.

[0062] Pour point depressants (PPD), otherwise known as lube oil flow improvers (LOFIs) lower the temperature. Compared to VM, LOFIs generally have a lower number average molecular weight. Like VM, LOFIs can be grafted with grafting materials such as, for example, maleic anhydride, and the grafted material can be reacted with, for example, amines, amides, nitrogen-containing heterocyclic compounds or alcohol, to form multifunctional additives.

[0063] In the present invention it may be necessary to include an additive which maintains the stability of the viscosity of the blend. Thus, although polar group-containing additives achieve a suitably low viscosity in the pre-blending stage it has been observed that some compositions increase in viscosity when stored for prolonged periods. Additives which are effective in controlling this viscosity increase include the long chain hydrocarbons functionalized by reaction with mono- or dicarboxylic acids or anhydrides which are used in the preparation of the ashless dispersants as hereinbefore disclosed. In another preferred embodiment, the lubricating oil compositions of the present invention contain an effective amount of a long chain hydrocarbons functionalized by reaction with mono- or dicarboxylic acids or anhydrides.

[0064] When lubricating compositions contain one or more of the above-mentioned additives, each additive is typically blended into the base oil in an amount that enables the additive to provide its desired function. Representative effective amounts of such additives, when used in crankcase lubricants, are listed below. All the values listed (with the exception of detergent values) are stated as mass percent active ingredient (A.I.).

ADDITIVE	MASS % (Broad)	MASS % (Preferred)
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 - 2.5
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
Viscosity Modifier	0.01 - 10	0.25 - 3
Base stock	Balance	Balance

[0065] Preferably, the Noack volatility of the fully formulated lubricating oil composition (oil of lubricating viscosity plus all additives) will be no greater than 18, such as no greater than 14, preferably no greater than 10, mass %. Lubricating oil compositions useful in the practice of the present invention may have an overall sulfated ash content of from 0.5 to 2.0, such as from 0.7 to 1.4, preferably from 0.6 to 1.2, mass %.

[0066] It may be desirable, although not essential to prepare one or more additive concentrates comprising additives (concentrates sometimes being referred to as additive packages) whereby several additives can be added simultaneously to the oil to form the lubricating oil composition.

[0067] The final composition may employ from 5 to 25, preferably 5 to 22, typically 10 to 20, mass % of the concentrate, the remainder being oil of lubricating viscosity.

EXAMPLES

Example 1

Synthesis of Detergent of the Invention

[0068] Glycerol mono-oleate (24.3g), xylene (202.0g), methanol (361.5g), water (6.8g) and Group I base oil (9.6g) were provided in a reactor. Under constant stirring, the mixture was heated stepwise to 160°C wherein:

Neutralisation
at 30°C, calcim hydroxide (114.0g) was added; and, at 40°C, alkylated sulfonic acid (155.7g) dissolved in xylene (126.8g) and then alkylated salicylic acid (330.4g) dissolved in xylene (76.3) were added;

Overbasing
at 28°C, carbon dioxide addition was started to add all (39.3g) over 180 minutes.

Distillation and Dilution
at 65°C, base oil (57.4g) was added; at 160°C, vacuum was applied before cooling to ambient temperature. Xylene (485g) was added and the mixture stirred. The mixture was then centrifuged and the solvent distilled.

Formulations

[0069] Three lubricating oil formulations were prepared, each containing 4 mmol of sulfonate, 16 mmol of salicylate, having the same co-additives in the same proportions, and having the same TBN.

Formulation 1: contained the detergent of Example 1

[0070]

Formulation A (reference): containing a hybrid sulfonate/salicylate detergent but no glycerol mono-oleate (GMO).
Formulation B (comparison): contained a hybrid sulfonate/salicylate detergent and subsequently added GMO, in the same concentration as Formulation 1.

TESTING

[0071] Each formulation was subjected to the HFRR (High Frequency Reciprocating Rig) testing described as follows: The apparatus used is described in ASTM D6079. 2mL of oil is added to the sample reservoir and a specific program run (shown below) with a load of 400 g and a frequency of 40 Hz. The average of the recorded coefficient of friction over the last stage (at 140 °C) is used to compare the formulations.

Step Number	Temperature (in °C)	Time (in minutes)	Description of Step
1	40	1	Hold/Stabilise Temperature
2	40	5	Run/Measure Friction (5 second intervals)
3	60	1	Hold/Stabilise Temperature
4	60	5	Run/Measure Friction (5 second intervals)
5	80	1	Hold/Stabilise Temperature
6	80	5	Run/Measure Friction (5 second intervals)
7	100	1	Hold/Stabilise Temperature
8	100	5	Run/Measure Friction (5 second intervals)
9	120	1	Hold/Stabilise Temperature
10	120	5	Run/Measure Friction (5 second intervals)
11	140	1	Hold/Stabilise Temperature

(continued)

Step Number	Temperature (in °C)	Time (in minutes)	Description of Step
12	140	5	Run/Measure Friction (5 second intervals)

[0072] The end of test results were as follows:

Formulation	Coefficient of Friction
1 (Invention)	0.099
A (reference)	0.119
B (comparison)	0.111

[0073] The results show the clear advantage of the invention over the referenced and comparison formulations.

Stability Tests

[0074] Improvement in overall stability of this invention was investigated using additive package stability studies, the packages being the mixture of lubricant componentry prior to the addition of the base oil to create the finished lubricant.

[0075] A comparison below is shown between two packages where identical levels of overbased metal detergent and at least one amide-or ester-based surfactant are included in a formulated product. In the comparison package, the additional surfactant is blended into the package, and in the invention package the surfactant is delivered as a co-surfactant in the overbased detergent.

Formulation	Comparison	Invention
Description	**Surfactant addition to package**	**Surfactant inclusion in overbased detergent**
start	C, B	C, B
4 Days	SH	C, B
2 weeks	SF, SH	SF, SH
6 weeks	2.6% SFL, SH	0.9% FL, H
12 weeks	3.5% SFL, SH	1.5% SFL, H

[0076] Key:

C, B	Clear, Bright
SH	Slightly Hazy
H	Hazy
SF	Slightly floculated
FL	Floculated lower layer
SFL	Slightly floculated lower layer
x%	Measured level of separated constituents

[0077] The above results show that the Invention Formulation provides a considerable improvement in formulation compatibility and stability over the Comparison Formulation. This is emphasised by the results after 12 weeks where there is a significant reduction in flocculation material of from 3.5% to 1.5%.

Claims

1. The use of an overbased metal detergent in which two or more different surfactant groups, one being a hydrocarbyl-substituted hydroxybenzoate and another being a sulfonate group, are incorporated therein during its overbasing,

and which has been manufactured in the presence of at least one amide- or ester-based co-surfactant, said use being as an additive in a motor vehicle lubricating oil composition to provide lubricant frictional benefits, exemplified by improved high frequency reciprocating rig performance thereof, and/or improved stability of the overbased detergent in the composition in comparison with an analogous lubricating oil composition made by admixing said overbased metal detergent and said at least one amide- or ester-based co-surfactant.

2. The use of claim 1 where the hydrocarbyl-substituted hydroxybenzoate is an alkylsalicylate.

3. The use of claim 1 or claim 2 where the metal is calcium or magnesium.

4. The use of any of claims 1 to 3 where the mole/mole ratio of hydroxybenzoate to sulfonate is in the range of 1:1 to 4:1.

5. The use of any of claims 1 to 4 where the co-surfactant is ester-based and is selected from: glycerol monoesters and esters of long chain polycarboxylic acids with diols.

6. The use of any of claims 1 to 5 where the metal ratio of the detergent is in the range of 3:1 to 7:1.

7. The use of any of claims 1 to 6 where the co-surfactant constitutes up to 20, such as 1 to 20 mass % of the mass of the detergent.

8. A method of providing lubricant frictional benefits, exemplified by improved high frequency reciprocating rig performance, in a motor vehicle lubricating oil composition comprising the steps of

(i) making a stable overbased complex/hybrid calcium detergent incorporating hydrocarbyl-substituted hydroxybenzoate and hydrocarbyl-substituted sulfonate surfactant groups; and
(ii) blending the detergent, with other additive components, into the lubricating oil composition,

wherein at least one amide- or ester-based co-surfactant is incorporated into the detergent in step (i) and not as another additive component in step(ii).

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EUROPEAN SEARCH REPORT

Application Number
EP 16 15 1609

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X Y	EP 2 045 313 A1 (INFINEUM INT LTD [GB]) 8 April 2009 (2009-04-08) * paragraphs [0005], [0014], [0016], [0039], [0040], [0045], [0085]; claims; tables 1,2 * -----	1-8 1-8	INV. C10M159/20 ADD. C10N10/04 C10N30/06 C10N40/25
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Y	WO 97/46646 A1 (EXXON CHEMICAL PATENTS INC [US]; SKINNER PHILIP [GB]; LENACK ALAIN [FR) 11 December 1997 (1997-12-11) * page 14, line 28 to page 15, line 38; page 19, line 18 to page 20, line 8; page 23, lines 14-17; claims 1-3,25-28,36; examples 39,64 * -----	1-8	
			TECHNICAL FIELDS SEARCHED (IPC)
			C10M

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
Munich	13 April 2016	Renoth, Heinz

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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