

Process for Producing an Overbased Metal Detergent

Field of Invention

[0001] The present invention relates to a process for producing an overbased metal detergent.

5 [0002] More specifically, the present invention relates to a process for preparing an overbased metal sulfonate having a high total base number (TBN).

[0003] The present invention further relates to a process for producing a high TBN metal sulfonate detergent for use in lubricants. Lubricants that include detergents are useful in lubrication applications and particularly in engine oils. Engine oils are used in many
10 engines including 2-stroke or 4-stroke engines.

Background of the Invention

[0004] The delivery of compounds comprising a high total base number to marine diesel applications is important. During the combustion process of fuels in engines, a high build-up of acids is usually formed as a by-product. A high building up of acid leads to
15 corrosive effects on the components of a marine diesel application and results in particularly high rates of wear.

[0005] Overbased compounds can be used as detergents, particularly in lubricants and can be utilized to neutralise such acids. Overbased detergents are generally oil-soluble particles comprising a metal salt core and a surfactant outer-shell.

20 [0006] WO/PCT application 2005/042677A1 (Kocsis, et al. 05/12/2005) discloses a process for preparing an overbased detergent. The process comprises a nine step process including the steps of; (1) providing a metal salt selected from the group consisting of a hydrocarbyl-substituted organic acid, a hydrocarbyl-substituted phenyl, a phenate, a hydrocarbyl-substituted carboxylate and mixtures thereof; (2) further providing methanol and
25 a mixture of alcohols containing two to about seven carbon atoms, wherein the mole ratio of methanol to the mixture of alcohols is about 2.2 or less, to form a mixture; (3) further providing a basic metal compound; (4) reacting the mixture of steps (3) with carbon dioxide to form a carbonated overbased metal sulfonate; (5) performing steps (3) and (4) at least three additional times upon the product of step (4); (6) thereafter removing at least a portion of the

water produced in steps (1) to (5) and of the alcohols introduced in step (2); (7) performing step (2) again, upon the product of step (6); (8) performing the steps (3) and (4) at least two additional times upon the product of step (7); and (9) thereafter removing a substantial portion of the water and of the alcohols from the composition.

5 [0007] It is further disclosed that the oil medium is present in an amount such that the weight ratio of acid corresponding to the metal salt of (1) to the oil medium is 0.3 to 1.4; and wherein step (6) is required when the hydrocarbyl substituted organic acid is a hydrocarbyl substituted sulfonic acid.

[0008] United States patent 6,444,625 (Muir et al. 09/03/2002) discloses a high
10 viscosity overbased sulfonate detergent and also marine cylinder oils containing high viscosity overbased sulfonate detergents. It is disclosed that the overbased calcium sulfonate detergent comprises a TBN of 400 or more and having a viscosity of at least 180mm² per second at 100°C.

[0009] A process for preparing high viscosity overbased calcium sulfonate is also
15 disclosed in US 6,444,625 comprising the steps of; (1) providing a sulfonic acid to the reactor; (2) adding a lime reactant to the reactor for neutralisation and over-basing; (3) adding a aliphatic C₁ to C₄ alcohol and a hydrocarbon solvent, to form a process mixture in the reactor, carbonating the process mixture by injecting carbon dioxide into the reactor, adding an oil to the process mixture to form a product mixture, clarifying the product mixture by removing
20 any solids, removing water and any remaining hydrocarbons from the product mixture after clarification, and isolating an overbased calcium sulfonate having a high TBN of at least 400, wherein, during carbonation the exotherm of the reaction is maintained at a temperature between 27°C and 57°C.

[0010] United States patent 5,384,053 (Cane, et al. 01/24/1995) discloses a process for
25 the production of a lubricating oil additive. This document discloses a process carried out with a starting overbased compound and reacting the overbased compound at elevated temperatures in the presence of a glycol. The process disclosed in this document utilizes a carboxylic acid during post-treatment of the highly overbased products. The process does not disclose a process of producing a highly overbased compound from a non-overbased starting

compound. The use of glycol in the process necessitates the need for the process to be carried out at elevated temperatures as the step of alcohol stripping of the glycol must be done at high temperatures to be effective.

[0011] A problem with the above processes is that there is a low uptake of metal salt to form the resultant overbased sulfonate detergent product which results in a slow filtration rate of the product due to a build-up of solid which blocks the filtration pathway.

[0012] In addition, the disclosed technology provides a lubricant composition which exhibits improved frictional performance (i.e. lower friction), improved anti-wear performance, and improved fuel economy.

Summary of the Invention

[0013] According to a first embodiment of the present invention, there is provided a process for preparing an overbased metal detergent in an oil medium comprising the steps of:

- (1) providing an organic acid selected from a group consisting of:
 - a hydrocarbyl-substituted organic sulfonic acid,
 - a mixture of a hydrocarbyl-substituted organic sulfonic acids,
 - a metal salt of said organic acid, and
 - mixtures thereof,
- (2) further providing at least one mono-alcohol;
- (3) further providing a basic metal compound;
- (4) further providing a carboxylic acid having 6 to 30 carbon atoms,
- (5) reacting the mixture of step (4) with carbon dioxide to form a carbonated overbased metal sulfonate;

wherein the resultant overbased metal detergent has a metal equivalent to sulfonic acid substrate ratio of 5:1 to 27:1. In one embodiment, steps (1) through (5) are performed sequentially, i.e., (1) followed by (or mixed or reacted with) (2) followed by (or mixed or reacted with) (3) followed by (or mixed or reacted with) (4), and thereafter reacted as in step (5). In other embodiments steps (1) through (4) may be performed in other orders or simultaneously.

[0014] In one embodiment the process defined by the invention is not an emulsion. Likewise the product of the process in one embodiment is not an emulsion. By emulsion it is meant to be a colloidal suspension of one immiscible liquid in another e.g., a water-in-oil, or oil-in-water emulsion.

5 [0015] The process may comprise an additional step (6) where steps (3), (4) and (5) are performed at least two additional times. The product of either step (5) or step (6) may be heated to at least 150°C in an additional step (7). The product of step (7) may be cooled in a further step (8).

[0016] The carboxylic acid may consist of 6 to 24 carbon atoms. The carboxylic acid
10 may be saturated and/or unsaturated. The carboxylic acid may be provided at 1 to 20 wt %. Alternatively the carboxylic acid may be provided at 2 to 20 wt %. Alternatively the carboxylic acid may be added at 4 to 8 wt % and may be about 7 wt %. The carboxylic acid may be stearic acid.

[0017] The at least one mono-alcohol may comprise 2 to 10 carbon atoms.
15 Alternatively, at least one mono-alcohol may comprise 2 to 7, 2 to 6, 2 to 5 or 3 to 5 carbon atoms. The at least one mono-alcohol may comprise branched or linear alkyl chains or mixtures thereof.

[0018] The at least one mono-alcohol may be one or a combination of the following:
ethanol, propan-1-ol, propan-2-ol, isopropanol, butan-1-ol, butan-2-ol, isobutanol, pentan-1-
20 ol, pentan-2-ol, penta-3-ol, isopentanol, hexan-1-ol, hexan-3-ol, heptan-1-ol, heptan-2-ol, heptan-3-ol, heptan-4-ol or mixtures thereof. The at least one mono-alcohol may contain at least one butanol and at least one amyl alcohol

[0019] Methanol may be provided at step (2). The mole ratio of methanol to at least one mono-alcohol may be below 2.2:1. Alternatively, the mole ratio of methanol to the at
25 least one mono-alcohol may be 1.70:1, 0.9:1 to 1.60:1, 1:1 to 1.50:1, 1:1 to 1:1.45 or 1.1:1 to 1.40:1.

[0020] The basic metal compound may be an alkali metal or alkaline earth metal oxide, hydroxide, mixtures thereof, or reactive equivalents. In one embodiment the basic metal compound is calcium oxide, calcium hydroxide, or mixtures thereof. Alternatively, the

basic metal compound may be sodium hydroxide. Alternatively, the basic metal compound may be magnesium oxide and/or magnesium hydroxide.

[0021] Any residual solids and any residual water and alcohols may be substantially or completely removed from the product.

5 **[0022]** Between 10 and 20 wt % of the total amount of the basic metal compound may be added at each occurrence of step (3).

[0023] An oil medium may be present. The oil medium may be substantially free of hydrocarbon solvent other than oil of lubricating viscosity. Suitable oils may have a kinematic viscosity at 100°C of 3 cSt (or mm²/s) to 20 cSt (or mm²/s).

10 **[0024]** The organic acid of step (1) may be a hydrocarbyl-substituted sulfonic acid and may be represented by the formula:



wherein each R¹ is independently a hydrocarbyl group having between 6 and 40 carbon atoms; A is a cyclic or acyclic hydrocarbon group; and k is 1 – 5.

15 **[0025]** The total base number (TBN) of the overbased metal salt of the hydrocarbyl-substituted sulfonic acid may be at least 400. The total base number of the metal salt of the hydrocarbyl-substituted sulfonic acid may be between 450 to 550, or 450 to 500.

[0026] The metal ratio of the metal salt of the hydrocarbyl-substituted sulfonic acid may be at least 20.

20 **[0027]** According to a second aspect of the present invention, there is provided a method for lubricating an internal combustion engine, comprising supplying thereto a lubricant composition comprising the detergent prepared by the process of:

- (1) providing a metal salt selected from a group consisting of a hydrocarbyl-substituted organic acid or a mixture of hydrocarbyl-substituted organic acids,
- 25 (2) further providing at least one mono-alcohol;
- (3) further providing a basic metal compound;
- (4) further providing a carboxylic acid having 6 to 30 carbon atoms;
- (5) reacting the mixture of step (4) with carbon dioxide to form a carbonated overbased metal sulfonate;

wherein the resultant overbased metal detergent has a metal equivalent to sulfonic acid substrate ratio of 5:1 to 27:1, and preferably 7:1 to 20:1 (or 5 to 27, or 7 to 20).

Detailed Description of the Invention

[0028] The present invention provides a process for preparing an overbased metal detergent in an oil medium.

[0029] As used herein, the Total Base Number (TBN) is a measure of the final overbased detergent containing the oil used in processing i.e. the final product has not been diluted in additional oil nor has the oil been removed after processing.

[0030] The overbased metal salt of a hydrocarbyl-substituted organic acid is generally formed by causing a reaction between an overbased neutral salt with a metal basic compound forming an overbased metal salt having a high Total Base Number.

[0031] All % values provided herein specifically refer to percentage by weight, unless otherwise specified.

[0032] It is further identified that the process of the present invention is to provide an overbased metal detergent, i.e. one that does not form part of a two phase system of matter or colloid.

Hydrocarbon Solvent

[0033] The process of the present invention may be carried out in the presence of hydrocarbon solvent in addition to the oil of lubricating viscosity. Alternatively, the process may be free of hydrocarbon solvent other than the oil of lubricating viscosity.

[0034] If present, hydrocarbon solvents can include aliphatic hydrocarbons or aromatic hydrocarbons. Examples of suitable aliphatic hydrocarbons include iso-butyl, hexane, heptane, octane, nonane, decane, undecane, dodecane, tridecane and mixtures thereof. Examples of aromatic hydrocarbons include xylene, toluene and mixtures thereof.

The Metal Basic Compound

[0035] The metal basic compound is used to supply excess basicity to the overbased material. The metal basic compound can be a hydroxide or oxide of the metal. The metal can be monovalent, divalent, or trivalent. When monovalent, the metal ion M can be an alkali metal, preferably lithium, sodium, or potassium. When potassium is used, it can be used in

combination with other metals. When divalent, the metal ion M can be an alkaline earth metal, preferably magnesium, calcium, barium or mixtures thereof and most preferably calcium which can be used alone or in combination with other metals. When trivalent, the metal ion M can be aluminium, which can be used alone or in combination with other metals.

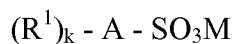
5 [0036] Some suitable examples of metal basic compounds 3 with hydroxide functionality include lithium hydroxide, potassium hydroxide, sodium hydroxide, magnesium hydroxide, calcium hydroxide, barium hydroxide and aluminium hydroxide. Suitable elements of metal basic compounds with oxide functionality include lithium oxide, magnesium oxide, calcium oxide and barium oxide. The oxides and/or hydroxides can be
10 used alone or in combination. The oxides or hydroxides can be hydrated or dehydrated, although hydrated is preferred. In one embodiment the metal basic compound is calcium hydroxide, which can be used alone or as mixtures thereof with other metal basic compounds. Calcium hydroxide is often referred to as lime. In one embodiment the metal basic compound 3 is calcium oxide which can be used alone or as mixtures thereof with other metal basic
15 compounds.

[0037] The overbased metal salt can be formed from the hydrocarbyl-substituted organic sulfonic acid and have metal ratios not exceeding 40:1 (or 40). Often, salts having weight ratios of 2:1 to 35:1 are used.

Metal Salt of a Hydrocarbyl-Substituted Organic Sulfonic Acid

20 [0038] The metal salt may be selected from the group consisting of a hydrocarbyl-substituted organic sulfonic acid.

[0039] In one embodiment of the invention the metal salt selected from the group consisting of a hydrocarbyl-substituted organic acid, a hydrocarbyl-substituted phenol and mixtures thereof, includes a metal salt of the hydrocarbyl-substituted sulfonic acid including
25 those represented by the formula:



wherein, each R^1 is independently a hydrocarbyl group. Preferably the hydrocarbyl group consists of ethylene, propylene, butylene or natural derived groups having 6 to 40, preferably 8 to 35 or 9 to 30 and most preferably 15 to 36 carbon atoms; A can be cyclic or acyclic

moieties or mixtures thereof. The hydrocarbyl group is preferably selected from the group consisting of an alkyl, cycloalkyl, aryl, acyl and mixtures thereof. Most preferably the hydrocarbyl group is an alkyl group, k is preferably 1 and R^1 is a branched alkyl group with 6 to 40 carbon atoms. M is a valence of a calcium ion, sodium ion, magnesium ion, or mixtures thereof. Valence is the number of “bonds” an atom or ion may be capable of forming, with one or more other atoms or ions. For example, a calcium or magnesium ion may typically have a valence of two, meaning the number of $(R^1)_k - A - SO_3$ anions associated with the “M” may be two. One of the valences of Ca or Mg may be associated with an $(R^1)_k - A - SO_3$ anion, and the second valence may be associated with a second $(R^1)_k - A - SO_3$ anion or it may be associated with another anion such as OH or CO_3 . The valence of sodium is one, meaning one $(R^1)_k - A - SO_3$ anion may be associated with a sodium ion.

[0040] The metal salt of the hydrocarbyl-substituted sulfonic acid has a hydrocarbyl-substituted sulfonic group that includes natural, synthetic or mixtures thereof. Suitable examples of the hydrocarbyl-substituted sulfonic acid include polypropene benzenesulfonic acid; and monoalkyl and dialkyl benzenesulfonic acids wherein the alkyl groups contain at least 10 carbons for example, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29 or 30 carbons and mixtures thereof.

[0041] Examples of suitable alkyl group include branched and/or linear decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, octadecenyl, nonadecyl, eicosyl, un-eicosyl, do-eicosyl, tri-eicosyl, tetra-eicosyl, penta-eicosyl, hexa-eicosyl or mixtures thereof.

[0042] Preferred examples of hydrocarbyl-substituted sulfonic acid include polypropene benzenesulfonic acid and C_{16} - C_{24} alkyl benzenesulfonic acid or mixtures thereof. Other preferred examples include toluene derived sulfonic acids.

[0043] When A is cyclic suitable groups include phenyl or fused bicyclic such as naphthalene, indenyl, indanyl, bicyclopentadienyl and mixtures thereof. Although A includes a fused bicyclic ring, phenyl rings are preferred. When A is a chain, the chain can be linear, branched and mixtures thereof, although linear is preferred. Suitable groups include derivatives of carboxylic acids containing 7 to 30, preferably 7 to 20, more preferably 8 to 20

and most preferably 8 to 15 carbon atoms. Further the chain can be saturated or unsaturated, although saturated is preferred.

[0044] The overbased detergent often has a low in-process viscosity and a low final viscosity. As used herein the term “low” used in “low in-process viscosity” and a “low final
5 viscosity” defines a viscosity that is lower than would be expected from a conventional overbased metal detergent.

[0045] The final product often has a final viscosity of less than $300 \text{ mm}^2\text{s}^{-1}$, preferably less than $200 \text{ mm}^2\text{s}^{-1}$, more preferably less than $190 \text{ mm}^2\text{s}^{-1}$ and most preferably less than $180 \text{ mm}^2\text{s}^{-1}$ at 100°C . Bulk viscosities at this level are easier to pump and handle.

10 [0046] Often the product when using overbased metal salt of hydrocarbyl-substituted sulfonic acid is a detergent and especially an overbased metal sulfonate with a TBN (Total Base Number) of at least 400, more preferably at least 425, and more preferably at least 450, even more preferably at least 490. The overbased sulfonate detergent could have a TBN of about 500.

15 [0047] Preferably in the first step of the process reaction pathway, a metal salt of a phenate such as sulfur-containing phenate, an alkylene (preferably methylene) coupled phenate or mixtures thereof may be employed. The preparation of the phenate materials listed above are known in the art.

The Carboxylic Acid

20 [0048] The carboxylic acid may comprise an acid containing 6 to 30 carbon atoms or any combination or mixture of acids therein. In one embodiment, the carboxylic acid contains 6 to 24 carbon atoms, 12 to 20 carbon atoms, or 16 to 18 carbon atoms. The carboxylic acid may be linear, branched, or mixtures thereof. In one embodiment, the carboxylic acid can be saturated and/or unsaturated. Acids which have a diacid functionality or hydroxyl-substituted
25 acids are not suitable. Tartaric acid and citric acid are also not suitable. In one embodiment, the carboxylic acid is stearic acid.

[0049] Examples of a suitable carboxylic acids include 2-methyl-2-heptanoic acid, 5-methyl-hexanoic acid, 3-methyl-2-heptanoic acid, 2,4,4-trimethyl-2-pentanoic acid, 4,4-dimethyl-2-pentanoic acid, 3-ethyl-2-hexanoic acid, 2-heptanoic acid, 2,3-dimethyl-2-

pentanoic acid, 3,5-dimethyl-2-hexanoic acid, 2-methyl-2-pentanoic acid, 3,4,4-trimethyl-2-pentanoic acid, 3-propyl-2-hexanoic acid, 4-methyl-2-pentanoic acid, 2,4-dimethyl-2-pentanoic acid, 3-ethyl-2-pentanoic acid, 3,4-dimethyl-2-pentanoic acid, 4-methyl-2-hexanoic acid, 2,4-dimethyl-2-hexanoic acid, 3-butyl-2-heptanoic acid, 2,5-dimethyl-2-hexanoic acid, 2-methyl-2-hexanoic acid, 3-ethyl-2-methyl-2-pentanoic acid, decanoic acid, isodecanoic acid, dodecanoic acid, tridecanoic acid, butadecanoic acid, myristic acid, pentadecanoic acid, palmitic acid, hexadecanoic acid, heptadecanoic acid, stearic acid, octadecanoic acid, icosyldecanoic acid, icosanoic acid or mixtures thereof. In one embodiment the carboxylic acid may be stearic acid.

[0050] The carboxylic acid(s) chosen from the group above is preferably added to the process at 1 to 20%, 2 to 20%, preferably 4 to 7%, or most preferably 7% of reactants.

[0051] Preferably, stearic acid is added incrementally in the process. The use of a carboxylic acid and in particular stearic acid in the process reaction, through incremental addition is advantageous. Without being bound by theory it is believed that the acid locates to a micelle of the carbonate core. This leads to a co-solubilization of the acid with the metal carbonate significantly lowering the viscosity of the reaction mixture, therefore increasing the rate and efficiency of filtration. The in-process addition of a carboxylic acid further reduces the amount of water needed to reduce the viscosity during the reaction.

Mono-alcohols

[0052] The alcohols may include methanol and at least one mono-alcohol containing 2 to 10, containing 2 to 7, preferably 2 to 6, more preferably 2 to 5 and most preferably 3 to 5 carbon atoms. The mono-alcohols containing 2 to 10 carbon atoms can include branched or linear alkyl chains or mixtures thereof, although branched is preferred.

[0053] The mono-alcohols can contain ethanol, propan-1-ol, isopropanol, butan-1-ol, butan-2-ol, isobutanol, pentan-1-ol, pentan-2-ol, penta-3-ol, isopentanol, hexan-1-ol, hexan-3-ol, heptan-1-ol, heptan-2-ol, heptan-3-ol, isooctyl, 2-ethylhexanol, nonanol, decanol, heptan-4-ol or mixtures thereof. Preferably the mixture of alcohols contains at least one butanol and at least one amyl alcohol. The mixture of alcohols is commercially available as isoamyl alcohol from Union Carbide or other suppliers.

[0054] In one embodiment only mono-alcohols are used. Diols are not generally utilized. Mono-alcohols are advantageous over diols during the final stripping of this alcohol; this can be carried out at much lower temperatures, i.e. less than 160°C.

Oil Medium

5 [0055] The invention further includes an oil medium (considered to be distinct and not part of the hydrocarbon solvent described above), especially an oil of lubricating viscosity. The oil includes natural and synthetic oils, oil derived from hydrocracking, hydrogenation, hydrofinishing, unrefined, refined and re-refined oils or mixtures thereof.

[0056] Unrefined oils are those obtained directly from a natural or synthetic source
10 generally without (or with little) further purification treatment.

[0057] Refined oils are similar to the unrefined oils except they have been further treated in one or more purification steps to improve one or more properties. Purification techniques are known in the art and include solvent extraction, secondary distillation, acid or base extraction, filtration, percolation and the like.

15 [0058] Re-refined oils are also known as reclaimed or reprocessed oils, and are obtained by processes similar to those used to obtain refined oils and often are additionally processed by techniques directed to removal of spent additives and oil breakdown products.

[0059] Natural oils useful in making the inventive lubricants include animal oils, vegetable oils (e.g. castor oil, lard, oil), mineral lubricating oils such as liquid petroleum oils
20 and solvent-treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic or mixed paraffinic-naphthenic types and oils derived from coal or shale or mixtures thereof.

[0060] Synthetic lubricating oils are useful and include hydrocarbon oils such as polymerised and interpolymerised olefins (e.g. polybutylenes, polypropylenes, propyleneisobutylene copolymers); poly(1-hexenes), poly(1-octenes), poly(1-decenes), and
25 mixtures thereof; alkyl-benzenes (e.g. dodecylbenzenes, tetradecylbenzenes, di-(2-ethylhexyl)-benzenes); polyphenyls (e.g. biphenyls, terphenyls, alkylated polyphenyls); alkylated diphenyl ethers and alkylated diphenyl sulfides and the derivatives, analogs and homologs thereof or mixtures thereof.

[0061] Other synthetic lubricating oils include liquid esters of phosphorous-containing acids (e.g. tricresyl phosphate, trioctyl phosphate, and the diethyl ester of decane phosphonic acid), and polymeric tetrahydrofurans. Synthetic oils may be produced by Fischer-Tropsch reactions and often may be hydroisomerised Fischer-Tropsch hydrocarbons or waxes

5 [0062] Oils of lubricating viscosity can also be defined as specified in the American Petroleum Institute (API) Base Oil Interchangeability Guidelines. The five base oil groups are as follows: Group I (sulfur content >0.03 wt %, and/or <90 wt % saturates, viscosity index 80-120); Group II (sulfur content ≤ 0.03 wt %, and ≥ 90 wt % saturates, viscosity index 80-120); Group III (sulfur content ≤ 0.03 wt %, and ≥ 90 wt % saturates, viscosity index ≥ 120);
10 Group IV (all polyalphaolefins (PAOs)); and Group V (all others not included in Groups I, II, III, or IV). The oil of lubricating viscosity comprises an API Group I, II, III, IV, V oil and mixtures thereof. Preferably the oil of lubricating viscosity is an API Group I, II, III oil or mixtures thereof.

Optional Performance Additives

15 [0063] The detergent can be incorporated into a lubricating oil composition that optionally includes at least one other performance additive selected from the group consisting of metal deactivators, detergents other than those prepared by the process of the invention, dispersants, antioxidants, antiwear agents, corrosion inhibitors, anti-scuffing agents, extreme pressure agents, foam inhibitors, demulsifiers, friction modifiers, viscosity modifiers, pour
20 point depressants and mixtures thereof. Often fully-formulated lubricating oil will contain one or more of these additives.

[0064] One such additive is a dispersant. Dispersants are well known in the field of lubricants and include primarily what is known as ashless-type dispersants and polymeric dispersants. Ashless type dispersants are characterized by a polar group attached to a
25 relatively high molecular weight hydrocarbon chain. Typical ashless dispersants include nitrogen-containing dispersants such as N-substituted long chain alkenyl succinimides, also known as succinimide dispersants. Succinimide dispersants are more fully described in U.S. Patents 4,234,435 and 3,172,892. Another class of ashless dispersant is high molecular weight esters, prepared by reaction of a hydrocarbyl acylating agent and a polyhydric

aliphatic alcohol such as glycerol, pentaerythritol, or sorbitol. Such materials are described in more detail in U.S. Patent 3,381,022. Another class of ashless dispersant is Mannich bases. These are materials which are formed by the condensation of a higher molecular weight, alkyl substituted phenol, an alkylene polyamine, and an aldehyde such as formaldehyde and are described in more detail in U.S. Patent 3,634,515. Other dispersants include polymeric dispersant additives, which are generally hydrocarbon-based polymers which contain polar functionality to impart dispersancy characteristics to the polymer. Dispersants can also be post-treated by reaction with any of a variety of agents. Among these are urea, thiourea, dimercaptothiadiazoles, carbon disulfide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, nitriles, epoxides, boron compounds, and phosphorus compounds. References detailing such treatment are listed in U.S. Patent 4,654,403. The amount of dispersant in the present composition can typically be 1 to 10 wt %, or 1.5 to 9.0 percent, or 2.0 to 8.0 percent, all expressed on an oil-free basis.

[0065] Another component may be an antioxidant. Antioxidants encompass phenolic antioxidants, which may comprise a butyl substituted phenol containing 2 or 3 t-butyl groups. The para position may also be occupied by a hydrocarbonyl group or a group bridging two aromatic rings. The latter antioxidants are described in greater detail in U.S. Patent 6,559,105. Antioxidants also include aromatic amines, such as nonylated diphenylamine. Other antioxidants include sulfurized olefins, titanium compounds, and molybdenum compounds. U.S. Pat. No. 4,285,822, for instance, discloses lubricating oil compositions containing a molybdenum and sulfur containing composition. Typical amounts of antioxidants will, of course, depend on the specific antioxidant and its individual effectiveness, but illustrative total amounts can be 0.01 to 5, or 0.15 to 4.5, or 0.2 to 4 percent by weight. Additionally, more than one antioxidant may be present, and certain combinations of these can be synergistic in their combined overall effect.

[0066] Viscosity improvers (also sometimes referred to as viscosity index improvers or viscosity modifiers) may be included in the compositions of this invention. Viscosity improvers are usually polymers, including polyisobutenes, poly(meth)acrylates (PMA) and

poly(meth)acrylic acid esters, hydrogenated diene polymers, polyalkylstyrenes, esterified styrene-maleic anhydride copolymers, hydrogenated alkenylarene-conjugated diene copolymers and polyolefins. PMA's are prepared from mixtures of methacrylate monomers having different alkyl groups. The alkyl groups may be either straight chain or branched chain groups containing from 1 to 18 carbon atoms. Most PMA's are viscosity modifiers as well as pour point depressants.

[0067] Another additive is an antiwear agent. Examples of anti-wear agents include phosphorus-containing antiwear/extreme pressure agents such as metal thiophosphates, phosphoric acid esters and salts thereof, phosphorus-containing carboxylic acids, esters, ethers, and amides; and phosphites. In certain embodiments a phosphorus antiwear agent may be present in an amount to deliver 0.01 to 0.2 or 0.015 to 0.15 or 0.02 to 0.1 or 0.025 to 0.08 percent by weight phosphorus. Often the antiwear agent is a zinc dialkyldithiophosphate (ZDP). For a typical ZDP, which may contain 11 percent P (calculated on an oil free basis), suitable amounts may include 0.09 to 0.82 percent by weight. Non-phosphorus-containing anti-wear agents include borate esters (including borated epoxides), dithiocarbamate compounds, molybdenum-containing compounds, and sulfurized olefins.

The Overbased Material (The Product)

[0068] The overbased material is the product formed following the process of the present invention.

[0069] Detergents in general are typically overbased materials, otherwise referred to as overbased or super-based salts, which are generally homogenous Newtonian systems having, by a metal content, in excess of that which would be present for neutralisation according to the stoichiometry of the metal and the detergent anion. The amount of excess metal is commonly expressed in terms of metal ratio, that is, the ratio of the total equivalent of the metal to the equivalent of the acidic organic compound. Overbased materials are prepared by reacting an acid material (such as carbon dioxide) with an acidic or organic compound, an inert reaction medium (e.g. mineral oil), a stoichiometric excess of a metal base, and a promoter such as a phenyl or alcohol. The acidic organic metal will normally have a sufficient number of carbon atoms, to provide oil solubility.

Industrial Application

[0070] The metal salt selected from the group consisting of a hydrocarbyl-substituted organic acid; a hydrocarbyl-substituted phenol and mixtures thereof of the present invention are useful as detergents in lubricants for internal combustion engines, for example diesel fuelled engines, gasoline fuelled engines, natural gas fuelled engines or mixed gasoline/alcohol fuelled engines.

[0071] A method for lubricating an internal combustion engine, comprising supplying thereto a lubricant comprising the composition as described herein is also provided. The invention is suitable for 2-stroke or 4-stroke engines, in particular marine diesel engines, especially 2-stroke marine diesel engines.

[0072] The overbased metal detergent can be used as part of a lubricating composition. The lubricating composition may be useful in an internal combustion engine, a driveline device, a hydraulic system, a grease, a turbine, or a refrigerant.

[0073] If the lubricating composition is part of a grease composition, the composition further comprises a thickener. The thickener may include simple metal soap thickeners, soap complexes, non-soap thickeners, metal salts of such acid-functionalized oils, polyurea and diurea thickeners, calcium sulfonate thickeners or mixtures thereof. Thickeners for grease are well known in the art. The overbased metal detergent of the present invention can be used in the preparation of a calcium sulfonate grease.

[0074] The process may provide a method of lubricating an internal combustion engine. The engine components may have a surface of steel or aluminium.

[0075] An aluminium surface may be derived from an aluminium alloy that may be a eutectic or a hyper-eutectic aluminium alloy (such as those derived from aluminium silicates, aluminium oxides, or other ceramic materials). The aluminium surface may be present on a cylinder bore, cylinder block, or piston ring having an aluminium alloy, or aluminium composite.

[0076] The internal combustion engine may or may not have an Exhaust Gas Recirculation system. The internal combustion engine may be fitted with an emission control

system or a turbocharger. Examples of the emission control system include diesel particulate filters (DPF), or systems employing selective catalytic reduction (SCR).

[0077] In one mode the internal combustion engine may be a diesel fuelled engine (typically a heavy duty diesel engine), a gasoline fuelled engine, a natural gas fuelled engine, a mixed gasoline/alcohol fuelled engine, or a hydrogen fuelled internal combustion engine. The internal combustion engine may be a diesel fuelled engine and in another mode a gasoline fuelled engine. The internal combustion engine may be a heavy duty diesel engine.

[0078] The internal combustion engine may be a 2-stroke or 4-stroke engine. Suitable internal combustion engines include marine diesel engines, aviation piston engines, low-load diesel engines, and automobile and truck engines. The marine diesel engine may be lubricated with a marine diesel cylinder lubricant (typically in a 2-stroke engine), a system oil (typically in a 2-stroke engine), or a crankcase lubricant (typically in a 4-stroke engine).

[0079] The lubricant composition for an internal combustion engine may be suitable for any engine lubricant irrespective of the sulfur, phosphorus or sulfated ash (ASTM D-874) content.

[0080] The sulfur content of the engine oil lubricant may be 1 % or less, or 0.8 % or less, or 0.5 % or less, or 0.3 % or less. In one mode the sulfur content may be in the range of 0.001 % to 0.5 %, or 0.01 % to 0.3 %. The phosphorus content may be 0.2 % or less, or 0.12 % or less, or 0.1 % or less, or 0.085 % or less, or 0.08 % or less, or even 0.06 % or less, 0.055 % or less, or 0.05 % or less.

[0081] The phosphorus content may be 0.04 % to 0.12 %. The phosphorus content may be 100 ppm to 1000 ppm, or 200 ppm to 600 ppm.

[0082] The total sulfated ash content may be 0.3 % to 1.2 %, or 0.5 % to 1.1 % of the lubricating composition. In one mode the sulfated ash content may be 0.5 % to 1.1 % of the lubricating composition.

[0083] The lubricating composition may be an engine oil, wherein the lubricating composition may be characterised as having at least one of (i) a sulfur content of 0.5 % or less, (ii) a phosphorus content of 0.12 % or less, and (iii) a sulfated ash content of 0.5 % to 1.1 % of the lubricating composition.

[0084] In different embodiments the lubricating composition may have a composition as described in the following table:

Additive	Embodiments (wt %)		
	A	B	C
Additive of Invention	0.05 to 1	0.2 to 3	0.5 to 2
Dispersant	0.05 to 12	0.75 to 8	0.5 to 6
Dispersant Viscosity Modifier	0 or 0.05 to 5	0 or 0.05 to 4	0.05 to 2
Additional Detergent	0 or 0.05 to 15	0.1 to 10	0.2 to 8
Antioxidant	0 or 0.05 to 15	0.1 to 10	0.5 to 5
Antiwear Agent	0 or 0.05 to 15	0.1 to 10	0.3 to 5
Friction Modifier	0 or 0.05 to 6	0.05 to 4	0.1 to 2
Viscosity Modifier	0 or 0.05 to 10	0.5 to 8	1 to 6
Any Other Performance Additive	0 or 0.05 to 10	0 or 0.05 to 8	0 or 0.05 to 6
Oil of Lubricating Viscosity	Balance to 100	Balance to 100	Balance to 100

Specific Embodiment

5 **[0085]** The following examples provide an illustration of the invention. These examples are non-exhaustive and are not intended to limit the scope of the invention.

[0086] To produce an oil diluted 500 TBN overbased sulfonate detergent, a series of separate carbonation increments are carried out over the overbasing period. The processing of a 500 TBN detergent in this way is however not easy. Several main issues have so far prevented current processes being scaled up to plant level. A six stage process has been investigated (PCT/US2004/036152); however, one issue is that there is a significant increase in viscosity during the final two carbonation steps, making the resultant detergent unmanageable on a larger scale. To mitigate this unmanageable increase in viscosity, an intermediate strip has been employed (PCT/US2004/036152). However, the additional intermediate strip step is detrimental to the plant's time cycles and hence throughput. High

levels of solids in both the six stage reaction and also the six stage reaction with additional intermediate strip step are also a problem as high solid levels can lead to slow filtration rates.

[0087] A key development has been the removal of the intermediate strip step. However, removal of the intermediate strip step alone had the detrimental effect of severely increasing in process viscosities.

[0088] Referring to table 1, a number of reactions were carried out under differing conditions in order to prepare overbased calcium sulfonates with the combination of high TBN (i.e. greater than 400 TBN even when oil-diluted), increased TBN/Ash ratio, and improved processability (measured in terms of filtration time and solids formation).

Table 1 – Summary of Preparative Examples

Example	Fatty Acid	%Acid Added	TBN	%Ca	Metal Ratio ¹
COMP EX 2	None	0	507	19.2	17
EX 3	Stearic	10	514	18.5	17
EX 4	Stearic	7	483	19.1	17
EX 5	Stearic	7	401	17	14
COMP EX 6	None	0	400	15	13

1. Metal ratio as defined in [0069] with the detergent anion limited to the sulfonate.

Example 1. Neutral Salt Formation.

[0089] To a flange flask (5L) is charged diluent mineral oil (1388 g), mixed isobutyl and amyl alcohols (117 g), polyisobutenyl succinic anhydride (294g), calcium alkylphenate detergent (containing 69% oil) (258 g), calcium hydroxide (207 g), water (26 g) and calcium chloride (12 g). The mixture is heated to 50°C and stirred at 300 r.p.m. under nitrogen. At this time, the alkylbenzene sulfonic acid (C20-24) (1830 g) is added dropwise at a rate to ensure that the temperature of the mixture does not exceed 75°C. After the addition is complete, the mixture is heated to 100°C for 1 hour and then to 150°C, at which temperature

the majority of the volatile solvent is removed by distillation. The product is the neutral calcium salt in diluent oil.

Comparative Example 2. (COMP EX 2) 500 TBN overbased calcium detergent baseline.

[0090] To a flange flask (2L) was added the neutral salt mixture from Ex. 1 (500 g),
5 mixed isobutyl and amyl alcohols (80 g), methanol (48 g) and diluent mineral oil (283 g) with
stirring, at 47°C. At this temperature, calcium hydroxide (94.5 g) was added and the mixture
was stirred for 20 minutes. Carbon dioxide gas, about 40 g, is blown through the mixture at
this temperature over 45 minutes. A second addition of calcium hydroxide (93 g) is added
and stirred for 20 minutes. An additional amount of CO₂ gas, about 52 g, is added over 1
10 hour. A third portion of calcium hydroxide (93 g) is added and stirred for 20 minutes. An
additional aliquot of CO₂ gas, about 52 g, is added over 1 hour. A fourth portion of calcium
hydroxide (93 g) is added and stirred for 20 minutes. A further quantity of CO₂ gas, about 52
g, is added over 1 hour. The reaction mixture is then heated to 150 °C to remove the volatile
solvents to provide a crude mixture. To the mixture is then added mixed isobutyl and amyl
15 alcohols (80 g), methanol (48 g) with stirring, at 47°C. At this temperature, calcium hydroxide
(93.5 g) was added and the mixture was stirred for 20 minutes. Carbon dioxide gas, about 52
g, is blown through the mixture at this temperature over 1 hour. The final calcium hydroxide
(93 g) was then added and stirred for 20 minutes. An additional amount of CO₂ gas, about 52
g, is added over 1 hour. Thereafter, the reaction mixture is heated to 150°C to remove volatile
20 solvents and provide a crude mixture with a solids level of 24%. The mixture is filtered
through Diatomaceous earth filter aid at a rate of 79 g/hr to give the desired product, having
an analysis of calcium 19.2%, TBN (total base number, as mg KOH/g) 507, sulfated ash
63.8%, and KV100 (kinematic viscosity at 100 °C) of 181 mm²/s (cSt).

Example 3. (EX 3) 500 TBN overbased calcium detergent with stearic acid (10%).

25 [0091] To a flange flask (2L) was added the neutral salt mixture from Ex. 1 (500 g),
mixed isobutyl and amyl alcohols (80 g), methanol (48 g) and diluent mineral oil (181.5 g)
with stirring, at 47°C. At this temperature, calcium hydroxide (94.5 g) and stearic acid (25.7
g) was added and the mixture was stirred for 20 minutes. Carbon dioxide gas, about 36 g, is
blown through the mixture at this temperature over 44 minutes. A second addition of calcium

hydroxide (93 g) and stearic acid (25.7 g) is added and stirred for 20 minutes. An additional amount of CO₂ gas, about 50 g, is added over 1 hour. A third portion of calcium hydroxide (93 g) and stearic acid (25.7 g) is added and stirred for 20 minutes. An additional aliquot of CO₂ gas, about 50 g, is added over 1 hour. A fourth portion of calcium hydroxide (93 g) and stearic acid (25.7 g) is added and stirred for 20 minutes. A further quantity of CO₂ gas, about 50 g, is added over 1 hour. The fifth portion of calcium hydroxide (93.5 g) and stearic acid (25.7 g) was added and the mixture was stirred for 20 minutes. Carbon dioxide gas, about 50 g, is blown through the mixture over 1 hour. The final calcium hydroxide (93 g) and stearic acid (25.7 g) was then added and stirred for 20 minutes. An additional amount of CO₂ gas, about 52 g, is added over 1 hour. Thereafter, the reaction mixture is heated to 150°C to remove volatile solvents and provide a crude mixture with a solids level of 10.4%. The mixture is filtered through Diatomaceous earth filter aid at a rate of 28 g/hr to give the desired product, having an analysis of calcium 18.5%, TBN (total base number, as mg KOH/g) 514, sulfated ash 62.7%, and KV100 (kinematic viscosity at 100 °C) of 946 mm²/s (cSt).

Example 4. (EX 4) 475 TBN overbased calcium detergent with stearic acid (7%).

[0092] To a flange flask (2L) was added the neutral salt mixture from Ex. 1 (500 g), mixed isobutyl and amyl alcohols (80 g), methanol (48 g) and diluent mineral oil (310 g) with stirring, at 47°C. At this temperature, calcium hydroxide (94.5 g) and stearic acid (18.2 g) was added and the mixture was stirred for 20 minutes. Carbon dioxide gas, about 35 g, is blown through the mixture at this temperature over 42 minutes. A second addition of calcium hydroxide (93 g) and stearic acid (18.2 g) is added and stirred for 20 minutes. An additional amount of CO₂ gas, about 50 g, is added over 1 hour. A third portion of calcium hydroxide (93 g) and stearic acid (18.2 g) is added and stirred for 20 minutes. An additional aliquot of CO₂ gas, about 50 g, is added over 1 hour. A fourth portion of calcium hydroxide (93 g) and stearic acid (18.2 g) is added and stirred for 20 minutes. A further quantity of CO₂ gas, about 50 g, is added over 1 hour. The fifth portion of calcium hydroxide (93.5 g) and stearic acid (18.2 g) was added and the mixture was stirred for 20 minutes. Carbon dioxide gas, about 50 g, is blown through the mixture over 1 hour. The final calcium hydroxide (93 g) and stearic acid (18.2 g) was then added and stirred for 20 minutes. An additional amount of CO₂ gas,

about 52 g, is added over 1 hour. Thereafter, the reaction mixture is heated to 150°C to remove volatile solvents and provide a crude mixture with a solids level of 9.2%. The mixture is filtered through Diatomaceous earth filter aid at a rate of 136 g/hr to give the desired product, having an analysis of calcium 19.1%, TBN (total base number, as mg
5 KOH/g) 483, sulfated ash 58.4%, and KV100 (kinematic viscosity at 100 °C) of 211 mm²/s (cSt).

Example 5 (EX 5) 400 TBN overbased calcium detergent with stearic acid (7%).

[0093] To a flange flask (2L) was added the neutral salt mixture from Ex. 1 (440 g), mixed isobutyl and amyl alcohols (73 g), methanol (44 g) and diluent mineral oil (288 g) with
10 stirring, at 47°C. At this temperature, calcium hydroxide (67 g) and stearic acid (16.7 g) was added and the mixture was stirred for 20 minutes. Carbon dioxide gas, about 35 g, is blown through the mixture at this temperature over 42 minutes. A second addition of calcium hydroxide (67 g) and stearic acid (16.7 g) is added and stirred for 20 minutes. An additional amount of CO₂ gas, about 38 g, is added over 1 hour. A third portion of calcium hydroxide
15 (67 g) and stearic acid (16.7 g) is added and stirred for 20 minutes. An additional aliquot of CO₂ gas, about 38 g, is added over 1 hour. A fourth portion of calcium hydroxide (67 g) and stearic acid (16.7 g) is added and stirred for 20 minutes. A further quantity of CO₂ gas, about 38 g, is added over 1 hour. The fifth portion of calcium hydroxide (67 g) and stearic acid (16.7 g) was added and the mixture was stirred for 20 minutes. Carbon dioxide gas, about 38
20 g, is blown through the mixture over 1 hour. The final calcium hydroxide (67 g) and stearic acid (16.7 g) was then added and stirred for 20 minutes. An additional amount of CO₂ gas, about 38g, is added over 1 hour. Thereafter, the reaction mixture is heated to 150°C to remove volatile solvents and provide a crude mixture with a solids level of 7.2%. The mixture is filtered through Diatomaceous earth filter aid to give the desired product, having an
25 analysis of calcium 16.9%, TBN (total base number, as mg KOH/g) 401, sulfated ash 51.5%, and KV100 (kinematic viscosity at 100 °C) of 81 mm²/s (cSt).

Comparative Example 6 (COMP EX 6) 400 TBN Overbased calcium detergent baseline

[0094] To a flange flask (3L) was added the neutral salt mixture from Ex. 1 (500 g), mixed isobutyl and amyl alcohols (116 g), methanol (96 g) and diluent mineral oil (463 g)

with stirring, at 47°C. At this temperature, calcium hydroxide (72.5 g) was added and the mixture was stirred for 20 minutes. Carbon dioxide gas, about 41 g, is blown through the mixture at this temperature over 45 minutes. A second addition of calcium hydroxide (72.5 g) is added and stirred for 20 minutes. An additional amount of CO₂ gas, about 41 g, is added over 1 hour. A third portion of calcium hydroxide (72.5 g) is added and stirred for 20 minutes. An additional aliquot of CO₂ gas, about 41 g, is added over 1 hour. A fourth portion of calcium hydroxide (72.5 g) is added and stirred for 20 minutes. A further quantity of CO₂ gas, about 41 g, is added over 1 hour. The fifth portion of calcium hydroxide (72.5 g) was added and the mixture was stirred for 20 minutes. Carbon dioxide gas, about 41 g, is blown through the mixture over 1 hour. The final calcium hydroxide (72.5 g) was then added and stirred for 20 minutes. An additional amount of CO₂ gas, about 41g, is added over 1 hour. Thereafter, the reaction mixture is heated to 150°C to remove volatile solvents and provide a crude mixture with a solids level of 7.2%. The mixture is filtered through Diatomaceous earth filter aid to give the desired product, having an analysis of calcium 15.5%, TBN (total base number, as mg KOH/g) 400, sulfated ash 52%, and KV100 (kinematic viscosity at 100 °C) of 110 mm²/s (cSt).

[0095] The overbased calcium sulfonate detergents are evaluated based on several factors including filterability, bulk kinematic viscosity, TBN to ash ratio, and solids formation. Solids formation is determined by centrifugation. Prior to filtration a sample of the crude mixture is dissolved in hexane (25:75 by volume) and placed into a centrifuge tube. The sample is then centrifuged at 1600 rpm for 20 minutes. The solids settle to the bottom of the tube and are recorded as ml of solids. This value is multiplied by 4 which gives a percentage solids in the bulk detergent.

[0096] Comparison of overbased calcium sulfonate detergents (summarized in Table 2) shows the benefit of employing stearic acid during overbasing of neutral calcium sulfonate. Comparative Example 2 (COMP EX 2) is conventional calcium overbased to 500 TBN without addition of a fatty acid; however an intermediate strip step is employed to maintain viscosity control. While the target TBN is achieved, there is a high level of solids, indicative of a lack of product stability.

[0097] In Example 3 stearic acid was utilized at 10% of the reaction mixture; the acid was added incrementally. This improved final solid levels by reducing the solid levels from 24% to 10.4%. However, the viscosity of the final product was high at 946 cSt (or mm²/s) at 100 °C relative to the baseline reaction (EX 2) which required an intermediate strip; (as per PCT/US2004/036152). Target TBN/Ash ratio is achieved and addition of diluent oil may be carried out to reduce in process viscosity without altering product performance.

[0098] Therefore a reaction whereby the target was 475 TBN, with additional oil with respect to Example 3, was performed (Example 4). This reaction incorporated the incremental addition of stearic acid at 7% (rather than at 10%). This had the desired effect of good in-process viscosity, low final solid levels, good filtration rates (double the rate of baseline reaction (EX 2)) and good final viscosity. In addition, the highest ratio of TBN to sulfated ash.

[0099] Example 5 is an attempt to produce a lower TBN (~400 comparable to commercial overbased calcium sulfonate (COMP EX 6) with improved process conditions as well as improved product performance.

Table 2 – Preparative Results

Example	% Solid	Filtration Rate (g/hr)	TBN/%Ash	KV100
COMP EX2	24	79.3	7.95	181*
EX 3	10.4	80.0	8.20	946
EX 4	9.2	136.0	8.27	211
EX 5	7.2	N/A	7.86	81
COMP EX6	6-8%	N/A	7.55	110

*Includes intermediate stripping

[0100] In summary a high TBN sulfonate (overbased metal detergent) was achieved omitting the intermediate strip step and utilizing incremental additions of stearic acid. This resulted in low solids, good in-process viscosity, good filtration rates and good final viscosity.

Lubricating Compositions

[0101] A series of 0W-20 engine lubricants in Group III base oil of lubricating viscosity are prepared containing the additives described above as well as conventional additives including polymeric viscosity modifier, ashless succinimide dispersant, additional overbased detergents, antioxidants (combination of phenolic ester and diarylamine), zinc dialkyldithiophosphate (ZDDP), as well as other performance additives as follows (Table 3). The phosphorus, sulfur and ash contents of each of the examples are also presented in the table in part to show that each example has a similar amount of these materials and so provide a proper comparison between the comparative and invention examples.

Table 3 – Lubricating Oil Composition Formulations¹

	CEX 7	EX 8	EX 9	CEX 10
Group III Base Oil	Balance to 100%	Balance to 100%	Balance to 100%	Balance to 100%
COMP EX 2	0.83			
EX 4		0.89		
EX 5			1.05	
COMP EX 6				1.06
TOTAL AO ²	1.4	1.4	1.4	1.4
Other Detergent ³	0.4	0.39	0.37	0.30
ZDDP (2°)	0.79	0.79	0.79	0.79
Friction Modifiers ⁴	0.75	0.75	0.75	0.75
Additional Additives ⁵	4.5	4.5	4.5	4.5
%Phosphorus	0.073	0.074	0.075	0.076
%Sulfur	0.203	0.203	0.201	0.208
%Ash	0.90	0.90	0.89	0.86
TBN from Ca Detergent	4.26	4.27	4.25	4.27

1 – All amounts shown above are in wt % and are on an oil-free basis unless otherwise noted.

2 – AO includes a mixture of hindered phenol and diarylamine

3 – Additional detergent includes small amounts of overbased sodium sulfonate and low overbased calcium sulfonate to balance soap and sulfated ash

4 – Ashless friction modifiers include fatty acid amides and polyacid imides

5 – The additional additives used in the examples include dispersants, a viscosity modifier, and an antifoam agent, and include some amount of diluent oil. The same additive package is used in each of the examples

Testing

[0102] The lubricating oil composition examples summarized in Table 3 are evaluated for fuel economy improvement as measured by a friction torque test (FTT) (Table 4). The impact of friction on fuel economy has been well established. Reduction in friction has been linked to improvements in measured fuel economy.

[0103] The Friction Torque Test (FTT) provides a measure of friction torque of an engine assembly, which is driven by an electric motor. The FTT procedure involves both a preparation phase and a measurement phase. The preparation phase consists of: (a) multiple flushing cycles at high temperature and low engine revolutions with high detergent flushing oil and test sample to minimize potential additive carry over effect from the preceding test, (b) initial friction stabilization (transient) step at high oil temperature and fix (lower) engine rpm to facilitate metal surfaces and additive chemistry actions as well as intermediate heating / cooling cycles at low to medium engine speeds to achieve engine oil temperatures specified in test conditions. The measurement phase comprises both steady and sweep mode friction torque measurements for varying engine speed / oil temperature combinations defined by test conditions that are set based on actual vehicle operating conditions referring to industrial or OEM specific fuel economy testing drive cycles.

[0104] The lubricant formulations are tested in a motor-driven engine assembly friction tester at variable speed conditions at 88°C. This test measures the frictional torque of the engine lubricated with the test formulation. The results are typically presented as a percent frictional torque reduction versus a standard baseline as a function of speed varying from e.g., 500 RPM (revolutions per minute) to 2500 RPM.

Table 4 – Torque Reduction Ratio

	CEX 7	EX 8	EX 9	CEX 10
RPM (at 88°C)	%TORQUE REDUCTION RATIO*			
500	6.90	9.20	7.59	6.44
1000	4.36	5.23	4.80	3.20
1500	3.86	4.50	3.54	2.79
2000	2.93	3.60	2.93	2.09
2500	2.43	2.97	2.30	1.89

*Measured v. industry standard reference oil

[0105] The results indicate that all four lubricants have improved frictional performance versus a common baseline. However, the lubricants containing the detergents according to the invention (EX 8 and EX 9) demonstrate significant improvement in torque at lower speeds. In fact, EX 8 containing the highest TBN:ash ratio detergent provided the best performance under all conditions of the test. Lubricant EX 9, containing 400 TBN detergent, performed comparably to CEX 7 which contained high TBN calcium sulfonate made via a conventional process with intermediate stripping (COMP EX 2) but utilized a detergent having better stability and filterability (EX 5). Comparative lubricant CEX 10 formulated with a commercial 400 TBN calcium detergent made by a conventional process showed the lowest improvement in torque reduction.

[0106] 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. The products formed thereby, including the products formed upon employing lubricant 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 lubricant composition prepared by admixing the components described above.

[0107] Each of the documents referred to above is incorporated herein by reference. Except in the Examples, or where otherwise explicitly indicated, all numerical quantities in this description specifying amounts of materials, reaction conditions, molecular weights, number of carbon atoms, and the like, are to be understood as modified by the word "about." Unless otherwise indicated, each chemical or composition referred to herein should be interpreted as being a commercial grade material which may contain the isomers, by-products, derivatives, and other such materials which are normally understood to be present in the commercial grade. However, the amount of each chemical component is presented exclusive of any solvent or diluent oil, 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 may be used together with ranges or amounts for any of the other elements.

[0108] As used herein, the term "hydrocarbyl substituent" or "hydrocarbyl group" is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group having a carbon atom directly attached to the remainder of the molecule and having predominantly hydrocarbon character. Examples of hydrocarbyl groups include: hydrocarbon substituents, including aliphatic, alicyclic, and aromatic substituents; substituted hydrocarbon substituents, that is, substituents containing non-hydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbon nature of the substituent; and hetero substituents, that is, substituents which similarly have a predominantly hydrocarbon character but contain other than carbon in a ring or chain. A more detailed definition of the term "hydrocarbyl substituent" or "hydrocarbyl group" is described in paragraphs [0118] to [0119] of International Publication WO2008147704, or a similar definition in paragraphs [0137] to [0141] of published application US 2010-0197536.

[0109] While the invention has been explained in relation to its preferred embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.

Claims

1. A process for preparing an overbased metal detergent in an oil medium comprising the steps of:
- 5 (1) providing an organic acid selected from a group consisting of:
a hydrocarbyl-substituted organic sulfonic acid,
a mixture of a hydrocarbyl-substituted organic sulfonic acids,
a metal salt of said organic acid, and
mixtures thereof,
- 10 (2) further providing at least one mono-alcohol;
(3) further providing a basic metal compound;
(4) further providing a carboxylic acid having 6 to 30 carbon atoms
(5) reacting the mixture of step (4) with carbon dioxide to form a carbonated overbased metal sulfonate;
- 15 wherein the resultant overbased metal detergent has a metal equivalent to sulfonic acid substrate ratio of 5:1 to 27:1.
2. A process as claimed in claim 1, wherein the resultant overbased metal detergent has a metal equivalent to sulfonic acid substrate ratio of 7:1 to 20:1.
- 20 3. A process as claimed in claim 1 comprising an additional step (6) wherein steps (3), (4) and (5) are performed at least two additional times.
4. A process as claimed in claim 3, wherein the product of either step (5) or step (6) is
25 heated to at least 150°C in an additional step (7).
5. A process as claimed in claim 4, wherein the product of step (7) may be cooled in a further step (8).

6. A process as claimed in any of the preceding claims, wherein the carboxylic acid has 6 to 24 carbon atoms.

7. A process as claimed in any of the preceding claims, wherein the carboxylic acid has 12 to 20 carbon atoms, or 16 to 18 carbon atoms.

8. A process as claimed in claim 7, wherein the carboxylic acid is stearic acid.

9. A process as claimed in any of the preceding claims, wherein the carboxylic acid is saturated.

10. A process as claimed in any of the preceding claims wherein the carboxylic acid is unsaturated.

11. A process as claimed in any of the preceding claims, wherein the carboxylic acid may be provided at 1 to 20 wt % of reactants.

12. A process as claimed in claim 11, wherein the carboxylic acid is provided as 2 to 20 wt %, or 4 to 8 wt % of reactants.

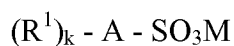
13. A process as claimed in any of the preceding claims, wherein the at least one mono-alcohol comprises 2 to 10 carbon atoms.

14. A process as claimed in any of the preceding claims, wherein any residual solids and any residual water and alcohols are substantially or completely removed from the product.

15. A process as claimed in any of the preceding claims, wherein between 10 and 20 wt % of the total amount of the basic metal compound may be added at each occurrence of step (3).

16. A process as claimed in any of the preceding claims, wherein an oil medium is present.

17. A process as claimed in any of the preceding claims, wherein the metal salt of step (1) is a metal salt of a hydrocarbyl-substituted sulfonic acid and is represented by the formula:



wherein each R^1 is independently a hydrocarbyl group having between 6 and 40 carbon atoms; A is a cyclic or acyclic hydrocarbon group; M is a valence of at least one metal ion; and k is 1 to 5.

18. A process as claimed in claim 17, wherein M is a valence of calcium, sodium, or magnesium.

19. An overbased metal detergent prepared by the process of any preceding claim 1 to 18.

20. A lubricating composition comprising an oil of lubricating viscosity and an overbased detergent prepared according to claim 19.

21. A method for lubricating an internal combustion engine, comprising supplying thereto a lubricant composition of claim 20.