

TITLE

PROCESS FOR PREPARING OVERBASED ALKALINE EARTH METAL ALKYLHYDROXYBENZOATE

BACKGROUND OF THE INVENTION

5 [0001] Detergents are known additives for lubricating compositions. properties. One type of detergent is alkaline-earth metal hydroxybenzoates. There is a need in the art to provide improved processes for making alkaline-earth metal hydroxybenzoates.

SUMMARY OF THE INVENTION

10 [0002] The present invention is directed to a process for preparing an alkaline earth metal alkylhydroxybenzoate.

[0003] The process of the present invention involves preparing an overbased alkaline earth metal alkylhydroxybenzoate using the following steps: (a) reacting an alkylphenol with an alkali metal hydroxide in the presence of a diluent oil to produce an alkali metal alkylphenate; (b) carboxylating the alkali metal alkylphenate obtained in step (a) with carbon dioxide so that at least 50 mol% of the alkali metal alkylphenate is converted to an alkali metal alkylhydroxybenzoate; (c) acidifying the alkali metal alkylhydroxybenzoate obtained in step (b) with an aqueous solution of a strong acid to produce an alkylhydroxybenzoic acid and an alkali metal salt of the strong acid; (d) separating the alkali metal salt of a strong acid from the alkylhydroxybenzoic acid; (e) adding methane sulfonic acid, mono-alcohol, water, and an alkaline earth metal base to the alkylhydroxybenzoic acid to form an alkaline earth metal alkylhydroxybenzoate and at least one alkaline earth metal sulfonic acid salt; (f) reacting the alkaline earth metal alkylhydroxybenzoate with at least one acidic overbasing material in the presence of the at least one alkaline earth metal sulfonic acid salt and the monoalcohol.

DETAILED DESCRIPTION OF THE INVENTION

25 [0004] Prior to discussing the present invention in detail, the following terms will have the following meanings unless expressly stated to the contrary.

Definitions

30 [0005] The term “alkali metal” or “alkaline metal” refers to lithium, sodium or potassium.

[0006] The term “alkaline earth metal” refers to calcium, barium, magnesium and strontium.

[0007] The term “alkyl” refers to both straight- and branched-chain alkyl groups.

[0008] The term “alkylphenate” means a metal salt of an alkylphenol.

[0009] The term “alkylphenol” means a phenol having one or more alkyl substituents, wherein at least one of the alkyl substituents has a sufficient number of carbon atoms to impart oil solubility to the phenol.

[0010] The term “aryl group” is a substituted or non-substituted aromatic group, such as the phenyl, tolyl, xylyl, ethylphenyl and cumenyl groups.

[0011] The term “hydrocarbyl” means an alkyl or alkenyl group.

[0012] The term “hydrocarbyl phenol” refers to a phenol having one or more hydrocarbyl substituent; at least one of which has sufficient number of carbon atoms to impart oil solubility to the phenol.

[0013] The term “lime” refers to calcium hydroxide, also known as slaked lime or hydrated lime.

[0014] The term “overbased” refers to a class of metal salts or complexes. Overbased products are metal salts or complexes characterized by a metal content in excess of that which would be present according to the stoichiometry of the metal and the particular acidic organic compound reacted with the metal, e.g., a carboxylic acid.

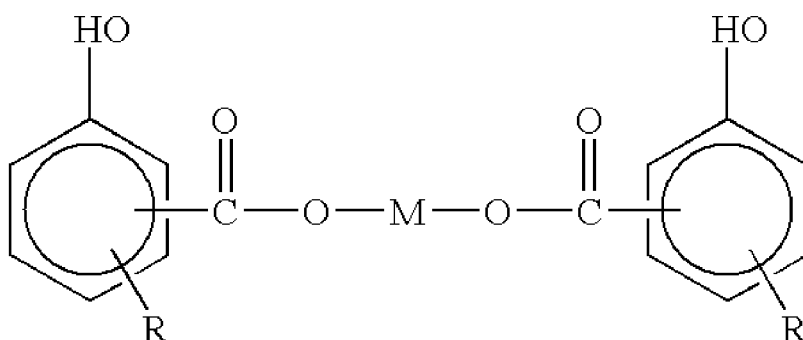
[0015] The term “phenate” means a metal salt of a phenol.

[0016] The term “Total Base Number” or “TBN” refers to the equivalent number of milligrams of KOH needed to neutralize 1 gram of a product. Therefore, a high TBN reflects strongly overbased products and, as a result, a higher base reserve for neutralizing acids. The TBN of a product can be determined by ASTM Standard No. D2896 or equivalent procedure.

Overbased Alkaline Earth Metal Alkylhydroxybenzoate

[0017] The present invention provides a process for preparing an overbased alkaline earth metal alkylhydroxybenzoate. Alkaline earth metal alkylhydroxybenzoate prepared using the process of the present invention will typically have a structure as shown below as Formula (I).

Formula (I)



wherein R is a linear aliphatic group, branched aliphatic group or a mixture of linear and branched aliphatic groups. Preferably, R is an alkyl or alkenyl group. More preferably, R is an alkyl group. M is an alkaline earth metal selected of the group consisting of calcium, barium, magnesium, strontium. Calcium and magnesium are the preferred alkaline earth metal. Calcium is more preferred. When R is a linear aliphatic group, the linear alkyl group typically comprises from 12 to 40 or 14 to 30 or 16 to 20 carbon atoms. When R is a branched aliphatic group, the branched alkyl group typically comprises at least 9 or about 9 to 40, or about 9 to 24, or 10 to 18 carbon atoms. Such branched aliphatic groups are preferably derived from an oligomer of propylene or butene. R can also represent a mixture of linear or branched aliphatic groups. When R represents a mixture of aliphatic groups, the alkaline-earth metal alkylhydroxybenzoic acid employed in the present invention may contain a mixture of linear groups, a mixture of branched groups, or a mixture of linear and branched groups. Thus, R can be a mixture of linear aliphatic groups, for example, an alkyl group selected from the group consisting of C14-C16, C16-C18, C18-C20, C20-C22, C20-C24 and C20-C28 alkyl and mixtures thereof and derived from normal alpha olefins. In some embodiments, these mixtures include at least 95 mole % or even 98 mole % of alkyl groups and originating from the polymerization of ethylene.

[0018] The —COOM group of Formula (I) can be in the ortho, meta or para position with respect to the hydroxyl group.

[0019] The alkaline earth metal alkylhydroxybenzoates of the present invention can be any mixture of alkaline-earth metal alkylhydroxybenzoic acid having the —COOM group in the ortho, meta or para position.

[0020] The alkaline earth metal alkylhydroxybenzoates of the present invention are generally soluble in oil.

[0021] In one embodiment, the TBN of the overbased alkaline earth metal alkylhydroxybenzoate detergent is greater than 250, for example from about 250 to 450 or even about 300 to 400. In another embodiment, the overbased alkaline earth metal alkylhydroxybenzoate of the present invention, the TBN is from about 100 to 250, or about 140 to 230.

Process

[0022] The process for preparing the overbased alkaline earth metal alkylhydroxybenzoate of the present invention involves the following steps: (a) reacting an alkylphenol with an alkali metal hydroxide in the presence of a diluent oil to produce an alkali metal alkylphenate; (b) carboxylating the alkali metal alkylphenate obtained in step (a) with carbon dioxide so that at least 50 mol% of the alkali metal alkylphenate is converted to an alkali metal alkylhydroxybenzoate; (c) acidifying the alkali metal alkylhydroxybenzoate obtained in step (b) with an aqueous solution of a strong acid to produce an alkylhydroxybenzoic acid and an alkali metal salt of the strong acid; (d) separating the alkali metal salt of a strong acid from the alkylhydroxybenzoic acid; (e) adding methane sulfonic acid, mono-alcohol, water, and a molar excess of an alkaline earth metal base to the alkylhydroxybenzoic acid to form an alkaline earth metal alkylhydroxybenzoate and at least one alkaline earth metal sulfonic acid salt; (f) reacting the alkaline earth metal alkylhydroxybenzoate with at least one acidic overbasing material in the presence of the at least one alkaline earth metal sulfonic acid salt and the monoalcohol. Each of these process steps will be described in more detail below.

[0023] A. Formation of the Alkali Metal Alkylphenate

[0024] In the first step, alkylphenols are neutralized using an alkali metal base in the presence of a diluent oil to form the alkali metal alkylphenate. The alkylphenols used in the present invention may contain up to 100 wt % linear hydrocarbyl groups, up to 100 wt % branched hydrocarbyl groups, or both linear and branched hydrocarbyl groups. In one embodiment, the linear hydrocarbyl group is alkyl and such linear alkyl group contains from about 12 to 40 carbon atoms or about 14 to 30 carbon atoms or even 16 to 20 carbon atoms. In one embodiment, the branched hydrocarbyl group is alkyl and contains at least 9 carbon atoms or from about 9 to 40 carbon atoms, or from about 9 to 24 carbon atoms

or even from about 10 to 18 carbon atoms. In one embodiment, the hydrocarbyl phenols may contain a mixture of linear and branched hydrocarbyl phenols, for example, up to 85 wt % of linear hydrocarbyl phenol (preferably at least 35 wt % linear hydrocarbyl phenol) in mixture with at least 15 wt % of branched hydrocarbyl phenol. In another embodiment, the hydrocarbyl phenols are 100% linear alkylphenols.

[0025] Branched alkylphenols can be obtained by reaction of phenol with a branched olefin, generally originating from propylene. They consist of a mixture of monosubstituted isomers, the great majority of the substituents being in the para position, very few being in the ortho position, and hardly any in the meta position.

[0026] Linear alkylphenols can be obtained by reaction of phenol with a linear olefin, generally originating from ethylene. They include of a mixture of monosubstituted isomers in which the proportion of linear alkyl substituents in the ortho, meta, and para positions is much more uniformly distributed. Linear alkylphenols may contain alkyl substituents with some branching which increases the amount of para substituents and may also increase the relative reactivity towards alkali metal bases.

[0027] The alkali metal bases that can be used for carrying out this step include the oxides or hydroxides of lithium, sodium or potassium. In one embodiment, potassium hydroxide is preferred. In another embodiment, sodium hydroxide is preferred.

[0028] In this reaction step, a molar excess of alkali metal base is employed. The ratio of alkali metal base:alkylphenol in this step is preferably from about 1.005:1 to 1.2 :1, or 1.05:1 to 1.1:1, or 1.01:1 to 1.08:1.

[0029] The step of forming the alkali metal alkylphenate is carried out in the presence of a diluent oil. In one embodiment, the diluent oil is selected from Group I, Group II, or Group III oils or mixtures thereof. The diluent oil preferably has a viscosity of 2-8 cSt (KV100, measured by ASTM D445-100). In one embodiment, the diluent oil makes up 25 wt% to 50 wt% of the total reaction mixture.

[0030] Upon completion of this reaction step, any water is removed by methods known to those skilled in the art, including distillation, flash vaporization, vacuum stripping. Water is removed until the mixture contains less than 0.5 wt% water.

[0031] B. Carboxylation

[0032] This carboxylation step is conducted by bubbling carbon dioxide (CO₂) into the reaction medium originating from the preceding neutralization step and is continued

until at least 50 mol %, or even at least 75 mol%, or even at least 80 mol% of the alkali metal alkylphenate has been converted to an alkali metal alkylhydroxybenzoate (as measured as hydroxybenzoic acid by potentiometric determination).

[0033] The diluent oil content in the mixture remains the same as in the previous step.

5 [0034] C. Acidification

[0035] The objective of this step is to acidify the alkylhydroxybenzoate salt diluted in the oil to give an alkylhydroxybenzoic acid. Any acid stronger than alkylhydroxybenzoic acid could be utilized. For example, hydrochloric acid, sulfuric acid, perchloric acid, or phosphoric acid may be used in the present invention.

10 [0036] The acidification step is conducted with an acid having a pKa of less than 2.5. In another embodiment, an acid is used which has an H⁺ equivalent excess of acid versus potassium hydroxide of 1 H⁺ equivalent %, or 5 H⁺ equivalent %, or 10 H⁺ equivalent % or 20 H⁺ equivalent %, the acidification is complete. In one embodiment, an acid is used which has 1 H⁺ equivalent % to 5 H⁺ equivalent %.

15 [0037] In one embodiment, sulfuric acid is used. Sulfuric acid may be diluted in water to a concentration of 35 wt% to 99 wt%, or 40 wt% to 60 wt%, or even 45 wt% to 55 wt%. The quantity of sulfuric acid used relative to the hydroxybenzoate (salicylate), on a per mole of hydroxybenzoate basis, is 0.5 mole, or at least 0.5 mole, or even 0.5 mole to 0.6 mole of sulfuric acid.

20 [0038] The acidification reaction is carried out under agitation or with any suitable mixing system at a temperature from about room temperature to 95° C., for example 75°C to 95°C.

[0039] Following completion of the acidification reaction, water is removed by distillation, vacuum stripping, or flash vaporization, while continuing agitation of the reaction product.

25 [0040] D. Separation

[0041] The product from the acidification step, is an oil phase solution containing the alkylhydroxybenzoic acid. The product is filtered to remove the solid alkali metal salt from the oil phase which contains the alkylhydroxybenzoic acid and any remaining alkylphenol in the diluent oil.

30 [0042] E. Overbasing

[0043] In this step, a sulfonic acid, at least one mono-alcohol, water, and an alkaline earth metal base is added to the alkylhydroxybenzoic acid to form an alkaline earth metal alkylhydroxybenzoate and at least one alkaline earth metal sulfonic acid salt.

[0044] The sulfonic acid may be selected from acids such as methane sulfonic acid, para-tolunene sulfonic acid, and dodecylbenzene sulfonic acid or mixtures thereof. In one embodiment, the sulfonic acid comprises or consists of methane sulfonic acid. In one embodiment, the methane sulfonic acid is an aqueous solution comprising 70 wt% to 98 wt % methane sulfonic acid in water. In another embodiment, the methane sulfonic acid is diluted to 15 wt% methane sulfonic acid in water.

[0045] In one useful mono-alcohols include methanol, ethanol, propanol, isopropanol, butanol, isobutanol, t-butyl alcohol, amyl alcohol and mixtures thereof. In one embodiment, the mono-alcohol comprises or consists of methanol. In another embodiment, the mono-alcohol comprises or consists of butanol. In another embodiment, the mono-alcohol is a mixture of methanol and butanol. In one embodiment, the mono-alcohol comprises or consists of a mixture of ethanol and butanol. The ratio of methanol:butanol can be from 1:3 to 3:1.

[0046] The alkaline earth metal base is selected from calcium oxide, calcium hydroxide, magnesium oxide or magnesium hydroxide. In one embodiment, the alkaline earth metal base comprises or consists of calcium oxide. In another embodiment, the alkaline earth metal base comprises or consists of calcium hydroxide.

[0047] In the reaction mixture, the ratio of mono-alcohol to alkaline earth metal base is 0.1:1 to 10:1 or 0.2:1 to 4:1 and the ratio of methane sulfonic acid to alkaline earth metal base is from 0.001:1 to 0.2:1 or from 0.01:1 to 0.1:1.

[0048] The overbasing of the alkaline earth metal alkylhydroxybenzoate may be carried out by any method known by a person skilled in the art.

[0049] Generally, the overbasing reaction is carried out in a reactor containing about 10 wt% to about 70 wt% of the alkylhydroxybenzoic acid, about 1 wt % to 30 wt % alkylphenol, about 1 wt % to 50 wt % diluent oil.

[0050] The degree of overbasing may be controlled by the quantity of the alkaline earth metal, carbon dioxide and the reactants added to the reaction mixture and the reaction conditions used during the carbonation process.

[0051] In the overbasing process, the alkaline earth metal base is added such that the ratio of alkaline earth metal base:alkylhydroxy benzoic acid ratio is from 1:1 to 10:1 or from 1:1 to 5:1 by equivalents to provide an overbased alkaline earth metal hydroxybenzoate having a TBN of 100 to 250 or from 5:1 to 10:1 by equivalents to provide an overbased alkaline earth metal hydroxybenzoate having a TBN of greater than 250. In addition, the ratio of carbon dioxide to alkaline earth metal base is from 0.6:1 to 1:1, for example, 0.8:1 by equivalents.

[0052] In one embodiment, the process for preparing an overbased alkaline earth metal alkylhydroxybenzoate of the present invention is carried out in the absence of elemental sulfur, that is none of the reactants, solvents, diluent oils or other components introduce elemental sulfur to the reaction process. It would be understood by one skilled in the art that the use of methane sulfonic acid would not introduce elemental sulfur to the reaction.

Filter Aid Unit Consumption

[0053] Filter Aid Unit Consumption (FAUC) as used herein is the minimum weight percentage (based on the total weight of the material to be filtered) of a particular filter aid (diatomaceous earth) required to obtain a filtration oil flow rate of at least 0.44g/min/cm² using a filter aid having an oil flow rate from 0.41 g/min/cm² to 0.56 g/min/cm² determined using an oil having a viscosity of 36 cSt to 37 cSt at 40°C.

[0054] The oil flow rate of a particular filter aid is determined by placing a 10-15mm thick filter cake of 16 grams of filter aid on a 4-inch Buchner funnel. The flow rate of an oil having a viscosity of 36 cSt to 37 cSt at 40°C passing through the filter aid material is measured under 385 torr of vacuum. The flow rate is measured by collecting the filtered oil on a scale over a predetermine amount of time.

[0055] FAUC is measured using a lab pressure leaf filter unit and a diatomaceous earth filter aid having a oil flow rate of 0.41 g/min/cm² to 0.56 g/min/cm² determined using the process set forth above. Crude detergent product from the overbasing step is preheated to 150 °C for 10 minutes before 8 wt% (based on the total weight of the crude detergent) of the filter aid is added to the crude detergent. The mixture of crude detergent and filter aid is then filtered through the pressure leaf filter at 150 °C at 5 PSIG to set the filter pad. The filtered material is then pre-heated at 150 °C for 10 minutes before the second pass at 35 PSIG. The detergent in oil phase is collected in a jar on a balance, allowing a flow rate in g/min to be determined. A “passing” flow rate is >0.44g/min/cm². If the sample passes at

8%, the amount of filter aid is decreased to 4 wt% for the second trial. If the sample fails at 8%, the amount of filter aid is increased to 12 wt% for the second trial. The rest of the trials follow the attached workflow until a minimum percentage of filter aid that obtains a passing filtration rate is determined.

5 Filter Aid Unit Consumption Workflow

Run	%Filter Aid*							
1	8							
2	If 8% passes				If 8% fails			
	4				12			
3	If 4% passes		If 4% fails		If 12% passes		If 12% fails	
	2		6		10		14	
4	If 2% passes	If 2% fails	If 6% passes	If 6% fails	If 10% passes	If 10% fails	If 14% passes	If 14% fails
	1	3	5	7	9	11	13	15

* Diatomaceous earth filter aid having a oil flow rate of 0.41 g/min/cm² to 0.56 g/min/cm² using an oil having a viscosity of 36 cSt to 37 cSt at 40°C.

[0056] In one embodiment of the present invention, the process of the present invention unexpectedly reduces filter aid unit consumption. For example, the process of the present invention results in a product that has a FAUC of 2 wt% to 3 wt%.

Lubricating Oil Composition

[0057] The present invention also relates to lubricating oil compositions containing an overbased alkaline earth metal alkylhydroxybenzoate prepared by the process of the present invention.

Oils of Lubricating Viscosity

[0058] Lubricating composition of the present invention comprises an oil of lubricating viscosity. Such oils include natural and synthetic oils, oil derived from hydrocracking, hydrogenation, and hydrofinishing, unrefined, refined, re-refined oils or mixtures thereof. A more detailed description of unrefined, refined and rerefined oils is provided in International Publication W02008/147704, paragraphs [0054] to [0056] (a similar disclosure is provided in US Patent Publication 2010/ 0197536, see [0072] to [0073]). A more detailed description of natural and synthetic lubricating oils is described in paragraphs [0058] to [0059] respectively of W02008/ 147704 (a similar disclosure is provided in US Patent Publication 2010/0197536, see [0075] to [0076]). Synthetic oils

may also be produced by Fischer-Tropsch reactions and typically may be hydroisomerized Fischer-Tropsch hydrocarbons or waxes. In one embodiment, oils may be prepared by a Fischer-Tropsch gas-to-liquid synthetic procedure as well as other gas-to-liquid oils.

[0059] Oils of lubricating viscosity may also be defined as specified in the April 2008 version of “Appendix E—API Base Oil Interchangeability Guidelines for Passenger Car Motor Oils and Diesel Engine Oils”, section 1.3 Subheading 1.3. “Base Stock Categories”. The API Guidelines are also summarized in U.S. Pat. No. 7,285,516 (see column 11, line 64 to column 12, line 10). The five base oil groups are as follows:

Base Oil Category	Sulfur (%)	Saturates (%)	Viscosity Index
Group I	>0.03 and/or	<90	80 to 120
Group II	≤0.03 and	≥90	80 to 120
Group III	≤0.03 and	≥90	≥120
Group IV	All polyalphaolefins (PAO)		
Group V	All others not included in Groups I, II, III, or IV		

[0060] The amount of the oil of lubricating viscosity present in the lubricating composition is typically the balance remaining after subtracting from 100 weight % (wt %) the sum of the amount of the compound of the invention and the other performance additives.

[0061] The lubricating composition may be in the form of a concentrate and/or a fully formulated lubricant. If the lubricating composition of the invention (comprising the additives disclosed herein) is in the form of a concentrate which may be combined with additional oil to form, in whole or in part, a finished lubricant, the ratio of the of these additives to the oil of lubricating viscosity and/or to diluent oil include the ranges of 1:99 to 99:1 by weight, or 80:20 to 10:90 by weight.

[0062] In one embodiment, the base oil has a kinematic viscosity at 100° C. from 2 mm²/s (centi Stokes-cSt) to 16 mm²/s, from 3 mm²/s to 10 mm²/s, or even from 4 mm²/s to 8 mm²/s.

[0063] Base oil solvency may be measured as the ability of unadditized base oil to act as a solvent for polar constituents. In general, base oil solvency decreases as the base oil group moves from Group I to Group IV (PAO). That is, solvency of base oil may be ranked as follows for oil of a given kinematic viscosity: Group I>Group II>Group III>Group IV. Base oil solvency also decreases as the viscosity increases within a base oil group; base

oil of low viscosity tends to have better solvency than similar base oil of higher viscosity. Base oil solvency may be measured by aniline point (ASTM D611).

[0064] In one embodiment of the present invention, the base oil component of the lubricating composition comprises at least 30 wt %, at least 40 wt%, at least 50 wt%, at least 60 wt%, at least 70 wt%, or at least 80 wt% of a Group I, Group II, or a Group III base oil or mixtures thereof. In addition, the lubricant composition comprises less than 50 wt % or less than 40 wt%, or less than 30 wt%, or less than 20 wt% of Group IV (i.e. polyalphaolefin) base oil. In another embodiment, the base oil comprises less than 10 wt % of Group IV base oil. In another embodiment, the lubricating composition is substantially free of (i.e. contains less than 0.5 wt %) of a Group IV (polyalphaolefin) base oil.

[0065] Ester base fluids, which are characterized as Group V oils, have high levels of solvency as a result of their polar nature. Addition of low levels (typically less than 10 wt %) of ester to a lubricating composition may significantly increase the resulting solvency of the base oil mixture. Esters may be broadly grouped into two categories: synthetic and natural. An ester base fluid would have a kinematic viscosity at 100° C. suitable for use in an engine oil lubricant, such as between 2 cSt and 30 cSt, or from 3 cSt to 20 cSt, or even from 4 cSt to 12 cSt.

[0066] Synthetic esters may comprise esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids and alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkyl malonic acids, and alkenyl malonic acids) with any of variety of monohydric alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, and 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 of tetraethylene glycol and two moles of 2-ethylhexanoic acid. Other synthetic esters include those made from C5 to C12 monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol, and tripentaerythritol. Esters can also be monoesters of monocarboxylic acids and monohydric alcohols.

[0067] Natural (or bio-derived) esters refer to materials derived from a renewable biological resource, organism, or entity, distinct from materials derived from petroleum or equivalent raw materials. Natural esters include fatty acid triglycerides, hydrolyzed or partially hydrolyzed triglycerides, or transesterified triglyceride esters, such as fatty acid methyl ester (or FAME). Suitable triglycerides include, but are not limited to, palm oil, soybean oil, sunflower oil, rapeseed oil, olive oil, linseed oil, and related materials. Other sources of triglycerides include, but are not limited to, algae, animal tallow, and zooplankton. Methods for producing bio-lubricants from natural triglycerides are described in, e.g., United States Patent Publication 2011/0009300A1.

Other Additive Components

[0068] The compositions of the invention may optionally comprise one or more other additional performance additives. These additional performance additives may include, but are not limited to, one or more dispersants, including borated dispersants, anti-wear additives, detergents, metal deactivators, viscosity modifiers, detergents, friction modifiers, antiwear agents, corrosion inhibitors, dispersant viscosity modifiers, extreme pressure agents, foam inhibitors, demulsifiers, pour point depressants, seal swelling agents, and any combination or mixture thereof. Typically, fully-formulated lubricating oil will contain one or more of these performance additives, and often a package of multiple performance additives.

[0069] In one embodiment, the invention provides a lubricating composition further comprising a detergent. In one embodiment, the detergent may be an alkali or alkaline earth metal sulfonate detergent, an alkali or alkaline earth metal salicylate detergent, an alkali or alkali earth metal salixarate detergent, or an alkali or alkaline earth metal phenate detergent. The detergent may be an overbased detergent. Overbased detergents, otherwise referred to as overbased or superbased salts, are characterized by a metal content in excess of that which would be necessary for neutralization according to the stoichiometry of the metal and the particular acidic organic compound reacted with the metal. Overbased detergents are known in the art and the lubricating composition of the present invention may contain detergents that are now known or hereafter developed and understood to be useful in the present invention to those skilled in the art.

[0070] In one embodiment, the detergent may comprise an overbased metal-containing sulfonate detergent. Overbased metal-containing sulfonate detergents may include calcium

salts, magnesium salts, sodium salts, or mixtures thereof of one or more sulfonates. Other useful metals may include titanium and zirconium. Overbased sulfonates typically have a total base number of 250 to 600, or 300 to 500. In one embodiment, the sulfonate detergent may be predominantly a linear alkylbenzene sulfonate detergent having a metal ratio of at least 8 as is described in paragraphs [0026] to [0037] of US Patent Publication 2005065045 (and granted as US 7,407,919). The linear alkyl group may be attached to the benzene ring anywhere along the linear chain of the alkyl group, but often in the 2, 3 or 4 position of the linear chain, and in some instances, predominantly in the 2 position, resulting in the linear alkylbenzene sulfonate detergent.

[0071] In one embodiment, the lubricating composition may comprise an alkali or alkaline earth metal salicylate detergent or salixarate detergent or mixture thereof. The metal containing salicylate or salixarate detergent may be an overbased detergent. Useful salicylate and salixarate detergents may include calcium salts, magnesium salts, sodium salts or mixtures thereof. Other useful metals may include titanium and zirconium.

[0072] In one embodiment, the lubricating composition may contain a metal containing sulfur coupled alkyl phenol compound. Such compounds may be exemplified by alkali and alkaline earth metal containing phenate detergents, such as magnesium phenate detergents, calcium phenate detergents and sodium phenate detergents and further including overbased metal containing phenate detergents, all of which are known in the art.

[0073] In one embodiment, the detergent comprises or consists of a calcium detergent. In another embodiment, the detergent may comprise a mixture of calcium and magnesium containing detergents such as those disclosed herein where the detergent mixture may provide 800 to 1300 ppm calcium and 450 to 800 ppm magnesium and in another embodiment 900 to 1200 ppm calcium and 500 to 750 ppm magnesium.

[0074] According to some embodiments, the total amount of soap contributed by the detergent may be from about 0.08 or 1.0 to less than 0.9 or 0.7 or 0.5 or 0.4 or 0.3 or 0.25 wt. % with respect to the lubricating composition. The lubricating composition may be free or substantially free of phenate soap. As used herein the term "soap" means the surfactant portion of a detergent and does not include a metal base, such as calcium carbonate. The soap term may also be referred to as a detergent substrate. For example,

the sulfonate detergents described herein, the soap or substrate may be a neutral salt of an alkylbenzenesulfonic acid.

[0075] Metal-containing detergents may also contribute sulfated ash to a lubricating composition. Sulfated ash may be determined by ASTM D874. In one embodiment, the lubricating composition of the invention comprises a metal-containing detergent in an amount to deliver at least 0.4 wt. % sulfated ash to the total composition. In another embodiment, the metal-containing detergent is present in an amount to deliver at least 0.6 wt. % sulfated ash, or at least 0.75 wt. % sulfated ash, or even at least 0.9 wt. % sulfated ash to the lubricating composition.

[0076] In some embodiments, the lubricating compositions of the present invention may contain an organophosphorous anti-wear agent. The organo-phosphorus anti-wear agent may be a metal free organo-phosphorus anti-wear agent. The organo-phosphorus agent may contain sulfur or may be sulfur-free. Sulfur-free phosphorus-containing antiwear agents may be phosphites, phosphonates, alkylphosphate esters, amine or ammonium phosphate salts, or mixtures thereof.

[0077] Phosphorus esters such as the dihydrocarbon and trihydrocarbon phosphites, e.g., dibutyl phosphite, diheptyl phosphite, dicyclohexyl phosphite, pentylphenyl phosphite; dipentylphenyl phosphite, tridecyl phosphite, distearyl phosphite and polypropylene substituted phenol phosphite; metal thiocarbamates such as zinc dioctyldithiocarbamate and barium heptylphenol diacid; amine salts of alkyl and dialkylphosphoric acids or derivatives including, for example, the amine salt of a reaction product of a dialkyldithiophosphoric acid with propylene oxide and subsequently followed by a further reaction with P₂O₅; and mixtures thereof (as described in US 3,197,405).

[0078] Amine phosphates may be amine salts of (i) monohydrocarbylphosphoric acid, (ii) dihydrocarbylphosphoric acid, (iii) hydroxy-substituted di-ester of phosphoric acid, or (iv) phosphorylated hydroxy-substituted di- or tri-ester of phosphoric acid. The amine salt of a sulfur-free phosphorus-containing compound may be salts of primary amines, secondary amines, tertiary amines, or mixtures thereof.

[0079] Amine phosphate salts may be derived from mono- or di- hydrocarbyl phosphoric acid (typically alkyl phosphoric acid), or mixtures thereof. The alkyl of the mono- or di- hydrocarbyl phosphoric acid may comprise linear or branched alkyl groups of 3 to 36 carbon atoms. The hydrocarbyl group of the linear or branched

hydrocarbylphosphoric acid may contain 4 to 30, or 8 to 20 carbon atoms. Examples of a suitable hydrocarbyl group of the hydrocarbyl phosphoric acid may include isopropyl, n-butyl, sec-butyl, amyl, 4-methyl-2-pentyl (i.e., methylamyl), n-hexyl, n-heptyl, n-octyl, iso-octyl, 2-ethylhexyl, nonyl, 2-propylheptyl, decyl, dodecyl, tetradecyl, hexadecyl, octadecyl, oleyl, or combinations thereof. In one embodiment, the phosphate is a mixture of mono- and di- (2-ethyl)hexylphosphate.

[0080] Examples of suitable primary amines include ethylamine, propylamine, butylamine, 2-ethylhexylamine, octylamine, and dodecylamine, as well as such fatty amines as n-octylamine, n-decylamine, n-dodecylamine, n-tetradecylamine, n-hexadecylamine, n-octadecylamine and oleyamine. Other useful fatty amines include commercially available fatty amines such as "Armeen®." amines (products available from Akzo Chemicals, Chicago, Ill.), such as Armeen C, Armeen O, Armeen O L, Armeen T, Armeen H T, Armeen S and Armeen S D, wherein the letter designation relates to the fatty group, such as coco, oleyl, tallow, or stearyl groups.

[0081] In one embodiment, the metal-free phosphorus anti-wear agent may be present in the lubricant composition in amount of 0.01 to 5 wt %, or 0.1 to 3.2 wt %, or 0.35 to 1.8 wt %, or 0.5 to 1.5 wt %, or 0.5 to 0.9 wt %. In one embodiment, the metal-free phosphorus anti-wear agent may be present in an amount to provide 0.01 wt % to 0.15 wt % phosphorus, or 0.01 to 0.08 wt % phosphorus, or 0.025 to 0.065 wt % phosphorus to the composition.

[0082] In another embodiment, the lubricating composition of the present invention is free of or substantially free of phosphorous or phosphorous containing agents.

[0083] In one embodiment, the invention provides a lubricating composition which further includes an ashless antiwear agent different from the organo-phosphorus antiwear agent described above. Examples of suitable antiwear agents include hydroxy-carboxylic acid derivatives such as esters, amides, imides or amine or ammonium salt, sulfurized olefins, thiocarbamate-containing compounds, such as thiocarbamate esters, thiocarbamate amides, thiocarbamic ethers, alkylene-coupled thiocarbamates, and bis(S-alkyldithiocarbamyl) disulphides.

[0084] In one embodiment, an ashless antiwear agent may include a compound derived from a hydroxycarboxylic acid. In one embodiment the ashless antiwear agent is derived from at least one of hydroxy-polycarboxylic acid di-ester, a hydroxy-polycarboxylic acid

di-amide, a hydroxy-polycarboxylic acid imide, and a hydroxy-polycarboxylic acid ester amide. In one embodiment the ashless antiwear agent is derived from a hydroxy-polycarboxylic acid imide.

5 [0085] Examples of a suitable a hydroxycarboxylic acid include citric acid, tartaric acid, lactic acid, glycolic acid, hydroxy-propionic acid, hydroxyglutaric acid, or mixtures thereof. In one embodiment ashless antiwear agent is derived from tartaric acid, citric acid, hydroxy-succinic acid, dihydroxy mono-acids, mono-hydroxy diacids, or mixtures thereof. In one embodiment the ashless antiwear agent includes a compound derived from tartaric acid or citric acid. In one embodiment the ashless antiwear agent includes a
10 compound derived from tartaric acid.

[0086] US Patent Application 2005/198894 discloses suitable hydroxycarboxylic acid compounds, and methods of preparing the same.

[0087] Canadian Patent 1 183 125; US Patent Publication numbers 2006/0183647 and US-2006-0079413; U.S. Patent Application No. 60/867,402; and British Patent 2 105743
15 A. all disclose examples of suitable tartaric acid derivatives. The antiwear agent may in one embodiment include a tartrate or tartramide as disclosed in International Publication WO 2006/044411 or Canadian Patent CA 1 183 125. The tartrate or tartramide may contain alkyl-ester groups, where the sum of carbon atoms on the alkyl groups is at least 8. The antiwear agent may in one embodiment include a citrate.

20 [0088] An ashless phosphorus-free antiwear agent may be present at 0.1 to 5 wt %, 0.1 wt % to 3 wt %, or 0.2 to 3 or 0.1 wt % to 1.5 wt %, or 0.5 wt % to 1.1 wt % of the lubricating composition.

[0089] In one embodiment, the invention may also provide a lubricating composition which further includes a metal dialkyldithiophosphate. Typically, the metal
25 dialkyldithiophosphate may be a zinc dialkyldithiophosphate (ZDDP), or mixtures thereof. Zinc dialkyldithiophosphates are known in the art. The zinc dialkyldithiophosphate may be present at 0 wt % to 3 wt %, or 0.1 wt % to 1.5 wt %, or 0.5 wt % to 0.9 wt % of the lubricating composition. In another embodiment, ZDDP is present in amounts such that the total zinc contributed to the lubricant composition does not exceed 0.15 weight percent
30 of the composition, for example, zinc may be presents in amounts of from 0 wt % to 0.15 wt %, or even less than 0.14 wt %, or even less than 0.11 wt %, or even less than 0.09 wt%, or even less than 0.07 wt%, or even less than 0.05 wt%, or even less than 0.03 wt%

and in another embodiment 0.01 wt % to 0.14 wt %. In another embodiment, the lubricating composition is substantially free of zinc.

[0090] The zinc dialkyldithiophosphate may be derived from primary alcohols, secondary alcohols, or combinations thereof. Typically, they are derived from primary and secondary alcohols containing 3 to 12 carbon atoms and combinations thereof. In one embodiment the zinc alkyldithiophosphate comprises at least 25 mol % secondary alkyl groups, or at least 40 mol % secondary alkyl groups, or at least 75 mol % secondary alkyl groups, or at least 90 mol % secondary alkyl groups.

[0091] Polymeric viscosity index improvers, also referred to as viscosity modifiers (VM) or dispersant viscosity modifiers (DVM, may be useful in the compositions disclosed herein. The dispersant viscosity modifier may be generally understood to be a functionalized, i.e. derivatized, form of a polymer similar to that of the polymeric viscosity modifier. The polymeric viscosity modifier may be an olefin (co)polymer, a poly(meth)acrylate (PMA), or mixtures thereof. In one embodiment, the polymeric viscosity modifier is an olefin (co)polymer or dispersant viscosity modifier derived therefrom.

[0092] The olefin polymer may be derived from isobutylene or isoprene. In one embodiment, the olefin polymer is prepared from ethylene and a higher olefin within the range of C3-C10 alpha-mono-olefins, for example, the olefin polymer may be prepared from ethylene and propylene.

[0093] Useful olefin polymers, in particular, ethylene-a-olefin copolymers have a number average molecular weight ranging from 4500 to 500,000, for example, 5000 to 100,000, or 7500 to 60,000, or 8000 to 45,000.

[0094] The formation of functionalized ethylene-a-olefin copolymer is well known in the art, for instance those described in U.S. Patent US 7,790,661 column 2, line 48 to column 10, line 38. Additional detailed descriptions of similar functionalized ethylene-a-olefin copolymers are found in International Publication W02006/015130 or U.S. Patents 4,863,623; 6,107,257; 6,107,258; 6,117,825; and US 7,790,661. In one embodiment, the functionalized ethylene-a-olefin copolymer may include those described in U.S. Patent 4,863,623 (see column 2, line 15 to column 3, line 52) or in International Publication W02006/015130 (see page 2, paragraph [0008] and preparative examples are described paragraphs [0065] to [0073]).

[0095] In one embodiment, the lubricating composition comprises a dispersant viscosity modifier (DVM). The DVM may comprise an olefin polymer that has been modified by the addition of a polar moiety.

[0096] The olefin polymers are functionalized by modifying the polymer by the addition of a polar moiety. In one useful embodiment, the functionalized copolymer is the reaction product of an olefin polymer grafted with an acylating agent. In one embodiment, the acylating agent may be an ethylenically unsaturated acylating agent. Useful acylating agents are typically α,β -unsaturated compounds having at least one ethylenic bond (prior to reaction) and at least one, for example two, carboxylic acid (or its anhydride) groups or a polar group which is convertible into said carboxyl groups by oxidation or hydrolysis. The acylating agent grafts onto the olefin polymer to give two carboxylic acid functionalities. Examples of useful acylating agents include maleic anhydride, chlormaleic anhydride, itaconic anhydride, or the reactive equivalents thereof, for example, the corresponding dicarboxylic acids, such as maleic acid, fumaric acid, cinnamic acid, (meth)acrylic acid, the esters of these compounds and the acid chlorides of these compounds.

[0097] In one embodiment, the functionalized ethylene-a-olefin copolymer comprises an olefin copolymer grafted with the acyl group, which is further functionalized with a hydrocarbyl amine, a hydrocarbyl alcohol group, amino- or hydroxy- terminated polyether compounds, and mixtures thereof.

[0098] In one embodiment, the hydrocarbyl amine may be selected from aromatic amines, aliphatic amines, and mixtures thereof. In one embodiment, the hydrocarbyl amine component may comprise at least one aromatic amine containing at least one amino group capable of condensing with said acyl group to provide a pendant group and at least one additional group comprising at least one nitrogen, oxygen, or sulfur atom, wherein said aromatic amine is selected from the group consisting of (i) a nitrosubstituted aniline, (ii) an amine comprising two aromatic moieties linked by a $C(=O)NR-$ group, a $-C(=O)O-$ group, an $-O-$ group, an $N=N-$ group, or an $-SO_2-$ group where R is hydrogen or hydrocarbyl, one of said aromatic moieties bearing said condensable amino group, (iii) an aminoquinoline, (iv) an aminobenzimidazole, (v) an N,N' -dialkylphenylenediamine, (vi), an aminodiphenyl amine (also N -phenylphenylenediamine), (vii) a ring-substituted benzylamine, and (viii) a methylene-coupled dimer of aminodiphenyl amine.

[0099] In one embodiment, lubricating composition may comprise a poly(meth)acrylate polymeric viscosity modifier. As used herein, the term “(meth)acrylate” and its cognates means either methacrylate or acrylate, as will be readily understood.

5 [0100] In one embodiment, the poly(meth)acrylate polymer is prepared from a monomer mixture comprising (meth)acrylate monomers having alkyl groups of varying length. The (meth)acrylate monomers may contain alkyl groups that are straight chain or branched chain groups. The alkyl groups may contain 1 to 24 carbon atoms, for example, 1 to 20 carbon atoms.

10 [0101] In one embodiment, the poly(meth)acrylate polymer comprises a dispersant monomer; dispersant monomers include those monomers which may copolymerize with (meth)acrylate monomers and contain one or more heteroatoms in addition to the carbonyl group of the (meth)acrylate. The dispersant monomer may contain a nitrogen-containing group, an oxygen-containing group, or mixtures thereof.

15 [0102] Dispersant monomers may be present in an amount up to 5 mol percent of the monomer composition of the (meth)acrylate polymer. In one embodiment, the poly(meth)acrylate is present in an amount 0 to 5 mol percent, 0.5 to 4 mol percent, or 0.8 to 3 mol percent of the polymer composition. In one embodiment, the poly(meth)acrylate is free of or substantially free of dispersant monomers.

20 [0103] In one embodiment, the poly(meth)acrylate polymer (P) is a block or tapered block copolymer that comprises at least one polymer block (B1) that is insoluble or substantially insoluble in the base oil and a second polymer block (B2) that is soluble or substantially soluble in the base oil.

25 [0104] In one embodiment, the poly(meth)acrylate polymers may have an architecture selected from linear, branched, hyper-branched, cross-linked, star (also referred to as “radial”), or combinations thereof. Star or radial refers to multi -armed polymers. Such polymers include (meth)acrylate-containing polymers comprising 3 or more arms or branches, which, in some embodiments, contain at least about 20, or at least 50 or 100 or 200 or 350 or 500 or 1000 carbon atoms. The arms are generally attached to a multivalent organic moiety which acts as a “core” or “coupling agent.” The multi-armed polymer may
30 be referred to as a radial or star polymer, or even a “comb” polymer, or a polymer otherwise having multiple arms or branches as described herein.

[0105] Linear poly(meth)acrylates, random, block or otherwise, may have weight average molecular weight (Mw) of 1000 to 400,000 Daltons, 1000 to 150,000 Daltons, or 15,000 to 100,000 Daltons. In one embodiment, the poly(meth)acrylate may be a linear block copolymer with a Mw of 5,000 to 40,000 Daltons, or 10,000 to 30,000 Daltons. Radial, cross-linked or star copolymers may be derived from linear random or di-block copolymers with molecular weights as described above. A star polymer may have a weight average molecular weight of 10,000 to 1,500,000 Daltons, or 40,000 to 1,000,000 Daltons, or 300,000 to 850,000 Daltons.

[0106] Another class of polymeric viscosity modifiers is styrene-diene (SD) copolymers, such as styrene isoprene (SI) and styrene butadiene (SBR). Styrenediene copolymers may be linear or radial (star-shaped), and generally contain one or more distinct blocks of styrene attached to one or more distinct blocks of hydrogenated diene

[0107] In some embodiments, the lubricating compositions may comprise 0.05 wt% to 4 wt%, or 0.08 wt% to 2 wt%, or 0.1 to 1 wt% of the one or more polymeric viscosity modifiers and/or dispersant viscosity modifiers. In other embodiments, the lubricating composition may be free of or substantially free of polymeric viscosity modifiers.

[0108] In one embodiment, the invention provides a lubricating composition further comprising a molybdenum compound. The molybdenum compound may be selected from the group consisting of molybdenum dialkyldithiophosphates, molybdenum dithiocarbamates, amine salts of molybdenum compounds, and mixtures thereof. The molybdenum compound may provide the lubricating composition with 0 to 1000 ppm, or 5 to 1000 ppm, or 10 to 750 ppm, or 5 ppm to 300 ppm, or 20 ppm to 250 ppm of molybdenum.

[0109] In one embodiment, the invention provides a lubricating composition further comprising a friction modifier. Examples of friction modifiers include long chain fatty acid derivatives of amines, fatty esters, or epoxides; fatty imidazolines such as condensation products of carboxylic acids and polyalkylene-polyamines; amine salts of alkylphosphoric acids; fatty alkyl tartrates; fatty alkyl tartrides; or fatty alkyl tartrides. The term fatty, as used herein, can mean having a C8-22 linear alkyl group.

[0110] Friction modifiers may also encompass materials such as sulfurized fatty compounds and olefins, molybdenum dialkyldithiophosphates, molybdenum dithiocarbamates, sunflower oil or monoester of a polyol and an aliphatic carboxylic acid.

[0111] In one embodiment, the friction modifier may be selected from the group consisting of long chain fatty acid derivatives of amines, long chain fatty esters, or long chain fatty epoxides; fatty imidazolines; amine salts of alkylphosphoric acids; fatty alkyl tartrates; fatty alkyl tartrimides; and fatty alkyl tartramides. The friction modifier may be present at 0.05 wt % to 6 wt %, or 0.05 wt % to 4 wt %, or 0.1 wt % to 2 wt % of the lubricating composition.

[0112] In one embodiment, the friction modifier may be a long chain fatty acid ester. In another embodiment the long chain fatty acid ester may be a mono-ester or a diester or a mixture thereof, and in another embodiment the long chain fatty acid ester may be a triglyceride.

[0113] Other performance additives such as corrosion inhibitors include those described in paragraphs 5 to 8 of US Application US05/038319, published as WO2006/047486, octyl octanamide, condensation products of dodecenyl succinic acid or anhydride and a fatty acid such as oleic acid with a polyamine. In one embodiment, the corrosion inhibitors include the Synalox® (a registered trademark of The Dow Chemical Company) corrosion inhibitor. The Synalox® corrosion inhibitor may be a homopolymer or copolymer of propylene oxide. The Synalox® corrosion inhibitor is described in more detail in a product brochure with Form No. 118-01453-0702 AMS, published by The Dow Chemical Company. The product brochure is entitled "SYNALOX Lubricants, High-Performance Polyglycols for Demanding Applications."

[0114] The lubricating composition may further include metal deactivators, including derivatives of benzotriazoles (typically tolyltriazole), dimercaptothiadiazole derivatives, 1,2,4-triazoles, benzimidazoles, 2-alkyldithiobenzimidazoles, or 2-alkyldithiobenzothiazoles; foam inhibitors, including copolymers of ethyl acrylate and 2-ethylhexylacrylate and copolymers of ethyl acrylate and 2-ethylhexylacrylate and vinyl acetate; demulsifiers including trialkyl phosphates, polyethylene glycols, polyethylene oxides, polypropylene oxides and (ethylene oxide-propylene oxide) polymers; and pour point depressants, including esters of maleic anhydride-styrene, polymethacrylates, polyacrylates or polyacrylamides.

[0115] Pour point depressants that may be useful in the compositions of the invention further include polyalphaolefins, esters of maleic anhydride-styrene, poly(meth)acrylates, polyacrylates or polyacrylamides.

[0116] Embodiments of the present invention are defined in the following clauses:

[0117] CLAUSE 1: A process for preparing an overbased alkaline earth metal alkylhydroxybenzoate comprising the steps of: (a) reacting an alkylphenol with an alkali metal hydroxide in the presence of a diluent oil to produce an alkali metal alkylphenate; (b) carboxylating the alkali metal alkylphenate obtained in step (a) with carbon dioxide so that at least 50 mol% of the alkali metal alkylphenate is converted to an alkali metal alkylhydroxybenzoate; (c) acidifying the alkali metal alkylhydroxybenzoate obtained in step (b) with an aqueous solution of a strong acid to produce an alkylhydroxybenzoic acid and an alkali metal salt of the strong acid; (d) separating the alkali metal salt of a strong acid from the alkylhydroxybenzoic acid; (e) adding methane sulfonic acid, mono-alcohol, water, and an alkaline earth metal base to the alkylhydroxybenzoic acid to form an alkaline earth metal alkylhydroxybenzoate and at least one alkaline earth metal sulfonic acid salt; (f) reacting the alkaline earth metal alkylhydroxybenzoate with at least one acidic overbasing material in the presence of the at least one alkaline earth metal sulfonic acid salt and the monoalcohol.

[0118] CLAUSE 2: The process of clause 1, wherein the process is carried out in the absence of elemental sulfur.

[0119] CLAUSE 3: The process of any preceding clause, wherein the alkali metal hydroxide is selected from the group consisting of potassium hydroxide, sodium hydroxide, lithium hydroxide, or mixtures thereof.

[0120] CLAUSE 4: The process of any preceding clause wherein the molar ratio of alkali metal hydroxide to alkylphenol is from 1.005:1 to 1.2:1, or 1.05:1 to 1.1:1, or 1.01:1 to 1.08:1.

[0121] CLAUSE 5: The process of any preceding clause wherein the alkali metal hydroxide comprises or consists of potassium hydroxide.

[0122] CLAUSE 6: The process of any preceding clause, wherein the diluent oil has a viscosity of 2 cSt to 8 cSt (KV100 measured by ASTM D445-100)

[0123] CLAUSE 7: The process of any preceding clause, wherein at least 50 mol%, or at least 75 mol%, or at least 80 mol% of the alkali metal phenate is converted to alkali metal alkylhydroxybenzoate.

[0124] CLAUSE 8: The process of any preceding clause, wherein the strong acid comprises or consists of a strong acid having a pKa of less than 2.5.

[0125] CLAUSE 9: The process of any preceding clause, wherein the strong acid is selected from the group consisting of sulfuric acid, hydrochloric acid, perchloric acid, phosphoric acid, or mixtures thereof.

5 [0126] CLAUSE 10: The process of any preceding clause, wherein the strong acid is sulfuric acid diluted in water to a concentration of 35 wt% to 99 wt% or 40 wt% to 60 wt% or 45 wt% to 55 wt%.

[0127] CLAUSE 11: The process of any preceding clause, wherein the mono-alcohol comprises a mono-alcohol having 1 to 5 carbon atoms.

10 [0128] CLAUSE 12: The process of any preceding clause, wherein the mono-alcohol is selected from the group consisting of butanol, methanol, ethanol, propanol, isopropanol, isobutanol, t-butyl alcohol, amyl alcohol, or mixtures thereof.

[0129] CLAUSE 13: The process of any preceding clause, wherein the mono-alcohol comprises a mixture of butanol and methanol.

15 [0130] CLAUSE 14: The process of clause 13, wherein the ratio of methanol to butanol is from 1:3 to 3:1.

[0131] CLAUSE 15: The process of any preceding clause, wherein the alkaline earth metal base is selected from calcium oxide, calcium hydroxide, or mixtures thereof.

[0132] CLAUSE 16: The process of any preceding clause, wherein the alkaline earth metal base is calcium hydroxide.

20 [0133] CLAUSE 17: The process of any preceding clause, wherein the ratio of mono-alcohol to alkaline earth metal base is 0.1:1 to 10:1 or 0.2:1 to 4:1.

[0134] CLAUSE 18: The process of any preceding clause, wherein the ratio of methane sulfonic acid to alkaline earth metal base is from 0.001:1 to 0.2:1 or from 0.01:1 to 0.1:1.

25 [0135] CLAUSE 19: The process of any preceding clause, wherein the ratio of alkaline earth metal base to alkyl hydroxybenzoic acid is from 1:1 to 10:1 equivalents or 1:1 to 5:1 equivalents to provide an overbased alkaline earth metal hydroxybenzoate having a TBN of 100 to 250.

30 [0136] CLAUSE 20: The process of any preceding clause wherein the ratio of alkaline earth metal base to alkyl hydroxybenzoic acid is from 5:1 to 10:1 to provide an overbased alkaline earth metal hydroxybenzoate having a TBN of greater than 250.

[0137] CLAUSE 21: The process of any preceding clause, wherein the acidic overbasing material comprises or consists of carbon dioxide.

[0138] CLAUSE 22: The process of any preceding clause, wherein the ratio of alkaline earth metal base to carbon dioxide is 0.6:1 to 1:1 or 0.8:1 to 1:1 equivalents.

5 [0139] CLAUSE 23: The process of any preceding clause, wherein the overbased alkaline earth metal alkylhydroxybenzoate has an oil free TBN from 70 to 600 or 100 to 550 or 150 to 450, or 200 to 350.

[0140] CLAUSE 24: The process according to any preceding clause, wherein the alkylphenol contains a linear alkyl group, a branched alkyl group, or a mixture thereof.

10 [0141] CLAUSE 25: The process according to clause 24, wherein the alkylphenol contains a linear alkyl group having from 12 to 40 or 14 to 30 carbon atoms or 16 to 20 carbon atoms.

[0142] CLAUSE 26: The process according to clause 25, wherein the linear alkyl group is derived from the polymerization of ethylene.

15 [0143] CLAUSE 27: The process according to any of clauses 1 to 24, wherein the alkylphenol contains a branched alkyl group having at least 9, or 9 to 40, or 9 to 24 carbon atoms.

[0144] CLAUSE 28: The process according to any of clauses 1 to 24 wherein the alkyl phenol contains 100% linear alkyl phenols.

20 [0145] CLAUSE 29: An overbased alkaline earth metal alkylhydroxybenzoate detergent prepared by the process of any preceding clauses.

[0146] CLAUSE 30: A lubricating oil composition comprising the alkaline earth metal alkylhydroxbenzoate detergent of clause 29.

25 [0147] CLAUSE 31: A method of lubricating an engine, comprising supplying to the engine the lubricating oil composition of clause 30.

[0148] CLAUSE 32: The use of the process of any of clauses 1 to 28 in order to reduce the filter aid unit consumption in the manufacture of an alkaline earth metal alkylhydroxybenzoate.

30 [0149] The following examples provide illustrations of the invention. These examples are non-exhaustive and are not intended to limit the scope of the invention.

EXAMPLES

[0150] In the Examples, the following test methods were employed:

- Oil viscosity is KV100 measured according to ASTM D445-100.
- TBN (not oil free) is measured according to ASTM D2896A.
- Filter Aid Unit Consumption (FAUC) is measured using a lab pressure leaf filter unit and a diatomaceous earth filter aid having a oil flow rate of 0.41 g/min/cm² to 0.56 g/min/cm² determined using the process set forth above . Crude detergent product from the overbasing step is preheated to 150 °C for 10 minutes before 8 wt% (based on the total weight of the crude detergent) of the filter aid is added to the crude detergent. The mixture of crude detergent and filter aid is then filtered through the pressure leaf filter at 150 °C at 5 PSIG to set the filter pad. The filtered material is then pre-heated at 150 °C for 10 minutes before the second pass at 35 PSIG. The detergent in oil phase is collected in a jar on a balance.
- Crude sediment is measured by placing a volume of 25 mL of sample in a 100 mL graduated cylinder containing 75 mL of heptane. It is mixed thoroughly and centrifuged at 2,000 rpm for 20 minutes. The % crude sediment (by volume) = tube volume x 4.
- Turbidity is measured by taking 20 vol% of the filtered sample and mixing it with 80 vol% oil and measuring using a Monitek 151 Turbidimeter. Turbidity is reported in 22 Jackson Turbidity Units (JTU).

Example X

[0151] 1595 kg alkyl phenol (a mixture of C14,16,18 saturated alkyl groups) is mixed with 684 kg 4cSt Group II oil. 562 kg KOH base solution (45%, aq) is added at a rate to maintain the batch temperature at 90 °C maximum. After adding the base solution, the mixture is heated to 150 °C to produce potassium alkyl phenate. Water is removed by distillation. The temperature is then adjusted to 125 °C. 311 kg of CO₂ is added to the dehydrated mixture evenly over 12 hours to produce potassium alkylhydroxybenzoate. 442 kg 4cSt oil and 31 kg water are added. The TBN (not oil free) of the product of this step is determined to be 82.3 mg KOH/g. The conversion of potassium alkyl phenate to potassium alkylhydroxybenzoate was 83.7% by mole measured by NMR.

Example Y

[0152] The product of Example X (499 kg) is treated by dropwise addition with 74.6 kg aqueous solution of sulfuric acid (50 wt. %) at 70 °C over 3 hours. After acid addition is complete, the reaction mixture is stirred for an additional 2 hours at 85 °C. The mixture

is then heated until all the water is removed. The resultant slurry is then hot filtered to remove potassium sulfate over a filter cloth to yield a brown oil (mixture of alkyl hydroxybenzoic acid, alkyl phenol and oil). Oil was calculated by mass balance to be 39% by weight of the total product of this step.

5 Example 1

[0153] The product of Example Y (2000 g) is mixed with 250g methanol and 250g n-butanol followed by addition of 353 g hydrated lime to make a slurry. The slurry is mixed for 30 min at 40 °C. 70 g of water is added. The reaction mixture is then heated to 60 °C and held for 1 hr at 60 °C. CO₂ is added over 90 min at a rate of 1.6 g/min. The reaction mixture is then heated to 150 °C under 40mmHg for 30 min to remove the water, methanol, and n-butanol. 90 g of oil is added to adjust the amount of oil to be 35wt%. Crude sediment is 2.8 vol%. FAUC is 8wt%. Turbidity is 22 JTU. The TBN of the filtered detergent product is 215 mg KOH/g. Oil free TBN is calculated to be 330 mg KOH/g. The filtered product (alkylhydroxybenzoate, calcium carbonate, oil) is further diluted with oil (about 15 560g) to have a final TBN of 170 mg KOH/g (not oil free).

Example 2

[0154] The product of Example Y (2000g) is mixed with 250g methanol, 250g n-butanol and 18.3g methanesulfonic acid (70wt% water) followed by the addition of 353g hydrated lime. The slurry is mixed for 30 min at 40 °C. 70 g of water is added. The reaction mixture is then heated to 60 °C and held for 1 hr at 60 °C. CO₂ is added over 90 min at a rate of 1.6 g/min. The reaction mixture is then heated under 40mmHg to remove all water, methanol, and n-butanol. 90g of oil is added in the end to adjust the amount of oil to be 35wt%. Crude sediment is 0.05 vol%. FAUC is 2wt%. Turbidity is 38 JTU. The TBN of the filtered detergent product is 211 mg KOH/g. Oil Free TBN is calculated to be 325 mg KOH/g. The filtered product is further diluted with oil (about 560g) to have a final TBN of 170 mg KOH/g.

Example 3

[0155] The product of Example Y (2000g) is mixed with 250g methanol and 250g n-butanol. 353g hydrated lime is added. The slurry is mixed for 30 min at 40 °C. 70 g of water is added. The mixture is then heated to 60 °C and held for 1 hr at 60 °C. CO₂ is added over 90 min at a rate of 1.6 g/min. 173g hydrated lime is added under N₂ and mixed for 10 min. CO₂ is added over 1 hr at 1.6 g/min. Another 173g hydrated lime is added

under N₂ and mixed for 10 min. Additional CO₂ is added for 1 hr at 1.6 g/min. The reaction mixture is heated to 150 °C under 40mmHg to remove all water, methanol, and n-butanol. 90g of oil was added to adjust the amount of oil to 35wt%. Crude sediment is 8 vol%. The TBN of the filtered detergent product is 341 mg KOH/g. Oil free TBN is calculated to be 525 mg KOH/g. FAUC is 8wt%. Turbidity is 11.7 JTU.

Example 4

[0156] The product of Example Y (2000 g) is mixed with 250g methanol, 250g n-butanol and 21g methanesulfonic acid (70% in water). 353g hydrated lime is added. The slurry is mixed for 30 min at 40 °C. 70 g of water is added. The reaction mixture is then heated to 60 °C and held for 1 hr at 60 °C. CO₂ is added over 90 min at a rate of 1.6 g/min. 173g hydrated lime is added under N₂ and mixed for 10 min. Additional CO₂ is added over 1 hr at 1.6 g/min. An additional 173 g of hydrated lime is then added under N₂ and mixed for 10 min. CO₂ is added for 1 hr at 1.6 g/min. The reaction mixture is heated to 150 °C under 40mmHg to remove all water, methanol, and n-butanol. Crude sediment is 1.6 vol%. 90 g of oil was added to adjust the amount of oil to 35wt%. The TBN of the filtered detergent product is 334 mg KOH/g. Oil free TBN is calculated to be 514 mg KOH/g. FAUC is 3wt%. Turbidity is 32 JTU.

[0157] Each of the detergent examples above were evaluated and the results are summarized in Table 1.

Table 1

[0158] Filter Aid Unit Consumption

Measurement	Method	Example 1 564C-27583	Example 2 564C-27606	Example 3 564C-27624	Example 4 564C-27778
Filter Aid Consumption Unit (FAUC) ¹		8 %	2 %	8%	3%
Filter Flowrate (g/min/cm ²)	Measured	>0.44	>0.44	>0.44	>0.44
Crude Sediment (vol%)	25% vol in hexane and centrifuged	2.8 %	0.05 %	8 %	1.6 %
JTU, Turbidity	20% vol in Oil	22	38	11.7	32
TBN	ASTM D2896A	215	211	341	343
TBN (oil-free)(calculated) ²	Calculated	330	325	535	514

¹ Diatomaceous Earth Filter Aid having an oil flow rate of 37-51ml/min determined by the method described herein.

² Measured TBN / wt fraction of non-oil components.

5 **[0159]** 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.

10

What is claimed is:

1. A process for preparing an overbased alkaline earth metal alkylhydroxybenzoate comprising the steps of:

(a) reacting an alkylphenol with an alkali metal hydroxide in the presence of a diluent oil to produce an alkali metal alkylphenate;

(b) carboxylating the alkali metal alkylphenate obtained in step (a) with carbon dioxide so that at least 50 mol% of the alkali metal alkylphenate is converted to an alkali metal alkylhydroxybenzoate;

(c) acidifying the alkali metal alkylhydroxybenzoate obtained in step (b) with an aqueous solution of a strong acid to produce an alkylhydroxybenzoic acid and an alkali metal salt of the strong acid;

(d) separating the alkali metal salt of a strong acid from the alkylhydroxybenzoic acid;

(e) adding methane sulfonic acid, mono-alcohol, water, and an alkaline earth metal base to the alkylhydroxybenzoic acid to form an alkaline earth metal alkylhydroxybenzoate and at least one alkaline earth metal sulfonic acid salt;

(f) reacting the alkaline earth metal alkylhydroxybenzoate with at least one acidic overbasing material in the presence of the at least one alkaline earth metal sulfonic acid salt and the monoalcohol.

2. The process of claim 1, wherein the process is carried out in the absence of elemental sulfur.

3. The process of claim 1 or 2, wherein the alkali metal hydroxide is selected from the group consisting of potassium hydroxide, sodium hydroxide, lithium hydroxide, or mixtures thereof.

4. The process of any preceding claim, wherein the diluent oil has a viscosity of 2 cSt to 8 cSt (KV100 measured by ASTM D445-100).

5. The process of any preceding claim, wherein the strong acid comprises or consists of a strong acid having a pKa of less than 2.5.

6. The process of any preceding claim, wherein the strong acid is selected from the group consisting of sulfuric acid, hydrochloric acid, perchloric acid, phosphoric acid or mixtures thereof.

5

7. The process of any preceding claim, wherein the mono-alcohol comprises a mono-alcohol having 1 to 5 carbon atoms.

8. The process of any preceding claim, wherein the mono-alcohol is selected from the group consisting of butanol, methanol, ethanol, propanol, isopropanol, isobutanol, t-butyl alcohol, amyl alcohol, or mixtures thereof.

10

9. The process of any preceding claim, wherein the mono-alcohol comprises a mixture of butanol and methanol.

15

10. The process of any preceding claim, wherein the alkaline earth metal base is selected from calcium oxide, calcium hydroxide, or mixtures thereof.

20

11. The process of any preceding claim, wherein the alkaline earth metal base is calcium hydroxide.

12. The process of any preceding claim, wherein the acidic overbasing material comprises or consists of carbon dioxide.

25

13. The process of any preceding claim, wherein the overbased alkaline earth metal alkylhydroxybenzoate has an oil free TBN greater than 250.

30

14. The process of any preceding claim, wherein the overbased alkaline earth metal alkylhydroxybenzoate has an oil free TBN from 70 to 600 or 100 to 550 or 150 to 450, or 200 to 350.

15. The process according to any preceding claim, wherein the alkylphenol contains a linear alkyl group, a branched alkyl group, or a mixture thereof.

16. The process according to claim 15, wherein the alkylphenol contains a linear alkyl group having from 12 to 40 or 14 to 30 carbon atoms or 16 to 20 carbon atoms.

17. The process according to claim 16, wherein the linear alkyl group is derived from the polymerization of ethylene.

18. The process according to any of claims 1 to 15, wherein the alkylphenol contains a branched alkyl group having at least 9, or 9 to 40, or 9 to 24 carbon atoms.

19. An overbased alkaline earth metal alkylhydroxybenzoate prepared by the process of any preceding claim.

20. A lubricating oil composition comprising the alkaline earth metal alkylhydroxybenzoate of claim 19.

21. A method of lubricating an engine, comprising supplying to the engine the lubricating oil composition of claim 20.

22. The use of the process of any of claims 1 to 18 in order to reduce the filter aid unit consumption in the manufacture of an alkaline earth metal alkylhydroxybenzoate.