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(54) Title: METHOD FOR PREPARING A SULFURIZED ALKALINE EARTH METAL DODECYLPHENATE

(57) Abstract: An overbased sulfurized alkaline earth metal alkylphenate is prepared by reacting an alkylphenol with an alkaline earth metal hydroxide or an alkaline earth metal oxide and sulfur in the presence of an alkylene glycol or dialkylene glycol, or ether thereof and in the presence of an oil of lubricating viscosity, and optionally further reacting the product thereof with carbon dioxide; thereby forming a sulfurized alkaline earth metal alkylphenate composition in oil. The composition is heated and subjected to steam stripping followed by filtration. The resulting product exhibits an improved rate and efficiency of filtration.



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TITLE

Method for Preparing a Sulfurized Alkaline Earth Metal Dodecylphenate

BACKGROUND OF THE INVENTION

5 [0001] The disclosed technology relates to a process for preparing a sulfurized alkaline earth metal dodecylphenate exhibiting improved ease of filterability.

[0002] Phenol-based detergents are known. Among these are phenates based on phenolic monomers, linked with sulfur bridges or alkylene bridges such as methylene linkages derived from formaldehyde. The phenolic monomers themselves are typically substituted with an aliphatic hydrocarbyl group to provide a measure of oil solubility.

10 [0003] One commonly employed step in the commercial manufacture of metal phenates, including overbased metal phenates, is filtration. The filtration typically occurs after the overbasing process, and slow filtration can have a negative impact on production and economics, in terms of filtration time or alternatively in amount of filter aid usage required to maintain an acceptable flow rate. Moreover, recipe modifications designed to reduce the amount of monomeric phenolic species may tend to lead to worse filtration performance. This is of increasing significance because certain alkylphenols and products prepared from them have come under increased scrutiny due to their association as potential endocrine disruptive materials. In particular, alkylphenol detergents which are based on oligomers of C₁₂ alkyl phenols may contain residual monomeric C₁₂ alkyl phenol species. There has been interest, therefore, in developing alkyl-substituted phenate detergents, for uses in lubricants, fuels, and as industrial additives, which contain a reduced amount of dodecylphenol component.

20 [0004] An early reference to basic sulfurized polyvalent metal phenates is U.S. Patent 2,680,096, Walker et al., June 1, 1954; see also U.S. Patent 3,372,116, Meinhardt, March 6, 1968. Additionally, U.S. Patent 3,036,971, Otto, May 29, 1962, discloses lubricating oils containing carbonated basic sulfurized calcium phenates. Its preparation includes the use of a glycol containing less than 6 carbon atoms.

25 [0005] U.S. Patent 3,464,970, Sakai et al., September 2, 1969, similarly discloses an overbased sulfurized calcium phenate by heating a mixture of phenolic compounds, dihydric alcohol, elementary sulfur and calcium compounds. Somewhat later, U.S. Patent 5,024,773, Liston, June 18, 1991, discloses a method of preparing group II metal overbased sulfurized alkylphenols involving use of a sulfurization catalyst. The product is said to have lower crude sediment, higher Total Base Number, and lower viscosity.

[0006] EP 601721, Ethyl Petroleum, June 15, 1994, discloses a process for preparing overbased phenates.

[0007] PCT publication WO 2013/119623, Lubrizol, August 15, 2013, discloses a sulfurized alkaline earth metal (e.g., calcium) dodecylphenate prepared by reacting dodecylphenol with calcium hydroxide or calcium oxide in an amount of about 0.3 to about 0.7 moles per mole of dodecylphenol charged and an alkylene glycol in an amount of about 0.13 to about 0.6 moles per mole of dodecylphenol charged; and reacting the product of the first step with sulfur in an amount of about 1.6 to about 3 moles per mole of dodecylphenol charged. The product thus prepared has reduced levels of monomeric dodecylphenol.

[0008] The disclosed technology provides a method for preparing phenate detergent with improved filterability efficiency. In certain embodiments, the disclosed technology may also provide a product which contains a reduced amount of monomeric dodecylphenol within an oligomeric dodecylphenol composition.

SUMMARY OF THE INVENTION

[0009] The disclosed technology provides a process for preparing a sulfurized alkaline earth metal alkylphenate, optionally overbased, comprising:

- (a) reacting (i) an alkylphenol, wherein the alkyl group contains 6 to 24 carbon atoms, with (ii) an alkaline earth metal hydroxide or an alkaline earth metal oxide in an amount of 0.4 to 10 moles per mole of alkylphenol charged to the reaction; and (iii) a sulfur source in an amount to provide 0.8 to 3 moles sulfur (as S) per mole of alkylphenol charged to the reaction; in the presence of (iv) an alkylene glycol or dialkylene glycol, or ether thereof, in an amount of 0.2 to 2 moles per mole of alkylphenol charged to the reaction; and including in the reaction mixture (v) an oil of lubricating viscosity; and optionally further reacting the product thereof with (vi) carbon dioxide; thereby forming a sulfurized alkaline earth metal alkylphenate composition in oil;
- (b) heating said alkylphenate composition to 120 to 280°C or 200 to 250°C;
- (c) supplying steam to said alkylphenate composition;
- (d) removing said steam under reduced pressure; and
- (e) filtering the resulting composition to provide, as the filtrate, a sulfurized alkaline earth metal alkylphenate in oil.

[0010] The disclosed technology further provides the product prepared by the foregoing process; a lubricant composition comprising an oil of lubricating viscosity and the

foregoing product; and a method for lubricating an internal combustion engine, comprising supplying thereto the foregoing lubricant composition.

DETAILED DESCRIPTION OF THE INVENTION

[0011] Various preferred features and embodiments will be described below by way of non-limiting illustration.

[0012] One of the materials used in the presently disclosed technology is a sulfur-bridged phenolic compound. Such materials in general, their methods of preparation, and use in lubricants are well known from, for instance, the above-referenced U.S. Patent 2,680,096, Walker et al. They may be prepared starting from phenol or, alternatively, a short chain alkyl phenol such as cresol (*o*-, *m*-, or *p*-methylphenol), or mixtures thereof, any of which are readily available as starting materials. The alkylation of phenol and its homologues is well known, typically by catalyzed reaction of an olefin, often an α -olefin, with phenol (or with cresol or another homologue, as the case may be). Alkylation of phenol is described in greater detail in the Kirk-Othmer *Encyclopedia of Chemical Technology*, third edition (1978) vol. 2, pages 82-86, John Wiley and Sons, New York.

[0013] Linking of alkyl-substituted (or more generally, hydrocarbyl-substituted) phenols to form oligomeric species is also well known. They may be linked together to make sulfur bridged species, which may include bridges of single sulfur atoms ($-S-$) or multiple sulfur atoms (e.g., $-S_n-$ where n may be 2 to 8, typically 2 or 3). Typically there may be 1, 2, or 3, or often 1, S atom per linkage. Sulfurized phenols may be prepared by reaction with a sulfur source, that is, an active sulfur species such as sulfur monochloride or sulfur dichloride as described on pages 79-80 of the Kirk-Othmer reference or with elemental sulfur, as described, for instance, in US 2,680,096. Sulfurization (with sulfur) may be conducted in the presence of a basic metal compound such as calcium hydroxide or calcium oxide, thus preparing a metal salt, as described in greater detail, below.

[0014] The process of the disclosed technology begins with an alkylphenol which comprises an alkylphenol wherein the alkyl group contains 6 to 24 carbon atoms, and in certain embodiments, 8 to 18 or 9 to 15 or 10 to 14 carbon atoms, or 12 carbon atoms. Such a material may include a dodecylphenol (e.g., tetrapropenylphenol, "TPP") such as, in one embodiment, paradodecylphenol, ("PDDP"). Other substituted phenols may be present in TPP as well as PDDP, but in certain embodiments the PDDP may comprise

at least 50 weight percent of the monomeric phenolic component and may be 50 to 100 weight percent, or 60 to 99% or 70 to 98% or 80 to 97% or 90-96% or 95 to 98%.

Typically, a commercial grade of TPP may be used, such that phenolic components other than PDDP will be those materials that are present along with PDDP in the com-

mercial grade material. Thus, a certain amount of other isomers may be present, pre-
dominantly ortho-dodecylphenol or meta-dodecylphenol, but there may also be an
amount of unsubstituted phenol and an amount of unreacted dodecene, as well as a
certain amount (typically a minor amount) of dialkylated material. Moreover, since
dodecylphenols are typically prepared by the reaction of a propylene tetramer with a
phenol, certain amounts of material having C9 or C15 alkyl groups, or a mixture of alkyl
groups having 9 (or fewer) to 15 (or more) carbon atoms, may also be present. Some of
these may result from reaction with propylene trimer or pentamer. Characteristically,
the amount of such other materials may be 5 or 15 to 50 percent or 20 to 40, or 25 to 35,
or 35 to 40 percent by weight, in commercial PDDP. The amounts of PDDP referred to
herein generally refer to the total amount of the commercial grade, which would include
such isomers, byproducts, and other materials. However, when the amount of "residual
TPP" is reported, those amounts normally include mixtures of closely related monomer-
ic materials such as ortho- and para- isomers from C9 to C15 alkylphenols, typically
excluding dialkylated materials.

[0015] The TPP or other alkylphenol may be, in one embodiment, initially reacted
with a basic alkaline earth metal material, typically an oxide or a hydroxide, where the
alkaline earth metal may typically be calcium or magnesium, or in some embodiments,
calcium. Suitable basic materials include calcium (or magnesium) hydroxide or calcium
(or magnesium) oxide, typically calcium hydroxide. The reaction may be carried out in
the presence of an alkylene glycol and sulfur. The amount of the alkaline earth metal
hydroxide or oxide may typically be an amount to provide 0.4 to 10 moles of the metal
oxide or hydroxide per mole of the alkylphenol (such as TPP) that is charged to the
reaction. Alternative amounts may be 0.5 to 8 moles or 0.8 to 6 or 1 to 5 or 1.3 to 3 or 1.5
to 2 or 1.7 to 1.9 moles per moles of alkylphenol. Since alkaline earth metals are divalent,
the broadest above-mentioned amounts would correspond to 0.8 to 20 equivalents per
mole of the alkylphenol. For amounts less than 1 equivalent per equivalent, the alkylphe-
nol will not be completely salted or neutralized; for amounts of about 1 equivalent/-
equivalent, a substantially neutral salt may be obtained. For amounts in excess of 1

equivalent/ equivalent, an overbased salt may be obtained, as described in greater detail below. In another embodiment, the alkylphenol may be initially reacted with a sulfur source to form a sulfur-bridged material, and thereafter reacted with the selected amount of alkaline earth metal oxide or hydroxide to effect neutralization.

5 **[0016]** An alkylene glycol (that is, diol) is typically present, especially during the neutralization reaction. The alkylene glycol may be ethylene glycol or it may, alternatively, be a heavier glycol such as 1,2- or 1,3-propylene glycol or a butylene glycol. As it is often considered to be desirable able to remove the alkylene diol after the reaction is complete, use of a diol having 6 or fewer or 5, 4, or 3 or fewer carbon atoms, or a normal
10 boiling point of less than 230 or 220 or 210 °C may be desirable. Ethylene glycol may typically be used. Alternatively, a dialkylene glycol may be used, that is, a material of the general structure HO-R-O-R-OH, where R represents an alkylene group (the two R groups may be the same or different). Alternatively, one or both of the -OH groups of the alkylene- or dialkylene-glycol may be replaced by an ether group, that is, an alkoxy group
15 which may contain 1 to 4 or 1 to 2 carbon atoms, such as methoxy, -OCH₃.

[0017] The amount of the alkylene glycol or dialkylene glycol, or ether thereof that is present in the reaction mixture may be 0.2 to 2 moles per mole of alkylphenol charged to the reaction. Alternative amounts may be 0.4 to 1.5, or 1.0 to 1.5, or 0.5 to 1.2, or 0.6 to 1, or 0.5 to 0.8, or 0.65 to 0.8 moles per mole.

20 **[0018]** Another component of the reaction mixture will be a sulfur source which may be elemental sulfur, which will typically form sulfur-bridges or linkages between the aromatic groups of two or more alkylphenol molecules, thereby forming species that may be considered dimeric or oligomeric species. The amount of the sulfur source charged to the reaction mixture will typically be an amount to provide 0.8 to 3 moles of
25 sulfur (calculated assuming monomeric S units, molecular weight 32) per mole of alkylphenol charged to the reaction. Other amounts may be 1 to 2.5 or 1 to 2 or 1.2 to 1.8 or 1.3 to 1.5 moles per mole.

[0019] The reaction of the above-described components may be conducted in a solvent or other medium such as an oil of lubricating viscosity, also referred to as a base
30 oil. If a volatile medium is used, it may be subsequently removed from the reaction mixture by evaporation or other means, e.g., steam-stripping. If a base oil is used as the medium, it may be retained in the reaction medium since, in some embodiments, the overbased product will be used in the presence of diluent oil. The base oil may be

selected from any of the base oils in Groups I-V of the American Petroleum Institute (API) Base Oil Interchangeability Guidelines, namely

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 (PAOs)		
Group V	All others not included in Groups I, II, III or IV		

Groups I, II and III are mineral oil base stocks. The oil of lubricating viscosity can include natural or synthetic oils and mixtures thereof. Mixture of mineral oil and synthetic oils, e.g., polyalphaolefin oils and/or polyester oils, may be used.

[0020] Natural oils include animal oils and vegetable oils (e.g. vegetable acid esters) as well as mineral lubricating oils such as liquid petroleum oils and solvent-treated or acid treated mineral lubricating oils of the paraffinic, naphthenic, or mixed paraffinic-naphthenic types. In one embodiment, the oil of lubricating viscosity will be a mineral oil. Hydro treated or hydrocracked oils are also useful oils of lubricating viscosity. Oils of lubricating viscosity derived from coal or shale are also useful.

[0021] Synthetic oils include hydrocarbon oils and halosubstituted hydrocarbon oils such as polymerized and interpolymerized olefins and mixtures thereof, alkylbenzenes, polyphenyl, alkylated diphenyl ethers, and alkylated diphenyl sulfides and their derivatives, analogs and homologues thereof. Alkylene oxide polymers and interpolymers and derivatives thereof, and those where terminal hydroxyl groups have been modified by, e.g., esterification or etherification, are other classes of synthetic lubricating oils. Other suitable synthetic lubricating oils comprise esters of dicarboxylic acids and those made from C5 to C12 monocarboxylic acids and polyols or polyol ethers. Other synthetic lubricating oils include liquid esters of phosphorus-containing acids, polymeric tetrahydrofurans, silicon-based oils such as poly-alkyl-, polyaryl-, polyalkoxy-, or polyaryloxy-siloxane oils, and silicate oils. Other synthetic oils include those produced by Fischer-Tropsch reactions, typically 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.

[0022] Unrefined, refined, and rerefined oils, either natural or synthetic (as well as mixtures thereof) of the types disclosed hereinabove can be used. Unrefined oils are

those obtained directly from a natural or synthetic source without further purification treatment. 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. Rerefined oils are obtained by processes similar to those used to obtain refined oils applied to refined oils which have been already used in service. Rerefined oils often are additionally processed to remove spent additives and oil breakdown products.

[0023] The amount of oil of lubricating viscosity present during the reaction of the alkylphenol with the sulfur source and the alkaline earth compound may be an amount suitable to provide a mixture that can be readily processed, that is, stirred and otherwise handled. To the extent that the final product will be used as a lubricant additive, the oil may serve as the conventional diluent oil in which the product is commercially supplied. Additional oil may be added subsequently if desired, in order to adjust the concentration, viscosity, or other parameters of the final product. The amount of oil included in the above-described reaction mixture may be 10 to 100 parts by weight per 100 parts by weight of alkylphenol charged to the reaction. Alternative amounts may be 15 to 50, or 20 to 50, or 20 to 60, or 21 to 40, or 22 to 30, or 23 to 28 parts by weight per 100 parts by weight of the alkylphenol charged to the reaction mixture. Such amounts may be present at the time of initial mixture of the alkylphenol with other reactants, or the initial amount of oil may be less and then increased to any of the above values during subsequent processing. In one embodiment, the oil of lubricating viscosity is present in any of the above-identified amounts at the time of the removal of the steam in step (d), described below. In certain embodiments the oil of lubricating viscosity will be present during the step of neutralizing the sulfur-bridged phenol but need not be present during the sulfurization step, if the sulfurization is conducted in a step prior to neutralization.

[0024] In the case where the amount of alkaline earth metal hydroxide or oxide is present in an amount in excess of the stoichiometric amount needed to neutralize the alkylphenol moieties, the resulting salt is said to be overbased. Overbased materials in general, otherwise referred to as overbased or superbased salts, are generally homogeneous Newtonian systems characterized by a metal content in excess of that which would be present for neutralization according to the stoichiometry of the metal and the particular acidic organic compound reacted with the metal. Overbased materials are prepared by reacting an acidic material (typically an inorganic acid or lower carboxylic acid, typically carbon dioxide) with a mixture comprising an acidic organic compound (in this

instance, the sulfurized phenol or phenate), a reaction medium of at least one inert, organic solvent (e.g., mineral oil, naphtha, toluene, xylene) for said acidic organic material, a stoichiometric excess of a metal base, and a promoter such as a phenol or alcohol. The amount of excess metal is commonly expressed in terms of metal ratio.

- 5 The term "metal ratio" is the ratio of the total equivalents of the metal to the equivalents of the acidic organic compound. A neutral metal salt has a metal ratio of one. A salt having 4.5 times as much metal as present in a normal salt will have metal excess of 3.5 equivalents, or a ratio of 4.5.

[0025] In order to facility preparation of an overbased detergent, the basic composi-
10 tion may be optionally further reacted with carbon dioxide. Such treatment will convert excess basicity arising from the stoichiometric excess of alkaline earth hydroxide or oxide to the carbonate. The amount of carbon dioxide may be an amount added until an excess is observed that is not absorbed by the reaction mixture. Such an amount will depend on the amount of basic alkaline earth material that is present, and any other basic
15 materials, but in some embodiments may amount to 0.5 to 2 or 1 to 1.5 or 1.1 to 1.3 or 0.9 to 1.1 moles per mole alkylphenol charged. In some embodiments, the amount of carbon dioxide supplied may be 10 to 50 parts by weight per 100 parts by weight of alkylphenol charged to the system, alternatively 12 to 25 or 15 to 20 parts per 100 parts. The reaction with the carbon dioxide may take place over 1 to 10 hours, or 2 to 8 or 3 to
20 6 or 3.5 to 5 hours.

[0026] Overbased detergents are often characterized by Total Base Number (TBN, as measured by ASTM D-2896). TBN is the amount of strong acid needed to neutralize all of the overbased material's basicity, expressed as potassium hydroxide equivalents (mg KOH per gram of sample). Since overbased detergents are commonly provided in a
25 form which contains a certain amount of diluent oil, for example, 40-50% oil, the actual TBN value for such a detergent will depend on the amount of such diluent oil present, irrespective of the "inherent" basicity of the overbased material. For the purposes of the present invention, the TBN of an overbased detergent is to be recalculated to an oil-free basis, except as noted. Detergents which are useful in the present technology typically
30 have a TBN (oil-free basis) of 100 to 800, and in one embodiment 150 to 750, and in another, 400 to 700. In certain embodiments, the amount of alkaline earth metal hydroxide or oxide will be the amount suitable to provide a product with a TBN of 200 to 600 on an oil-free basis; such materials are typically considered "overbased." Products that

are substantially “neutral,” that is, not overbased or not significantly overbased, may nevertheless exhibit a TBN of 100-350. The overall TBN of the composition, including oil, will be derived from the TBN contribution of the individual components. In the case of a final lubricant formulation, the various components contributing TBN may include dispersants, the detergents, and other basic materials.

[0027] Metal compounds useful in making basic metal salts are generally any Group 1 or Group 2 metal compounds (CAS version of the Periodic Table of the Elements). The Group 1 metals of the metal compound include Group 1a alkali metals such as sodium, potassium, and lithium, as well as Group 1b metals such as copper. The Group 2 metals of the metal base include the Group 2a alkaline earth metals such as magnesium, calcium, and barium, as well as the Group 2b metals such as zinc or cadmium. In one embodiment the Group 2 metals are magnesium, calcium, barium, or zinc, and in another embodiment magnesium or calcium or, in particular, calcium. In certain embodiments the metal is calcium or sodium or a mixture of calcium and sodium. Generally the metal compounds are delivered as metal salts. The anionic portion of the salt can be hydroxide, oxide, carbonate, borate, or nitrate.

[0028] Such overbased materials are well known to those skilled in the art. Patents describing techniques for making basic salts of sulfonic acids, carboxylic acids, (hydrocarbyl-substituted) phenols, phosphonic acids, and mixtures of any two or more of these include U.S. Patents 2,501,731; 2,616,905; 2,616,911; 2,616,925; 2,777,874; 3,256,186; 3,384,585; 3,365,396; 3,320,162; 3,318,809; 3,488,284; and 3,629,109.

[0029] The order of addition of the components for the above-described reaction, and the conditions of reaction, can be varied as will be apparent to the person skilled in the art. For instance, the alkylphenol, the alkaline earth metal compound, sulfur source, and alkylene glycol or dialkylene glycol, and oil, may be added to a reaction vessel simultaneously or in varying orders of addition. In one embodiment, the alkylphenol may be first mixed (in oil) with an approximately stoichiometric amount of the alkaline earth metal compound and thereafter sulfur may be charged to the mixture, along with the glycol material. The sulfur may be supplied in one or in multiple charges. Likewise, the alkaline earth metal compound may be provided in one or in multiple charges. Particularly if the product is to be overbased, addition of the alkaline earth metal compound and treatment with carbon dioxide may be done in multiple stages. In another embodiment, the alkylphenol may be first reacted with the sulfur source, in the presence

of the alkylene glycol (or dialkylene glycol, or ether thereof) in the absence (or in the presence) of oil, and thereafter the resulting sulfur-bridged component may be reacted with the alkaline earth metal compound, typically in the presence of oil.

[0030] During the reaction sequence, the mixture is typically maintained at elevated temperature, such as 80 to 150 °C, or 100 to 149 °C, or 95 to 130 °C, or 100 to 125 °C. Temperatures and reaction times may vary depending on the order of addition of reagents; if different reagents are added in different stages or times, the temperature and reaction time of each stage may be adjusted as will be apparent to the skilled person. In one embodiment the temperature of the reaction mixture is increased during a first stage, in that the alkylphenol may be initially heated to 90 to 110 °C, e.g., about 100 °C, and after the other components are added, the mixture may be further heated to 120 to 130 °C, e.g., about 124 or 125 °C. Alternatively, reaction with the sulfur may be conducted at an elevated temperature, such as 160 to 230 °C, or 170 to 230 °C, or 180 to 230 °C, or 190 to 225, or 200 to 220, or 210 to 220 °C. At any stage during the reaction, volatile materials may be removed by distillation or they may be retained in the reaction mixture. The reaction mixture may be maintained at an elevated temperature for a period of time sufficient to permit reaction to occur to the desired extent, which will, of course, depend to some extent on the temperature selected. Typical overall times of reaction may be ½ to 20 hours, or 1 to 10, or 2 to 9, or 3 to 8, or 4 to 7, or 5 to 6 hours.

[0031] Following reaction and, if desired, treatment with carbon dioxide, the reaction mixture will be subjected to treatment with steam. In this steam-treatment process, the alkylphenate composition thus prepared will be heated to 120 to 280 °C or alternatively 200 to 250 °C, or 210 to 230, or 216 to 240 °C, and steam will be supplied thereto. The steam may be provided at superatmospheric pressure and at a temperature of 120 °C to 250 °C, or alternatively 190-240 °C, but in any event should be supplied as steam and not as liquid water. Supplying the steam at superatmospheric pressure means that the steam may be provided from a source of steam at superatmospheric pressure; the actual contact between the steam and the reaction mixture is not necessarily conducted at superatmospheric pressure.

[0032] The steam which has been added is subsequently removed, and with it a portion of the volatile byproducts or unreacted components from the reaction mixture. The steam will be both added and removed in a continuous or semi-continuous manner commonly referred to as steam stripping, which is a well-known industrial process. If

desired, the steam may be re-used in multiple passes through the reaction mixture, or it may be used once after a single pass. The steam (and other volatile components) may be removed under reduced pressure of 1.3 to 53 kPa (10 to 400 mmHg), or alternatively 2.7-13 or 4.0-6.6 kPa (20-100 mmHg or 30-50 mmHg). The total amount of steam employed in the stripping process may be 1 to 40 parts by weight steam per 100 parts by weight of alkylphenol charged to the reaction, or alternatively 3 to 36, or 10 to 30, parts by weight. Greater than 36 or 40 parts by weight of steam may also be used, although the relative benefit obtained by using higher amounts may be less.

[0033] After the steam stripping, the reaction mixture will contain a commercial grade of overbased, sulfur-bridged alkylphenate in oil. The mixture will typically be filtered to remove any insoluble materials. This filtration may be conducted at 130-200°C or 149-185°C and may make use of a filter aid such as diatomaceous earth in a method which is well known to those skilled in the art. In brief, the filter aid may be mixed with the batch to be filtered and the mixture passed through any of several types of pressure leaf filters, such as those using screens or cloth, to form a cake of filter aid. The cake of filter aid performs the actual removal of solids. The filtration may optionally be assisted by vacuum. Since, a small amount of liquid and dissolved solids are necessarily retained within the filter cake, it is desirable that the smallest possible amount of filter aid be used in order to provide the highest yield of product.

[0034] The preparation of the optionally overbased, sulfur-bridged alkylphenate by means of the disclosed technology provides a material with significantly improved filterability and ease of filtration. In an industrial environment, improved filterability is reflected in a reduced amount of filter aid required to permit effective filtration. If too little filter aid is used, the filter will become plugged, resulting in reduced flow of filtrate and inefficiency in production of product. If excessive filter aid is used or required, the filtrate may flow unimpeded but an unacceptably large amount of liquid will be retained in the filter pad, with a loss of yield. It is therefore desired to have an amount of filter aid sufficient to absorb all the solid materials, but still having porosity or channels to permit flow of the filtrate liquids therethrough.

[0035] Filtration efficiency may thus be expressed in terms of filter aid usage consumption (FAUC). FAUC, which is expressed in units of weight percent of the final batch yield, may be determined by a manual batch test or series of batch tests, in which filter aid is added in increasing amounts until the amount is just sufficient to obtain good

flow of filtrate. "Good flow" is defined as a filtration time of no longer than 60 seconds or, alternatively, 90 seconds, for a mixture of 100 mL sample mixed with 100 mL diluent oil, containing the specified amount of filter aid, through a screen filter assisted by vacuum to provide a sensibly dry filter cake. In certain embodiments, the present technology can be employed with a FAUC of less than 3 percent, such as 0.5 to 2.5 percent or 0.8 to 2 percent or 1 to 1.5 percent.

[0036] It is unexpected that treatment of the optionally overbased alkylphenate with a steam-stripping step should lead to improved filterability. It has been recognized that the presence of water in the overbasing process can cause the CaCO_3 component formed thereby to convert to the vaterite form, which leads to problems with solubility and filtration. It appears that contact with high temperature steam has a contrary impact on filterability.

[0037] The sulfurized calcium alkylphenate prepared by the disclosed technology may also have a reduced level of free monomeric alkylphenate or alkylphenol than materials prepared by conventional means without the steam-stripping step. When the alkylphenol starting material is a tetrapropenyl phenol (TPP) such as, in one instance, paradodecyl phenol (PDDP), the resulting product may thereby be reduced in amount of residual, monomeric or unreacted, PDDP or its salt.

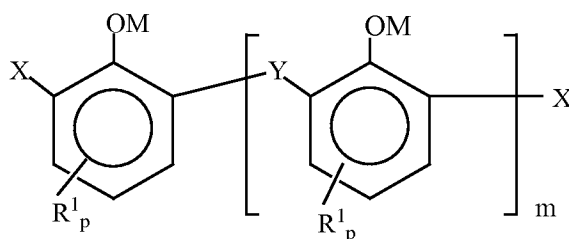
[0038] The amount of monomeric TPP within the product may be determined, if desired, by reverse phase ultra-high performance liquid chromatography by comparison with calibration standards prepared containing known amounts of TPP, using a UV detector at 225 nm. The solvent for the sample may be a mixture of 15% acetic acid in methyl-t-butyl ether. Suitable conditions may involve injection of a 2 μL sample of filtered material onto a 100x2.1 mm Waters UPLC® column with 1.7 μm particle size packing. The column temperature may be 40 °C and a flow rate of eluent may be 0.35 $\mu\text{L}/\text{min}$, with a gradient of eluent composition from 75% methanol/25% water to 100% methanol. The TPP monomer amount is determined by integration of the appropriate peaks.

[0039] The materials of the disclosed technology are typically employed in an oil to form a composition that may be used as a lubricant. The oil is typically referred to as an oil of lubricating viscosity, and various types thereof have been described above. The amount of the oil of lubricating viscosity present in a lubricant is typically the balance remaining after subtracting from 100 weight % the sum of the amount of the compound of the disclosed technology and the other performance additives.

[0040] The bridged phenolic compound may be used as one component of a lubricant formulation. Its amount, when so used, may vary depending on the end-use application. When used in a passenger car lubricant it may be present as low as 0.1 weight percent, and when used in a marine diesel cylinder lubricant it may be present in amounts as high as 25 percent by weight of the lubricant. Therefore, suitable ranges may include 0.1 to 25%, or 0.5 to 20%, or 1 to 18% or 3 to 13 % or 5 to 10%., or 0.7 to 5 weight percent or 1 to 3 weight percent, all on an oil-free basis. Similar overall amounts may also be used if the bridged phenolic compound is not overbased.

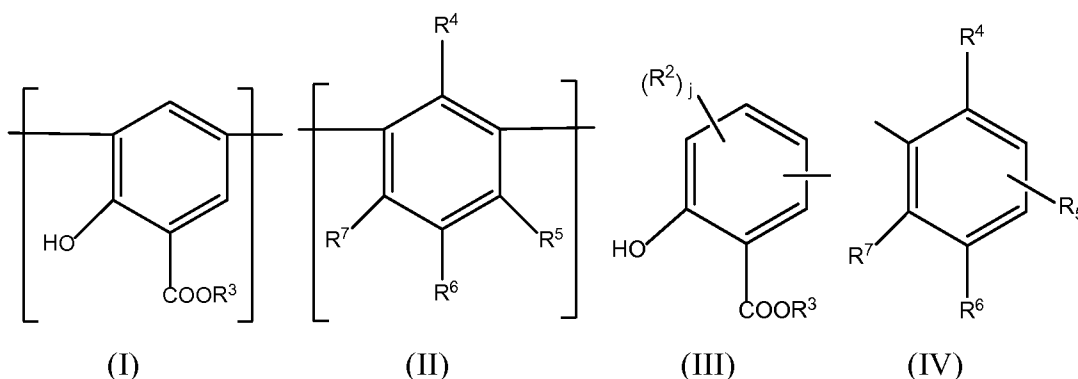
[0041] In lubricants containing the material of the disclosed technology, either a single detergent (that of the disclosed technology) or multiple detergents may be present. If there are multiple detergents, the additional detergents may be additional phenate detergents, or they may be detergents of other types. An example of another type of detergent is a sulfonate detergent, prepared from a sulfonic acid. Suitable sulfonic acids include sulfonic and thiosulfonic acids, including mono or polynuclear aromatic or cycloaliphatic compounds. Certain oil-soluble sulfonates can be represented by $R^2T(SO_3^-)_a$ or $R^3(SO_3^-)_b$, where a and b are each at least one; T is a cyclic nucleus such as benzene or toluene; R^2 is an aliphatic group such as alkyl, alkenyl, alkoxy, or alkoxyalkyl; $(R^2)-T$ typically contains a total of at least 15 carbon atoms; and R^3 is an aliphatic hydrocarbyl group typically containing at least 15 carbon atoms. The groups T, R^2 , and R^3 can also contain other inorganic or organic substituents. In one embodiment the sulfonate detergent may be a predominantly linear alkylbenzenesulfonate detergent having a metal ratio of at least 8 as described in paragraphs [0026] to [0037] of US Patent Application 2005-065045. In some embodiments 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.

[0042] In one embodiment, an overbased material is an overbased saligenin detergent. Overbased saligenin detergents are commonly overbased magnesium salts which are based on saligenin derivatives. A general example of such a saligenin derivative can be represented by the formula



where X is -CHO or -CH₂OH, Y is -CH₂- or -CH₂OCH₂-, and the -CHO groups typically comprise at least 10 mole percent of the X and Y groups; M is hydrogen, ammonium, or a valence of a metal ion (that is, if M is multivalent, one of the valences is satisfied by the illustrated structure and other valences are satisfied by other species such as anions or by another instance of the same structure), R₁ is a hydrocarbyl group of 1 to 60 carbon atoms, m is 0 to typically 10, and each p is independently 0, 1, 2, or 3, provided that at least one aromatic ring contains an R¹ substituent and that the total number of carbon atoms in all R¹ groups is at least 7. When m is 1 or greater, one of the X groups can be hydrogen. In one embodiment, M is a valence of a Mg ion or a mixture of Mg and hydrogen. Saligenin detergents are disclosed in greater detail in U.S. Patent 6,310,009, with special reference to their methods of synthesis (Column 8 and Example 1) and preferred amounts of the various species of X and Y (Column 6).

[0043] Salixarate detergents are overbased materials that can be represented by a compound comprising at least one unit of formula (I) or formula (II) and each end of the compound having a terminal group of formula (III) or (IV):

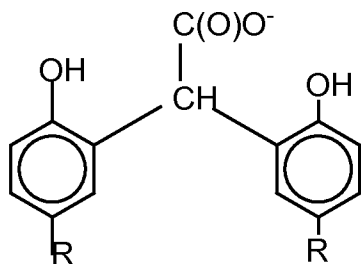


such groups being linked by divalent bridging groups A, which may be the same or different. In formulas (I)-(IV) R³ is hydrogen, a hydrocarbyl group, or a valence of a metal ion; R² is hydroxyl or a hydrocarbyl group, and j is 0, 1, or 2; R⁶ is hydrogen, a hydrocarbyl group, or a hetero-substituted hydrocarbyl group; either R⁴ is hydroxyl and R⁵ and R⁷ are independently either hydrogen, a hydrocarbyl group, or hetero-substituted hydrocarbyl group, or else R⁵ and R⁷ are both hydroxyl and R⁴ is hydrogen, a hydro-

carbyl group, or a hetero-substituted hydrocarbyl group; provided that at least one of R^4 , R^5 , R^6 and R^7 is hydrocarbyl containing at least 8 carbon atoms; and wherein the molecules on average contain at least one of unit (I) or (III) and at least one of unit (II) or (IV) and the ratio of the total number of units (I) and (III) to the total number of units of (II) and (IV) in the composition is 0.1:1 to 2:1. The divalent bridging group "A," which may be the same or different in each occurrence, includes $-CH_2-$ and $-CH_2OCH_2-$, either of which may be derived from formaldehyde or a formaldehyde equivalent (e.g., paraform, formalin).

[0044] Salixarate derivatives and methods of their preparation are described in greater detail in U.S. patent number 6,200,936 and PCT Publication WO 01/56968. It is believed that the salixarate derivatives have a predominantly linear, rather than macrocyclic, structure, although both structures are intended to be encompassed by the term "salixarate."

[0045] Glyoxylate detergents are similar overbased materials which are based on an anionic group which, in one embodiment, may have the structure



wherein each R is independently an alkyl group containing at least 4 or 8 carbon atoms, provided that the total number of carbon atoms in all such R groups is at least 12 or 16 or 24. Alternatively, each R can be an olefin polymer substituent. The acidic material upon from which the overbased glyoxylate detergent is prepared is the condensation product of a hydroxyaromatic material such as a hydrocarbyl-substituted phenol with a carboxylic reactant such as glyoxylic acid or another omega-oxoalkanoic acid. Overbased glyoxylic detergents and their methods of preparation are disclosed in greater detail in U.S. Patent 6,310,011 and references cited therein.

[0046] This supplemental overbased detergent can also be an overbased salicylate, e.g., an alkali metal or alkaline earth metal salt of a substituted salicylic acid. The salicylic acids may be hydrocarbyl-substituted wherein each substituent contains an average of at least 8 carbon atoms per substituent and 1 to 3 substituents per molecule. The substituents can be polyalkene substituents. In one embodiment, the hydrocarbyl

substituent group contains 7 to 300 carbon atoms and can be an alkyl group having a molecular weight of 150 to 2000. Overbased salicylate detergents and their methods of preparation are disclosed in U.S. Patents 4,719,023 and 3,372,116.

[0047] Other overbased detergents can include overbased detergents having a Mannich base structure, as disclosed in U.S. Patent 6,569,818.

[0048] The amount of any supplemental overbased detergent or detergents, if present in a lubricant, may be 0.1 to 20, or 0.5 to 18, or 1, 2, or 3 to 13 percent by weight.

[0049] Lubricants prepared using the materials of the presently-disclosed technology will typically contain one or more additional additive of the types that are known to be used as lubricant additives. 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 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, dimercaptiothiadiazoles, 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 weight percent, or 1.5 to 9.0 percent, or 2.0 to 8.0 percent, all expressed on an oil-free basis.

[0050] Another component is 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 hydrocarbyl group, an ester-containing group, or a group bridging two aromatic rings. Antioxidants also include aromatic amine, such as nonylated diphenylamines or (optionally alkylated) phenyl-naphthylamine. 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. U.S. Patent Application Publication 2006-0217271 discloses a variety of titanium compounds, including titanium alkoxides and titanated dispersants, which materials may also impart improvements in deposit control and filterability. Other titanium compounds include titanium carboxylates such as neodecanoate. 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 percent by weight or 0.15 to 4.5 percent or 0.2 to 4 percent. Additionally, more than one antioxidant may be present, and certain combinations of these can be synergistic in their combined overall effect.

[0051] 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, polymethacrylic acid esters, hydrogenated diene polymers, polyalkylstyrenes, esterified styrene-maleic anhydride copolymers, hydrogenated alkenylarene-conjugated diene copolymers and polyolefins. Multifunctional viscosity improvers, which also have dispersant and/or antioxidant properties are known and may optionally be used.

[0052] 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 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. Non-phosphorus-containing anti-wear agents include borate esters (including borated epoxides), dithiocarbamate compounds, molybdenum-containing compounds, and sulfurized olefins.

[0053] Other materials that may be used as antiwear agents include tartrate esters, tartramides, and tartrimides. Examples include oleyl tartramide (the imide formed from

oleylamine and tartaric acid) and alkyl diesters (from, e.g., mixed C12-16 alcohols). Other related materials that may be useful include esters, amides, and imides of other hydroxy-carboxylic acids in general, including hydroxy-polycarboxylic acids, for instance, acids such as tartaric acid, citric acid, lactic acid, glycolic acid, hydroxy-
5 propionic acid, hydroxyglutaric acid, and mixtures thereof. These materials may also impart additional functionality to a lubricant beyond antiwear performance. These materials are described in greater detail in US Publication 2006-0079413 and PCT publication WO2010/077630. Such derivatives of (or compounds derived from) a hydroxy-carboxylic acid, if present, may typically be present in the lubricating composition in an amount of 0.1 weight % to 5 weight %, or 0.2 weight % to 3 weight %, or
10 greater than 0.2 weight % to 3 weight %.

[0054] Other additives that may optionally be used in lubricating oils include pour point depressing agents, extreme pressure agents, color stabilizers and anti-foam agents. In one embodiment the lubricant may comprise at least one of a supplemental overbased detergent, a dispersant, an antioxidant, a viscosity improver, an anti-wear agent, a pour
15 point depressant, or an extreme pressure agent.

[0055] Lubricants containing the materials of the disclosed technology may be used for the lubrication of a wide variety of mechanical devices, including internal combustion engines, both two-stroke cycle and four-stroke cycle, spark-ignited and compression-ignited, sump-lubricated or non-sump-lubricated. The engines may be run on a variety of fuels including gasoline, diesel fuel, alcohols, bio-diesel fuel, and hydrogen, as well as mixtures of these (such as gasoline-alcohol mixtures, e.g., E-10, E-15, E-85).
20

[0056] The disclosed lubricants are suitable for use as lubricants for marine diesel engines, particularly as cylinder lubricants. In one embodiment, the present technology provides a method for lubricating an internal combustion engine, comprising supplying thereto a lubricant comprising the composition as described herein. The invention is suitable for 2-stroke or 4-stroke engines, including marine diesel engines, such as 2-stroke marine diesel engines.
25

[0057] 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
30

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 found in paragraphs [0137] to [0141] of published application US 2010-0197536.

[0058] The amount of each chemical component described is presented exclusive of any solvent or diluent oil, which may be customarily present in the commercial material, that is, on an active chemical basis, unless otherwise indicated. However, 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.

[0059] It is known that some of the materials described above may interact in the final formulation, so that the components of the final formulation may be different from those that are initially added. For instance, metal ions (of, e.g., a detergent) can migrate to other acidic or anionic sites of other molecules. The products formed thereby, including the products formed upon employing the composition of the present invention in its intended use, may not be susceptible of easy description. Nevertheless, all such modifications and reaction products are included within the scope of the present invention; the present invention encompasses the composition prepared by admixing the components described above.

EXAMPLES

[0060] Example 1. A calcium overbased alkylphenol sulfide is manufactured via a process as set forth generally in Example 1 of PCT Publication WO2013/119623 (Lubrizol), August 15, 2013, although typically conducted on a larger, commercial scale, and without the specific stripping step as described therein. That is, as it is generally described in WO2013/119623: to a 3 L four-necked round-bottom flask, equipped with a thermowell and nitrogen inlet, with subsurface sparge tube, a Dean-Stark trap, Friedrichs condenser, and a scrubber, is charged 501.0 g para-dodecylphenol (PDDP). The PDDP is heated to 100 °C and 59.6 g hydrated lime and 22.7 g ethylene glycol are added. The temperature is increased to 121 °C and 163.9 g sulfur is added. The mixture

is heated over the course of 20 minutes to 215 °C and maintained at that temperature for an additional 6 hours, at which time 123.3 g diluent oil is added and the reaction is allowed to cool. During this reaction, 32.9 g distillate is collected from the reactor.

[0061] The material in the reactor is heated to 135 °C, and 204.4 g hydrated lime,

5 138.2 g ethylene glycol, 43.3 g alkylbenzenesulfonic acid, and 173.5 g decyl alcohol are added. The mixture is heated to 168 °C and maintained at that temperature for 10 minutes, until liquid is no longer readily distilling. Flow of carbon dioxide is begun at 17-25 L/hr (0.6-0.9 ft³/hr) and continued for 4 hours.

[0062] Volatile materials are removed from a commercial-scale product correspond-
10 ing to Example 1, above, by the stripping process described either in Example 2 or Reference Example 3, below:

[0063] Example 2. A batch of carbon dioxide-treated material is stripped by circu-
lating the batch, originating in a feed tank, through an external heat exchanger and then
a flash tank, and finally back to the feed tank, for a period of time referred to as “strip-
15 back.” During the strip-back, the external heat exchanger batch exit temperature target
it 218-238°C. Heat is also applied directly to the stripper feed tank throughout the strip-
back phase, until the batch reaches a target temperature of 218-226°C. The flash tank is
operated at a target pressure of 8-16 kPa (60-120 mm Hg absolute), with a residence
time of approximately 3 minutes. Flow through the flash tank provides 2 to 3 volumet-
20 ric turnovers of the batch through the flash tank during the strip-back phase, over
approximately 6 hours. Thereafter, the liquid outflow from the flash tank is redirected
to a filter-feed tank, with stripping conditions otherwise maintained. Throughout the
stripping process, steam is fed to the flash tank via a sub-surface inlet line, at an approx-
imately uniform rate, targeting delivery of approximately 18 parts by weight total steam
25 (based on 100 parts by weight of initial alkylphenol reactant, before sulfur coupling and
neutralization/overbasing). The batch is filtered by use of 1 weight% filter aid (FAUC).

[0064] Example 3 (Reference). A batch of carbon dioxide-treated material is
stripped as described in Example 2, except that no steam is fed to the flash tank at any
time. The batch is filtered by use of 3.5 weight % filter aid (FAUC).

30 [0065] Each of the documents referred to above is incorporated herein by reference,
including any prior applications, whether or not specifically listed above, from which
priority is claimed. The mention of any document is not an admission that such docu-
ment qualifies as prior art or constitutes the general knowledge of the skilled person in

any jurisdiction. 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." It is to be understood that the upper and lower amount, range, and ratio limits set forth herein may be independently combined. Similarly, the ranges and amounts for each element of the invention can be used together with ranges or amounts for any of the other elements.

[0066] As used herein, the transitional term "comprising," which is synonymous with "including," "containing," or "characterized by," is inclusive or open-ended and does not exclude additional, un-recited elements or method steps. However, in each recitation of "comprising" herein, it is intended that the term also encompass, as alternative embodiments, the phrases "consisting essentially of" and "consisting of," where "consisting of" excludes any element or step not specified and "consisting essentially of" permits the inclusion of additional un-recited elements or steps that do not materially affect the essential or basic and novel characteristics of the composition or method under consideration. The expression "consisting of" or "consisting essentially of," when applied to an element of a claim, is intended to restrict all species of the type represented by that element, notwithstanding the presence of "comprising" elsewhere in the claim.

[0067] While certain representative embodiments and details have been shown for the purpose of illustrating the subject invention, it will be apparent to those skilled in this art that various changes and modifications can be made therein without departing from the scope of the subject invention. In this regard, the scope of the invention is to be limited only by the following claims. In certain jurisdictions, recitation of one or more of narrower values for a numerical range or recitation of a narrower selection of elements from a broader list means that such recitations represent preferred embodiments.

4152-01

What is claimed is:

1. A process for preparing a sulfurized alkaline earth metal alkylphenate, comprising:

5 (a) reacting

(i) an alkylphenol, wherein the alkyl group contains about 6 to about 24 carbon atoms, with:

(ii) an alkaline earth metal hydroxide or an alkaline earth metal oxide in an amount of about 0.4 to about 10 moles per mole of alkylphenol charged to the reaction; and

10 (iii) a sulfur source in an amount to provide about 0.8 to about 3 moles sulfur (as S) per mole of alkylphenol charged to the reaction; in the presence of

(iv) an alkylene glycol or dialkylene glycol, or ether thereof, in an amount of about 0.2 to about 2 moles per mole of alkylphenol charged to the reaction; and including in the reaction mixture

15 (v) an oil of lubricating viscosity; and optionally further reacting the product thereof with:

(vi) carbon dioxide; thereby forming a sulfurized alkaline earth metal alkylphenate composition in oil;

20 (b) heating said alkylphenate composition to about 120 to 280°C or 200 to about 250°C;

(c) supplying steam to said alkylphenate composition;

(d) removing said steam under reduced pressure; and

(e) filtering the resulting composition to provide, as the filtrate, a sulfurized alkaline earth metal alkylphenate in oil.

25 2. The process of claim 1 wherein the alkylphenol comprises p-dodecylphenol.

3. The process of claim 1 or claim 2 wherein the alkaline earth metal hydroxide or oxide comprises calcium hydroxide.

30 4. The process of any one of claims 1 to 3 wherein the amount alkaline earth metal hydroxide or oxide is about 1 to about 5 moles per mole of alkylphenol charged to the reaction.

5. The process of any one of claims 1 to 4 wherein the optional further reacting with carbon dioxide in optional step (vi) is conducted.

6. The process of any of claims 1 through 5 wherein the amount of alkaline earth metal hydroxide or oxide is suitable to provide a product with a total base number of about 200 to about 600 on an oil free basis.

7. The process of any of claims 1 through 5 wherein the amount of the alkaline earth metal hydroxide or oxide is suitable to provide a product with a total base number of about 100 to about 350.

8. The process of any one of claims 1 to 7 wherein the sulfur source comprises elemental sulfur and the amount of sulfur is about 1 to about 2.5 moles per mole of alkylphenol charged to the reaction.

9. The process of any one of claims 1 through 8 wherein the alkylene glycol or dialkylene glycol, or ether thereof, comprises ethylene glycol or propylene glycol.

10. The process of any one of claims 1 through 9 wherein the alkylene glycol or dialkylene glycol, or ether thereof, comprises ethylene glycol.

11. The process of any one of claims 1 through 10 wherein the amount of alkylene glycol is about 1.0 to about 1.5 moles per mole of alkylphenol charged to the reaction.

12. The process of any one of claim 1 through 11 wherein the oil of lubricating viscosity comprises a mineral oil.

13. The process of any one of claims 1 through 12 wherein the oil of lubricating viscosity is present at the time of removal of the steam in step (d) in an amount of about 20 to about 60 parts by weight per 100 parts by weight of alkylphenol charged to the reaction.

14. The process of any one of claims 1 through 13 wherein the optional reaction with carbon dioxide is conducted and the amount of carbon dioxide supplied is about 10 to about 50 parts by weight per 100 parts by weight of alkylphenol charged to the reaction.

15. The process of any one of claims 1 through 14 wherein the steam is supplied at superatmospheric pressure and at a temperature of about 120°C to about 250°C.

16. The process of any one of claims 1 through 15 wherein volatile materials are removed along with removal of the steam.

17. The process of any one of claims 1 through 16 wherein the steam is removed at a pressure of about 1.3 to about 53 kPa (10 to 400 mmHg).

18. The process of any one of claims 1 through 17 wherein the amount of steam is about 3 to about 36 parts by weight per 100 parts by weight of alkylphenol charged to the reaction.

19. The process of any one of claims 1 through 18 wherein the filtration employs the use of a filter aid.

20. The product prepared by the process of any of claims 1 through 19.

21. A lubricant composition comprising an oil of lubricating viscosity and the product of claim 20.

22. The lubricant composition of claim 21 further comprising at least one of a supplemental overbased detergent, a dispersant, an antioxidant, a viscosity improver, an anti-wear agent, a pour point depressant, or an extreme pressure agent.

23. A method for lubricating an internal combustion engine, comprising supplying thereto the lubricant composition of claim 21 or claim 22.

24. A method for improving the filterability of an alkaline earth metal in a process comprising (a) reacting

(i) an alkylphenol, wherein the alkyl group contains about 6 to about 24 carbon atoms, with:

(ii) an alkaline earth metal hydroxide or an alkaline earth metal oxide in an amount of about 0.4 to about 10 moles per mole of alkylphenol charged to the reaction; and

(iii) a sulfur source in an amount to provide about 0.8 to about 3 moles sulfur (as S) per mole of alkylphenol charged to the reaction; in the presence of

(iv) an alkylene glycol or dialkylene glycol, or ether thereof, in an amount of about 0.2 to about 2 moles per mole of alkylphenol charged to the reaction; and including in the reaction mixture

(v) an oil of lubricating viscosity; and optionally further reacting the product thereof with:

(vi) carbon dioxide; thereby forming a sulfurized alkaline earth metal alkylphenate composition in oil;

(b) heating said alkylphenate composition to about 120 to 280°C or 200 to about 250°C; said improvement comprising:

(c) supplying steam to said alkylphenate composition; and

(d) removing said steam under reduced pressure; prior to

(e) filtering the resulting composition to provide, as the filtrate, a sulfurized alkaline earth metal alkylphenate in oil.

25. The method of claim 24 wherein the filtering is accomplished by use of a filter aid and the amount of said filter aid used is less than about 3 weight percent based on the final batch yield.

26. The method of claim 25 wherein the amount of filter aid used is about 0.8 to about 2 weight percent based on the final batch yield.

27. A method for reducing the amount of monomeric alkylphenol in the product of a process comprising (a) reacting

(i) an alkylphenol, wherein the alkyl group contains about 6 to about 24 carbon atoms, with:

(ii) an alkaline earth metal hydroxide or an alkaline earth metal oxide in an amount of about 0.4 to about 10 moles per mole of alkylphenol charged to the reaction; and

(iii) a sulfur source in an amount to provide about 0.8 to about 3 moles sulfur (as S) per mole of alkylphenol charged to the reaction; in the presence of

(iv) an alkylene glycol or dialkylene glycol, or ether thereof, in an amount of about 0.2 to about 2 moles per mole of alkylphenol charged to the reaction; and including in the reaction mixture

(v) an oil of lubricating viscosity; and optionally further reacting the product thereof with:

(vi) carbon dioxide; thereby forming a sulfurized alkaline earth metal alkylphenate composition in oil; (b) heating said alkylphenate composition to about 120 to 280°C or 200 to about 250°C; said reduction arising from:

(c) supplying steam to said alkylphenate composition; and

(d) removing said steam under reduced pressure; prior to

(e) filtering the resulting composition to provide, as the filtrate, a sulfurized alkaline earth metal alkylphenate in oil.

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2015/021949

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C10M135/02 C10M159/22 C07G99/00
 ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C10M C07G C10N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2013/119623 A1 (LUBRIZOL CORP [US]; WALKER GARY M [GB]; SOWERBY ROGER L [US]; ROSKI JA) 15 August 2013 (2013-08-15) cited in the application paragraph [0001]; claim 1; example 1 -----	1-27
A	EP 0 601 721 A2 (ETHYL PETROLEUM ADDITIVES INC [US]) 15 June 1994 (1994-06-15) page 2, line 45 - line 48 -----	1-27
A	EP 2 055 761 A2 (CHEVRON ORONITE CO [US]) 6 May 2009 (2009-05-06) paragraph [0055] -----	1-27



Further documents are listed in the continuation of Box C.



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Information on patent family members

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