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(54) **Phenate detergent preparation**

(57) A sulphurised calcium phenate detergent prepared by the following stages:

i) reacting one or more alkyl phenol materials comprising hydrogenated distilled cashew nut shell liquid with first defined amounts of a calcium salt and of a promoter, and with sulphur, in the presence of a process solvent; and
(ii) reacting the product of stage (i) with second defined amounts of the calcium salt and of the promoter and carbonating the product;

the total amount of calcium salt and of promoter being such as to provide a sulphurised phenate of desired TBN, and the first amount of each of the calcium salt and of the promoter in stage (i), relative to its total amount in the method, being less than 50, expressed as a molar percentage.

The sulphurised calcium phenate has a kinematic viscosity at 100°C of greater than 750 and less than 1200 cSt.

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Description**FIELD OF THE INVENTION**

5 **[0001]** This invention relates to making a sulphurised calcium alkyl phenate detergent and to use of the detergent in internal combustion engine lubrication.

BACKGROUND OF THE INVENTION

10 **[0002]** Sulphurised calcium alkyl phenate detergents are well known additive components for internal combustion engine crankcase lubricating oil compositions. However, certain alkylphenol sources (nonylphenol, tetrapropenylphenol) used in their manufacture are classified as reproductive toxins; accordingly, there is a desire to identify other phenol sources.

15 **[0003]** The art describes a way of meeting this problem. Thus, US-A-5,910,468 ('468) describes the preparation of sulphurised calcium alkyl phenate from, as the phenol source, distilled or hydrogenated-distilled cashew nut shell liquid (CNSL). Distilled CNSL is a mixture of biodegradable meta-hydrocarbyl substituted phenols, where the hydrocarbyl group is linear and unsaturated, including cardanol. Catalytic hydrogenation of distilled CNSL gives rise to a mixture of meta-hydrocarbyl substituted phenols predominantly rich in 3-pentadecylphenol.

20 **[0004]** A problem with the process described in '468 is to improve the oxidative stability of the sulphurised calcium alkyl phenate detergents thereby produced.

SUMMARY OF THE INVENTION

25 **[0005]** The above problem is met according to the invention by using hydrogenated distilled CNSL as the phenol source and by making the phenate in a two-stage process in which the amounts of calcium salt and of promoter are controlled.

[0006] The invention provides, in a first aspect, a method of making a sulphurised calcium phenate detergent comprising the stages:

30 (i) reacting one or more alkyl phenol materials comprising hydrogenated distilled cashew nut shell liquid with first defined amounts of a calcium salt (such as calcium oxide or calcium hydroxide) and of an alcohol (such as a mono-, di or poly-hydric alcohol, preferably a 1,2-vicinal diol), and with sulphur, preferably elemental sulphur, in the presence of a solvent; and

35 (ii) reacting the product of stage (i) with second defined amounts of the calcium salt and of the alcohol and carbonating the product;

the total amount of calcium salt and of promoter being such as to provide a sulphurised calcium phenate of desired TBN, and the first amount of each of the calcium salt and of the promoter in stage (i), relative to its total amount in the method, being less than 50, such as less than 30, such as 20 or less, expressed as a molar percentage. Stage (ii) does not include sulphur.

[0007] The invention provides, in a second aspect, a sulphurised calcium phenate detergent obtainable by the method of the first aspect of the invention. The sulphurised calcium phenate detergent has a kinematic viscosity at 100°C of greater than 750 and less than 1200 cSt, preferably greater than 800 to less than 1150 cSt, as measured by ASTM D445.

45 **[0008]** The invention provides, in a third aspect, a lubricating oil composition comprising, in a major amount, an oil of lubricating viscosity and, in a minor amount, a detergent of the second aspect of the invention.

[0009] The invention provides, in a fourth aspect, a lubricating oil composition comprising, in a major amount, an oil of lubricating viscosity and, in a minor amount, a detergent of the second aspect of the invention.

50 **[0010]** The invention provides, in a fifth aspect, a method of operating an internal combustion engine comprising fuelling the engine and lubricating the engine with the lubricating oil composition of the fourth aspect of the invention.

[0011] In this specification, the following words and expressions, if and when used, have the meanings ascribed below:

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

55 "comprising" or any cognate word specifies the presence of stated features, steps, or integers or components, but does not preclude the presence or addition of one or more other features, steps, integers, components or groups thereof; the expressions "consists of" or "consists essentially of" or cognates may be embraced within "comprises" or cognates, wherein "consists essentially of" permits inclusion of substances not materially affecting the charac-

teristics of the composition to which it applies;

"major amount" means 50 mass % or more of a composition, preferably 60 mass % or more, even more preferably 70 mass % or more;

"minor amount" means less than 50 mass % of a composition, preferably less than 40 mass %, even more preferably less than 30 mass %;

"TBN" means total base number as measured by ASTM D2896.

[0012] Furthermore in this specification, if and when used:

"calcium content" is as measured by ASTM D4951;

"phosphorus content" is as measured by ASTM D5185;

"sulphated ash content" is as measured by ASTM D874;

"sulphur content" is as measured by ASTM D2622;

"KV 100" means kinematic viscosity at 100°C as measured by ASTM D445.

[0013] Also, it will be understood that various components used, essential as well as optimal and customary, may react under conditions of formulation, storage or use and that the invention also provides the product obtainable or obtained as a result of any such reaction.

[0014] Further, it is understood that any upper and lower quantity, range and ratio limits set forth herein may be independently combined.

DETAILED DESCRIPTION OF THE INVENTION

Method

[0015] In the method of the invention, note may be made of the following:

Calcium salt and alcohol

[0016] The calcium salt is preferably calcium oxide or calcium hydroxide; the alcohol, which is also known as the promoter, has the function of phase transferring the calcium from the solid phase into the liquid organic phase and is preferably a mono-, di- or poly-hydric alcohol, such as a 1, 2-vicinal diol, for example ethylene glycol.

[0017] The total amount of calcium salt and of alcohol used must be such as to provide a sulphurised calcium phenate of desired TBN. To provide a detergent of improved oxidative stability, the first amounts (i.e. in stage (i)) of each of the calcium salt and of the promoter, relative to their respective total amounts, are less than 50, such as less than 30, such as 20 or less, expressed as molar percentages. Preferably, the first amounts of each of the calcium salt and of the alcohol, expressed as molar percentages of their total amounts, are not less than 5 such as not less than 10.

Alkyl phenol materials

[0018] A characteristic structural feature of the alkyl phenol materials used in the invention is meta hydrocarbyl-substitution of the aromatic ring where the substituent is attached to the ring at its first (C1) carbon atom. This structural feature is not available by chemical alkyl phenol synthesis such as the Friedel-Crafts reaction of phenol with olefins. The latter typically gives mixtures of ortho and para alkyl phenols (but only around 1% of meta alkyl phenols), and where attachment of the alkyl group to the aromatic ring is at the second (C2) or higher carbon atom.

[0019] Cardanol, the product obtained by distilling technical CNSL, typically contains 3-pentadecylphenol (3%); 3-(8-pentadecenyl) phenol (34-36 %); 3-(8, 11-pentadecadienyl) phenol (21-22%); and 3-(8, 11, 14-pentadecatrienyl) phenol (40-41%), plus a small amount of 5-(pentadecyl) resorcinol (c. 10%), also referred to as cardol. Technical CNSL contains mainly cardanol plus some polymerized material. Cardanol may therefore be expressed as containing significant amounts of meta-linear hydrocarbyl substituted phenol, where the hydrocarbyl group has the formula $C_{15}H_{25-31}$ and is attached to the aromatic ring at its first carbon atom (C1).

[0020] Thus, both cardanol and technical CNSL contain significant quantities of material having long linear unsaturated side chains and only small quantities of material with long linear saturated side chains. The present invention employs material where a major proportion, preferably all of the phenol, contains material with long linear saturated side chains. Such latter material is obtainable by hydrogenating cardanol; a preferred example is 3-(pentadecyl) phenol, where the pentadecyl group is linear and is attached to the aromatic ring at its first carbon atom. It may constitute 50 or more, 60 or more, 70 or more, 80 or more, or 90 or more, mass % of the additive of the invention. It may contain small quantities of 3-(pentadecyl) resorcinol. The invention does not include technical CNSL.

Carboxylic acid or anhydride (co-surfactant)

[0021] The method may be carried out in the presence of a carboxylic acid or anhydride (which is also known as a co-surfactant) such as a long chain carboxylic acid (e.g. stearic acid or lauric acid, oleic acid or alkylsalicylic acid) or the related esters; a long chain carboxylic amide (e.g. tallow amine); a long chain ethoxylated amine; a phenol or alkyl phenol or methylene bridged alkyl phenol; a hydrocarbyl substituted anhydride or succinic anhydride (e.g. polyisobutene succinic anhydride); or a long chain alkylaryl sulphonic acid.

[0022] The carboxylic acid or anhydride (co-surfactant) may be present in the range of 1-20, such as 4-12, such as 4-10, such as 4-8, preferably 6-8, mass % based on the total mass of alkyl phenol. Preferably, the carboxylic acid or anhydride (co-surfactant) is provided in step (ii) to avoid the possibility of its adverse interaction with elemental sulphur in step (i).

Solvent

[0023] Process solvents are added to the reaction mixture in order to decrease viscosity of the reaction mixture during synthesis. As is known by those skilled in the art, lowering the viscosity allows improved dispersion of carbon dioxide in the reaction mixture therefore promoting efficient carbonation. These solvents are typically high boiling (>140°C) and unreactive under the conditions used. Examples include isodecanol, cyclohexanol and 2-ethylhexanol.

Carbonation Temperature

[0024] Carbonation is preferably effected at temperatures of greater than 100°C. Carbonation preferably takes place at temperatures from 120 to 210°C, more preferably from 140 to 190°C, most preferably from 150 to 180°C and even most preferably from 160 to 175°C.

Lubricating Oil Composition

[0025] An oil of lubricating viscosity provides a major proportion of the composition and may be any oil suitable for lubricating an internal combustion engine.

[0026] It may range in viscosity from light distillate mineral oils to heavy lubricating oils. Generally, the viscosity of the oil ranges from 2 to 40 nm²/sec, as measured at 100°C.

[0027] Natural oils include animal oils and vegetable oils (e.g., castor oil, lard oil); liquid petroleum oils and hydrorefined, solvent-treated or acid-treated mineral oils of the paraffinic, naphthenic and mixed paraffinic-naphthenic types. Oils of lubricating viscosity derived from coal or shale also serve as useful base oils.

[0028] Synthetic lubricating oils include hydrocarbon oils and halo-substituted hydrocarbon oils such as polymerized and interpolymerized olefins (e.g., polybutylenes, polypropylenes, propylene-isobutylene copolymers, chlorinated polybutylenes, poly(1-hexenes), poly(1-octenes), poly(1-decenes)); alkybenzenes (e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di(2-ethylhexyl)benzenes); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenols); and alkylated diphenyl ethers and alkylated diphenyl sulphides and derivative, analogues and homologues thereof.

[0029] Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc., constitute another class of known synthetic lubricating oils. These are exemplified by polyoxyalkylene polymers prepared by polymerization of ethylene oxide or propylene oxide, and the alkyl and aryl ethers of polyoxyalkylene polymers (e.g., methyl-polyiso-propylene glycol ether having a molecular weight of 1000 or diphenyl ether of poly-ethylene glycol having a molecular weight of 1000 to 1500); and mono- and polycarboxylic esters thereof, for example, the acetic acid esters, mixed C3-C8 fatty acid esters and C 13 oxo acid diester of tetraethylene glycol.

[0030] Another suitable class of synthetic lubricating oils comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids and alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkylmalonic acids, alkenyl malonic acids) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether,

propylene glycol). Specific examples of such esters includes 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.

[0031] Esters useful as synthetic oils also include those made from C5 to C12 monocarboxylic acids and polyols and polyol esters such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol and tripentaerythritol.

[0032] Silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy- or polyaryloxysilicone oils and silicate oils comprise another useful class of synthetic lubricants; such oils include tetraethyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl)silicate, tetra-(4-methyl-2-ethylhexyl)silicate, tetra-(p-tert-butyl-phenyl) silicate, hexa-(4-methyl-2-ethylhexyl)disiloxane, poly(methyl)siloxanes and poly(methylphenyl)siloxanes. Other synthetic lubricating oils include liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, diethyl ester of decylphosphonic acid) and polymeric tetrahydrofurans.

[0033] Unrefined, refined and re-refined oils can be used in lubricants of the present invention. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. For example, a shale oil obtained directly from retorting operations; petroleum oil obtained directly from distillation; or ester oil obtained directly from esterification and used without further treatment, are unrefined oils. Refined oils are similar to unrefined oils except that the oil is further treated in one or more purification steps to improve one or more properties. Many such purification techniques, such as distillation, solvent extraction, acid or base extraction, filtration and percolation, are known to those skilled in the art. Re-refined oils are obtained by processes similar to those used to provide refined oils but begin with oil that has already been used in service. Such re-refined oils are also known as reclaimed or reprocessed oils and are often subjected to additional processing using techniques for removing spent additives and oil breakdown products.

[0034] The American Petroleum Institute (API) publication "Engine Oil Licensing and Certification System", Industry Services Department, Fourteenth Edition, December 1996, Addendum 1, December 1998 categorizes groups of base stocks. As an example of an oil of lubricating viscosity that may be used in a lubricating oil composition of the present invention, there may be mentioned an oil containing 50 mass % or more of a basestock containing greater than or equal to 90 % saturates and less than or equal to 0.03% sulphur or a mixture thereof. Preferably, it contains 60, such as 70, 80 or 90, mass % or more of said basestock or a mixture thereof. The oil of lubricating viscosity may consist or substantially consist of said basestock or a mixture thereof.

[0035] Oil of lubricating viscosity may provide 50 mass% or more of the composition. Preferably, it provides 60, such as 70, 80 or 90, mass % or more of the composition.

[0036] The lubricating oil composition may, for example, be a marine diesel cylinder lubricant ("MDCL") or a trunk piston engine oil ("TPEO").

Engines

[0037] The phenates of the invention may be used in lubricants for a range of internal combustion engines (spark-ignited or compression-ignited) such as motor vehicle engines and marine engines. Of the latter, there may be mentioned two-stroke marine diesel cross-head engines and marine trunk piston engines.

EXAMPLES

[0038] The present invention is illustrated by but in no way limited to the following examples.

Preparation of calcium phenate detergent

[0039] The general process was as tabulated and described below:

<u>Process description</u>	<u>Process detail</u>
Sulphurisation temperature	140-190°C
Sulphurisation time	2-8 hours
Carbonation temperature	160-175°C
Carbonation time	2-10 hours
Sulphur source	S ₈
Sulphur charge	0.20 moles S ₈ / CNSL molecule (1.60 moles S / CNSL molecule)
Ca salt	CaO
TOTAL Ca CHARGE (≡CNSL*)	1.43 moles

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(continued)

<u>Process description</u>	<u>Process detail</u>
Promoter	ethylene glycol (EG)
TOTAL PROMOTER CHARGE (=CNSL)	2.60 moles
Promoter addition temperature (stage (i))	140°C
CO ₂ charge	125 mole% (= Ca salt)
Oil	150N mineral oil
Oil charged for synthesis (=CNSL)	22 mass%
Reaction solvent	isodecanol
Co-surfactant	stearic acid

(* means with respect to the total hydrogenated CNSL charge, i.e. for each mole of CNSL material used, 1.43 moles of the calcium source were added)

Step (i)

[0040] Hydrogenated distilled CNSL (ex Sigma Aldrich, Cardolite Corporation or synthesized from cardanol sourced from various providers) is sulphurised using elemental sulphur (added in one or two steps) in the presence of calcium oxide, solvent and ethylene glycol.

Step (ii)

[0041] Further ethylene glycol, calcium oxide (such as to provide the required TBN), a co-surfactant and CO₂ are added to the reaction mixture of step (i).

[0042] The synthesis is completed by vacuum distillation, filtration or centrifugation, and, if necessary, dilution in oil.

[0043] The product was filtered, and diluted to the required TBN with base oil if necessary.

[0044] A set of calcium phenate detergents was prepared employing various charges of ethylene glycol promoter and of Ca in each of steps (i) and (ii).

Tests

[0045] The above calcium phenate detergents were blended into otherwise identical marine lubricant formulations (each to contain 9.125 mass % of the detergent), which were subjected to the following test.

Differential Scanning Calorimetry (pDSC) - [European method no: CECL-85-T-99].]

[0046] The test method is performed as follows; ramp at 40°C/min from 50°C to 210°C under an atmosphere of air (100psi and zero flow) then hold at that temperature for up to 2 hours. Open Seiko Aluminium pans are used.

[0047] This measures oil induction time and indicates oxidative stability: a higher value indicates a better result. The results are set out in the table below.

Example	% EG and Ca (step (i))	% EG and Ca (step (ii))	Kinematic Viscosity (cSt) at 100 °C	pDSC (mins)
1	30	70	919	93.7
2	50	50	1084	82.8
A (comparative)	70	30	707	74.5
B (comparative)	100	0	346	75.3

- The percentages are molar percentages; equal molar proportions of EG and Ca were present.
- Examples 1 and 2 are examples of the invention, and Examples A and B are reference examples that are for comparative purposes only.

[0048] The results demonstrate that the use of lower amounts of alcohol and calcium in step (i) in Examples 1 and 2 noticeably increased oxidative stability in comparison with the reference examples (A and B) which included greater than 50% of the total alcohol and calcium in step (i).

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Claims

1. A method of making a sulphurised calcium phenate detergent comprising the steps of:

10 (i) reacting one or more alkyl phenol materials comprising hydrogenated distilled cashew nut shell liquid with first defined amounts of a calcium salt (such as calcium oxide or calcium hydroxide) and of an alcohol, with sulphur, preferably elemental sulphur, in the presence of a solvent; and
 (ii) reacting the product of step (i) with second defined amounts of the
 15 calcium salt and of the alcohol and carbonating the product;
 the total amount of calcium salt and of alcohol being such as to provide a sulphurised calcium phenate of desired TBN; and wherein the first amount of each of the calcium salt and of the alcohol in step (i), relative to its total amount in the method, being less than 50, preferably less than 30, more preferably 20 or less, expressed as a molar percentage.

20 2. The method of claim 1, wherein step (ii) is carried out in the absence of sulphur.

3. The method of claims 1 or 2, wherein the alcohol is a mono-, di- or poly-hydric alcohol, preferably a 1,2-vicinal diol.

25 4. The method of any one of the preceding claims wherein the molar percentage of the first amount of each of the calcium salt and of the alcohol is not less than 5 such as not less than 10.

5. The method of any one of the preceding claims wherein the calcium salt is calcium oxide or calcium hydroxide.

30 6. The method of any one of the preceding claims wherein the alkyl phenol material comprises 3-pentadecylphenol.

7. The method of any one of the preceding claims carried out in the presence of a carboxylic acid or anhydride.

8. The method of claim 7, wherein the carboxylic acid or anhydride is stearic acid or a polyisobutene succinic anhydride.

35 9. A sulphurised calcium phenate detergent obtainable by the method of any one of claims 1-8, the sulphurised calcium phenate detergent having a kinematic viscosity at 100°C of greater than 750 and less than 1200 cSt, preferably greater than 800 and less than 1150 cSt, as measured by ASTM D445.

40 10. Use of the detergent of claim 9 in a marine crankcase lubricant.

11. Use of the detergent of claim 9 in a marine crankcase lubricant to improve the oxidative stability of the lubricant as measured using Differential Scanning Calorimetry (pDSC) (European method no. CECIL-85-T-99) in comparison with that of a lubricant containing a detergent made by a single-stage calcium salt addition process.

45 12. A lubricating oil composition comprising, in a major amount, an oil of lubricating viscosity and, in a minor amount, a detergent of claim 9.

50 13. The lubricating oil composition of claim 12, wherein the oil of lubricating viscosity contains 50 mass % or more of a basestock containing greater than or equal to 90 % saturates and less than or equal to 0.03 % sulphur or a mixture thereof.

14. The lubricating oil composition of claim 12 or claim 13 in the form of a marine diesel cylinder lubricant.

55 15. The lubricating oil composition of claim 12 or claim 13 in the form of a marine diesel trunk piston engine oil.

16. A method of operating an internal combustion diesel engine comprising fuelling the engine, and lubricating the engine with a lubricating oil composition of any of claims 12-15.



EUROPEAN SEARCH REPORT

Application Number
EP 13 18 5404

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X,D	US 5 910 468 A (DOHHEN KHEM CHAND [IN] ET AL) 8 June 1999 (1999-06-08)	9-16	INV. C10M159/22
Y	* claims 1,3 *	1-8	C10M177/00
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X	----- US 6 339 052 B1 (DOHHEN KHEM CHAND [IN] ET AL) 15 January 2002 (2002-01-15) * paragraphs [0012], [0013], [0028] *	1-16	
Y	----- US 5 244 588 A (KOSHIMA HIROAKI [JP] ET AL) 14 September 1993 (1993-09-14) * column 3, lines 21-23; examples 1,3 *	1-8	

			TECHNICAL FIELDS SEARCHED (IPC)
			C10M
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 3 December 2013	Examiner Bertrand, Samuel
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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03-12-2013

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REFERENCES CITED IN THE DESCRIPTION

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