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(54) Title: LUBRICATING COMPOSITIONS CONTAINING SULPHONATES

(57) Abstract: A lubricating composition containing (a) a detergent package containing (i) an oligomeric reaction product of (1) a hydrocarbyl-substituted phenol; (2) an aldehyde; and (3) a carboxyl-substituted phenol or a carboxyl-substituted phenylamine; and salts of the reaction product; (ii) a sulphonate; and (iii) optionally a phenate; (b) a dispersant; and (c) an oil of lubricating viscosity, wherein the sulphonate detergent is overbased with a metal ratio of about 12.5:1 to about 40:1. The composition is suitable for internal combustion engines, particularly marine diesel applications to provide improved cleanliness properties, antiwear performance or deposit control.



WO 2006/041810 A1

TITLE

Lubricating Compositions Containing Sulphonates

FIELD OF INVENTION

5           The present invention relates to a lubricating composition containing a detergent package a dispersant and an oil of lubricating viscosity. The invention further relates to the use of the lubricating composition in marine diesel cylinder lubricants.

BACKGROUND OF THE INVENTION

10   **[0001]**   It is known to add various additives to an oil of lubricating viscosity for diesel or gasoline engines to reduce wear and improve cleanliness. In diesel engines an oil of lubricating viscosity is used particularly to reduce wear of cylinder liners and piston rings. Often engine operating temperatures and pressures are sufficient to break down the film of the oil of lubricating viscosity  
15   on the internal walls of the cylinder. As a consequence of this, the cylinder experiences increased wear and decreased engine cleanliness due to deposits. Formation of high levels of deposits around the piston rings can also result in excessive wear.

**[0002]**   International Publication WO 03/018728 A1 (Moreton et al.)  
20   discloses a lubricating composition containing a metal salt of linear compounds containing phenolic and salicylic units or derivatives thereof. The lubricating composition may also contain an ashless dispersant and a zinc dithiophosphate.

**[0003]**   US Patent 6,277,794, Dunn, discloses the use of a marine diesel engine lubricant composition containing (a) an overbased metal detergent  
25   having a TBN of at least 300 and/or (b) a metal detergent other than component (a), provided that if detergent (b) is present the composition does not contain a minor amount of an extreme pressure additive; and (c) ashless antiwear additives; and (d) an oil of lubricating viscosity.

**[0004]**   US Patent 6,339,051, Carey et al., discloses diesel cylinder oils with  
30   improved cleanliness and load carrying capabilities by using an additive package containing at least one detergent, an antioxidant, an antiwear agent and

a dispersant. The detergent component contains at least one of an overbased phenate, phenylate, salicylate or sulphonate.

[0005] US Patent 6,376,434, Katafuchi, discloses lubricating oil compositions for diesel engines containing at least one of (a) overbased  
5 sulphonate, overbased phenates and overbased salicylates; and (b) a bis-type succinic imide compound.

[0006] US Patent 6,551,965, Nagamatsu, discloses a marine diesel lubricating oil composition containing an overbased alkyl sulphonate detergent and an overbased sulphurised alkylphenate detergent. The overbased  
10 sulphurised alkylphenate has a TBN of 110 or more.

[0007] British Patent application GB 2,328,217A discloses marine diesel lubricating oil compositions containing a polyalkylene succinimide compound for improving anti-wear. The lubricating oil composition can further include up to 6% of at least one highly overbased detergent selected from alkyl or alkenyl  
15 phenates, alkyl or alkenyl phenate-carboxylates, alkyl or alkenyl aromatic sulphonates; and mixtures thereof.

[0008] European Patent application EP 1,086,960 discloses a lubricating oil composition containing novel succinimide compounds and at least one detergent selected from overbased sulphonates, phenates and salicylates of alkaline earth  
20 metals.

[0009] It would be advantageous to have a lubricating composition with at least one of cleanliness properties, antiwear performance and deposit control. The present invention provides a lubricating composition with at least one of cleanliness properties, antiwear performance and deposit control.

## 25 SUMMARY OF THE INVENTION

[0010] The present invention provides a lubricating composition comprising:

(a) a detergent package comprising:

(i) an oligomeric reaction product of (1) a hydrocarbyl-substituted phenol; (2) an aldehyde; and (3) a carboxyl-substituted phenol  
30 or a carboxyl-substituted phenylamine; or a salt of the reaction product;

(ii) a sulphonate; and

(iii) optionally a phenate;

(b) a optionally dispersant; and

(c) an oil of lubricating viscosity,

wherein the sulphonate detergent is overbased with a metal ratio of about 12.5:1 to about 40:1.

**[0011]** The invention further provides a process to prepare a lubricating composition comprising mixing:

(a) a detergent package comprising:

(i) an oligomeric reaction product of (1) a hydrocarbyl-substituted phenol; (2) an aldehyde; and (3) a carboxyl-substituted phenol or a carboxyl-substituted phenylamine; or a salt of the reaction product;

(ii) a sulphonate; and

(iii) optionally a phenate;

(b) optionally a dispersant; and

(c) an oil of lubricating viscosity,

wherein the sulphonate detergent is overbased with a metal ratio of about 12.5:1 to about 40:1.

**[0012]** The invention further provides a method for lubricating an internal combustion engine, comprising supplying thereto a lubricant comprising the composition as described herein.

#### DETAILED DESCRIPTION OF THE INVENTION

**[0013]** The present invention provides a lubricating composition comprising:

(a) a detergent package comprising:

(i) an oligomeric reaction product of (1) a hydrocarbyl-substituted phenol; (2) an aldehyde; and (3) a carboxyl-substituted phenol or a carboxyl-substituted phenylamine; or a salt of the reaction product;

(ii) a sulphonate; and

(iii) optionally a phenate;

(b) optionally a dispersant; and

(c) an oil of lubricating viscosity,

wherein the sulphonate detergent is overbased with a metal ratio of about 12.5:1 to about 40:1.

[0014] The total base number (TBN) of the lubricating composition in one embodiment is 30 or higher, in another embodiment 40 or higher, in another embodiment 50 or higher and in another embodiment 60 or higher. Examples of the TBN of the lubricating composition include 65, 70, 75 or 80.

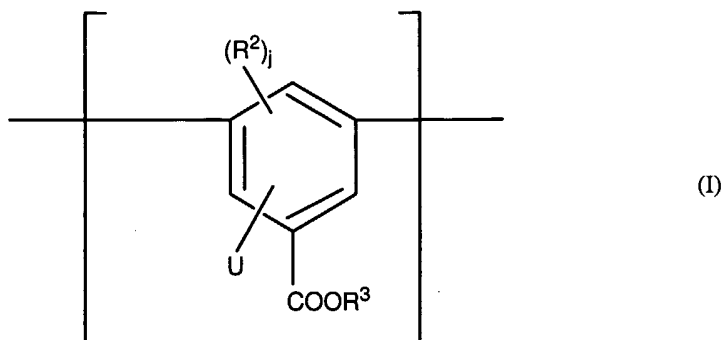
Oligomeric Reaction Product

[0015] The invention includes an oligomeric reaction product of (1) a hydrocarbyl-substituted phenol; (2) an aldehyde; and (3) a carboxyl-substituted phenol or a carboxyl-substituted phenylamine; or a salt of the reaction product. The oligomeric reaction product is a detergent. In one embodiment the oligomeric reaction product is a metal salt and in another embodiment the oligomeric product is metal-free. The oligomeric reaction product is commercially available from The Lubrizol Corporation.

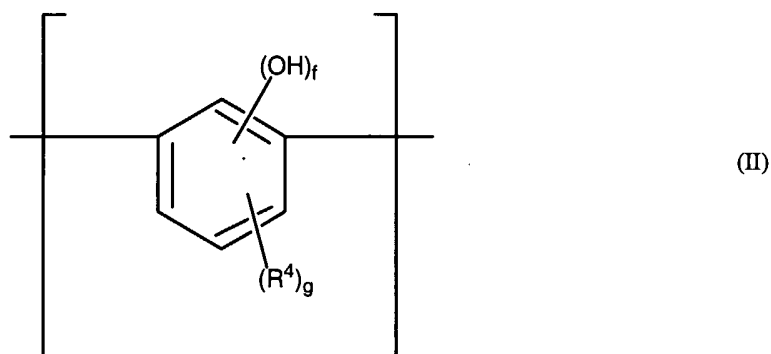
[0016] The hydrocarbyl-substituted phenol in one embodiment contains an alkyl group containing 1 to 60 carbon atoms, in another embodiment 4 to 50 carbon atoms, in another embodiment 6 to 40 carbon atoms and in another embodiment 7 to 30 carbon atoms, for instance 10, 12, 14 or 16. The alkyl substituent is often derived from a polyolefin which may be a homopolymer from one olefin monomer or a copolymer from a mixture of two or more olefin monomers. The molecular weight Mw of the homopolymer and/or copolymer in one embodiment is 250 to 5000, in another embodiment 350 to 3000 and in another embodiment 450 to 2000, for instance 550, 1000 or 1600. The olefin monomer may be an alpha-olefin, an internal olefin, or a polyene and includes ethylene, propylene, butene isomers, pentene isomers, decene isomers, and dienes. Useful polyolefins are polypropylenes and polyisobutylenes. Methods to prepare the polyolefins and the alkylphenols via alkylation of phenol with olefins or polyolefins are well known.

[0017] The aldehyde in one embodiment has 1 to 6 carbon atoms and in another embodiment 1 to 3 carbon atoms. The aldehyde may be formaldehyde in one of its reactive forms such as formalin or paraformaldehyde.

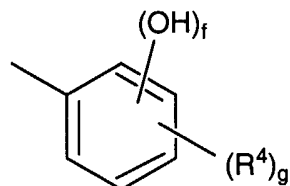
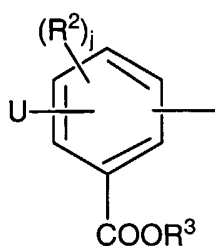
[0018] The oligomeric reaction product in one embodiment is represented by a substantially linear compound comprising at least one unit of the formulae (I) or (II):



5 or



each end of the compound having a terminal group of formulae (III) or (IV):



such groups being linked by divalent bridging groups, which may be the same or different for each linkage; wherein in formulas (I)-(IV)  $f$  is 1, 2 or 3, in one embodiment 1 or 2;  $U$  is  $-OH$ ,  $-NH_2$ ,  $-NHR^1$ ,  $-N(R^1)_2$  or mixtures thereof,  $R^1$  is a hydrocarbyl group containing 1 to 5 carbon atoms;  $R^2$  is hydroxyl or a hydrocarbyl group and  $j$  is 0, 1, or 2;  $R^3$  is hydrogen or a hydrocarbyl group;  $R^4$  is a hydrocarbyl group or a substituted hydrocarbyl group;  $g$  is 1, 2 or 3, provided at least one  $R^4$  group contains 8 or more carbon atoms; and wherein

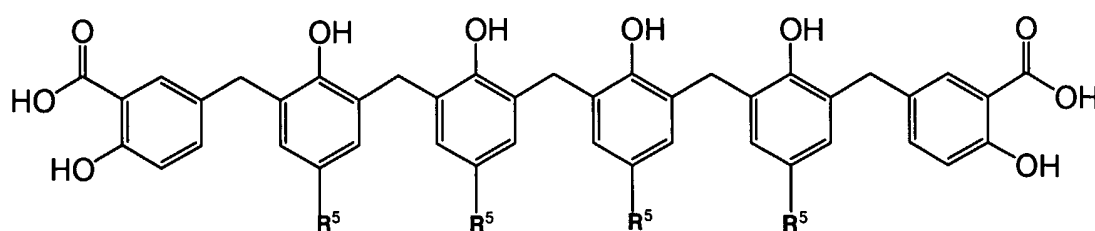
the molecules on average contain at least one of unit (I) or (III) and at least one of unit (II) or (IV) and the ratio of the total number of units (I) and (III) to the total number of units of (II) and (IV) in the composition is about 0.1:1 to about 2:1.

5    **[0019]**    The U group in formulae (i) and (iii) may be located in one or more positions ortho, meta, or para to the  $-\text{COOR}^3$  group. In one embodiment the U group is located ortho to the  $-\text{COOR}^3$  group. When the U group is a  $-\text{OH}$  group, formulae (i) and (iii) are derived from 2-hydroxybenzoic acid (often called salicylic acid), 3-hydroxybenzoic acid, 4-hydroxybenzoic acid or mixtures  
10    thereof. When U is a  $-\text{NH}_2$  group, formulae (i) and (iii) are derived from 2-aminobenzoic acid (often called anthranilic acid), 3-aminobenzoic acid, 4-aminobenzoic acid or mixtures thereof.

15    **[0020]**    The divalent bridging group, which may be the same or different in each occurrence, includes  $-\text{CH}_2-$  (methylene bridge) and  $-\text{CH}_2\text{OCH}_2-$  (ether bridge), either of which may be derived from an aldehyde such as formaldehyde or a formaldehyde equivalent (e.g., paraform, formalin), ethanal or propanal.

20    **[0021]**    In one embodiment the oligomeric reaction product is a metal salt and the metal is often mono-valent, di-valent or mixtures thereof. In one embodiment the metal is an alkali metal or alkaline earth metal such as magnesium, calcium, potassium or sodium. In one embodiment the metal is magnesium, in another embodiment calcium and in another embodiment potassium. When the oligomeric reaction product is a metal salt the product is often referred to as a salixarate or metal salixarate. In one embodiment the oligomeric reaction product contains a metal and in an amount sufficient to  
25    neutralise the product. In one embodiment the oligomeric reaction product contains metal present in an amount sufficient to overbase the product. In one embodiment the oligomeric reaction product contains the organic compound represented by formulae (I) or (II) as defined above.

30    **[0022]**    It is believed that a significant fraction of oligomeric reaction product molecules (prior to neutralisation) may be represented on average by the following formula:



(V)

wherein each  $R^5$  can be the same or different, and are hydrogen or an alkyl group, provided at least one  $R^5$  is alkyl. In a one embodiment,  $R^5$  is a polyisobutene group (especially of molecular weight 200 to 1,000, or 550).

5 Significant amounts of di-or trinuclear species may also be present containing one salicylic end group of formula (III).

[0023] The oligomeric reaction product and derivatives thereof are described in greater detail in U.S. patent number 6,200,936 and PCT Publications WO 01/56968 and WO 03/18728. In one embodiment the oligomeric reaction product additionally provides antiwear performance.

[0024] The oligomeric reaction product is present at in one embodiment at 0.01 to 15, in another embodiment 0.05 to 10, in another embodiment 0.1 to 8 and another embodiment 0.2 to 5 weight percent of the lubricating composition.

#### Overbased Sulphonate Detergent

15 [0025] The invention further includes a sulphonate detergent. The sulphonate detergent of the composition includes compounds represented by the formula:



wherein each  $R^6$  is a hydrocarbonyl group in one embodiment containing 6 to 40 carbon atoms, in another embodiment 8 to 25 carbon atoms and in another embodiment 9 to 20 carbon atoms; A may be independently a cyclic or acyclic hydrocarbon group; M is hydrogen, a valence of a metal ion, an ammonium ion or mixtures thereof; and k is an integer of 0 to 5, for example 0, 1, 2, 3, 4, 5. In one embodiment k is 1, 2 or 3, in another embodiment 1 or 2 and in another embodiment 1. In non-overbased precursors of the sulfonate detergent, M can be hydrogen and be present, for example, on less than 30%, in another embodiment less than 20%, in another embodiment less than 10% and in another embodiment less than 5% of the available M entities. When the sulfonate



detergent is overbased, most or substantially all of the M entities will represent metal ions.

[0026] In one embodiment k is 1 and R<sup>6</sup> is a branched alkyl group with 6 to 40 carbon atoms. In one embodiment k is 1 and R<sup>6</sup> is a linear alkyl group with 6 to 40 carbon atoms.

[0027] Examples of suitable sulphonic acids capable of forming the overbased sulphonate detergent include polypropene benzene sulphonic acid, undecyl benzene sulphonic acid, dodecyl benzene sulphonic acid, tridecyl benzene sulphonic acid, tetradecyl benzene sulphonic acid, pentadecyl benzene sulphonic acid, hexadecyl benzene sulphonic acid and mixtures thereof. In one embodiment the sulphonic acid includes undecyl benzene sulphonic acid, dodecyl benzene sulphonic acid, tridecyl benzene sulphonic acid, tetradecyl benzene sulphonic acid, octadecyl benzene sulphonic acid, tetraeicosyl benzene sulphonic acid or mixtures thereof. In one embodiment of the invention the sulphonic acid is a polypropene benzene sulphonic acid, where the polypropene often contains 18 to 30 carbon atoms.

[0028] In one embodiment of the invention the sulphonate components are calcium polypropene benzenesulphonate and calcium monoalkyl and dialkyl benzenesulphonates wherein the alkyl groups contain at least 10 carbons, for example 11, 12, 13, 14, or 15 carbon atoms.

[0029] When M is a valence of a metal ion, the metal may be monovalent, divalent, trivalent or mixtures of such metals. When monovalent, the metal M includes an alkali metal such as lithium, sodium, or potassium and when divalent, the metal M includes an alkaline earth metal such as magnesium, calcium or barium. When trivalent, the metal M may be aluminium. In one embodiment the metal is an alkaline earth metal. In one embodiment the metal is calcium.

[0030] When A is a cyclic hydrocarbon group, suitable groups include phenyl or fused bicyclic groups such as naphthalene, indenyl, indanyl, bicyclopentadienyl or mixtures thereof. In one embodiment A is a benzene ring.

[0031] When A is an acyclic hydrocarbon group, the carbon chain may be linear or branched. In one embodiment A is an acyclic linear hydrocarbon

group. Suitable groups include derivatives of carboxylic acids containing 7 to 30 carbon atoms, in another embodiment 7 to 20 carbon atoms, in another embodiment 8 to 20 carbon atoms and in another embodiment 8 to 15 carbon atoms. Further the chain may be saturated or unsaturated.

5 [0032] The overbased sulphonate detergent in one embodiment has a TBN (total base number) of at least 350, in another embodiment at least 400, in another embodiment at least 425, in another embodiment at least 450 and in another embodiment at least 475. In one embodiment the overbased sulphonate detergent has a TBN of 400 or 500.

10 [0033] The sulphonate detergent is present in one embodiment at 0.1 to 35, in another embodiment 2 to 30, in another embodiment 5 to 25 and in another embodiment 10 to 25 weight percent of the lubricating composition.

#### Overbasing the Detergent

[0034] In one embodiment the detergents of (i) or (ii) or both are overbased.

15 Overbased materials, otherwise referred to as overbased or superbased salts, are generally single phase, homogeneous Newtonian systems characterised by a metal content in excess of that which would be present for neutralisation according to the stoichiometry of the metal and the particular acidic organic compound reacted with the metal. The overbased materials are prepared by

20 reacting an acidic material (typically an inorganic acid or lower carboxylic acid, often carbon dioxide) with a mixture comprising an acidic organic compound, a reaction medium comprising at least one organic solvent and promoter such as phenol or a mixture of alcohols. A mixture of alcohols typically contains methanol and at least one alcohol with 2 to 7 carbon atoms, and may contain 50-

25 60 mole percent methanol. The acidic material will normally have a sufficient number of carbon atoms to provide a degree of solubility in oil. The amount of excess metal is commonly expressed in terms of substrate to metal ratio. The term "substrate to metal ratio" is the ratio of the total equivalents of the metal to the equivalents of the substrate. An overbased sulphonate detergent in one

30 embodiment has a metal ratio of 12.5:1 to 40:1, in another embodiment 13.5:1 to 40:1, in another embodiment 14.5:1 to 40:1, in another embodiment 15:1 to 40:1; in another embodiment 15.5:1 to 40:1 and in another embodiment 16.5:1

to 40:1. Furthermore the overbased sulphonate detergent often has a low in-process viscosity and a low final viscosity.

[0035] A sulphonate detergent with 500 TBN and its preparation are disclosed in U.S. Patent 5,792,732. In Example 2 thereof, a 500 TBN all-linear alkylbenzene sulphonate is prepared by reacting an alkyl benzene sulphonate from Witco Corp. (now known as Crompton) with  $\text{Ca}(\text{OH})_2$  and  $\text{CaO}$  in n-heptane and methanol and bubbling with  $\text{CO}_2$ . It is also reported in the aforementioned patent (col. 5) that a 500 TBN overbased sulphonate containing highly branched alkylbenzene sulphonate is available from Witco Corp. (now known as Crompton) as Petronate® C-500. Another method for preparing an overbased sulphonate detergent of high metal ratio is disclosed in U.S. Patent 6,444,625 (see, for instance, column 3, bottom). The latter process includes providing a sulphonic acid to a reactor, adding a lime reactant for neutralization and overbasing, adding a lower aliphatic  $\text{C}_1$  to  $\text{C}_4$  alcohol and a hydrocarbon solvent, and carbonating the process mixture with carbon dioxide during which process the exotherm of the reaction is maintained between  $27^\circ\text{C}$  and  $57^\circ\text{C}$ . Alternatively, a high metal-ratio detergent may be prepared by using a mixture of short chain alcohols, with or without a hydrocarbon solvent, conducting the addition of lime reactants and carbon dioxide in multiple iterations, and, if desired the process of adding lime and carbon dioxide and of removal of volatile materials may be repeated. The overbased sulphonate detergent in the present invention may be used alone or with other overbased sulphonates. In one embodiment the sulphonate detergent is in a mixture with other sulphonate detergents. Alternatively a 500 TBN sulphonate detergent may be prepared by the process shown in Preparative Example S-1.

#### Preparative Example S-1

[0036] A sample of a 500 TBN sulphonate detergent is prepared using a flange vessel with flange and clip, overhead stirrer with paddle and polytetrafluoroethylene (PTFE) stirrer gland, Dean Stark trap and double surface condenser, a mantle/thermocouple temperature controller system, the equipment from just above the mantle to just below the condenser being covered with glass wool. The vessel is charged with 35.1 parts by weight of  $\text{C}_{16}\text{-C}_{24}$

alkylbenzene sulphonic acid and 31.8 parts by weight of mineral oil (SN 150) and heated to 30°C. The reactor is charged through a port with alcohols containing methanol and a mixture of iso-butanol/amyl alcohol present at 11.6 parts by weight. The weight ratio of methanol to the mixture of iso-butanol/amyl alcohol is 1.31. The reactor is charged with 14.9 parts by weight of calcium hydroxide and the mixture is heated to 54°C where carbon dioxide is added to form a carbonated product. The carbonated product is further treated three more times with similar (or equal) portions of calcium hydroxide and carbon dioxide. Water is removed by stripping before repeating the addition of alcohol, calcium hydroxide and carbon dioxide 2 times. The product is stripped and filtered.

#### Phenate Detergent

[0037] Optionally the detergent package further includes a phenate. Phenate detergents are known and include neutral and overbased metal salts of a sulphur-containing phenate, a non-sulphurised phenate or mixtures thereof. Suitable metal salts are the same as those described for the sulphonate detergent.

[0038] The phenate detergent in one embodiment has a TBN from 30 to 290, in another embodiment 40 to 265, in another embodiment 50 to 190 and in another embodiment 70 to 175. In one embodiment the sulphur containing phenate detergent has a TBN of 150 and in another embodiment a TBN of 225.

[0039] The sulphur containing phenate detergent in one embodiment has a metal ratio of not more than 4, in another embodiment not more than 3, in another embodiment not more than 2.7, in another embodiment not more than 2.5, in another embodiment not more than 2.3 and in another embodiment not more than 2.1.

[0040] The phenate detergent is present in one embodiment at 0 to 15, in another embodiment 0 to 10, in another embodiment 0 to 5 and in another embodiment 0.5 to 3 weight percent of the lubricating composition.

#### Dispersant

[0041] The invention optionally includes a dispersant. The dispersant is known and includes an ash-containing dispersant or an ashless-type dispersant. The dispersant may be used alone or in combination with other dispersants. In

one embodiment the ashless dispersant does not contain ash-forming metals. Ashless type dispersants are characterised by a polar group attached to a relatively high molecular weight hydrocarbon chain. Typical ashless dispersants include N-substituted long chain alkenyl succinimides. Examples of  
5 N-substituted long chain alkenyl succinimides include polyisobutylene succinimide with number average molecular weight of the polyisobutylene substituent in one embodiment from 350 to 5000, and in another embodiment 500 to 3000. Succinimide dispersants and their preparation are disclosed, for instance in US Patent 4,234,435. Succinimide dispersants are typically the  
10 imide formed from a polyamine, typically a poly(ethyleneamine).

**[0042]** In one embodiment the invention further comprises a dispersant. In one embodiment the dispersant is derived from polyisobutylene, an amine and zinc oxide to form a polyisobutylene succinimide complex with zinc.

**[0043]** Another class of ashless dispersant is Mannich bases. Mannich  
15 dispersants are the reaction products of alkyl phenols with aldehydes (especially formaldehyde) and amines (especially polyalkylene polyamines). The alkyl group typically contains at least 30 carbon atoms.

**[0044]** The dispersant may also be post-treated by conventional methods by a reaction with any of a variety of agents. Among these are urea, thiourea,  
20 dimercaptiothiadiazoles, carbon disulfide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, maleic anhydride, nitriles, epoxides, boron compounds, and phosphorus compounds.

**[0045]** In one embodiment of the invention the dispersant is borated using a variety of agents selected from the group consisting of the various forms of  
25 boric acid (including metaboric acid,  $\text{HBO}_2$ , orthoboric acid,  $\text{H}_3\text{BO}_3$ , and tetraboric acid,  $\text{H}_2\text{B}_4\text{O}_7$ ), boric oxide, boron trioxide, and alkyl borates.

**[0046]** The borated dispersant may be prepared by blending the boron compound and the N-substituted long chain alkenyl succinimides and heating them at a suitable temperature in one embodiment from 80°C to 250°C, in  
30 another embodiment 90°C to 230°C and in another embodiment 100°C to 210°C, until the desired reaction has occurred. The molar ratio of the boron compounds to the N-substituted long chain alkenyl succinimides is typically 10:1 to 1:4, in

another embodiment 4:1 to 1:3, and in another embodiment 1:2. An inert liquid may be used in performing the reaction. The liquid may include toluene, xylene, chlorobenzene, dimethylformamide and mixtures thereof.

5     [0047]     The dispersant is present in one embodiment from 0 wt % to 10 wt % or 0.01 to 10 wt %, in another embodiment 0.05 wt % to 7 wt %, in another embodiment 0.1 wt % to 5 wt % and in another embodiment 0.2 wt % to 3 wt % of the lubricating composition.

#### Oils of Lubricating Viscosity

10     [0048]     The invention further includes oil of lubricating viscosity. Such oils include natural and synthetic oils, oil derived from hydrocracking, hydrogenation, and hydrofinishing, unrefined, refined and re-refined oils and mixtures thereof.

[0049]     Unrefined oils are those obtained directly from a natural or synthetic source generally without (or with little) further purification treatment.

15     [0050]     Refined oils are similar to the unrefined oils except they have been further treated in one or more purification steps to improve one or more properties. Purification techniques are known in the art and include solvent extraction, secondary distillation, acid or base extraction, filtration, percolation and the like.

20     [0051]     Re-refined oils are also known as reclaimed or reprocessed oils, and are obtained by processes similar to those used to obtain refined oils and often are additionally processed by techniques directed to removal of spent additives and oil breakdown products.

25     [0052]     Natural oils useful in making the inventive lubricants include animal oils, vegetable oils (e.g., castor oil, lard oil), mineral lubricating oils such as liquid petroleum oils and solvent-treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic or mixed paraffinic-naphthenic types and oils derived from coal or shale or mixtures thereof.

30     [0053]     Synthetic lubricating oils are useful and include hydrocarbon oils such as polymerised and interpolymerised olefins (e.g., polybutylenes, polypropylenes, propyleneisobutylene copolymers); poly(1-hexenes), poly(1-octenes), poly(1-decenes), and mixtures thereof; alkyl-benzenes (e.g.

dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di-(2-ethylhexyl)-benzenes); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenyls); alkylated diphenyl ethers and alkylated diphenyl sulphides and the derivatives, analogs and homologs thereof or mixtures thereof.

5 [0054] Other synthetic lubricating oils include but are not limited to liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, and the diethyl ester of decane phosphonic acid), and polymeric tetrahydrofurans. Synthetic oils may be produced by Fischer-Tropsch reactions and typically may be hydroisomerised Fischer-Tropsch hydrocarbons or waxes.

10 [0055] Oils of lubricating viscosity may also be defined as specified in the American Petroleum Institute (API) Base Oil Interchangeability Guidelines. The five base oil groups are as follows: Group I (sulphur content  $>0.03$  wt %, and/or  $<90$  wt % saturates, viscosity index 80-120); Group II (sulphur content  $\leq 0.03$  wt %, and  $\geq 90$  wt % saturates, viscosity index 80-120); Group III (sulphur  
15 content  $\leq 0.03$  wt %, and  $\geq 90$  wt % saturates, viscosity index  $\geq 120$ ); Group IV (all polyalphaolefins (PAOs)); and Group V (all others not included in Groups I, II, III, or IV). The oil of lubricating viscosity comprises an API Group I, Group II, Group III, Group IV, Group V oil and mixtures thereof. In one embodiment the oil of lubricating viscosity is a monograde often with a SAE-50 or above  
20 grade.

[0056] The oil of lubricating viscosity is present in one embodiment at 10 wt % to 99.8 wt %, in another embodiment 30 wt % to 97.9 wt %, in another embodiment 46 wt % to 94.8 wt % and in another embodiment 57 wt % to 89 wt % of the lubricating composition.

## 25 Performance Additives

[0057] Optionally the lubricating composition may include at least one performance additive other than components (a)-(c), selected from the group consisting of metal deactivators, dispersant, antioxidants, antiwear agents, corrosion inhibitors, antiscuffing agents, extreme pressure agents, foam  
30 inhibitors, demulsifiers, friction modifiers, viscosity modifiers, pour point depressants and mixtures thereof. Typically, fully-formulated lubricating oil will contain one or more of these performance additives.

[0058] The total combined amount of the other performance additives present in one embodiment from 0 wt % to 15 wt %, in another embodiment 0 wt % to 13 wt %, in another embodiment 0.01 wt % to 11 wt % and in another embodiment 0.05 wt % to 7 wt % of the lubricating composition.

5 Antiwear Agent

[0059] In one embodiment of the invention the composition further comprises an antiwear agent such as a metal hydrocarbyl dithiophosphate. Examples of a metal hydrocarbyl dithiophosphate include zinc dihydrocarbyl dithiophosphates (often referred to as ZDDP, ZDP or ZDTP). In one  
10 embodiment the lubricating composition is free of a metal hydrocarbyl dithiophosphate.

[0060] In an alternative embodiment the antiwear agent is ashless i.e. the antiwear agent is metal-free. In one embodiment the metal-free antiwear agent is an amine salt. The ashless antiwear agent often contains an atom including  
15 sulphur, phosphorus, boron or mixtures thereof. In one embodiment the lubricating composition is free of an ashless antiwear agent.

[0061] The amine is often a primary amine, a secondary amine a tertiary amine or mixtures thereof. Often a primary amine and/or a secondary amine contains at least one hydrocarbyl group with the number of carbon atoms  
20 present in one embodiment from 2 to 30, in another embodiment 8 to 26, in another embodiment 10 to 20, and in another embodiment 11 to 18 such as 11 to 14.

[0062] Examples of primary amines useful in the present invention include ethylamine, propylamine, butylamine, 2-ethylhexylamine, octylamine and dodecylamine. Also suitable primary fatty amines which include n-octylamine,  
25 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, Illinois), such as Armeen C, Armeen O, Armeen OL, Armeen T, Armeen HT, Armeen S and Armeen SD, wherein the letter  
30 designation relates to the fatty group, such as coco, oleyl, tallow, or stearyl groups.



[0063] Examples of suitable secondary amines include dimethylamine, diethylamine, dipropylamine, dibutylamine, diamylamine, dihexylamine, diheptylamine, methylethylamine, ethylbutylamine and ethylamylamine. The secondary amines may be cyclic amines such as piperidine, piperazine and morpholine.

[0064] The amine may also be a tertiary-aliphatic primary amine. Often the aliphatic group is an alkyl group containing a number of carbon atoms in one embodiment from 2 to 30, in another embodiment 6 to 26 and in another embodiment 8 to 24. Often the tertiary alkyl primary amines are monoamines such as tert-butylamine, terthexylamine, 1-methyl-1-amino-cyclohexane, tert-octylamine, tert-decylamine, tertdodecylamine, tert-tetradecylamine, tert-hexadecylamine, tert-octadecylamine, terttetracosanylamine, and tert-octacosanylamine.

[0065] Mixtures of amines may also be used in the invention. Especially useful mixtures of amines are "Primene 81R" and "Primene JMT." Primene 81R and Primene JMT (both produced and sold by Rohm & Haas) are mixtures of C<sub>11</sub> to C<sub>14</sub> tertiary alkyl primary amines and C<sub>18</sub> to C<sub>22</sub> tertiary alkyl primary amines respectively.

[0066] The ashless antiwear agent may also include phosphoric acid esters or salt thereof; dialkyldithiophosphoric acid esters or salt thereof; phosphites; and phosphorus-containing carboxylic esters, ethers, and amides or mixtures thereof.

[0067] Other ashless antiwear agent compounds include sulphur-containing ashless anti-wear additives include thiocarbamate-containing compounds, such as thiocarbamate esters, thiocarbamate amides, thiocarbamic ethers, alkylene-coupled thiocarbamates, and bis(S-alkyldithiocarbamyl) disulphides. In one embodiment the lubricating composition is free of thiocarbamate-containing compounds.

[0068] The dithiocarbamate-containing compounds may be prepared by reacting a dithiocarbamate acid or salt with an unsaturated compound. The dithiocarbamatecontaining compounds may also be prepared by simultaneously reacting an amine, carbon disulfide and an unsaturated compound. Generally,

the reaction occurs at a temperature from 25°C to 125°C. US Patents 4,758,362 and 4,997,969 describe dithiocarbamate compounds and methods of making them.

[0069] Useful fatty amines include commercially available fatty amines such as "Armeen®" amines (products available from Akzo Chemicals, Chicago, Illinois), such as Armeen® C, Armeen® O, Armeen® OL, Armeen® T, Armeen® HT, Armeen® S and Armeen® SD, wherein the letter designation relates to the fatty group, such as coco, oleyl, tallow, or stearyl groups.

[0070] In an alternative embodiment of the invention, the ashless antiwear agent may be a monoester of a polyol and an aliphatic carboxylic acid, often an acid containing 12 to 24 carbon atoms. Often the monoester of a polyol and an aliphatic carboxylic acid is in the form of a mixture with a sunflower oil or the like, which may be present in the friction modifier mixture in one embodiment from 5 to 95, in another embodiment 10 to 90, in another embodiment 20 to 85 and in another embodiment 20 to 80 weight percent of the mixture. The aliphatic carboxylic acids (including a monocarboxylic acid) which form the esters are those acids containing in one embodiment 12 to 24 carbon atoms and in another embodiment 14 to 20 carbon atoms. In one embodiment the composition is free of a monoester of a polyol and an aliphatic carboxylic acid.

[0071] Polyols include diols, triols, and alcohols with higher numbers of alcoholic OH groups. Polyhydric alcohols include ethylene glycols, including di-, tri- and tetraethylene glycols; propylene glycols, including di-, tri- and tetrapropylene glycols; glycerol; butane diol; hexane diol; sorbitol; arabitol; mannitol; sucrose; fructose; glucose; cyclohexane diol; erythritol; and pentaerythritols, including di- and tripentaerythritol. Often the polyol is diethylene glycol, triethylene glycol, glycerol, sorbitol, pentaerythritol or dipentaerythritol.

[0072] Examples of carboxylic acids include dodecanoic acid, stearic acid, lauric acid, behenic acid, and oleic acid. The commercially available monoester is believed to include  $60 \pm 5$  percent by weight of the chemical species "glycerol monooleate," along with  $35 \pm 5$  percent glycerol dioleate, and less than 5 percent trioleate and oleic acid. The amounts of the monoesters, described

above, are calculated based on the actual, corrected, amount of polyol monoester present in any such mixture.

[0073] In one embodiment of the invention the antiwear agent is a borate ester. The borate ester may be prepared by the reaction of a boron compound and at least one compound selected from epoxy compounds, halohydrin compounds, epihalohydrin compounds, alcohols and mixtures thereof. Typically the alcohols include monohydric alcohols, dihydric alcohols, trihydric alcohols or higher alcohols.

[0074] Boron compounds suitable for preparing the borate ester include a boric acid (including metaboric acid,  $\text{HBO}_2$ , orthoboric acid,  $\text{H}_3\text{BO}_3$ , and a tetraboric acid,  $\text{H}_2\text{B}_4\text{O}_7$ ), a boric oxide, a boron trioxide and an alkyl borate. The borate ester may also be prepared from boron halides. The borated ester further contains at least one hydrocarbyl group often containing about 8 to about 30 carbon atoms. In one embodiment the lubricating composition is free of a borated ester.

[0075] The antiwear agent is present in one embodiment from 0 wt % to 8 wt %, in another embodiment 0 wt % to 6 wt %, in another embodiment 0.01 wt % to 4 wt % and in another embodiment 0.01 wt % to 2 wt % of the lubricating composition. The antiwear agent may be used alone or in combination with other antiwear agents. In one embodiment the lubricating composition is free of an antiwear agent

[0076] Other performance additives such as an antioxidant including a diphenylamine, a hindered phenol, a molybdenum dithiocarbamate, a sulphurised olefin and mixtures thereof and in one embodiment the lubricating composition is free of an antioxidant; corrosion inhibitors including octylamine octanoate, condensation products of dodecenyl succinic acid or anhydride and a fatty acid such as oleic acid with a polyamine; metal deactivators including derivatives of benzotriazoles, 1,2,4-triazoles, benzimidazoles, 2-alkyldithiobenzimidazoles or 2-alkyldithiobenzothiazoles; foam inhibitors including copolymers of ethyl acrylate and 2-ethylhexylacrylate and optionally vinyl acetate; demulsifiers including trialkyl phosphates, polyethylene glycols, polyethylene oxides, polypropylene oxides and (ethylene oxide-propylene oxide) polymers; pour point depressants including esters of maleic anhydride-

styrene, polymethacrylates, polyacrylates or polyacrylamides; viscosity modifiers including styrene-butadiene rubbers, ethylene-propylene copolymers, hydrogenated styrene-isoprene polymers, hydrogenated radical isoprene polymers, poly(meth)acrylate acid esters, polyalkyl styrenes, polyolefins, 5 polyalkylmethacrylates and esters of maleic anhydride-styrene copolymers; and friction modifiers including fatty acid derivatives such as amines, esters, epoxides, fatty imidazolines, condensation products of carboxylic acids and polyalkylene-polyamines and amine salts of alkylphosphoric acids may also be used in the composition of the invention.

10 Process

[0077] The invention also includes a process to prepare the lubricating composition of the present invention, comprising mixing:

(a) detergent package comprising:

15 (i) an oligomeric reaction product of (1) a hydrocarbyl-substituted phenol; (2) an aldehyde; and (3) a carboxyl-substituted phenol or a carboxyl-substituted phenylamine; or salts of the reaction product;

(ii) a sulphonate; and

(iii) optionally a phenate;

20 (b) optionally a dispersant; and

(c) an oil of lubricating viscosity,

wherein the sulphonate detergent is overbased with a metal ratio of about 12.5:1 to about 40:1.

[0078] The mixing conditions include a temperature in one embodiment from 25 15°C to 130°C, in another embodiment 20°C to 120°C and in another embodiment 25°C to 110°C; and for a period of time in one embodiment from 30 seconds to 48 hours, in another embodiment 2 minutes to 24 hours, and in another embodiment 5 minutes to 16 hours or 1 to 4 hours; and at pressures in one embodiment from 86.4 kPa to 266 kPa (650 mm Hg to 2000 mm Hg), in 30 another embodiment 91.8 kPa to 200 kPa (690 mm Hg to 1500 mm Hg), and in another embodiment 95.1 kPa to 133 kPa (715 mm Hg to 1000 mm Hg).

[0079] The process optionally includes mixing other performance additives as described above. The optional performance additives may be added sequentially, separately or as a concentrate.

5 [0080] If the present invention 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 each of the above-mentioned detergent and/or dispersant, as well as other components, to diluent oil is typically in the range of 80:20 to 10:90 by weight.

#### Industrial Application

10 [0081] The lubricating composition of the present invention is useful for an internal combustion engine, for example a diesel fuelled engine, a gasoline fuelled engine, a natural gas fuelled engine or a mixed gasoline/alcohol fuelled engine. In one embodiment the internal combustion engine is a 4-stroke and in another embodiment a 2-stroke engine. In one embodiment the diesel fuelled  
15 engine is a marine diesel engine.

[0082] In one embodiment of the invention provides a method for lubricating an internal combustion engine, comprising supplying thereto a lubricant comprising the composition as described herein. The use of the composition may impart one or more of cleanliness properties, antiwear performance and  
20 deposit control.

[0083] The following examples provide an illustration of the invention. These examples are non exhaustive and are not intended to limit the scope of the invention.

#### EXAMPLES

##### 25 Examples 1-10 and Reference Example 1

[0084] Lubricating compositions are prepared by mixing additives as defined in Table 1; and all additives contain conventional amounts of diluent oil. The compositions prepared are:

**Table 1: Compositions of the Invention**

Example	Sulphonate		Oligomeric Reaction Product			Dispersant	Oil
	a*	b*	c*	d*	e*	f*	g*
EX1	17.2			1		1.5	balance
EX2	17.2			2		1.5	balance
EX3	17.2			4		1.5	balance
EX4	17.2				1	1.5	balance
EX5	17.2				2	1.5	balance
EX6	17.2				4	1.5	balance
EX7	17.2			1	1	1.5	balance
EX8	17.2		2			1.5	balance
EX9		13.8	2			1.5	balance
EX10		13.8			2	1.5	balance
REF1	17.2					1.5	balance

Foot note to Table 1:

(a\*) is a 400 TBN sulphonate detergent;

5 (b\*) is a 500 TBN sulphonate;

(c\*) is metal salixarate detergent;

(d\*) is a metal-free oligomeric reaction product of (1) a 550 molecular weight hydrocarbyl-substituted phenol; (2) an aldehyde; and (3) a carboxyl-substituted phenol;

10 (e\*) is a dodecyl-substituted phenol equivalent of component (d\*);

(f\*) is a dispersant; and

(g\*) is an oil of lubricating viscosity.

#### Test 1: Panel Coker

15 **[0085]** Approximately 233g of sample is placed in a 250 ml Panel Coker apparatus and heated to 325°C. The sample is splashed against a metal plate for 15 seconds and then baked for 45 seconds. The splashing and baking cycle is continued for approximately 3 hours. The sample is cooled to room temperature

and the amount of deposits left on the metal plate is weighed. The results obtained by testing the lubricants of the indicated Examples are as shown:

<u>Example</u>	<u>Deposit (mg)</u>
EX1	220.3
EX2	132.5
EX3	92.1
EX4	105.9
EX5	60.4
EX6	47.2
EX7	107.1
EX8	60.9
EX9	125.8
EX10	122.3
REF1	346.2

- 5 [0086] The analysis of the data indicates that the lubricating composition of the invention has reduced deposit formation compared with the reference example. Consequently the invention provides one or more properties of cleanliness properties, antiwear performance and deposit control into a lubricating composition.

10 Examples 11 to 16 and Reference Example 2

[0087] Lubricating compositions are prepared by mixing additives as defined in Table 1; and all additives contain conventional amounts of diluent oil. The compositions prepared are:

**Table 2: Compositions of the Invention**

	Sulphonate	Phenate	Oligomeric Reaction Product		Dispersant	Antiwear additive			Oil
Example	a*	b*	c*	d*	e*	f*	g*	h*	i*
EX11	17.2		2		1.5				balance
EX12	17.2			2	1.5				balance
EX13	17.2			2	1.5	0.75	0.25	0.25	balance
EX14	17.2			2	1.5		0.75		balance
EX15	17.2	1	2		1.5				balance
EX16	17.2		2.5						balance
REF2	17.2				1.5				balance

Foot note to Table 1:

(a\*) to (e\*) are as defined above;

5 (e\*) is a dispersant;

(f\*) is a borated dispersant;

(g\*) is a zinc dialkyl dithiophosphate;

(h\*) is a sulphurised olefin;

(i\*) is an oil of lubricating viscosity.

10 **Test 1: Cameron Plint Wear Test**

**[0088]** The Cameron Plint TE-77™ is a reciprocating wear tester. In this test a steel ball upper specimen is reciprocated against a steel flat lower specimen. The Cameron Plint is then charged with 10 ml of the sample and heated to 50°C and held for 20 minutes. The samples (EX12 to 16) are then subject to a load of 150 N over two minutes while at the same time reciprocation is started at 10 Hz over 15 mm stroke length. Samples EX11 and REF1 are subjected to a load of 240 N. The sample is then heated to 350°C at 2°C per minute and then held at temperature for 3 hours. At the end of the test the onset of film failure is measured. The onset of film failure is determined by the temperature at which the oil film as measured by the contact potential, first falls to 80 % of its



starting value. The results obtained by testing the lubricants of the indicated Examples are as shown:

Example	Onset of Film Failure (240 N load) Temperature (°C)	Onset of Film Failure (150 N load) Temperature (°C)
REF2	230	-
EX11	340	-
EX12	-	290
EX13	-	270
EX14	-	200
EX15	-	260
EX16	-	300

[0089] The analysis of the data indicates that the lubricating composition of the invention has an increased temperature for the onset of film failure.

[0090] In summary the lubricating composition of the invention has one or more of cleanliness properties, antiwear performance and deposit control.

[0091] Each of the documents referred to above is incorporated herein by reference. Except in the Examples, or where otherwise explicitly indicated, all numerical quantities in this description specifying amounts of materials, reaction conditions, molecular weights, number of carbon atoms, and the like, are to be understood as modified by the word "about." Unless otherwise indicated, each chemical or composition referred to herein should be interpreted as being a commercial grade material which may contain the isomers, by-products, derivatives, and other such materials which are normally understood to be present in the commercial grade. However, the amount of each chemical component is presented exclusive of any solvent or diluent oil, which may be customarily present in the commercial material, unless otherwise indicated. It is to be understood that the upper and lower amount, range, and ratio limits set forth herein may be independently combined. Similarly, the ranges and amounts for each element of the invention may be used together with ranges or amounts for any of the other elements. As used herein, the expression "consisting essentially of" permits the inclusion of substances that do not materially affect the basic and novel characteristics of the composition under consideration.

Various materials are referred to herein as "ashless" because they, at least initially, do not contain ash-forming metals. It is recognized that such materials may associate with ash-forming metals when formulated in a lubricant; nevertheless, they are still to be considered "ashless."

5 [0092] 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:

10 hydrocarbon substituents, that is, aliphatic (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl, cycloalkenyl) substituents, and aromatic-, aliphatic-, and alicyclic-substituted aromatic substituents, as well as cyclic substituents wherein the ring is completed through another portion of the molecule (e.g., two substituents together form a ring);

15 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 (e.g., halo (especially chloro and fluoro), hydroxy, alkoxy, mercapto, alkylmercapto, nitro, nitroso, and sulfoxy);

20 hetero substituents, that is, substituents which, while having a predominantly hydrocarbon character, in the context of this invention, contain other than carbon in a ring or chain otherwise composed of carbon atoms. Heteroatoms include sulfur, oxygen, nitrogen; and encompass substituents as pyridyl, furyl, thienyl and imidazolyl. In general, no more than two, in one  
25 embodiment no more than one, non-hydrocarbon substituent will be present for every ten carbon atoms in the hydrocarbyl group; typically, there will be no non-hydrocarbon substituents in the hydrocarbyl group.

What is claimed is:

1. A lubricating composition comprising:

5 (a) a detergent package comprising:

(i) an oligomeric reaction product of (1) a hydrocarbyl-substituted phenol; (2) an aldehyde; and (3) a carboxyl-substituted phenol or a carboxyl-substituted phenylamine; or a salt of the reaction product;

10 (ii) a sulphonate; and

(iii) optionally a phenate;

(b) optionally a dispersant; and

(c) an oil of lubricating viscosity,

wherein the sulphonate detergent is overbased with a metal ratio of about 12.5:1

15 to about 40:1.

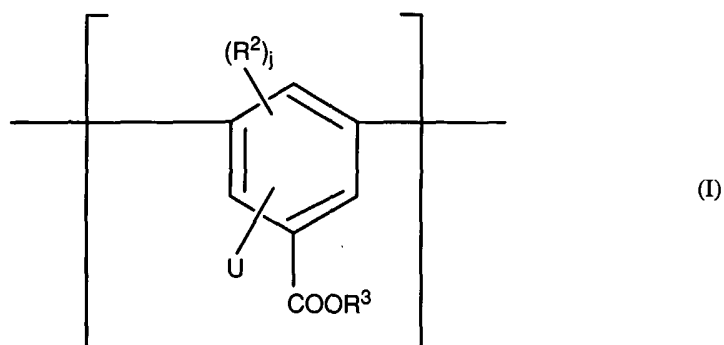
2. The lubricating composition of claim 1, wherein the lubricating composition has a total base number of 30 or higher.

20 3. The lubricating composition of claim 1, wherein the lubricating composition has a total base number of 50 or higher.

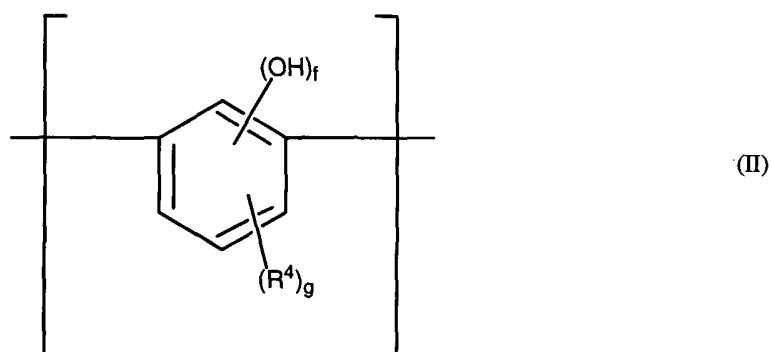
4. The lubricating composition of claim 1, wherein the sulphonate detergent metal ratio is 15:1 to 40:1.

25 5. The lubricating composition of claim 1, wherein the sulphonate detergent has a total base number of at least 350.

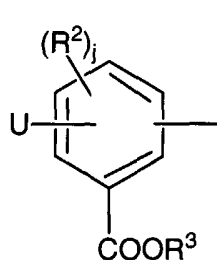
30 6. The lubricating composition of claim 1, wherein the oligomeric reaction product is a substantially linear compound comprising at least one unit of the formulae (I) or (II):



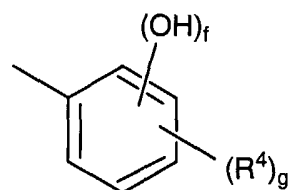
or



each end of the compound having a terminal group of formulae (III) or (IV):



(III)



(IV)

- 5 such groups being linked by divalent bridging groups, which may be the same or different for each linkage; wherein in formulas (I)-(IV)  $f$  is 1, 2 or 3;  $U$  is  $-OH$ ,  $-NH_2$ ,  $-NHR^1$ ,  $-N(R^1)_2$  or mixtures thereof,  $R^1$  is a hydrocarbyl group containing 1 to 5 carbon atoms;  $R^2$  is hydroxyl or a hydrocarbyl group and  $j$  is 0, 1, or 2;  $R^3$  is hydrogen or a hydrocarbyl group;  $R^4$  is a hydrocarbyl group or a substituted hydrocarbyl group;  $g$  is 1, 2 or 3, provided at least one  $R^4$  group contains 8 or more 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 about 0.1:1 to about 2:1.
- 10
- 15

7. The lubricating composition of claim 6, wherein the oligomeric reaction product is a metal salt.

8. A lubricating composition comprising:

(a) a detergent package comprising:

- 5           (i)    0.1 to 8 weight percent of an oligomeric reaction product of  
              (1) an hydrocarbyl-substituted phenol; (2) an aldehyde; and (3)  
              a carboxyl-substituted phenol or a carboxyl-substituted  
              phenylamine; and salts of the reaction product;  
              (ii)   5 to 25 weight percent of a sulphonate; and  
10           (iii)  0 to 10 weight percent of a phenate;  
              (b) 0.1 to 5 weight percent of a dispersant; and  
              (c) 46 to 94.8 weight percent of an oil of lubricating viscosity,

wherein the sulphonate detergent is overbased with a metal ratio of about 12.5:1 to about 40:1.

15   9. A process to prepare a lubricating composition comprising mixing:

(a) a detergent package comprising:

- (i) an oligomeric reaction product of (1) an hydrocarbyl-substituted  
              phenol; (2) an aldehyde; and (3) a carboxyl-substituted phenol or  
              a carboxyl-substituted phenylamine; and salts of the reaction  
20           product;  
              (ii) a sulphonate; and  
              (iii) optionally a phenate;  
              (b) a dispersant; and  
              (c) an oil of lubricating viscosity,

25   wherein the sulphonate detergent is overbased with a metal ratio of about 12.5:1 to about 40:1.

10. A method for lubricating an internal combustion engine, comprising supplying thereto a lubricant comprising the lubricating composition of claim 1.

11. The method of lubricating an internal combustion engine of claim 10,  
30   wherein the internal combustion engine is a marine diesel engine.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US2005/035600

## A. CLASSIFICATION OF SUBJECT MATTER

C10M163/00 C10N30/04 C10N30/06 C10N40/25 C10M159/20

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

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 practical, search terms used)

EPO-Internal, PAJ, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2004/102335 A1 (CARRICK VIRGINIA A ET AL) 27 May 2004 (2004-05-27) paragraph '0131!; example 2 -----	1,4-7, 9-11
E	WO 2005/112575 A (THE LUBRIZOL CORPORATION) 1 December 2005 (2005-12-01) paragraphs '0013!, '0019!, '0070!, '0097!, '0098!; examples -----	1-7,9-11
Y	US 6 339 051 B1 (CAREY VINCENT M ET AL) 15 January 2002 (2002-01-15) cited in the application the whole document -----	1-11
Y	WO 03/018728 A (THE LUBRIZOL CORPORATION) 6 March 2003 (2003-03-06) cited in the application claims; examples -----	1-11

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

\*A\* document defining the general state of the art which is not considered to be of particular relevance

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\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*&amp;\* document member of the same patent family

Date of the actual completion of the international search

27 January 2006

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US2005/035600

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