

A METHOD OF REDUCING THE RATE OF DEPLETION OF BASICITY OF A LUBRICATING OIL COMPOSITION IN USE IN AN ENGINE

FIELD OF THE INVENTION

5 This invention relates to a method of reducing the rate of depletion of basicity (as determined by ASTM D2896) of a lubricating oil composition in use in an engine, the lubricating oil composition including at least one oil-soluble overbased alkali or alkaline earth metal detergent. In particular, the invention relates to a method of reducing the rate of depletion of basicity (as determined by ASTM D2896) of a
10 lubricating oil composition in use in an engine, the lubricating oil composition including at least one oil-soluble overbased alkali or alkaline earth metal detergent, without increasing sulphated ash content (SASH). Preferably, the lubricating oil composition is a marine cylinder lubricant, a trunk piston engine oil, a gas engine oil or a crankcase lubricating oil composition (including a passenger car motor oil and a
15 heavy duty diesel motor oil).

BACKGROUND OF THE INVENTION

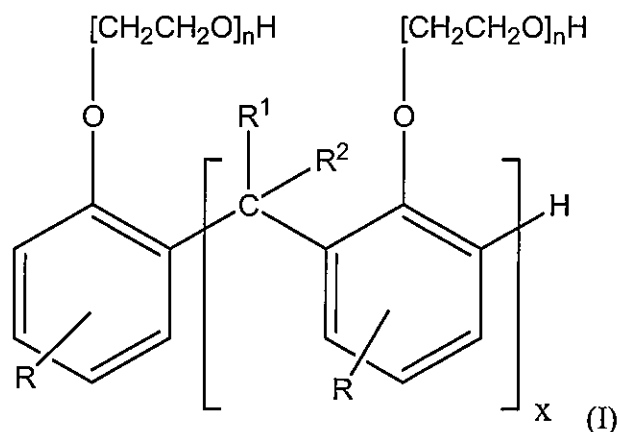
Lubricating oil compositions include oil-soluble overbased detergents to supply alkalinity to neutralize sulphur acids resulting from high sulphur fuels. They
20 also prevent harmful carbon and sludge deposits, which can lead to engine shut-down and repair. The overbased detergents usually have a TBN ranging from 50 to 500, preferably 250 to 450 mg KOH/g (ASTM D2896), and are usually overbased alkaline earth metal detergents such as overbased calcium sulphonates, phenates and salicylates. It is important that the basicity provided by the overbased detergents be
25 retained as long as possible, as this ensures longer oil life and better engine protection over a longer period of time. It is also important that ash levels are not increased because excessive sulphated ash levels can result in increased deposits on pistons and exhaust gas circuits, including heat recovery systems and after-treatment devices.

30 The present invention is concerned with the problem of reducing the rate of depletion of basicity (as determined by ASTM D2896) of a lubricating oil composition in use in an engine. The present invention is also concerned with the problem of reducing the rate of depletion of basicity (as determined by ASTM

D2896) of a lubricating oil composition in use in an engine without increasing sulphated ash content.

SUMMARY OF THE INVENTION

5 In accordance with a first aspect of the present invention, there is provided a method of reducing the rate of depletion of basicity (as determined by ASTM D2896) of a lubricating oil composition in use in an engine, the lubricating oil composition including at least one oil-soluble overbased alkali or alkaline earth metal detergent, which method comprises adding to the lubricating oil composition one or more
10 compounds of Formula (I):



wherein:

x is 1 to 50, preferably 1 to 40, more preferably 1 to 30;
15 R¹ and R² are H, hydrocarbyl groups having 1 to 12 carbon atoms, or hydrocarbyl groups having 1 to 12 carbon atoms and at least one heteroatom;
R is a hydrocarbyl group having 9 to 100, preferably 9 to 70, most preferably, 9 to 50, carbon atoms; and
n is 0 to 10, or alkaline earth metal salts of the compounds of formula (I).

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In the compounds of Formula (I), n is preferably 0. In the compounds of Formula (I), x is preferably 1. In the compounds of Formula (I), R is preferably 9 to 20 carbon atoms, more preferably 9 to 15. In the compounds of Formula (I), R is preferably branched.

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In the compounds of Formula (I), R¹ is preferably H, R² is preferably H and R is preferably in the para position in relation to the -O-[CH₂CH₂O]_nH group.

The compounds of Formula (I) are preferably methylene-bridged alkyl phenols or ethoxylated methylene-bridged alkyl phenols.

5 The compounds of Formula (I) preferably include less than 1 mole%, more preferably less than 0.5 mole% and most preferably less than 0.1 mole% of unreacted alkyl phenol.

10 In the compounds of Formula (I), preferably $n = 1$ for more than 60, more preferably more than 70, even preferably more than 80, even preferably more than 90, or most preferably more than 95, mole %.

15 In the compounds of Formula (I), preferably $n \geq 2$, such as di-oxyalkylated, tri-oxyalkylated and tetra-oxyalkylated, for less than 5 mole %.

 The alkaline earth metal salts of the compounds of Formula (I) are, for example, calcium, magnesium barium or strontium. Calcium or magnesium is preferred; calcium is especially preferred.

20 The lubricating oil composition is preferably a marine cylinder lubricant, a trunk piston engine oil, a gas engine oil or a crankcase lubricating oil composition (including a passenger car motor oil and a heavy duty diesel motor oil).

25 When the lubricating oil composition is a marine cylinder lubricant, the TBN (as measured by ASTM D2896) is preferably at least 20, more preferably at least 40 and to about 70 mgKOH/g.

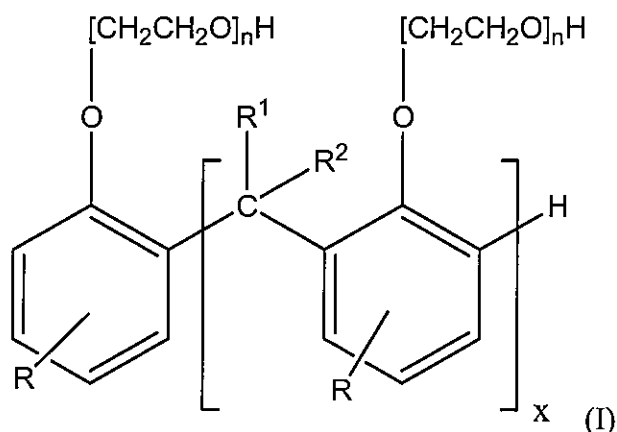
30 When the lubricating oil composition is a trunk piston engine oil, the TBN (as measured by ASTM D2896) is preferably at least 10, more preferably at least 20, and most preferably 30 to 55 mgKOH/g.

 When the lubricating oil composition is a gas engine oil, the TBN (as measured by ASTM D2896) is preferably at least 4, more preferably 5 to 15 mgKOH/g.

When the lubricating oil composition is a crankcase oil, the TBN (as measured by ASTM D2896) is preferably at least 5, more preferably at least 6 to 18 mgKOH/g.

5 The lubricating oil composition is preferably a marine cylinder lubricant.

In accordance with the present invention there is also provided use of one or more compounds of Formula (I):

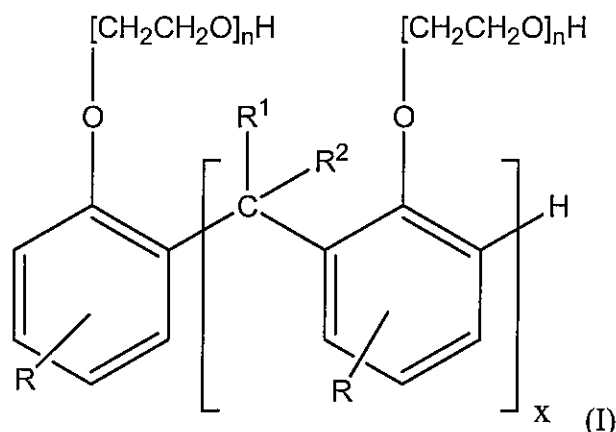


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wherein: x is 1 to 50, preferably 1 to 40, more preferably 1 to 30; R^1 and R^2 are H, hydrocarbyl groups having 1 to 12 carbon atoms, or hydrocarbyl groups having 1 to 12 carbon atoms and at least one heteroatom; R is a hydrocarbyl group having 9 to 100, preferably 9 to 70, most preferably, 9 to 50, carbon atoms; and n is 0 to 10, or
15 alkaline earth metal salts thereof, to reduce the rate of depletion of basicity (as determined by ASTM D2896) of a lubricating oil composition in use in an engine, the lubricating oil composition including at least one oil-soluble overbased alkali or alkaline earth metal detergent.

20 DETAILED DESCRIPTION OF THE INVENTION

Compounds of Formula (I) are shown below:



x is 1 to 50, preferably 1 to 40, more preferably 1 to 30;

R^1 and R^2 are H, hydrocarbyl groups having 1 to 12 carbon atoms, or hydrocarbyl groups having 1 to 12 carbon atoms and at least one heteroatom;

5 R is a hydrocarbyl group having 9 to 100, preferably 9 to 70, most preferably, 9 to 50, carbon atoms; and

n is 0 to 10, or alkaline earth metal salts thereof.

The alkaline earth metal salts of the compounds of Formula (I) are, for
10 example, calcium, magnesium barium or strontium. Calcium or magnesium is preferred; calcium is especially preferred.

In the compounds of Formula (I), n is preferably 0. In the compounds of
Formula (I), x is preferably 1. In the compounds of Formula (I), R is preferably 9 to
15 20 carbon atoms, more preferably 9 to 15. In the compounds of Formula (I), R is preferably branched. In the compounds of Formula (I), R^1 and R^2 are preferably H.

In the compounds of Formula (I), R^1 is preferably H, R^2 is preferably H, R is preferably in the para position in relation to the $-O-[CH_2CH_2O]_nH$ group, and n is preferably 1 or more, preferably 1 to 10. For further details of compounds of Formula
20 (I) when n is 1 or more, reference is made to EP 2374866A (the contents of which are incorporated herein). In the compounds of Formula (I), preferably $n = 1$ for more than 60, more preferably more than 70, even preferably more than 80, even preferably more than 90, or most preferably more than 95, mole %. In the compounds of
25 Formula (I), preferably $n \geq 2$, such as di-oxyalkylated, tri-oxyalkylated and tetra-oxyalkylated, for less than 5 mole %.

The compounds of Formula (I) preferably include less than 1 mole%, more preferably less than 0.5 mole% and most preferably less than 0.1 mole% of unreacted alkyl phenol.

- 5 Compounds of formula (I) have the advantage of being free of metals. Furthermore, they do not exhibit negative interactions with dispersants.

The compounds of Formula (I) are preferably hydrocarbyl phenol formaldehyde condensates. The term "hydrocarbyl" as used herein means that R is
10 primarily composed of hydrogen and carbon atoms and is bonded to the remainder of the molecule via a carbon atom, but does not exclude the presence of other atoms or groups in a proportion insufficient to detract from the substantially hydrocarbon characteristics of the group. The hydrocarbyl group is preferably composed of only hydrogen and carbon atoms. Advantageously, the hydrocarbyl group is an aliphatic
15 group, preferably alkyl or alkylene group, especially alkyl groups, which may be linear or branched. R is preferably an alkyl or alkylene group. R is preferably branched.

The hydrocarbyl phenol aldehyde condensate preferably has a weight average
20 molecular weight (Mw), as measured by GPC, in the range of 1000 to less than 6000, preferably less than 4000. The hydrocarbyl phenol aldehyde condensate preferably has a number average molecular weight (Mn), as measured by GPC, in the range of 900 to less than 4000, such as 3000. Mw/Mn is preferably in the range of 1.10 to 1.60.

25 The hydrocarbyl phenol aldehyde condensate is preferably one obtained by a condensation reaction between at least one aldehyde or ketone or reactive equivalent thereof and at least one hydrocarbyl phenol, in the presence of an acid catalyst such as, for example, an alkyl benzene sulphonic acid. The product is preferably subjected to stripping to remove any unreacted hydrocarbyl phenol, preferably to less than 5
30 mass %, more preferably to less than 3 mass %, even more preferably to less than 1 mass %, of unreacted hydrocarbyl phenol. Most preferably, the product includes less than 0.5 mass %, such as, for example, less than 0.1 mass % of unreacted hydrocarbyl phenol.

Although a basic catalyst can be used, an acid catalyst is preferred. The acid catalyst may be selected from a wide variety of acidic compounds such as, for example, phosphoric acid, sulphuric acid, sulphonic acid, oxalic acid and hydrochloric acid. The acid may also be present as a component of a solid material such as acid
5 treated clay. The amount of catalyst used may vary from 0.05 to 10 mass % or more, such as for example 0.1 to 1 mass % of the total reaction mixture.

When n is 1 or more in Formula (I), the compounds are preferably made by oxyalkylating a hydrocarbyl phenol condensate with ethylene carbonate (which is
10 preferred), propylene carbonate or butylene carbonate. Use of a carbonate for the oxyalkylation reaction is found to give rise to much better control of the “ n ” value and quantity, in comparison with use of ethylene oxide or propylene oxide. Furthermore, an appropriate choice of catalyst can provide a product consisting essentially entirely of mono-oxyalkyl (i.e. $n = 1$) content. Sodium salts are preferred, especially the
15 hydroxide and carboxylates, such as stearate.

In particular, the hydrocarbyl phenol aldehyde condensate is preferably branched dodecyl phenol formaldehyde condensate, such as, for example, a tetrapropenyl tetramer phenol formaldehyde condensate.
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The hydrocarbyl phenol aldehyde condensate is preferably present in the additive concentrate in an amount ranging from about 0.1 to 20 mass %, preferably from about 0.1 to 15 mass %, and more preferably from about 0.1 to 12 mass %, based on the mass of the concentrate.
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Lubricating oil compositions of the present invention comprise a major amount of an oil of lubricating viscosity and a minor amount of a compound of Formula I.

30 Oils of lubricating viscosity useful in the context of the present invention may be selected from natural lubricating oils, synthetic lubricating oils and mixtures thereof. The lubricating oil may range in viscosity from light distillate mineral oils to heavy lubricating oils such as gasoline engine oils, mineral lubricating oils and heavy duty diesel oils. Generally, the viscosity of the oil ranges from about 2 centistokes to

about 40 centistokes, especially from about 4 centistokes to about 20 centistokes, as measured at 100°C.

Natural oils include animal oils and vegetable oils (e.g., castor oil, lard oil);
5 liquid petroleum oils and hydrotreated, 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.
Synthetic lubricating oils include hydrocarbon oils and halo-substituted hydrocarbon oils such as polymerized and interpolymerized olefins (e.g., polybutylenes,
10 polypropylenes, propylene-isobutylene copolymers, chlorinated polybutylenes, poly(1-hexenes), poly(1-octenes), poly(1-decenes)); alkylbenzenes (e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di(2-ethylhexyl)benzenes); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenols); and alkylated diphenyl ethers and alkylated diphenyl sulfides and derivative, analogs and homologs
15 thereof. Also useful are synthetic oils derived from a gas to liquid process from Fischer-Tropsch synthesized hydrocarbons, which are commonly referred to as gas to liquid, or "GTL" base oils.

Alkylene oxide polymers and interpolymers and derivatives thereof where the
20 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
25 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 C₁₃ oxo acid diester of tetraethylene glycol.

Another suitable class of synthetic lubricating oils comprises the esters of
30 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.

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.

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 phosphorous-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, diethyl ester of decylphosphonic acid) and polymeric tetrahydrofurans.

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The oil of lubricating viscosity may comprise a Group I, Group II or Group III, base stock or base oil blends of the aforementioned base stocks. Preferably, the oil of lubricating viscosity is a Group II or Group III base stock, or a mixture thereof, or a mixture of a Group I base stock and one or more a Group II and Group III. Preferably, a major amount of the oil of lubricating viscosity is a Group II, Group III, Group IV or Group V base stock, or a mixture thereof. The base stock, or base stock blend preferably has a saturate content of at least 65%, more preferably at least 75%, such as at least 85%. Most preferably, the base stock, or base stock blend, has a saturate content of greater than 90%. Preferably, the oil or oil blend will have a sulfur content of less than 1%, preferably less than 0.6%, most preferably less than 0.4%, by weight.

Preferably the volatility of the oil or oil blend, as measured by the Noack volatility test (ASTM D5880), is less than or equal to 30%, preferably less than or equal to 25%, more preferably less than or equal to 20%, most preferably less than or

equal 16%. Preferably, the viscosity index (VI) of the oil or oil blend is at least 85, preferably at least 100, most preferably from about 105 to 140.

Definitions for the base stocks and base oils in this invention are the same as those found in the American Petroleum Institute (API) publication "Engine Oil Licensing and Certification System", Industry Services Department, Fourteenth Edition, December 1996, Addendum 1, December 1998. Said publication categorizes base stocks as follows:

- a) Group I base stocks contain less than 90 percent saturates and/or greater than 0.03 percent sulfur and have a viscosity index greater than or equal to 80 and less than 120 using the test methods specified in Table 1.
- b) Group II base stocks contain greater than or equal to 90 percent saturates and less than or equal to 0.03 percent sulfur and have a viscosity index greater than or equal to 80 and less than 120 using the test methods specified in Table 1.
- c) Group III base stocks contain greater than or equal to 90 percent saturates and less than or equal to 0.03 percent sulfur and have a viscosity index greater than or equal to 120 using the test methods specified in Table 1.
- d) Group IV base stocks are polyalphaolefins (PAO).
- e) Group V base stocks include all other base stocks not included in Group I, II, III, or IV.

Table I - Analytical Methods for Base Stock

Property	Test Method
Saturates	ASTM D 2007
Viscosity Index	ASTM D 2270
Sulfur	ASTM D 2622
	ASTM D 4294
	ASTM D 4927
	ASTM D 3120

Metal-containing or ash-forming detergents function both as detergents to reduce or remove deposits and as acid neutralizers or rust inhibitors, thereby reducing wear and corrosion and extending engine life. Detergents generally comprise a polar head with a long hydrophobic tail, with the polar head comprising a metal salt of an acidic organic compound. The salts may contain a substantially stoichiometric amount of the metal in which case they are usually described as normal or neutral salts, and would typically have a total base number or TBN (as can be measured by ASTM D2896) of from 0 to 80. A large amount of a metal base may be incorporated by reacting excess metal compound (e.g., an oxide or hydroxide) with an acidic gas (e.g., carbon dioxide). The resulting overbased detergent comprises neutralized detergent as the outer layer of a metal base (e.g. carbonate) micelle. Such overbased detergents may have a TBN of 150 or greater, and typically will have a TBN of from 250 to 500 or more.

Detergents that may be used include oil-soluble neutral and overbased sulfonates, phenates, sulfurized phenates, thiophosphonates, salicylates, and naphthenates and other oil-soluble carboxylates of a metal, particularly the alkali or alkaline earth metals, e.g., sodium, potassium, lithium, calcium, and magnesium. The most commonly used metals are calcium and magnesium, which may both be present in detergents used in a lubricant, and mixtures of calcium and/or magnesium with sodium. Particularly convenient metal detergents are neutral and overbased calcium sulfonates having TBN of from 20 to 500 TBN, and neutral and overbased calcium phenates and sulfurized phenates having TBN of from 50 to 450. Combinations of detergents, whether overbased or neutral or both, may be used.

Sulfonates may be prepared from sulfonic acids which are typically obtained by the sulfonation of alkyl substituted aromatic hydrocarbons such as those obtained from the fractionation of petroleum or by the alkylation of aromatic hydrocarbons. Examples included those obtained by alkylating benzene, toluene, xylene, naphthalene, diphenyl or their halogen derivatives such as chlorobenzene, chlorotoluene and chloronaphthalene. The alkylation may be carried out in the presence of a catalyst with alkylating agents having from about 3 to more than 70 carbon atoms. The alkaryl sulfonates usually contain from about 9 to about 80 or

more carbon atoms, preferably from about 16 to about 60 carbon atoms per alkyl substituted aromatic moiety.

5 The oil soluble sulfonates or alkaryl sulfonic acids may be neutralized with oxides, hydroxides, alkoxides, carbonates, carboxylate, sulfides, hydrosulfides, nitrates, borates and ethers of the metal. The amount of metal compound is chosen having regard to the desired TBN of the final product but typically ranges from about 100 to 220 mass % (preferably at least 125 mass %) of that stoichiometrically required.

10

Metal salts of phenols and sulfurized phenols are prepared by reaction with an appropriate metal compound such as an oxide or hydroxide and neutral or overbased products may be obtained by methods well known in the art. Sulfurized phenols may be prepared by reacting a phenol with sulfur or a sulfur containing compound such as 15 hydrogen sulfide, sulfur monohalide or sulfur dihalide, to form products which are generally mixtures of compounds in which 2 or more phenols are bridged by sulfur containing bridges.

Lubricating oil compositions of the present invention may further contain one 20 or more ashless dispersants, which effectively reduce formation of deposits upon use in engines, when added to lubricating oils. Ashless dispersants useful in the compositions of the present invention comprises an oil soluble polymeric long chain backbone having functional groups capable of associating with particles to be dispersed. Typically, such dispersants comprise amine, alcohol, amide or ester polar 25 moieties attached to the polymer backbone, often via a bridging group. The ashless dispersant may be, for example, selected from oil soluble salts, esters, amino-esters, amides, imides and oxazolines of long chain hydrocarbon-substituted mono- and polycarboxylic acids or anhydrides thereof; thiocarboxylate derivatives of long chain hydrocarbons; long chain aliphatic hydrocarbons having polyamine moieties attached 30 directly thereto; and Mannich condensation products formed by condensing a long chain substituted phenol with formaldehyde and polyalkylene polyamine. The most common dispersant in use is the well known succinimide dispersant, which is a condensation product of a hydrocarbyl-substituted succinic anhydride and a

poly(alkyleneamine). Both mono-succinimide and bis-succinimide dispersants (and mixtures thereof) are well known.

Preferably, the ashless dispersant is a "high molecular weight" dispersant
5 having a number average molecular weight ($\overline{M}_n$) greater than or equal to 4,000, such as between 4,000 and 20,000. The precise molecular weight ranges will depend on the type of polymer used to form the dispersant, the number of functional groups present, and the type of polar functional group employed. For example, for a polyisobutylene derivatized dispersant, a high molecular weight dispersant is one
10 formed with a polymer backbone having a number average molecular weight of from about 1680 to about 5600. Typical commercially available polyisobutylene-based dispersants contain polyisobutylene polymers having a number average molecular weight ranging from about 900 to about 2300, functionalized by maleic anhydride (MW = 98), and derivatized with polyamines having a molecular weight of from
15 about 100 to about 350. Polymers of lower molecular weight may also be used to form high molecular weight dispersants by incorporating multiple polymer chains into the dispersant, which can be accomplished using methods that are known in the art.

Preferred groups of dispersant include polyamine-derivatized poly α -olefin,
20 dispersants, particularly ethylene/butene α -olefin and polyisobutylene-based dispersants. Particularly preferred are ashless dispersants derived from polyisobutylene substituted with succinic anhydride groups and reacted with polyethylene amines, e.g., polyethylene diamine, tetraethylene pentamine; or a polyoxyalkylene polyamine, e.g., polyoxypropylene diamine,
25 trimethylolaminomethane; a hydroxy compound, e.g., pentaerythritol; and combinations thereof. One particularly preferred dispersant combination is a combination of (A) polyisobutylene substituted with succinic anhydride groups and reacted with (B) a hydroxy compound, e.g., pentaerythritol; (C) a polyoxyalkylene polyamine, e.g., polyoxypropylene diamine, or (D) a polyalkylene diamine, e.g.,
30 polyethylene diamine and tetraethylene pentamine using about 0.3 to about 2 moles of (B), (C) and/or (D) per mole of (A). Another preferred dispersant combination comprises a combination of (A) polyisobutenyl succinic anhydride with (B) a polyalkylene polyamine, e.g., tetraethylene pentamine, and (C) a polyhydric alcohol

or polyhydroxy-substituted aliphatic primary amine, e.g., pentaerythritol or trimethylolaminomethane, as described in U.S. Patent No. 3,632,511.

Another class of ashless dispersants comprises Mannich base condensation products. Generally, these products are prepared by condensing about one mole of an alkyl-substituted mono- or polyhydroxy benzene with about 1 to 2.5 moles of carbonyl compound(s) (e.g., formaldehyde and paraformaldehyde) and about 0.5 to 2 moles of polyalkylene polyamine, as disclosed, for example, in U.S. Patent No. 3,442,808. Such Mannich base condensation products may include a polymer product of a metallocene catalyzed polymerization as a substituent on the benzene group, or may be reacted with a compound containing such a polymer substituted on a succinic anhydride in a manner similar to that described in U.S. Patent No. 3,442,808. Examples of functionalized and/or derivatized olefin polymers synthesized using metallocene catalyst systems are described in the publications identified *supra*.

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The dispersant can be further post treated by a variety of conventional post treatments such as boration, as generally taught in U.S. Patent Nos. 3,087,936 and 3,254,025. Boration of the dispersant is readily accomplished by treating an acyl nitrogen-containing dispersant with a boron compound such as boron oxide, boron halide boron acids, and esters of boron acids, in an amount sufficient to provide from about 0.1 to about 20 atomic proportions of boron for each mole of acylated nitrogen composition. Useful dispersants contain from about 0.05 to about 2.0 mass %, e.g., from about 0.05 to about 0.7 mass % boron. The boron, which appears in the product as dehydrated boric acid polymers (primarily $(\text{HBO}_2)_3$), is believed to attach to the dispersant imides and diimides as amine salts, e.g., the metaborate salt of the diimide. Boration can be carried out by adding from about 0.5 to 4 mass %, e.g., from about 1 to about 3 mass % (based on the mass of acyl nitrogen compound) of a boron compound, preferably boric acid, usually as a slurry, to the acyl nitrogen compound and heating with stirring at from about 135°C to about 190°C, e.g., 140°C to 170°C, for from about 1 to about 5 hours, followed by nitrogen stripping. Alternatively, the boron treatment can be conducted by adding boric acid to a hot reaction mixture of the dicarboxylic acid material and amine, while removing water. Other post reaction processes commonly known in the art can also be applied.

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The dispersant may also be further post treated by reaction with a so-called "capping agent". Conventionally, nitrogen-containing dispersants have been "capped" to reduce the adverse effect such dispersants have on the fluoroelastomer engine seals.

5 Numerous capping agents and methods are known. Of the known "capping agents", those that convert basic dispersant amino groups to non-basic moieties (e.g., amido or imido groups) are most suitable. The reaction of a nitrogen-containing dispersant and alkyl acetoacetate (e.g., ethyl acetoacetate (EAA)) is described, for example, in U.S. Patent Nos. 4,839,071; 4,839,072 and 4,579,675. The reaction of a nitrogen-

10 containing dispersant and formic acid is described, for example, in U.S. Patent No. 3,185,704. The reaction product of a nitrogen-containing dispersant and other suitable capping agents are described in U.S. Patent Nos. 4,663,064 (glycolic acid); 4,612,132; 5,334,321; 5,356,552; 5,716,912; 5,849,676; 5,861,363 (alkyl and alkylene carbonates, e.g., ethylene carbonate); 5,328,622 (mono-epoxide); 5,026,495;

15 5,085,788; 5,259,906; 5,407,591 (poly (e.g., bis)-epoxides) and 4,686,054 (maleic anhydride or succinic anhydride). The foregoing list is not exhaustive and other methods of capping nitrogen-containing dispersants are known to those skilled in the art.

20 For adequate piston deposit control, a nitrogen-containing dispersant can be added in an amount providing the lubricating oil composition with from about 0.03 mass % to about 0.15 mass %, preferably from about 0.07 to about 0.12 mass %, of nitrogen.

25 Ashless dispersants are basic in nature and therefore have a TBN which, depending on the nature of the polar group and whether or not the dispersant is borated or treated with a capping agent, may be from about 5 to about 200 mg KOH/g. However, high levels of basic dispersant nitrogen are known to have a deleterious effect on the fluoroelastomeric materials conventionally used to form engine seals and,

30 therefore, it is preferable to use the minimum amount of dispersant necessary to provide piston deposit control, and to use substantially no dispersant, or preferably no dispersant, having a TBN of greater than 5. Preferably, the amount of dispersant employed will contribute no more than 4, preferably no more than 3 mg KOH/g of TBN to the lubricating oil composition. It is further preferable that dispersant

provides no greater than 30, preferably no greater than 25% of the TBN of the lubricating oil composition.

Additional additives may be incorporated in the compositions of the invention to enable them to meet particular requirements. Examples of additives which may be included in the lubricating oil compositions are metal rust inhibitors, viscosity index improvers, corrosion inhibitors, oxidation inhibitors, friction modifiers, other dispersants, anti-foaming agents, anti-wear agents and pour point depressants. Some are discussed in further detail below.

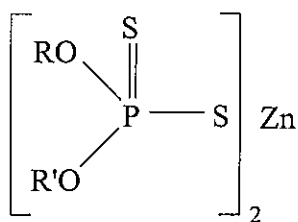
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Dihydrocarbyl dithiophosphate metal salts are frequently used as antiwear and antioxidant agents. The metal may be an alkali or alkaline earth metal, or aluminum, lead, tin, molybdenum, manganese, nickel or copper. The zinc salts are most commonly used in lubricating oil in amounts of 0.1 to 10, preferably 0.2 to 2 wt. %, based upon the total weight of the lubricating oil composition. They may be prepared in accordance with known techniques by first forming a dihydrocarbyl dithiophosphoric acid (DDPA), usually by reaction of one or more alcohol or a phenol with P_2S_5 and then neutralizing the formed DDPA with a zinc compound. For example, a dithiophosphoric acid may be made by reacting mixtures of primary and secondary alcohols. Alternatively, multiple dithiophosphoric acids can be prepared where the hydrocarbyl groups on one are entirely secondary in character and the hydrocarbyl groups on the others are entirely primary in character. To make the zinc salt, any basic or neutral zinc compound could be used but the oxides, hydroxides and carbonates are most generally employed. Commercial additives frequently contain an excess of zinc due to the use of an excess of the basic zinc compound in the neutralization reaction.

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The preferred zinc dihydrocarbyl dithiophosphates are oil soluble salts of dihydrocarbyl dithiophosphoric acids and may be represented by the following formula:

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wherein R and R' may be the same or different hydrocarbyl radicals containing from 1 to 18, preferably 2 to 12, carbon atoms and including radicals such as alkyl, alkenyl, aryl, arylalkyl, alkaryl and cycloaliphatic radicals. Particularly preferred as R and R' groups are alkyl groups of 2 to 8 carbon atoms. Thus, the radicals may, for example, be ethyl, n-propyl, i-propyl, n-butyl, i-butyl, sec-butyl, amyl, n-hexyl, i-hexyl, n-octyl, decyl, dodecyl, octadecyl, 2-ethylhexyl, phenyl, butylphenyl, cyclohexyl, methylcyclopentyl, propenyl, butenyl. In order to obtain oil solubility, the total number of carbon atoms (i.e. R and R') in the dithiophosphoric acid will generally be about 5 or greater. The zinc dihydrocarbyl dithiophosphate can therefore comprise zinc dialkyl dithiophosphates. The present invention may be particularly useful when used with lubricant compositions containing phosphorus levels of from about 0.02 to about 0.12 mass %, such as from about 0.03 to about 0.10 mass %, or from about 0.05 to about 0.08 mass %, based on the total mass of the composition. In one preferred embodiment, lubricating oil compositions of the present invention contain zinc dialkyl dithiophosphate derived predominantly (e.g., over 50 mol. %, such as over 60 mol. %) from secondary alcohols.

Oxidation inhibitors or antioxidants reduce the tendency of mineral oils to deteriorate in service. Oxidative deterioration can be evidenced by sludge in the lubricant, varnish-like deposits on the metal surfaces, and by viscosity growth. Such oxidation inhibitors include hindered phenols, alkaline earth metal salts of alkylphenolthioesters having preferably C₅ to C₁₂ alkyl side chains, calcium nonylphenol sulfide, oil soluble phenates and sulfurized phenates, phosphosulfurized or sulfurized hydrocarbons, phosphorous esters, metal thiocarbamates, oil soluble copper compounds as described in U.S. Patent No. 4,867,890, and molybdenum-containing compounds.

Typical oil soluble aromatic amines having at least two aromatic groups attached directly to one amine nitrogen contain from 6 to 16 carbon atoms. The

amines may contain more than two aromatic groups. Compounds having a total of at least three aromatic groups in which two aromatic groups are linked by a covalent bond or by an atom or group (e.g., an oxygen or sulfur atom, or a -CO-, -SO₂- or alkylene group) and two are directly attached to one amine nitrogen also considered
5 aromatic amines having at least two aromatic groups attached directly to the nitrogen. The aromatic rings are typically substituted by one or more substituents selected from alkyl, cycloalkyl, alkoxy, aryloxy, acyl, acylamino, hydroxy, and nitro groups.

Multiple antioxidants are commonly employed in combination. In one
10 preferred embodiment, lubricating oil compositions of the present invention contain from about 0.1 to about 1.2 mass % of aminic antioxidant and from about 0.1 to about 3 mass % of phenolic antioxidant. In another preferred embodiment, lubricating oil compositions of the present invention contain from about 0.1 to about 1.2 mass % of aminic antioxidant, from about 0.1 to about 3 mass % of phenolic antioxidant and a
15 molybdenum compound in an amount providing the lubricating oil composition from about 10 to about 1000 ppm of molybdenum.

Representative examples of suitable viscosity modifiers are polyisobutylene, copolymers of ethylene and propylene, polymethacrylates, methacrylate copolymers,
20 copolymers of an unsaturated dicarboxylic acid and a vinyl compound, interpolymers of styrene and acrylic esters, and partially hydrogenated copolymers of styrene/isoprene, styrene/butadiene, and isoprene/butadiene, as well as the partially hydrogenated homopolymers of butadiene and isoprene.

Friction modifiers and fuel economy agents that are compatible with the other
25 ingredients of the final oil may also be included. Examples of such materials include glyceryl monoesters of higher fatty acids, for example, glyceryl mono-oleate; esters of long chain polycarboxylic acids with diols, for example, the butane diol ester of a dimerized unsaturated fatty acid; oxazoline compounds; and alkoxylated alkyl-
30 substituted mono-amines, diamines and alkyl ether amines, for example, ethoxylated tallow amine and ethoxylated tallow ether amine.

Other known friction modifiers comprise oil-soluble organo-molybdenum compounds. Such organo-molybdenum friction modifiers also provide antioxidant

and antiwear credits to a lubricating oil composition. Examples of such oil soluble organo-molybdenum compounds include dithiocarbamates, dithiophosphates, dithiophosphinates, xanthates, thioxanthates, sulfides, and the like, and mixtures thereof. Particularly preferred are molybdenum dithiocarbamates, dialkyldithiophosphates, alkyl
5 xanthates and alkylthioxanthates.

Additionally, the molybdenum compound may be an acidic molybdenum compound. These compounds will react with a basic nitrogen compound as measured by ASTM test D-664 or D-2896 titration procedure and are typically hexavalent.
10 Included are molybdic acid, ammonium molybdate, sodium molybdate, potassium molybdate, and other alkaline metal molybdates and other molybdenum salts, e.g., hydrogen sodium molybdate, MoOCl_4 , MoO_2Br_2 , $\text{Mo}_2\text{O}_3\text{Cl}_6$, molybdenum trioxide or similar acidic molybdenum compounds.

15 Among the molybdenum compounds useful in the compositions of this invention are organo-molybdenum compounds of the formulae:



wherein R is an organo group selected from the group consisting of alkyl, aryl, aralkyl
20 and alkoxyalkyl, generally of from 1 to 30 carbon atoms, and preferably 2 to 12 carbon atoms and most preferably alkyl of 2 to 12 carbon atoms. Especially preferred are the dialkyldithiocarbamates of molybdenum.

Another group of organo-molybdenum compounds useful in the lubricating
25 compositions of this invention are trinuclear molybdenum compounds, especially those of the formula $\text{Mo}_3\text{S}_k\text{L}_n\text{Q}_z$ and mixtures thereof wherein the L are independently selected ligands having organo groups with a sufficient number of carbon atoms to render the compound soluble or dispersible in the oil, n is from 1 to 4, k varies from 4 through 7, Q is selected from the group of neutral electron donating compounds such as
30 water, amines, alcohols, phosphines, and ethers, and z ranges from 0 to 5 and includes non-stoichiometric values. At least 21 total carbon atoms should be present among all the ligand organo groups, such as at least 25, at least 30, or at least 35 carbon atoms.

A dispersant-viscosity index improver functions as both a viscosity index improver and as a dispersant. Examples of dispersant-viscosity index improvers include reaction products of amines, for example polyamines, with a hydrocarbyl-substituted mono-or di-carboxylic acid in which the hydrocarbyl substituent
5 comprises a chain of sufficient length to impart viscosity index improving properties to the compounds. In general, the viscosity index improver dispersant may be, for example, a polymer of a C₄ to C₂₄ unsaturated ester of vinyl alcohol or a C₃ to C₁₀ unsaturated mono-carboxylic acid or a C₄ to C₁₀ di-carboxylic acid with an unsaturated nitrogen-containing monomer having 4 to 20 carbon atoms; a polymer of
10 a C₂ to C₂₀ olefin with an unsaturated C₃ to C₁₀ mono- or di-carboxylic acid neutralized with an amine, hydroxyl amine or an alcohol; or a polymer of ethylene with a C₃ to C₂₀ olefin further reacted either by grafting a C₄ to C₂₀ unsaturated nitrogen-containing monomer thereon or by grafting an unsaturated acid onto the polymer backbone and then reacting carboxylic acid groups of the grafted acid with
15 an amine, hydroxy amine or alcohol.

Pour point depressants, otherwise known as lube oil flow improvers (LOFI), lower the minimum temperature at which the fluid will flow or can be poured. Such additives are well known. Typical of those additives that improve the low
20 temperature fluidity of the fluid are C₈ to C₁₈ dialkyl fumarate/vinyl acetate copolymers, and polymethacrylates. Foam control can be provided by an antifoamant of the polysiloxane type, for example, silicone oil or polydimethyl siloxane.

Some of the above-mentioned additives can provide a multiplicity of effects; thus for example, a single additive may act as a dispersant-oxidation inhibitor. This
25 approach is well known and need not be further elaborated herein.

In the present invention it may also be preferable to include an additive which maintains the stability of the viscosity of the blend. Thus, although polar group-
30 containing additives achieve a suitably low viscosity in the pre-blending stage it has been observed that some compositions increase in viscosity when stored for prolonged periods. Additives which are effective in controlling this viscosity increase include the long chain hydrocarbons functionalized by reaction with mono- or

dicarboxylic acids or anhydrides which are used in the preparation of the ashless dispersants as hereinbefore disclosed.

When lubricating compositions contain one or more of the above-mentioned additives, each additive is typically blended into the base oil in an amount that enables the additive to provide its desired function. Representative effect amounts of such additives, when used in different lubricants, are listed below. All the values listed are stated as mass percent active ingredient.

Marine Diesel Cylinder Lubricant ("MDCL")

A Marine Diesel Cylinder Lubricant may employ 10-35, preferably 13-30, most preferably 16-24, mass % of a concentrate or additive package, the remainder being base stock. It preferably includes at least 50, more preferably at least 60, even more preferably at least 70, mass % of oil of lubricating viscosity based on the total mass of MDCL.

Fully formulated MDCLs preferably have a TBN of at least 20, such as from about 30 to about 100 mg KOH/g (ASTM D2896). More preferably, compositions have a TBN of at least 40, such as from about 40 to about 70 mg KOH/g.

MDCLs preferably have a sulfated ash (SASH) content (ASTM D-874) of about 12 mass % or less, preferably about 11 mass % or less, more preferably about 10 mass % or less, such as 9 mass % or less.

The following may be mentioned as examples of typical proportions of additives in an MDCL:

Additive	Mass% a.i. (Broad)	Mass% a.i. (Preferred)
detergent(s)	1-20	3-15
dispersant(s)	0.5-5	1-3
ashless anti-wear agent(s)	0.1-1.5	0.5-1.3

pour point dispersant	0.03-1.15	0.05-0.1
base stock	balance	balance

Trunk Piston Engine Oil ("TPEO")

A Trunk Piston Engine Oil may employ 7-35, preferably 10-28, more preferably 12-24, mass % of a concentrate or additives package, the remainder being
5 base stock.

Fully formulated trunk piston engine oils preferably have a TBN of at least 10, such as from about 15 to about 60 mg KOH/g (ASTM D2896). More preferably, compositions have a TBN of at least 20, such as from about 30 to about 55 mg KOH/g.
10

Fully formulated trunk piston engine oils preferably have a sulfated ash (SASH) content (ASTM D-874) of about 7 mass % or less, preferably about 6.5 mass % or less, such as 6.3 mass % or less.

15 The following may be mentioned as typical proportions of additives in a TPEO:

Additive	Mass% a.i. (Broad)	Mass% a.i. (Preferred)
detergent(s)	0.5-12	2-8
dispersant(s)	0.5-5	1-3
ashless anti-wear agent(s)	0.1-1.5	0.5-1.3
oxidation inhibitor	0.2-2	0.5-1.5
rust inhibitor	0.03-0.15	0.05-0.1
pour point dispersant	0.03-1.15	0.05-0.1
base stock	balance	balance

Crankcase Lubricant

Fully formulated crankcase lubricating oil compositions preferably have a TBN of at least 6, such as from about 6 to about 18 mg KOH/g (ASTM D2896). More preferably, compositions have a TBN of at least 8.5, such as from about 8.5 or 9 to about 18 mg KOH/g.

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Fully formulated crankcase lubricating oil compositions preferably have a sulfated ash (SASH) content (ASTM D-874) of about 1.1 mass % or less, preferably about 1.0 mass % or less, more preferably about 0.8 mass % or less, such as 0.5 mass % or less.

10

The following may be mentioned as examples of typical proportions of additives in a crankcase lubricant (including passenger car motor oil and heavy duty diesel motor oil):

Additive	Mass% a.i. (Broad)	Mass% a.i. (Preferred)
Metal Detergents	0.1 - 15	0.2 - 9
Corrosion Inhibitor	0 - 5	0 - 1.5
Metal Dihydrocarbyl Dithiophosphate	0.1 - 6	0.1 - 4
Antioxidant	0 - 5	0.01 - 3
Pour Point Depressant	0.01 - 5	0.01 - 1.5
Antifoaming Agent	0 - 5	0.001 - 0.15
Supplemental Antiwear Agents	0 - 1.0	0 - 0.5
Friction Modifier	0 - 5	0 - 1.5
Viscosity Modifier	0.01 - 10	0.25 - 3
Basestock	Balance	Balance

15

Fully formulated lubricating oil compositions of the present invention preferably have a sulfur content of less than about 0.4 mass %. For crankcase applications, the fully formulated lubricating oil compositions preferably have a sulfur content of less than about 0.35 mass % more preferably less than about 0.3 mass %, such as less than about 0.20 mass %. Preferably, the Noack volatility (ASTM D5880) of the fully formulated lubricating oil composition (oil of lubricating viscosity plus all additives and additive diluent) will be no greater than 13, such as no greater than 12, preferably no greater than 10. Fully formulated lubricating oil compositions of the

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present invention preferably have no greater than 1200 ppm of phosphorus, such as no greater than 1000 ppm of phosphorus, or no greater than 800 ppm of phosphorus, such as no greater than 600 ppm of phosphorus, or no greater than 500 or 400 ppm of phosphorus.

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It may be desirable, although not essential to prepare one or more additive concentrates comprising additives (concentrates sometimes being referred to as additive packages) whereby several additives can be added simultaneously to the oil to form the lubricating oil composition. A concentration for the preparation of a lubricating oil composition of the present invention may, for example, contain from about 0.1 to about 30 mass %, preferably from 0.5 to 30 mass%, of one or more compounds of Formula (I); about 10 to about 40 mass % of a nitrogen-containing dispersant; about 2 to about 20 mass % of an aminic antioxidant, a phenolic antioxidant, a molybdenum compound, or a mixture thereof; about 5 to 40 mass % of a detergent; and from about 2 to about 20 mass % of a metal dihydrocarbyl dithiophosphate.

The final composition may employ from 5 to 25 mass %, preferably 5 to 18 mass %, typically 10 to 15 mass % of the concentrate, the remainder being oil of lubricating viscosity and viscosity modifier.

All weight (and mass) percents expressed herein (unless otherwise indicated) are based on active ingredient (A.I.) content of the additive, and/or additive-package, exclusive of any associated diluent. However, detergents are conventionally formed in diluent oil, which is not removed from the product, and the TBN of a detergent is conventionally provided for the active detergent in the associated diluent oil. Therefore, weight (and mass) percents, when referring to detergents are (unless otherwise indicated) total weight (or mass) percent of active ingredient and associated diluent oil.

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This invention will be further understood by reference to the following examples, wherein all parts are parts by weight (or mass), unless otherwise noted.

EXAMPLES

It is important that the basicity introduced into a lubricating oil composition be retained as long as possible. It is also important that the time at which TBN and TAN levels cross is as long as possible. Both of these measures ensure a longer oil life and better engine protection over a greater period of time.

Beaker tests were performed on three lubricating oil compositions: a reference oil, Example 1 and Example 2. The reference oil included 2.475 wt% of an overbased calcium sulphonate detergent having a TBN of 425 mgKOH/g in base oil. Example 1 included 2.475 wt% of an overbased calcium sulphonate detergent having a TBN of 425 mgKOH/g and 1.369 wt% of poly{[2-hydroxy-5-(tetrapropenyl)-1,3-phenylene]methylene} in base oil. Example 2 included 2.475 wt% of an overbased calcium sulphonate detergent having a TBN of 425 mgKOH/g and 1.369 wt% of poly{[2-hydroxyethoxy-5-(tetrapropenyl)-1,3-phenylene]methylene} in base oil. All three lubricating oil compositions had a TBN of 10.5 mgKOH/g (ASTM D2896).

The poly{[2-hydroxy-5-(tetrapropenyl)-1,3-phenylene]methylene} was prepared as follows:-

20

Para-tetrapropenylphenol (known as 'TPP') (1 mole equivalent, commercially available), alkylbenzene sulphonic acid (0.0033 mole% to TPP) and toluene (30mass% to TPP) were charged to a baffled reactor equipped with an overhead stirrer and a Dean and Stark reflux apparatus. A nitrogen blanket was used throughout. Stirring was increased to 160-170 rpm and the temperature was ramped up to 110°C over 40 mins. 36.5% formaldehyde solution (1.18 equiv. moles of formaldehyde to TPP used) was charged over 2 hrs at a constant rate. The temperature was maintained at 110°C throughout the addition. On completion of formaldehyde addition, the temperature was increased up to 120°C and maintained for 1 hr to remove the remaining water. The reaction was cooled to 90°C, then 50% sodium hydroxide solution (1.25 moles equiv to alkylbenzene sulphonic acid) was charged over 0.5 hrs. The temperature was ramped up to 130°C over 0.5 hrs and maintained for a further 1 hr to remove water. With apparatus set-up for distillation,

the intermediate was heated up to 130°C over 1 hr under vacuum to remove the toluene. Mineral oil was used to cutback product to 50% active ingredient.

5 The poly{[2-hydroxyethoxy-5-(tetrapropenyl)-1,3-phenylene]methylene} was prepared as follows:-

Para-tetrapropenylphenol (known as 'TPP') (1 mole equivalent, commercially available), alkylbenzene sulphonic acid (0.0033 mole% to TPP) and toluene (30mass% to TPP) were charged to a baffled reactor equipped with an overhead
10 stirrer and a Dean and Stark reflux apparatus. A nitrogen blanket was used throughout. The stirring rate was increased to 160-170 rpm. The temperature was ramped up to 110°C over 40 mins. 36.5% formaldehyde solution (1.18 equiv. moles of formaldehyde to TPP used) was charged over 2 hrs at a constant rate. The temperature was maintained at 110°C throughout the addition. On completion of
15 formaldehyde addition, the temperature was increased up to 120°C and maintained for 1 hr to remove the remaining water. The reaction was cooled to 90°C, then 50% sodium hydroxide solution (2.22 mass% to TPP) was charged over 0.5 hrs. The temperature was ramped up to 130°C over 0.5 hrs and maintained for a further 1 hr to remove water. With apparatus set-up for distillation, the intermediate was heated up
20 to 130°C over 1 hr under vacuum to remove the toluene. Xylene (30mass% to TPP) was charged whilst cooling down to 90°C. The Dean and Stark apparatus was switched from distillation to reflux. Ethylene carbonate (1.02 equivalent moles to TPP) was charged over 0.5 hrs using a dropping funnel. The temperature was ramped up to reflux point at 165°C over 1 hr. IR analysis was used to determine when
25 ethylene carbonate was fully consumed (typically after 2.5 hrs). The temperature was maintained at 165°C and vacuum distillation was used to remove xylene. Mineral oil was used to cutback product to 50% active ingredient.

The Beaker test involved titrating the oil formulation with 1.0M sulphuric acid,
30 and analyzing the TAN and TBN. The flow rate of acid was 10 ml/hr, the quantity of oil was 250g, the stirring rate was 300rpm and the oil temperature was 95 °C.

After each sample was tested, a centrifuge step was used to remove insoluble solids before oil analysis.

The results are as follows:

Reference Oil			
Acid Titration time /h	TAN ASTM D664	TBN ASTM D 4739	TBN (D4739) - TAN (D664)
0	0.44	8.8	8.38
0.25	1.73	5.3	3.57
0.5	1.58	4.7	3.12
1	1.56	4.4	2.84
1.5	1.77	4.0	2.23
2.5	1.63	1.6	-0.03

Example 1			
Acid Titration time /h	TAN ASTM D664	TBN ASTM D 4739	TBN (D4739) - TAN (D664)
0	0.71	6.7	5.97
0.25	1.20	6.1	4.9
0.5	1.22	5.1	3.9
1	1.27	4.8	3.5
1.5	1.33	4.0	2.7
2.5	1.30	3.9	2.6

Example 2			
Acid Titration time /h	TAN ASTM D664	TBN ASTM D 4739	TBN (D4739) - TAN (D664)
0	0.40	8.2	7.8
0.25	0.70	5.7	5.00
0.5	0.96	5.5	4.54
1	0.89	5.4	4.51
1.5	0.95	4.4	3.45
2.5	0.97	3.3	2.33

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The results are also shown in the attached Figure.

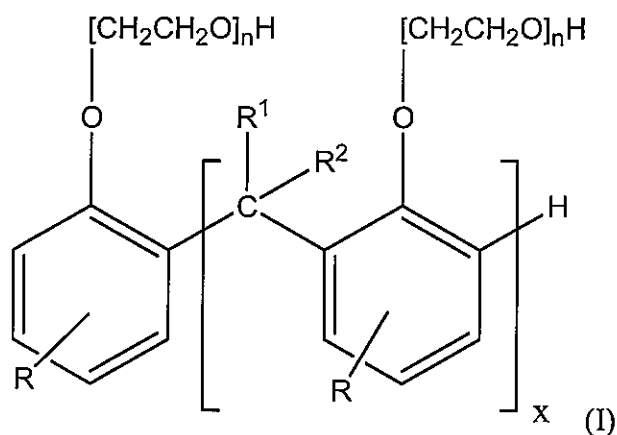
The results show that the reference oil reaches TAN and TBN crossover much earlier than Examples 1 and 2. Therefore, the base in the reference oil is depleted much sooner than the base in Examples 1 and 2. In fact, Examples 1 and 2 did not show TAN and TBN crossover even at the end of the test at 2.5 hours. Once lubricating oil compositions exhibit TAN and TBN crossover, the composition has

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insufficient base levels to neutralize any acid produced by an engine, which causes engine wear. These results are surprising as Examples 1 and 2 do not include any more base than the reference oil at the start of the test (i.e. all examples started the Beaker Test with a TBN of 10.5 mgKOH/g).

CLAIMS:

1. A method of reducing the rate of depletion of basicity (as determined by ASTM D2896) of a lubricating oil composition in use in an engine, the lubricating oil composition including at least one oil-soluble overbased alkali or alkaline earth metal detergent, which method comprises adding to the lubricating oil composition one or more compounds of Formula (I):



wherein:

x is 1 to 50, preferably 1 to 40, more preferably 1 to 30;

R¹ and R² are H, hydrocarbyl groups having 1 to 12 carbon atoms, or hydrocarbyl groups having 1 to 12 carbon atoms and at least one heteroatom;

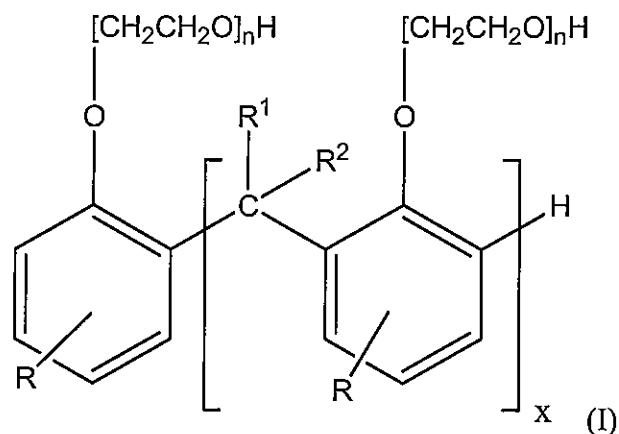
R is a hydrocarbyl group having 9 to 100, preferably 9 to 70, most preferably, 9 to 50, carbon atoms; and

n is 0 to 10, or alkaline earth metal salts thereof.

2. The method as claimed in claim 1, wherein n in Formula (I) is 0.
3. The method as claimed in any one of the preceding claims, wherein x in Formula (I) is 1.
4. The method as claimed in any one of the preceding claims, wherein R in Formula (I) is 9 to 20 carbon atoms, preferably 9 to 15.
5. The method as claimed in any one of the preceding claims, wherein R in Formula (I) is branched.

6. The method as claimed in any one of the preceding claims, wherein $R^1 = H$, $R^2 = H$ and R is in the para position in relation to the $-O-[CH_2CH_2O]_nH$ group in Formula (I).
7. The method as claimed in any one of the preceding claims, wherein the compounds of formula (I) include less than 1 mole%, preferably less than 0.5 mole% and most preferably less than 0.1 mole% of unreacted alkyl phenol.
8. The method as claimed in any one of the preceding claims, wherein $n = 1$ for more than 60, preferably more than 70, preferably more than 80, preferably more than 90, or most preferably more than 95, mole % of the compounds of formula (I).
9. The method as claimed in any one of the preceding claims, wherein the alkaline earth metal salts of the compounds of Formula (I) are calcium or magnesium.
10. The method as claimed in any one of the preceding claims, wherein $n \geq 2$, such as di-oxyalkylated, tri-oxyalkylated and tetra-oxyalkylated, for less than 5 mole % of the compounds of formula (I).
11. The method as claimed in any one of the preceding claims, wherein the compounds of formula (I) are methylene-bridged alkyl phenols or ethoxylated methylene-bridged alkyl phenols.
12. The method as claimed in any one of the preceding claims, wherein the lubricating oil composition has a TBN of 4 to 100 as measured by ASTM D2896, preferably a TBN of 5 to 75, even more preferably 6 to 70.
13. The method as claimed in any one of the preceding claims, wherein the lubricating oil composition is a marine cylinder lubricant, a trunk piston engine oil, a gas engine oil or a crankcase lubricating oil composition (including a passenger car motor oil and a heavy duty diesel motor oil).

14. Use of one or more compounds of Formula (I):



wherein: x is 1 to 50, preferably 1 to 40, more preferably 1 to 30; R^1 and R^2 are H, hydrocarbyl groups having 1 to 12 carbon atoms, or hydrocarbyl groups having 1 to 12 carbon atoms and at least one heteroatom; R is a hydrocarbyl group having 9 to 100, preferably 9 to 70, most preferably, 9 to 50, carbon atoms; and n is 0 to 10, or alkaline earth metal salts thereof, to reduce the rate of depletion of basicity (as determined by ASTM D2896) of a lubricating oil composition in use in an engine, the lubricating oil composition including at least one oil-soluble overbased alkali or alkaline earth metal detergent.