



(11) **EP 3 070 153 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
21.09.2016 Bulletin 2016/38

(21) Application number: **16164519.7**

(22) Date of filing: **30.08.2011**

(51) Int Cl.:
C10M 129/20 (2006.01) **C10L 1/18** (2006.01)
C10M 141/06 (2006.01) **C10M 141/10** (2006.01)
C10L 1/185 (2006.01) **C10L 1/19** (2006.01)
C10L 1/223 (2006.01) **C10L 1/24** (2006.01)
C10L 10/00 (2006.01) **C10L 1/224** (2006.01)
C10N 10/04 (2006.01) **C10N 30/10** (2006.01)
C10N 40/02 (2006.01) **C10N 40/04** (2006.01)
C10N 40/08 (2006.01) **C10N 40/20** (2006.01)
C10N 40/25 (2006.01) **C10N 40/26** (2006.01)
C10N 50/10 (2006.01)

(84) Designated Contracting States:
**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO
PL PT RO RS SE SI SK SM TR**

(30) Priority: **07.09.2010 US 380412 P**

(62) Document number(s) of the earlier application(s) in
accordance with Art. 76 EPC:
11755481.6 / 2 614 131

(71) Applicant: **The Lubrizol Corporation**
Wickliffe, OH 44092-2298 (US)

(72) Inventors:
• **CRAWLEY, Seth, L.**
Wickliffe, OH 44092-2298 (US)
• **CARRICK, Virginia, A.**
Wickliffe, OH 44092-2298 (US)

(74) Representative: **D Young & Co LLP**
120 Holborn
London EC1N 2DY (GB)

Remarks:

This application was filed on 08-04-2016 as a
divisional application to the application mentioned
under INID code 62.

(54) **HYDROXYCHROMAN DERIVATIVES AS ANTIOXIDANTS**

(57) A lubricant composition comprises a hydroxychroman derived antioxidant.

EP 3 070 153 A1

Description

FIELD OF THE INVENTION

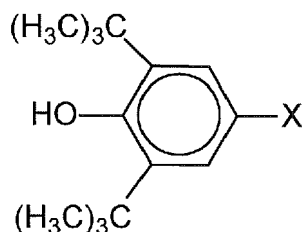
[0001] This invention relates to compositions suitable for use as lubricants and lubricant additive compositions which contain a hydroxychroman derived antioxidant, where said antioxidants themselves may also be described hydroxychroman compounds, and further optionally containing other additives suitable for lubricants such as a detergent or a dispersant. The present invention provides an economical antioxidant which has good performance properties when used in lubricant formulations especially for heavy duty diesel engines and passenger car crankcase engines.

BACKGROUND OF THE INVENTION

[0002] Antioxidants are an important class of additives since they are used to provide and/or improve the anti-oxidation performance of organic compositions, including lubricant compositions that contain organic components, by preventing or retarding oxidative and thermal decomposition. Antioxidants in some applications can result in an increase in volatility which can be undesirable due to required environmental regulations and/or performance standards.

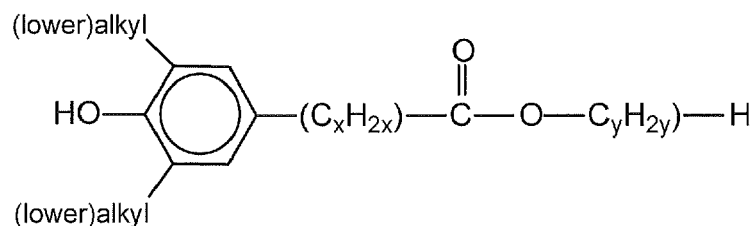
[0003] It is known to use a hindered, ester-substituted phenol antioxidant in an oil of lubricating viscosity to reduce oxidation breakdown and improve cleanliness.

[0004] U.S. Patent 5,523,007, Kristen et al., June 4, 1996, discloses a lubricant oil composition comprising a diesel engine lubricating oil and, as antioxidant, a compound of the formula



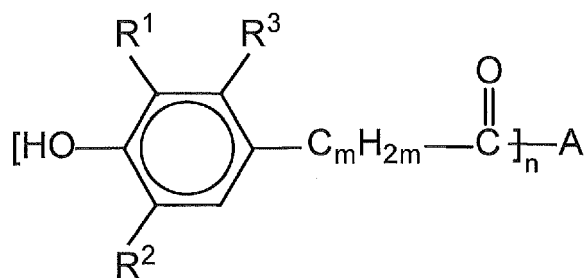
X can be $-\text{CH}_2-\text{CH}_2-\text{C}(=\text{O})-\text{OR}$ and R is a straight chain or branched alkyl radical of the formula $-\text{C}_n\text{H}_{2n+1}$ wherein n is an integer from 8 to 22.

[0005] U.S. Patent 3,285,855, Dexter et al., November 15, 1966, discloses stabilization of organic material with esters containing an alkylhydroxyphenyl group. The ester can have the structure



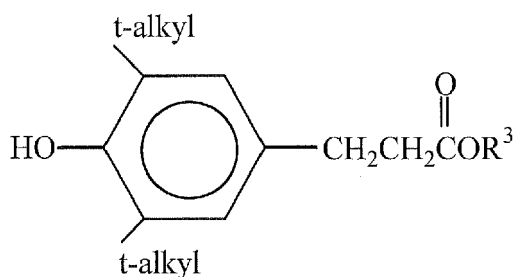
in which x has a value of from 0 to 6, inclusively, and y has a value of from 6 to 30, inclusively. The "lower alkyl" groups can be t-butyl. Organic materials which can be stabilized include, among many others, lubricating oil of the aliphatic ester type, and mineral oil.

[0006] U.S. Patent 5,206,414, Evans et al., April 27, 1993, discloses a process for the preparation of compounds of the general formula



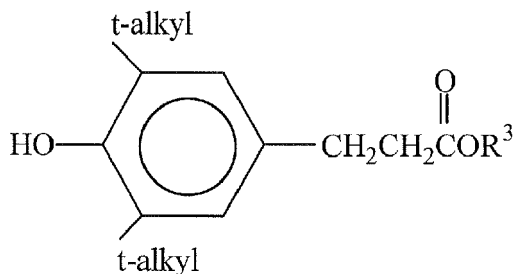
wherein R1 and R2 are identical or different and are hydrogen, C1-C18 alkyl, phenyl, C1-C4 alkyl-substituted phenyl, C7-C9 phenylalkyl, C5-C12 cycloalkyl or C1-C4 alkyl-substituted C5-C12 cycloalkyl, R3 is hydrogen or methyl, m is 0,1,2, or 3 and n is a number from 1 to 4 or 6, and A can be -OR4 where R4 can be C2-C45 alkyl.

[0007] U.S. Patent No. 6,559,105 of Abraham et al. involves lubricant compositions containing ester-substituted hindered phenol antioxidants.



wherein R3 is an alkyl group containing 2 to 6 carbon atoms, and a dispersant or a detergent, is a useful additive package for lubricant compositions.

[0008] U.S. Patent 6,787,663, Adams et al., September 7, 2004 discloses a process for the preparation of a hindered ester-substituted phenol and its use in a lubricant composition of the general formula

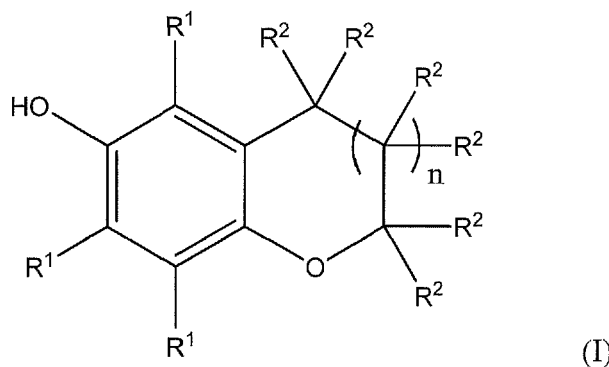


wherein R3 is an alkyl group containing 2 to 6 carbon atoms.

[0009] While materials such as the hindered phenols described above can provide good anti-oxidant performance in lubricating oils, their performance generally suffers at elevated temperatures. Increasingly, current engine technology is leading to increasing operating temperatures for engines and the lubricating oils on which they rely. For example, modern EGR, turbochargers, and the increased usage of smaller, more powerful and fuel efficient engines are leading to an increase in average engine operating temperatures. Therefore, there is a need for new antioxidant technology that provides at least as good performance as known antioxidant technology while also providing improved thermal stability and/or performance at elevated temperatures.

SUMMARY OF THE INVENTION

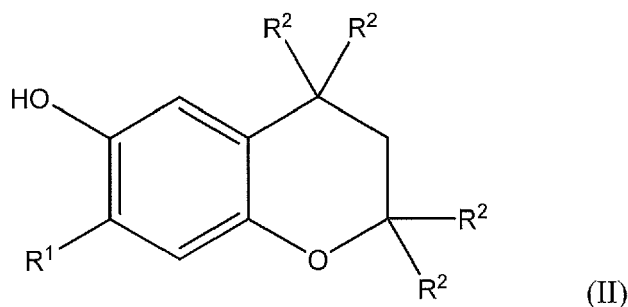
[0010] The present invention provides for a lubricating composition containing an oil of lubricating viscosity and an antioxidant having the formula:



wherein each R^1 is independently $-OR^2$, $-NH_2$, $-NR^2R^2$, $-SR^2$ or $-R^2$; each R^2 is independently a hydrogen, a hydrocarbyl group, or a $-C(=O)-X-R^3$ group where X is O , NR^3 or S and each R^3 is independently a hydrogen or a hydrocarbyl group; and n is 0 or 1; and where the two adjacent R^1 groups are hydrocarbyl groups, they may be linked to form a ring.

[0011] In some embodiments each R^1 in the formula above is independently a hydrogen or hydrocarbyl group containing from 1 to 20 carbon atoms and each R^2 is independently a hydrogen or hydrocarbyl group containing from 1 to 15 carbon atoms. In embodiments where one or more R^3 groups is present the R^3 group may be a hydrocarbyl group containing from 3 to 22 carbon atoms, or from 8 to 18 carbon atoms, or may be a 2-ethyl or isotridecyl group.

[0012] The invention further provides for lubricant compositions containing an antioxidant with the following formula:



wherein R^1 is hydrocarbyl group containing from 1 to 10 carbon atoms; and each R^2 is independently a hydrogen or hydrocarbyl group containing from 1 to 10 carbon atoms. Each R^2 in formula II may also be a $-C(=O)-X-R^3$ group where X is O , NR^3 or S and each R^3 is independently a hydrogen or a hydrocarbyl group.

[0013] The invention further provides for lubricant compositions as described above where the composition contains no more than 1200 ppm phosphorus, has a sulfur content of no more than 0.4 percent by weight, has a sulfated ash content of no more than 1.0 percent by weight, has a zinc dialkyldithiophosphate at a level of no less than 300 ppm, or any combinations thereof. In some embodiments the composition may have a phosphorus level of at least 300 ppm.

[0014] The invention further provides for methods of lubricating an internal combustion engine. Such methods include the step of supplying to the engine any of the lubricant compositions described herein.

[0015] The invention further provides a lubricant composition suitable for lubricating an internal combustion engine, comprising: (A) a major amount of an oil of lubricating viscosity; (B) a minor amount of at least one hydroxylchroman antioxidant, as described herein; and (C) a minor amount of at least one other additive selected from the group consisting of viscosity modifiers, pour point depressants, dispersants, detergents, antiwear agents, antioxidants are different from component (B), friction modifiers, corrosion inhibitors, seal swell agents, metal deactivators, foam inhibitors, and mixtures thereof.

[0016] The invention further provides for a lubricant concentrate suitable for use in preparing a lubricating composition suitable for lubricating an internal combustion engine, comprising: (A) a concentrate-forming amount of an oil of lubricating viscosity; (B) a minor amount of at least one hydroxylchroman antioxidant, as described herein; and (C) at least one other additive selected from the group consisting of viscosity modifiers, pour point depressants, dispersants, detergents, antiwear agents, antioxidants that are different from component (B), friction modifiers, corrosion inhibitors, seal swell agents, metal deactivators, foam inhibitors, and mixtures thereof.

[0017] The present invention further provides a method for lubricating an internal combustion engine, comprising: (A) supplying to said engine a lubricant comprising: (i) an oil of lubricating viscosity; (ii) a minor amount of at least one hydroxylchroman antioxidant, as described herein; and (iii) a minor amount of at least one other additive selected from the group consisting of viscosity modifiers, pour point depressants, dispersants, detergents, antiwear agents, antioxidants

that are different from component (ii), friction modifiers, corrosion inhibitors, seal swell agents, metal deactivators, foam inhibitors, and mixtures thereof.

DETAILED DESCRIPTION OF THE INVENTION

[0018] Various preferred features and embodiments will be described below by way of non-limiting illustration.

[0019] The present invention provides various compositions that comprise one or more hydroxymethane derived antioxidants, wherein said antioxidants may themselves also be described as hydroxymethane compounds, and methods of lubricating internal combustion engines utilizing such antioxidants. Such antioxidants have been discovered to provide superior performance in the harsher operating conditions becoming more and more common in modern engine technology. The drive to design smaller and more powerful engines along with the drive to increase fuel economy and reduce emissions, has led to higher demands on lubricants and lubricant additive technology. The antioxidants of the present invention have been found to provide superior performance compared to conventional antioxidants.

[0020] The compositions of the present invention comprise an oil of lubricant viscosity, one or more hydroxymethane derived antioxidants, and optionally one or more additional performance additives.

[0021] The lubricant composition of this invention can find use in various applications to include as a lubricant composition for an internal combustion engine to include a gasoline or spark-ignited engine such as a passenger car engine, a diesel or compression-ignited engine such as a heavy duty diesel truck engine, a natural gas fueled engine such as a stationary power engine, a two-cycle engine, aviation piston and turbine engines, marine and railroad diesel engines; for power transmissions such as an automatic or transaxle or farm tractor transmission; for gears such as industrial or automotive gears; for metalworking; for hydraulic systems; for special applications such as bearings which can require that the lubricant composition be a grease; and for hydrocarbon fuels for an internal combustion engine such as a gasoline or diesel fuel.

Oil of Lubricating Viscosity

[0022] The lubricant composition of the present invention can comprise (A) a major amount of an oil of lubricating viscosity. The oil of lubricating viscosity can function by providing lubrication and by serving as a medium to dissolve or disperse the other components or additives of the lubricant composition. The oil of lubricating viscosity can be a single oil or a mixture of two or more oils. The lubricating oil composition comprises of one or more base oils which are generally present in a major amount (i.e. an amount greater than 50 percent by weight). Generally, the base oil is present in an amount greater than 60 percent, or greater than 70 percent, or greater than 80 percent by weight of the lubricating oil composition. In one embodiment the base oil sulfur content can be 0.001 to 0.2 percent by weight, in another embodiment 0.0001 to 0.1 or 0.05 percent by weight.

[0023] The lubricating oil composition may have a kinematic viscosity as measured in ASTM D445, of up to about 16.3 mm²/s at 100°C, and in one embodiment 5 to 16.3 mm²/s (cSt) at 100°C, and in one embodiment 6 to 13 mm²/s (cSt) at 100°C. In one embodiment, the lubricating oil composition has an SAE Viscosity Grade of 0W, 0W-20, 0W-30, 0W-40, 0W-50, 0W-60, 5W, 5W-20, 5W-30, 5W-40, 5W-50, 5W-60, 10W, 10W-20, 10W-30, 10W-40 or 10W-50.

[0024] The lubricating oil composition may have a high-temperature/high-shear viscosity at 150°C as measured by the procedure in ASTM D4683 of up to 4 mm²/s (cSt), and in one embodiment up to 3.7 mm²/s (cSt), and in one embodiment 2 to 4 mm²/s (cSt), and in one embodiment 2.2 to 3.7 mm²/s (cSt), and in one embodiment 2.7 to 3.5 mm²/s (cSt).

[0025] The base oil used in the lubricant composition may be a natural oil, synthetic oil or mixture thereof, provided the sulfur content of such oil does not exceed the above-indicated sulfur concentration limit required for the inventive low-sulfur, low-phosphorus, low-ash lubricating oil composition. The natural oils that are useful include animal oils and vegetable oils (e.g., castor oil, lard oil) as well as mineral lubricating oils such as liquid petroleum oils and solvent treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic or mixed paraffinic-naphthenic types. Oils derived from coal or shale are also useful. Synthetic lubricating oils include hydrocarbon oils such as polymerized and interpolymerized olefins (e.g., polybutylenes, polypropylenes, and propylene isobutylene copolymers); poly(1-hexenes), poly(1-octenes), poly(1-decenes), etc. and mixtures thereof; alkylbenzenes (e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, and di-(2-ethylhexyl)benzenes); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenyls); alkylated diphenyl ethers and the derivatives, analogs and homologs thereof.

[0026] Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by e.g., esterification, etherification, constitute another class of known synthetic lubricating oils that can be used. These are exemplified by the oils prepared through polymerization of ethylene oxide or propylene oxide, the alkyl and aryl ethers of these polyoxyalkylene polymers (e.g., methyl-polypropylene glycol ether having an average molecular weight of about 1000, diphenyl ether of polyethylene glycol having a molecular weight of about 500-1000, diethyl ether of polypropylene glycol having a molecular weight of about 1000-1500, etc.) or mono- and polycarboxylic

esters thereof, for example, the acetic acid esters, mixed C₃-C₈ fatty acid esters, or the carboxylic acid diester of tetraethylene glycol.

[0027] Another suitable class of synthetic lubricating oils that can be used comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids, alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, dodecanedioic acid) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether and propylene glycol). Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer and the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid.

[0028] Esters useful as synthetic oils also include those made from C₅ to C₁₂ monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylol propane, pentaerythritol, dipentaerythritol and tripentaerythritol.

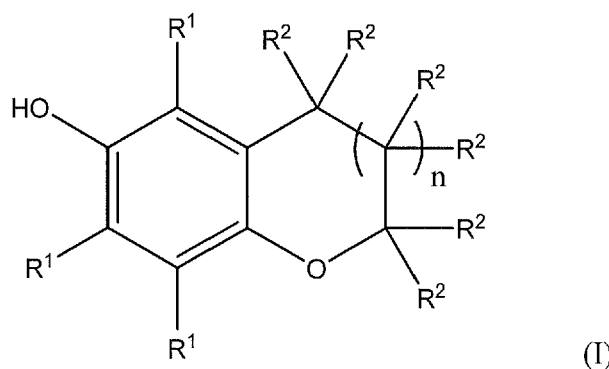
[0029] The oil can be a poly-alpha-olefin (PAO). Typically, the PAOs are derived from monomers having from 4 to 30, or from 4 to 20, or from 6 to 16 carbon atoms. Examples of useful PAOs include those derived from octene, decene and mixtures thereof. These PAOs may have a viscosity from 2 to 15, or from 3 to 12, or from 4 to 8 mm²/s (cSt), at 100°C. Examples of useful PAOs include 4 mm²/s (cSt) at 100°C poly-alpha-olefins, 6 mm²/s (cSt) at 100°C poly-alpha-olefins, and mixtures thereof. Mixtures of mineral oil with one or more of the foregoing PAOs may be used.

[0030] Unrefined, refined and rerefined oils, either natural or synthetic (as well as mixtures of two or more of any of these) of the type disclosed hereinabove can be used in the lubricants of the present invention. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. For example, a shale oil obtained directly from retorting operations, a petroleum oil obtained directly from primary distillation or ester oil obtained directly from an esterification process and used without further treatment would be an unrefined oil. 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. Many such purification techniques are known to those skilled in the art such as solvent extraction, secondary distillation, acid or base extraction, filtration, percolation, etc. Rerefined oils are obtained by processes similar to those used to obtain refined oils applied to refined oils which have been already used in service. Such rerefined oils are also known as reclaimed or reprocessed oils and often are additionally processed by techniques directed to removal of spent additives and oil breakdown products.

[0031] Additionally, synthetic oils may be produced by Fischer-Tropsch gas to liquid synthetic procedure as well as other gas-to-liquid oils. In one embodiment the polymer composition of the present invention is useful when employed in a gas-to-liquid oil. Often Fischer-Tropsch hydrocarbons or waxes may be hydroisomerised.

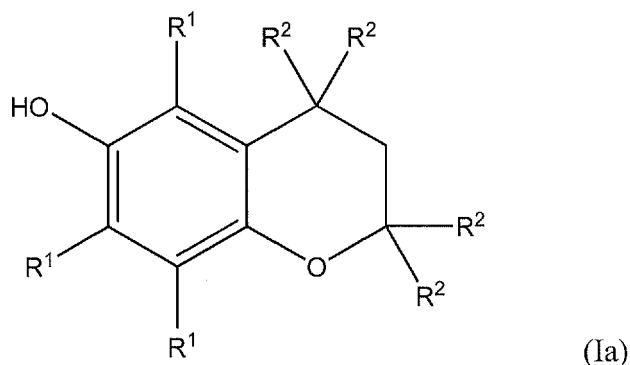
Hydroxychroman Derived Antioxidant

[0032] The antioxidant additives of the present invention are derived from hydroxychroman. As provided above, suitable antioxidants can be represented by the formula:



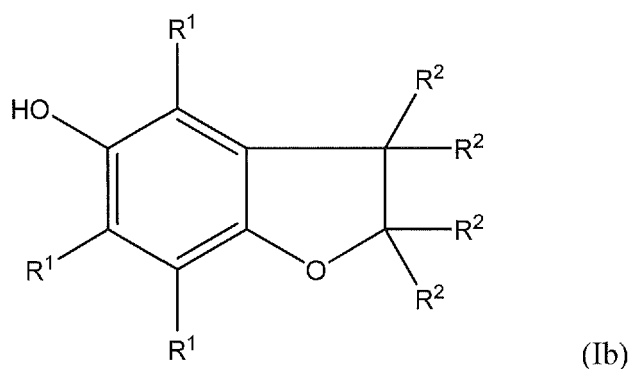
wherein each R¹ is independently -OR², -NH₂, -NR²R², -SR² or -R²; each R² is independently a hydrogen, a hydrocarbyl group, or a -C(=O)-X-R³ group where X is O, NR³ or S and each R³ is independently a hydrogen or a hydrocarbyl group; and n is 0 or 1; and where the two adjacent R¹ groups are hydrocarbyl groups, they may be linked to form a ring. In some embodiments each R¹ is independently hydrogen or a hydrocarbyl group.

[0033] The antioxidant may be chromanol having a hydroxy group located on the aromatic ring, i.e. as 6-chromanol. In such embodiments the antioxidant may be represented by the formula:



wherein each R^1 is independently $-OR^2$, $-NH_2$, $-NR^2R^2$, $-SR^2$ or $-R^2$; each R^2 is independently a hydrogen or hydrocarbyl group; and where the two adjacent R^1 groups are hydrocarbyl groups, they may be linked to form a ring. In some embodiments each R^1 is independently hydrogen or a hydrocarbyl group. Any of the R^2 groups in formula Ia may also be a $-C(=O)-X-R^3$ group where X is O, NR^3 or S and each R^3 is independently a hydrogen or a hydrocarbyl group.

[0034] Specific examples of suitable antioxidants include 2,3-dihydrobenzofuranol having a hydroxy group located on the aromatic ring. In such embodiments the antioxidant may be represented by the formula:



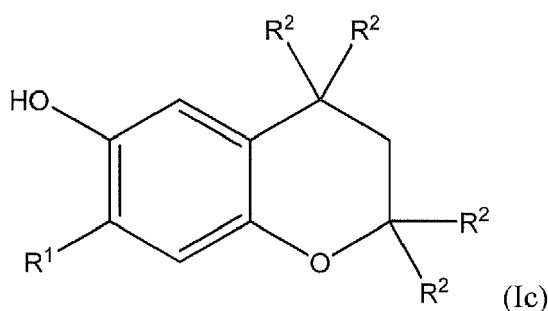
wherein each R^1 is independently $-OR^2$, $-NH_2$, $-NR^2R^2$, $-SR^2$ or $-R^2$; each R^2 is independently a hydrogen or hydrocarbyl group; and where the two adjacent R^1 groups are hydrocarbyl groups, they may be linked to form a ring. In some embodiments each R^1 is independently hydrogen or a hydrocarbyl group. Any of the R^2 groups in formula Ib may also be a $-C(=O)-X-R^3$ group where X is O, NR^3 or S and each R^3 is independently a hydrogen or a hydrocarbyl group.

[0035] In some embodiments, considering any of the formulas provided above: (i) at least one R^1 group of the antioxidant is a hydrocarbyl group, (ii) at least one R^2 group of the antioxidant is a hydrocarbyl group, or (iii) combinations thereof.

[0036] In still further embodiments, at least one of the R^1 groups adjacent to the hydroxy group is a hydrocarbyl group.

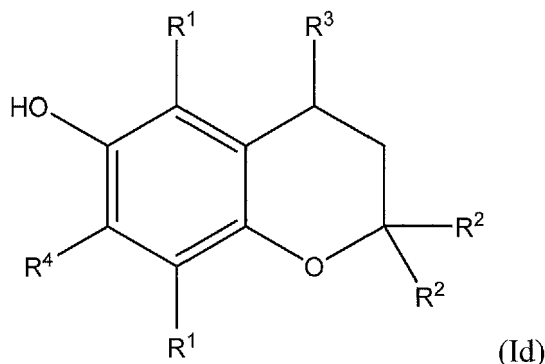
[0037] In other embodiments, considering any of the formulas provided above, each R^1 may be independently a hydrogen or hydrocarbyl group containing from 1 to 20 carbon atoms and each R^2 may be independently a hydrogen or hydrocarbyl group containing from 1 to 15 carbon atoms.

[0038] In some embodiments the antioxidant used in the compositions of the present invention may be represented by the following formula:



wherein R^1 is $-OR^2$, $-NH_2$, $-NR^2R^2$, $-SR^2$ or $-R^2$; and each R^2 is independently a hydrogen or hydrocarbyl group. In some embodiments R^1 is independently hydrogen or a hydrocarbyl group. In some embodiments, R^1 is a hydrocarbyl group containing from 1 to 10 carbon atoms and each R^2 is independently a hydrogen or hydrocarbyl group containing from 1 to 10 carbon atoms. Any of the R^2 groups in formula Ic may also be a $-C(=O)-X-R^3$ group where X is O, NR^3 or S and each R^3 is independently a hydrogen or a hydrocarbyl group.

[0039] In still other embodiments the antioxidant used in the compositions of the present invention may be represented by the following formula:



wherein R^1 is $-OR^2$, $-NH_2$, $-NR^2R^2$, $-SR^2$ or $-R^2$; each R^2 is independently a hydrogen or hydrocarbyl group; R^3 is hydrogen or hydrocarbyl group; and R^4 is a hydrogen or hydrocarbyl group. In some embodiments R^1 is independently hydrogen or a hydrocarbyl group. In some embodiments, R^1 is a hydrocarbyl group containing from 1 to 10 carbon atoms and each R^2 is independently a hydrogen or hydrocarbyl group containing from 1 to 10 carbon atoms. In some embodiments R^3 is a linear alkyl group containing from 1 to 10 carbon atoms. In some embodiments R^3 is a methyl group. In still other embodiments, where R^3 is a methyl group, both R^2 groups are methyl groups, all R^1 groups are hydrogen and R^4 is a branched alkyl group containing from 1 to 10 carbon atoms, or even from 3 to 10 or 8 carbon atoms. In some embodiments R^4 is a tert-butyl group. Any of the R^2 groups in formula Id may also be a $-C(=O)-X-R^3$ group where X is O, NR^3 or S and each R^3 is independently a hydrogen or a hydrocarbyl group.

[0040] The antioxidant (B) can be present on a weight basis in the lubricant composition of this invention at 0.1 to 10%, 0.3 to 8%, or 0.6 to 6%.

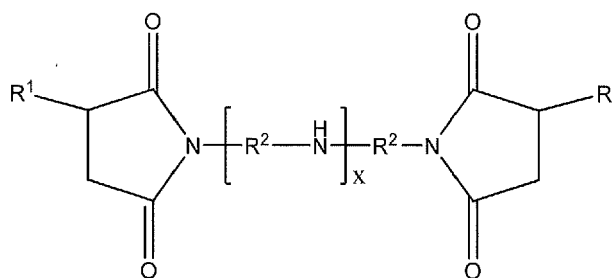
Additional Additives

[0041] The lubricant composition of the invention can optionally comprise (C) a minor amount of at least one other additive. The other additive (C) can comprise a member selected from the group consisting of a viscosity modifier, a pour point depressant, a dispersant, a detergent, an antiwear agent, an antioxidant that is different from component (B), a friction modifier, a corrosion inhibitor, a seal swell agent, a metal deactivator, a foam inhibitor, and a mixture thereof. The mixture of other additives can be 2 or more additives of the same type such as for example a sulfonate and phenate detergent, 2 or more additives of different types such as for example a detergent and dispersant and antiwear agent, or 2 or more additives of the same type as well as 2 or more additives of different types such as for example a sulfonate and phenate detergent and a dispersant and an antiwear agent.

[0042] The lubricant composition of the present invention may contain one or more dispersants. Carboxylic dispersants are reaction products of carboxylic acylating agents (acids, anhydrides, esters, etc.) containing at least 34 and preferably at least 54 carbon atoms which are reacted with nitrogen containing compounds (such as amines), organic hydroxy compounds (such as aliphatic compounds including monohydric and polyhydric alcohols, or aromatic compounds including phenols and naphthols), and/or basic inorganic materials. These reaction products include imide, amide, and ester reaction products of carboxylic ester dispersants.

[0043] Succinimide dispersants are a species of carboxylic dispersants. They are the reaction product of a hydrocarbyl substituted succinic acylating agent with an organic hydroxy compound or, an amine containing at least one hydrogen attached to a nitrogen atom, or a mixture of said hydroxy compound and amine. The term "succinic acylating agent" refers to a hydrocarbon-substituted succinic acid or succinic acid-producing compound (which term also encompasses the acid itself). Such materials typically include hydrocarbyl-substituted succinic acids, anhydrides, esters (including half esters) and halides.

[0044] Succinic based dispersants have a wide variety of chemical structures including typically structures such as



[0045] In the above structure, each R¹ is independently a hydrocarbyl group, such as a polyolefin-derived group having an M_n of 500 or 700 to 10,000. Typically the hydrocarbon based group is an alkyl group, frequently a polyisobutylene group derived from polyisobutylene having a molecular weight of 500 or 700 to 5000, or alternatively 1500 or 2000 to 5000. Alternatively expressed, the R¹ groups can contain 40 to 500 carbon atoms, for instance at least 50, e.g., 50 to 300 carbon atoms, such as aliphatic carbon atoms. The R² are alkylene groups, commonly ethylene (C₂H₄) groups. X is an integer and is not overly limited. In some embodiments X has the value within the range of zero, 1 or even 2 up to 10, or 6 or 4. Such molecules are commonly derived from reaction of an alkenyl acylating agent with a polyamine, and a wide variety of linkages between the two moieties is possible beside the simple imide structure shown above, including a variety of amides and quaternary ammonium salts. Succinimide dispersants are more fully described in U.S. Patents 4,234,435, 3,172,892 and 6,165,235.

[0046] Additional details and examples of the procedures for preparing the succinimide dispersants of the present invention are included in, for example, U.S. Pat. Nos. 3,172,892, 3,219,666, 3,272,746, 4,234,435, 6,440,905 and 6,165,235.

[0047] "Amine dispersants" are reaction products of relatively high molecular weight aliphatic halides and amines, preferably polyalkylene polyamines. Examples thereof are described, for example, in the following U.S. Patents: 3,275,554, 3,438,757, 3,454,555, and 3,565,804.

[0048] "Mannich dispersants" are the reaction products of alkyl phenols in which the alkyl group contains at least 30 carbon atoms with aldehydes (especially formaldehyde) and amines (especially polyalkylene polyamines). The materials described in the following U.S. Patents are illustrative: 3,036,003, 3,236,770, 3,414,347, 3,448,047, 3,461,172, 3,539,633, 3,586,629, 3,591,598, 3,634,515, 3,725,480, 3,726,882, and 3,980,569.

[0049] Post-treated dispersants are obtained by reacting carboxylic, amine or Mannich dispersants with reagents such as dimercaptiothiadiazoles, urea, thiourea, carbon disulfide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, nitriles epoxides, boron compounds, phosphorus compounds or the like. Exemplary materials of this kind are described in the following U.S. Patents: 3,200,107, 3,282,955, 3,367,943, 3,513,093, 3,639,242, 3,649,659, 3,442,808, 3,455,832, 3,579,450, 3,600,372, 3,702,757, and 3,708,422.

[0050] Polymeric dispersants are interpolymers of oil-solubilizing monomers such as decyl methacrylate, vinyl decyl ether and high molecular weight olefins with monomers containing polar substituents, e.g., aminoalkyl acrylates or acrylamides and poly-(oxyethylene)-substituted acrylates. Examples of polymer dispersants thereof are disclosed in the following U.S. Patents: 3,329,658, 3,449,250, 3,519,656, 3,666,730, 3,687,849, and 3,702,300.

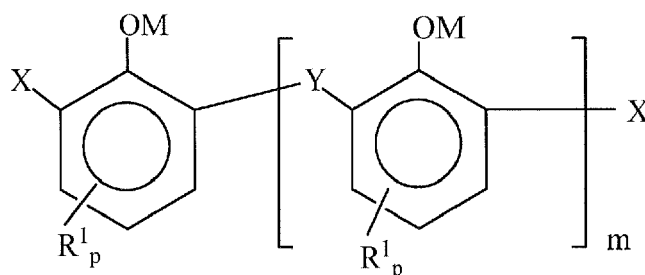
[0051] The composition can also contain one or more detergents, which are normally salts, and specifically overbased salts. Such overbased materials are well known to those skilled in the art. Patents describing techniques for making basic salts of sulfonic acids, carboxylic acids, (hydrocarbyl-substituted) phenols, phosphonic acids, and mixtures of any two or more of these include U.S. Patents 2,501,731; 2,616,905; 2,616,911; 2,616,925; 2,777,874; 3,256,186; 3,384,585; 3,365,396; 3,320,162; 3,318,809; 3,488,284; and 3,629,109. Overbased materials, otherwise referred to as overbased or superbased salts, are generally single phase, homogeneous Newtonian systems characterized by an amount of excess metal that which would be necessary for neutralization according to the stoichiometry of the metal and the particular acidic organic compound reacted with the metal. 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. A more detailed description of the term metal ratio is provided in "Chemistry and Technology of Lubricants", Second Edition, Edited by R. M. Mortier and S. T. Orszulik, pages 85 and 86, 1997. The overbased alkali or alkaline earth metal detergents suitable for use in the present invention may have a metal ratio of 0.8 to 10 or 3 to 9, or 4 to 8, or 5 to 7. The detergents may be overbased with calcium hydroxide. In different embodiments the alkali or alkaline earth metal detergents may have a total base number (TBN) of 30 or 50 to 400; or 200 to 350; or 220 to 300, and in another embodiment 255. In other embodiments the detergent has a TBN in the range of 30, 40 or 50 to 220, 205, or 190, and in another embodiment 150. In still other embodiments the detergent has a TBN of 300 or more, 350 or more, or 400 or more, or from 300 or 350 to 400, and in another embodiment 395.

[0052] In one embodiment the lubricant of the present invention can contain an overbased sulfonate detergent. Suitable sulfonic acids include sulfonic and thio-sulfonic acids. Sulfonic acids include the mono- or polynuclear aromatic or

cycloaliphatic compounds. Oil-soluble sulfonates can be represented for the most part by one of the following formulas: $R_2-T-(SO_3^-)_a$ and $R_3-(SO_3^-)_b$, where T is a cyclic nucleus such as typically benzene; R^2 is an aliphatic group such as alkyl, alkenyl, alkoxy, or alkoxyalkyl; $(R_2)+T$ typically contains a total of at least about 15 carbon atoms; and R_3 is an aliphatic hydrocarbon based group typically containing at least 15 carbon atoms. Examples of R_3 are alkyl, alkenyl, alkoxyalkyl, and carboalkoxyalkyl groups. The groups T, R_2 , and R_3 in the above formulas can also contain other inorganic or organic substituents in addition to those enumerated above such as, for example, hydroxy, mercapto, halogen, nitro, amino, nitroso, sulfide, or disulfide. In the above formulas, a and b are at least 1.

[0053] Another overbased material which can be present is an overbased phenate detergent. The phenols useful in making phenate detergents can be represented by the formula $(R_1)_a-Ar-(OH)_b$, wherein R_1 is defined above; Ar is an aromatic group (which can be a benzene group or another aromatic group such as naphthalene); a and b are independently numbers of at least one, the sum of a and b being in the range of two up to the number of displaceable hydrogens on the aromatic nucleus or nuclei of Ar. In one embodiment, a and b are independently numbers in the range of 1 to 4, or 1 to 2. R_1 and a are typically such that there is an average of at least 8 aliphatic carbon atoms provided by the R_1 groups for each phenol compound. Phenate detergents are also sometimes provided as sulfur-bridged species.

[0054] In one embodiment, the overbased material is an overbased detergent selected from the group consisting of overbased salixarate detergents, overbased saligenin detergents, overbased salicylate detergents, and overbased glyoxylate detergents, and mixtures thereof. Overbased saligenin detergents are commonly overbased magnesium salts which are based on saligenin derivatives. A general example of such a saligenin derivative can be represented by the formula

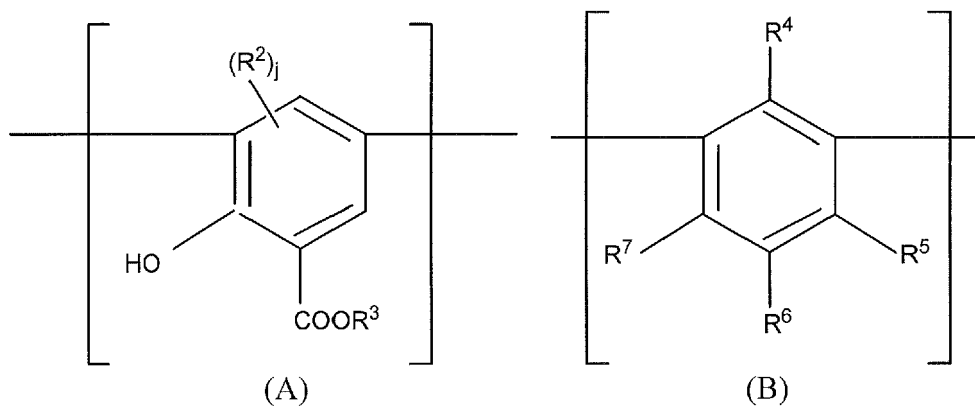


wherein X comprises $-CHO$ or $-CH_2OH$, Y comprises $-CH_2-$ or $-CH_2OCH_2-$, and wherein such $-CHO$ groups typically comprise at least 10 mole percent of the X and Y groups; M is hydrogen, ammonium, or a valence of a metal ion, R^1 is a hydrocarbon based group containing 1 to 60 carbon atoms, m is 0 to typically 10, and each p is independently 0, 1, 2, or 3, provided that at least one aromatic ring contains an R^1 substituent and that the total number of carbon atoms in all R^1 groups is at least 7. When m is 1 or greater, one of the X groups can be hydrogen. In one embodiment, M is an equivalent of a Mg ion or a mixture of Mg and hydrogen (and so in some embodiments can be less than a full Mg ion and/or include a partial Mg ion). Other metals include alkali metals such as lithium, sodium, or potassium; alkaline earth metals such as calcium or barium; and other metals such as copper, zinc, and tin.

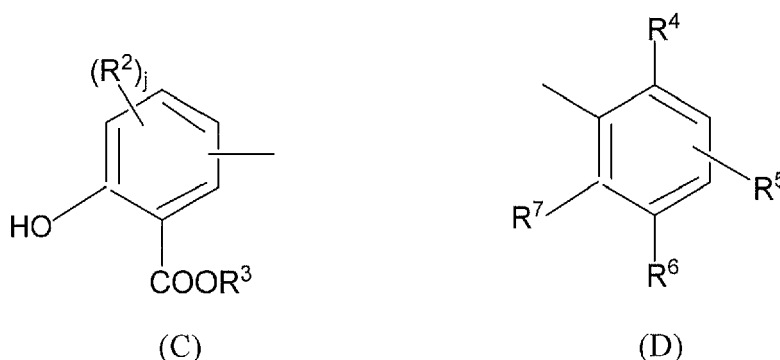
[0055] As used herein, the expression "represented by the formula" indicates that the formula presented is generally representative of the structure of the chemical in question. However, it is well known that minor variations can occur, including in particular positional isomerization, that is, location of the X, Y, and R groups at different position on the aromatic ring from those shown in the structure. The expression "represented by the formula" is expressly intended to encompass such variations.

[0056] Saligenin detergents are disclosed in greater detail in U.S. Patent 6,310,009, with special reference to their methods of synthesis (Column 8 and Example 1) and preferred amounts of the various species of X and Y (Column 6).

[0057] Salixarate detergents are overbased materials that can be represented by a substantially linear compound comprising at least one unit of formula (A) or formula (B):



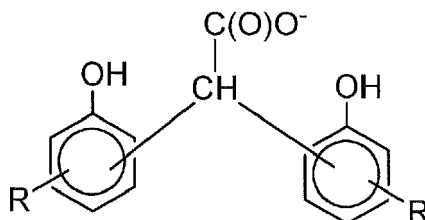
and wherein each end of the compound has a terminal group of formula (C) or formula (D):



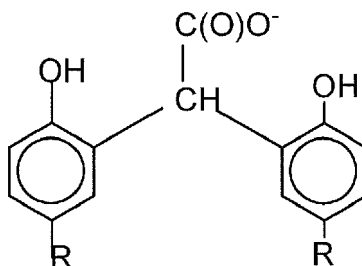
such groups being linked by divalent bridging groups A, which may be the same or different for each linkage; wherein in formulas (A)-(D) R³ is hydrogen or a hydrocarbyl group; R² is hydroxyl or a hydrocarbon based group and j is 0, 1, or 2; R⁶ is hydrogen, a hydrocarbyl group, or a hetero-substituted hydrocarbyl group; either R⁴ is hydroxyl and R⁵ and R⁷ are independently either hydrogen, a hydrocarbyl group, or hetero-substituted hydrocarbyl group, or else R⁵ and R⁷ are both hydroxyl and R⁴ is hydrogen, a hydrocarbyl group, or a hetero-substituted hydrocarbyl group; provided that at least one of R⁴, R⁵, R⁶ and R⁷ is hydrocarbyl containing at least 8 carbon atoms; and wherein the molecules on average contain at least one of unit (A) or (C) and at least one of unit (B) or (D) and the ratio of the total number of units (A) and (C) to the total number of units of (B) and (D) in the composition is about 0.1:1 to about 2:1. The divalent bridging group "A," which may be the same or different in each occurrence, includes -CH₂-(methylene bridge) and -CH₂OCH₂- (ether bridge), either of which may be derived from formaldehyde or a formaldehyde equivalent (e.g., paraform, formalin).

[0058] Salixarate derivatives and methods of their preparation are described in greater detail in U.S. patent number 6,200,936 and PCT Publication WO 01/56968. It is believed that the salixarate derivatives have a predominantly linear, rather than macrocyclic, structure, although both structures are intended to be encompassed by the term "salixarate."

[0059] Glyoxylate detergents are similar overbased materials which are based on an anionic group which, in one embodiment, may have the structure



and more specifically,



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

[0060] Another detergent can be a salicylate detergent. The alkylsalicylate can be an alkali metal salt or an alkaline earth metal salt of an alkylsalicylic acid which can in turn be prepared from an alkylphenol by Kolbe-Schmitt reaction. The alkylphenol can be prepared by a reaction of α -olefin having 8 to 30 carbon atoms (mean number) with phenol. Alternatively, calcium salicylate can be produced by direct neutralization of alkylphenol and subsequent carbonation.

[0061] In another embodiment of the invention component (C) can comprise an antioxidant comprising an aminic antioxidant that is different from component (B). In some embodiments this additional antioxidant comprises one or more of the antioxidants described above. In other embodiments the additional antioxidant is a hindered phenol that is different from component (B), a diarylamine, a sulfurized olefinic compound, a molybdenum containing antioxidant, and a mixture thereof. In additional embodiments of the invention the antioxidant can comprise an alkyl 3-(3,5-di-*t*-alkyl-4-hydroxyphenyl)propionate, such as an alkyl 3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionate where the alkyl group of the ester moiety has 1 or more carbon atoms, 2 or more carbon atoms, 2 to 30 carbon atoms, 2 to 20 carbon atoms, or 2 to 10 carbon atoms. In some embodiments this combination of antioxidants leads to additional improvements in the performance of the composition.

[0062] Component (C) can comprise an antiwear agent. The antiwear agent can comprise a zinc dialkyldithiophosphate. In some embodiments the compositions of the present invention contain a zinc dialkyldithiophosphate, and in some of these embodiments, the zinc dialkyldithiophosphate is present at a level of no less than 300 ppm (or in other embodiments the zinc dialkyldithiophosphate is present at a level such that the amount of phosphorus delivered to the composition from the additive is no less than 300 ppm), such that, in combination with some of the limits below, essentially all of the phosphorus present in the composition is delivered by the zinc dialkyldithiophosphate.

[0063] In some embodiments the compositions of the present invention further comprises a friction modifier, such as a hydroxy acid derived friction modifier, for example oleyl tartramide, or amide-based friction modifier such as oleyl amide.

[0064] The other additive or additives of component (C) can each be present in the lubricant composition on a weight basis at 0.001 to 14%, 0.001 to 11%, or 0.001 to 8%.

Sulfur, Phosphorus, Ash Content

[0065] The present invention provides a composition as described above. In some embodiments the composition has total sulfur content of no more than 0.4 percent weight and in other embodiments of no more than 0.3, 0.2, or even 0.1 percent by weight. In some embodiments the sulfur content of the compositions described herein is at least 0.01 or even 0.05 percent by weight. Often the major source of sulfur in the composition of the invention is derived from conventional diluent oil.

[0066] In some embodiments compositions described herein have a total phosphorus content of no more than 1200 ppm, and in other embodiments no more than 1000, 800, 500, 300, 200 or even 100 ppm. In some embodiments the compositions described herein have a phosphorus content within a range that includes a minimum value of 100 ppm.

[0067] In some embodiments the composition has a total sulfated ash content as determined by ASTM D-874 of no more than 1.0 percent by weight, and in other embodiments of no more than 0.7, 0.4, 0.3, 0.05 percent by weight. In some embodiments the sulfur content of the compositions described herein is at least 0.01 or even 0.05 percent by weight.

Lubricant Composition

[0068] The lubricant composition can be a lubricant composition for an application comprising those listed above. In one embodiment of the invention the lubricant composition can be a lubricant composition for an internal combustion

engine. The internal combustion engine can comprise a spark-ignited engine or a compression-ignited engine.

Concentrate Composition

[0069] Components (B) and (C) of the invention can be combined in a concentrated form as a concentrate composition for convenient and efficient handling and shipping prior to being diluted in a base stock or oil of lubricating viscosity for use in a lubricant composition for an application. A concentrate composition of the present invention can comprise a concentrate-forming amount of an oil of lubricating viscosity, at least one hindered-phenol-containing diester antioxidant as described above, and at least one other additive as described above. Each of the antioxidant and other additive or additives can be present in the concentrate composition on a weight basis at 1 to 99%, 5 to 85%, or 10 to 75%. The oil of lubricating viscosity can be present in the concentrate composition on a weight basis at 99 to 1%, 95 to 15%, or at 90 to 25%.

Preparation of Compositions

[0070] The lubricant and concentrate compositions of the invention can be prepared by admixing or mixing, usually with a mixing device, the components in any suitable order from ambient to an elevated temperature of 60°C, 80°C, or 100°C until the composition is homogeneous or the components are dispersed.

Method for Improving Lubricant Composition Performance

[0071] A method of the present invention for improving the performance of a lubricant composition comprises incorporating into the lubricant composition a performance-improving amount of a hydroxychroman derived antioxidant as described above where the lubricant composition comprises an oil of lubricating viscosity and at least one other additive as described above. The improvement in performance can comprise a decrease in volatility, an increase in oxidation inhibition, a reduction in deposits, or a combination thereof. The lubricant composition can be a lubricant composition for an internal combustion engine. The internal combustion engine can comprise a spark-ignited engine or a compression-ignited engine. The spark-ignited or compression-ignited engine can have an exhaust gas recirculation system. The spark-ignited or compression-ignited engine can have at least one exhaust treatment device comprising a catalytic converter, a catalyzed diesel particulate trap, a noncatalyzed diesel particulate trap, a diesel oxidation catalyst, a selective catalytic reduction catalyst, a lean NO_x catalyst, or a combination thereof. The lubricant composition can have normal or reduced levels of sulfated ash, phosphorus and sulfur as described above.

EXAMPLES

[0072] The invention will be further illustrated by the following examples, which set forth particularly advantageous embodiments. While the examples are provided to illustrate the present invention, they are not intended to limit it.

Example 1

[0073] A hydroxychroman derivative is prepared by adding to a 1-liter round bottom flask, equipped with a mechanical stirrer, thermowell, nitrogen inlet, Dean-Stark/Fredrich's condenser, 116.5 grams of 2-tert-butylbenzene-1,4-diol, 124.2 grams of 2-methylpentane-2,4-diol, 150 grams of heptane and 23.3 grams of Amberlyst 15. The reaction mixture is heated to reflux temperature to azeotrope water for a total of about 14 hours. The resulting material is then filtered using a frit funnel in order to remove the catalyst and the solvent is removed via vacuum stripping. The final material is a tan solid.

Example 2

[0074] A hydroxychroman derivative is prepared by adding to a 1-liter round bottom flask, equipped with a mechanical stirrer, thermowell, nitrogen inlet, Dean-Stark/Fredrich's condenser, 102.0 grams of 2-tert-butylbenzene-1,4-diol, 107.7 grams of 2,5-dimethyl-2,5-hexanediol, 150 grams of heptane and 22.0 grams of Amberlyst 15. The reaction mixture is heated to reflux temperature to azeotrope water for a total of about 14 hours. The resulting material is then filtered using a frit funnel in order to remove the catalyst and the solvent is removed via vacuum stripping. The final material is a tan solid.

Antioxidancy Performance Testing

[0075] The examples described above were prepared and then blended into samples for testing in antioxidant performance screen tests.

[0076] Each sample is prepared by blending the antioxidant additive being evaluated, if any, at the specified level, into a fully formulated engine oil composition. Each composition was blended into the same base oil, a mix of commercially available 100N and 160N mineral oils. Also included in each sample is an additive package. The additive package contains a combination of various lubricant additives including dispersants, detergents, antifoams, corrosion inhibitors, etc. The exact same additive package is present at the exact same treat level in each sample unless otherwise noted. The table below summarizes the samples prepared for the testing:

Table 1 - Sample Formulations in PBW

	Ex A (comp)	Ex B (Invent)	Ex C (Invent)	Ex D (comp)	Ex E (Invent)	Ex F (comp)
Base Oil ¹	100	100	100	100	100	100
Additive Pack ²	8.80	8.80	8.80	8.80	8.35	8.35
Hindered Phenol AO	0.45	0.00	0.00	0.58	0.00	0.45
Example 1 AO	0.00	0.45	0.00	0.00	0.35	0.00
Example 2 AO	0.00	0.00	0.45	0.00	0.00	0.00
1 - The base oil package used in all of the examples is a mixture of commercially available 100N and 160N mineral oils. 2 - The additive package used in Examples A to D is identical. The additive package used in Examples E and F is identical to that used in the other examples except that 0.45 pbw of an alkaryl amine believed to possibly contribute to lubricant antioxidancy performance was removed.						

[0077] Examples A, B and C compare the additives of the present invention against a conventional hindered phenol antioxidant on an equal treat rate basis, with treat rate measured by percent by weight. Example D, when compared to Example B, and Examples E and F, compare the additives of the present invention against a conventional hindered phenol antioxidant on an equal actives basis. In addition, Examples E and F were prepared using an additive package identical to that used in each of the other examples except that an alkaryl amine additive present in the full additive package, which is believed to possibly contribute to lubricant antioxidancy, was removed. Thus these examples ensure any improvement in antioxidancy performance is the result of the inventive additive.

[0078] The tests used to evaluate the samples are commonly used in the lubricant industry to evaluate the performance of antioxidant additives. The testing completed includes: (i) ASTM D7097, a bench-scale passenger car motor oil qualification test for GF-4 and GF-5. The test measures the amount of deposit generated on a steel rod heated at 285C. A lower result indicates a lower amount of deposit generation and so better performance. (ii) ASTM D6335, a bench-scale passenger car motor oil qualification test for GF-2. The test measures the amount of deposit generated on a steel rod when cycling the rod temperature from 200C to 480C. A lower result indicates a lower amount of deposit generation and so better performance. (iii) An in-house PDSC test was also used. This test uses a calorimetry method to determine the onset of oxidation activity in an oil sample and is used to rank the relative oxidative stabilities of a set of samples. Higher onset times indicate greater oxidative stability and so better performance.

[0079] The table below summarizes the results:

Table 2 - Test Results

	Ex A (comp)	Ex B (Invent)	Ex C (Invent)	Ex D (comp)	Ex E (Invent)	Ex F (comp)
<u>ASTM D7097</u>						
Total Deposits (mg)	54.6	42.3	47.3	47.2	77.3	82.4
<u>ASTMD6335</u>						
Total Deposits (mg)	--	--	--	--	21.8	29.3
<u>Oxidation Activity</u>						
Onset Time (min)	51.6	60.9	57.3	50.8	37.4	29.2

[0080] The results show that, as seen in Examples A, B and C, the hydroxychroman derivatives (see Examples B and C) give lower deposit levels and higher onset times than the conventional hindered phenolic antioxidants when treated at equal weight, thus indicating better oxidation stability.

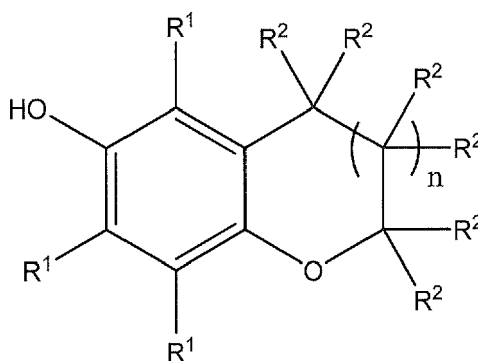
[0081] Furthermore, when the level of conventional hindered phenolic antioxidant is increased to compare to the hydroxychroman antioxidants on an equal actives basis (see Example D compared to Inventive Examples B and C), we still see better oxidative stability for both hydroxychroman derivatives and at least comparable, if not improved, deposit control.

[0082] When removing the additional amine antioxidant, as was done in Examples E and F while comparing the antioxidants at equal actives, we see better oxidation control and deposit control for the hydroxychroman derivatives compared to the conventional hindered phenolic antioxidants.

[0083] 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 indicates all percent values and ppm values herein are weight percent values and/or calculated on a weight basis and are relative to the overall composition to which the specific material is added. 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, 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 can 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.

[0084] In further aspects the present invention provides the compositions, processes and methods described in the following numbered paragraphs:

1. A lubricant composition comprising an oil of lubricating viscosity and an antioxidant having the formula:



wherein each R^1 is independently $-OR^2$, $-NH_2$, $-NR^2R^2$, $-SR^2$ or $-R^2$; each R^2 is independently a hydrogen, a hydrocarbyl group, or a $-C(=O)-X-R^3$ group where X is O, NR³ or S and each R³ is independently a hydrogen or a hydrocarbyl group; and n is 0 or 1; and where the two adjacent R^1 groups are hydrocarbyl groups, they may be linked to form a ring.

2. The lubricant composition of paragraph 1 wherein the antioxidant is a chromanol having a hydroxy group located on the aromatic ring.

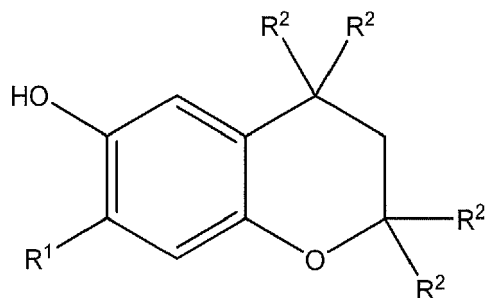
3. The lubricant composition of paragraph 1 wherein the antioxidant is a 2,3-dihydrobenzofuranol having a hydroxy group located on the aromatic ring.

4. The lubricant composition of paragraph 1 wherein: (i) at least one R^1 group of the antioxidant is a hydrocarbyl group, (ii) at least one R^2 group of the antioxidant is a hydrocarbyl group, or (iii) combinations thereof.

5. The lubricant composition of paragraph 1 wherein at least one of the R^1 groups adjacent to the hydroxy group is a hydrocarbyl group.

6. The lubricant composition of paragraph 1 wherein each R^1 is independently a hydrogen or hydrocarbyl group containing from 1 to 20 carbon atoms and each R^2 is independently a hydrogen or hydrocarbyl group containing from 1 to 15 carbon atoms.

7. The lubricant composition of paragraph 1 wherein the antioxidant has the formula:



wherein R¹ is hydrocarbyl group containing from 1 to 10 carbon atoms; and each R² is independently a hydrogen or hydrocarbyl group containing from 1 to 10 carbon atoms.

8. The lubricant composition of paragraph 1 wherein the composition contains no more than 1200 ppm phosphorus.

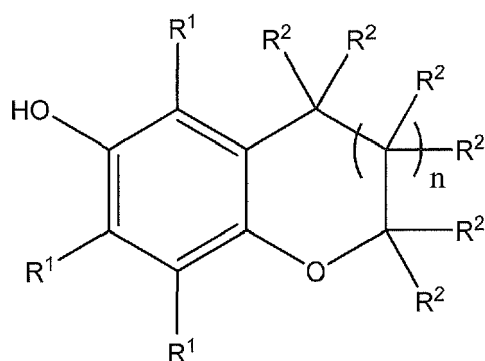
9. The lubricant composition of paragraph 8 wherein the composition has a sulfur content of no more than 0.4 percent by weight and a sulfated ash content of no more than 1.0 percent by weight.

10. The lubricant composition of paragraph 8 further comprising a zinc dialkyldithiophosphate at a level of no less than 300 ppm.

11. The lubricant composition of paragraph 1 further comprising an aminic antioxidant.

12. The lubricant composition of paragraph 1 further comprising a friction modifier.

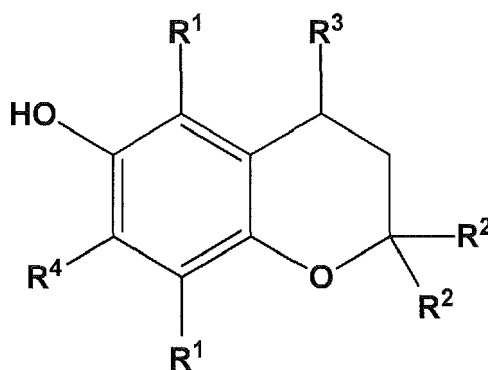
13. A method of lubricating an internal combustion engine comprising the steps of: (I) supplying to said engine a lubricant composition comprising an oil of lubricating viscosity and an antioxidant having the formula:



wherein each R¹ is independently -OR², -NH₂, -NR²R², -SR² or -R²; each R² is independently a hydrogen, a hydrocarbyl group, or a -C(=O)-X-R³ group where X is O, NR³ or S and each R³ is independently a hydrogen or a hydrocarbyl group; and n is 0 or 1; and where the two adjacent R¹ groups are hydrocarbyl groups, they may be linked to form a ring.

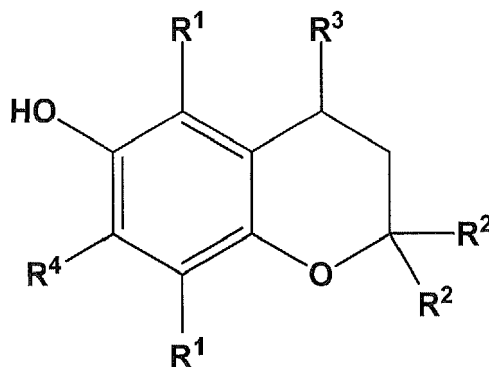
Claims

1. A lubricant composition comprising an oil of lubricating viscosity and an antioxidant having the formula:



wherein R^3 is a hydrogen or a hydrocarbyl group, both R^2 groups are methyl groups, all R^1 groups are hydrogen and R^4 is a branched alkyl group containing from 1 to 10 carbon atoms;
 wherein the antioxidant is present in the lubricant composition from 0.1 to 10 percent by weight;
 wherein the lubricant composition further comprises an aminic antioxidant;
 wherein the lubricant composition is an internal combustion engine lubricant composition, a power transmission lubricant composition, a gear lubricant composition, a metalworking lubricant composition, a hydraulic system lubricant composition, a bearings lubricant composition where the lubricant composition is a grease.

2. The lubricant composition of claim 1 wherein the composition contains no more than 1200 ppm phosphorus.
3. The lubricant composition of claim 2 wherein the composition has a sulfur content of no more than 0.4 percent by weight and a sulfated ash content of no more than 1.0 percent by weight.
4. The lubricant composition of claim 2 further comprising a zinc dialkyldithiophosphate present at a level such that the amount of phosphorus delivered to the composition is no less than 300 ppm.
5. A method of lubricating an internal combustion engine comprising the steps of: (I) supplying to said engine a lubricant composition comprising an oil of lubricating viscosity and an antioxidant having the formula:



wherein R^3 is a hydrogen or a hydrocarbyl group, both R^2 groups are methyl groups, all R^1 groups are hydrogen and R^4 is a branched alkyl group containing from 1 to 10 carbon atoms
 wherein the antioxidant is present in the lubricant composition from 0.1 to 10 percent by weight;
 wherein the lubricant composition further comprises an aminic antioxidant.

**PARTIAL EUROPEAN SEARCH REPORT**

Application Number

under Rule 62a and/or 63 of the European Patent Convention.
This report shall be considered, for the purposes of
subsequent proceedings, as the European search report

EP 16 16 4519

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	US 2 535 058 A (GLEIM WILLIAM K T ET AL) 26 December 1950 (1950-12-26) * the whole document *	1-5	INV. C10M129/20 C10L1/18 C10M141/06 C10M141/10 C10L1/185 C10L1/19 C10L1/223 C10L1/24 C10L10/00 C10L1/224
A	WO 2009/134716 A1 (DOW GLOBAL TECHNOLOGIES INC [US]; THOEN JOHAN [BE]; WOYDT MATHIAS [DE]) 5 November 2009 (2009-11-05) * page 9, line 1; claims 1-2 *	1-5	ADD. C10N10/04 C10N30/10 C10N40/02 C10N40/04 C10N40/08
A	EP 0 572 866 A1 (FUCHS PETROLUB AG OEL & CHEMIE [DE]) 8 December 1993 (1993-12-08) * claims 1, 12, 13, 21 *	1-5	
A	SCOTT J W ET AL: "6-HYDROXYCHROMAN-2-CARBOXYLIC ACIDS: NOVEL ANTIOXIDANTS", JOURNAL OF THE AMERICAN OIL CHEMISTS' SOCIETY, SPRINGER, BERLIN, DE, vol. 51, 1 April 1974 (1974-04-01), pages 200-203, XP008024186, ISSN: 0003-021X, DOI: 10.1007/BF02632894 * the whole document *	1-5	
----- -/-			TECHNICAL FIELDS SEARCHED (IPC) C10M

INCOMPLETE SEARCH

The Search Division considers that the present application, or one or more of its claims, does/do not comply with the EPC so that only a partial search (R.62a, 63) has been carried out.

Claims searched completely :

Claims searched incompletely :

Claims not searched :

Reason for the limitation of the search:

see sheet C

2

Place of search	Date of completion of the search	Examiner
Munich	12 August 2016	Greß, Tobias
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document		

EPO FORM 1503 03.82 (P04E07)



PARTIAL EUROPEAN SEARCH REPORT

Application Number

EP 16 16 4519

5

10

15

20

25

30

35

40

45

50

55

2

EPO FORM 1503 03.02 (P04C10)

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (IPC)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
A	US 5 811 380 A (WEITZ GENE C [US]) 22 September 1998 (1998-09-22) * claim 1; examples 1,3,9-10,12, 14-15 * -----	1-5	C10N40/20 C10N40/25 C10N40/26 C10N50/10
A	US 3 947 473 A (SCOTT JOHN WILLIAM ET AL) 30 March 1976 (1976-03-30) * claims 1-5 * * column 1, lines 13-24 * * column 35, lines 7-43 * -----	1-5	
			TECHNICAL FIELDS SEARCHED (IPC)

**INCOMPLETE SEARCH
SHEET C**

Application Number

EP 16 16 4519

Claim(s) completely searchable:

-

Claim(s) searched incompletely:

1-5

Reason for the limitation of the search:

In reply to the invitation to file a statement indicating the subject-matter to be searched, the applicant filed amended claims with his letter of 03-08-2016. However, these claims were received prior to the receipt of the European search report and are not considered as amended claims (Rule 137 (1) EPC), but merely as an indication of the subject-matter to be searched in respect of the claims originally filed. Having said that, neither the claims as filed nor the claims filed on 03-08-2016 meet the requirements of Article 76 EPC.

Thus, pursuant to Rule 63(2) EPC, the search report has been drawn up on the basis of claims 1 and 5 as originally filed wherein the antioxidant has been limited to the specific embodiment in orig. par. 39 which the applicant explicitly has indicated as basis for the claims filed on 03-08-2016 (i.e. formula (Id) wherein R1 is a hydrocarbyl group containing from 1 to 10 carbon atoms and each R2 is independently a hydrogen or hydrocarbyl group containing from 1 to 10 carbon atoms; R3 is hydrogen or hydrocarbyl group; and R4 is a hydrogen or hydrocarbyl group), which appears to comprise a reasonable and allowable definition of what is understood to be the invention for which protection is sought. The applicant's attention is drawn to the fact that the application will be further prosecuted on the basis of subject-matter for which a search has been carried out and that the claims should be limited to that subject-matter at a later stage of the proceedings (Rule 63(3) EPC).

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

EP 16 16 4519

5

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

12-08-2016

10

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2535058 A	26-12-1950	DE 909573 C US 2535058 A	22-04-1954 26-12-1950
-----	-----	-----	-----
WO 2009134716 A1	05-11-2009	CA 2722431 A1 EP 2271732 A1 KR 20110018327 A TW 201000623 A US 2011039741 A1 US 2013102507 A1 WO 2009134716 A1	05-11-2009 12-01-2011 23-02-2011 01-01-2010 17-02-2011 25-04-2013 05-11-2009
-----	-----	-----	-----
EP 0572866 A1	08-12-1993	DE 4217961 A1 EP 0572866 A1	02-12-1993 08-12-1993
-----	-----	-----	-----
US 5811380 A	22-09-1998	NONE	
-----	-----	-----	-----
US 3947473 A	30-03-1976	NONE	
-----	-----	-----	-----

15

20

25

30

35

40

45

50

55

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- US 5523007 A, Kristen [0004]
- US 3285855 A, Dexter [0005]
- US 5206414 A, Evans [0006]
- US 6559105 B, Abraham [0007]
- US 6787663 B, Adams [0008]
- US 4234435 A [0045] [0046]
- US 3172892 A [0045] [0046]
- US 6165235 A [0045] [0046]
- US 3219666 A [0046]
- US 3272746 A [0046]
- US 6440905 B [0046]
- US 3275554 A [0047]
- US 3438757 A [0047]
- US 3454555 A [0047]
- US 3565804 A [0047]
- US 3036003 A [0048]
- US 3236770 A [0048]
- US 3414347 A [0048]
- US 3448047 A [0048]
- US 3461172 A [0048]
- US 3539633 A [0048]
- US 3586629 A [0048]
- US 3591598 A [0048]
- US 3634515 A [0048]
- US 3725480 A [0048]
- US 3726882 A [0048]
- US 3980569 A [0048]
- US 3200107 A [0049]
- US 3282955 A [0049]
- US 3367943 A [0049]
- US 3513093 A [0049]
- US 3639242 A [0049]
- US 3649659 A [0049]
- US 3442808 A [0049]
- US 3455832 A [0049]
- US 3579450 A [0049]
- US 3600372 A [0049]
- US 3702757 A [0049]
- US 3708422 A [0049]
- US 3329658 A [0050]
- US 3449250 A [0050]
- US 3519656 A [0050]
- US 3666730 A [0050]
- US 3687849 A [0050]
- US 3702300 A [0050]
- US 2501731 A [0051]
- US 2616905 A [0051]
- US 2616911 A [0051]
- US 2616925 A [0051]
- US 2777874 A [0051]
- US 3256186 A [0051]
- US 3384585 A [0051]
- US 3365396 A [0051]
- US 3320162 A [0051]
- US 3318809 A [0051]
- US 3488284 A [0051]
- US 3629109 A [0051]
- US 6310009 B [0056]
- US 6200936 B [0058]
- WO 0156968 A [0058]
- US 6310011 B [0059]

Non-patent literature cited in the description

- Chemistry and Technology of Lubricants. 1997, 85, , 86 [0051]