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(54) **Low emission diesel lubricant with improved corrosion protection**

Emissionsarmes Schmiermittel mit verbessertem Korrosionsschutz

Lubrifiant à faible émission avec une protection améliorée contre la corrosion

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EP 1 479 752 B1

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DescriptionFIELD OF THE INVENTION

[0001] The present invention relates to engine lubricants for low emission diesel engines equipped with exhaust gas after-treatment systems that can be sensitive to lubricant constituents. Some of these types of after-treatment systems are known to be sensitive to fuel and lubricant constituents. In order to ensure the durability of these after-treatment systems, lubricants have been developed that feature low levels of ash, sulfur, and phosphorus. Ash, sulfur and phosphorus are present in many conventional lubricant additives such as detergents and zinc-dithiophosphates. To meet the requirement of maximum ash, sulfur and phosphorus levels, the low emission diesel lubricant ("LEDL") of the present invention has been developed using new components and component combinations.

[0002] Known LEDLs, which meet the requirement of maximum ash, sulfur and phosphorus levels, have been unable to meet minimum corrosion protection requirements. The new LEDL additive formulation described in this invention solves the corrosion problem while maintaining good performance in other areas. The formulation can be used in a finished oil blended with Group 1, 2, 3, or 4 base stocks or combinations thereof. The finished oil using this formulation may or may not contain a viscosity modifier, pour point depressant, and any ester added for solubility.

BACKGROUND OF THE INVENTION

[0003] There have heretofore been efforts to reduce the amount of sulfur in lubricating oil compositions.

[0004] For example, JP11-181463 teaches a gear oil that contains (a) 0.5-3 mass % of primary zinc dithiophosphoric acid, (b) 1.2-4 mass % of alkaline earth metal type detergent-dispersant, (c) 1.5-10 mass % of bis type alkenyl succinic acid imide or its derivative, (d) 0.3-3 mass % of amine salt of phosphate ester (e) 0.05-5 mass % of one or more sulfur compounds, and (f) a base oil that has less than 0.1 wt-% sulfur.

[0005] In order to further reduce the sulfur content in lubricating oil compositions, non-sulfur containing detergents may be employed. The preparation of both sulfur containing and non-sulfur containing hydrocarbyl phenates and hydrocarbyl salicylates is well known in the art.

[0006] U.S. Pat. No. 3,036,971 discloses preparing detergent dispersant additives based on sulfurized alkylphenates of high basicity alkaline earth metals. These additives are prepared by sulfurization of an alkylphenol, neutralization of the sulfurized alkylphenol with an alkaline earth metal base, then super-alkalization by carbonation of the alkaline earth metal base dispersed in the sulfurized alkylphenate.

[0007] French patent 1,563,557 discloses detergent additives based on sulfurized calcium alkylsalicylates. These additives are prepared by carboxylation of a potassium alkylphenate, exchange with calcium chloride, then sulfurization of the calcium alkylsalicylate obtained with sulfur in the presence of lime, a carboxylic acid and an alkylene glycol or alkyl ether of alkylene glycol.

[0008] French patent application 2,625,220 discloses superalkalized detergent-dispersant additives based on alkylphenates and alkylsalicylates. These additives are prepared by neutralization of an alkylphenol with an alkaline earth metal base in the presence of an acid and a solvent, distillation of the solvent, carboxylation, sulfurization and superalkalization by sulfur and an alkaline earth metal base in the presence of glycol and solvent, followed by carbonation and filtration.

[0009] US Patent No. 5,808,145 discloses a process that is able to improve substantially the performance of alkylphenate/alkylsalicylate additives, particularly in the tests relating to foaming, compatibility and dispersion in a new oil, and in the tests of stability towards hydrolysis. This process comprises neutralization with alkaline earth metal base of a mixture of linear and branched alkylphenols in the presence of a carboxylic acid, carboxylation by the action of carbon dioxide of the alkylphenate, followed by sulfurization and super-alkalization, then carbonation, distillation, filtration, and degassing in air.

[0010] European Patent Application Publication No. 0933417 discloses an unsulfurized, alkali metal-free detergent-dispersant additive, comprising a mixture of alkaline earth metal salts (alkylphenate/alkylsalicylate) and unreacted alkylphenol. This additive improves antioxidant properties, high temperature deposit control, and black sludge control.

[0011] U.S. Patent Nos. 6,162,770 and 6,262,001 teach an unsulfurized, alkali metal-free, detergent-dispersant composition having from 40% to 60% alkylphenol, from 10% to 40% alkaline earth alkylphenate, and from 20% to 40% alkaline earth single-aromatic-ring alkylsalicylate, and a process for preparing the same. This composition may have an alkaline earth double-aromatic-ring alkylsalicylate as long as the mole ratio of single-ring alkylsalicylate to double-aromatic-ring alkylsalicylate is at least 8:1. This composition may be produced by the three-step process involving neutralization of alkylphenols, carboxylation of the resulting alkylphenate, and filtration of the product of the carboxylation step. The detergent-dispersant produced by the method can be used in an engine lubricating composition to improve antioxidant properties, high temperature deposit control, and black sludge control.

[0012] EP-A-1167497 describes a lubricating oil composition having a low P content of 0.01 to 0.1 wt.%, and a sulfated

ash of 0.1 to 1 wt.%, which is composed of a) a major amount of mineral base oil having a low S content of at most 0.1 wt.%; b) an ashless alkenyl or alkyl-succinimide dispersant; c) a metal-containing detergent (non-sulfurized alkali metal or alkaline earth metal salt of an alkylsalicylic acid and/or non-sulfurized alkali metal or alkaline earth metal salt of an alkylphenol derivative having a Mannich base structure); d) Zn-DTP; e) an oxidation inhibitor (phenol compound and/or amine compound) and wherein the sulfur content is 0.01 to 0.3 wt. %. The lubricating oil composition shows good high temperature detergency notwithstanding its low S, P, and sulfated ash content, and is favourably employable in diesel engines using fuel of an extremely low sulfur content.

[0013] EP-A-0675191 describes a petroleum additive containing an alkaline earth metal salt of an aromatic hydroxy-carboxylic acid, wherein the alkaline earth metal salt is substantially free of an alkali metal and the ratio of salicylic acid skeleton to total benzene nuclei is 0.4:1 to 0.95:1. Also described is a process for producing an alkaline earth metal salt of an aromatic hydroxy-carboxylic acid involving: i) reacting an alkaline earth metal salt of a phenol with carbon dioxide; ii) reacting the resulting free phenol with an alkaline earth metal reagent in the presence of 2.0 to 15.0 mol of a dihydric alcohol per 1 mol of the alkaline earth metal reagent (when no water is added) or in the presence of 0.01 to 10.0 mol of water and 1.5 to 10.0 mol of a dihydric alcohol each per 1 mol of the alkaline earth metal reagent; and iii) repeating the reaction with carbon dioxide.

[0014] EP-A-0370555 relates to a process for the separation of a phenol from a mixture obtained by the carboxylation of the phenol and containing phenol, phenolate and the carboxylation products therefrom characterized in that the separation is carried out by selectively absorbing the phenol into the wall of a membrane, solubilizing the phenol in the membrane matrix, diffusing the phenol through the membrane and desorbing the phenol from the other wall.

[0015] It is desirable to find a low sulfur, ash and phosphorus lubricant with superior corrosion performance. The LEDL of the current invention is a low sulfur, ash, and phosphorus lubricant with superior corrosion performance.

[0016] The present invention provides a novel low emission diesel lubricant, or LEDL, comprising low levels of ash, sulfur and phosphorus, and LEDL also contains an unsulfurized, carboxylate-containing hydroxy-aromatic surfactant-based detergent-dispersant additive comprising a mixture of alkaline earth metal salts (hydrocarbyl phenate/hydrocarbyl salicylate) and a reduced amount of unreacted hydrocarbyl phenols. The present invention also relates to additive packages, concentrates and finished oil compositions comprising the same. Said hydrocarbyl salicylate is primarily single-aromatic-ring hydrocarbyl salicylate.

[0017] Said unsulfurized, carboxylate-containing additive containing said mixture in which said hydrocarbyl salicylate is primarily single-aromatic-ring hydrocarbyl salicylate improves antioxidant properties, high temperature deposit control, BN retention, corrosion control and black sludge control in lubricating oils. This invention is also directed, in part, to methods of preparing and using said novel LEDL.

[0018] The LEDL of the present invention has the following composition: a major amount of a base oil of lubricating viscosity, a hydroxy-aromatic surfactant-based detergent-dispersant additive containing less than 40 weight percent ("wt. %") free hydrocarbyl phenol; a dispersant; a wear inhibitor; and from 0 wt. % to 1.2 wt. % ash (as measured by ASTM D874); from 0.1 wt. % to 0.5 wt. % sulfur; and from 0.02 wt. % to 0.1 wt. % phosphorus. Preferably, the LEDL of the present invention comprise a major amount of a base oil of lubricating viscosity and from 0.4 wt. % to 1.0 wt. % ash; from 0.05 wt. % to 0.3 wt. % sulfur; and from 0.02 wt. % to 0.08 wt. % phosphorus. More preferably, said LEDL comprises a major amount of a base oil of lubricating viscosity and less than 1.0 wt. % ash; less than 0.3 wt. % sulfur; and less than 0.08 wt. % phosphorus. Most preferably, said LEDL comprises a major amount of a base oil of lubricating viscosity and from 0.4 wt. % to 1.0 wt. % ash; from 0.05 wt. % to 0.15 wt. % sulfur; and from 0.02 wt. % to 0.08 wt. % phosphorus.

[0019] The hydroxy-aromatic surfactant-based detergent-dispersant additive is unsulfurized. Said additive is a carboxylate-containing additive. Said additive comprises from 10 to 50% alkaline earth metal hydrocarbyl phenate; from 15 to 60% alkaline earth metal single-aromatic-ring hydrocarbyl salicylate; and from 0% to 50% organic diluent; and alkaline earth metal double-aromatic-ring hydrocarbyl salicylate; wherein the mole ratio of single-aromatic-ring hydrocarbyl salicylate to double-aromatic-ring hydrocarbyl salicylate is at least 8:1.

[0020] The LEDL comprises from 1.8 wt. % to 5.5 wt. % of said unsulfurized, carboxylate-containing, hydroxy-aromatic, surfactant-based, detergent-dispersant additive

[0021] In another embodiment, said LEDL further comprises from 1.0 wt. % to 4.0 wt. % borated dispersant; from 0.2 wt. % to 1.1 wt. % wear inhibitor; and from 0 wt. % to 0.5 wt. % corrosion inhibitor. More preferably, said dispersant is a succinimide; said wear inhibitor is zinc dithiophosphate; and said corrosion inhibitor is a neutralized terephthalic acid. Most preferably, said LEDL also comprises from 3.0 wt. % to 8.0 wt. % non-borated dispersant; from 0.6 wt. % to 1.4 wt. % calcium-sulfonate; from 0.1 wt. % to 0.5 wt. % molybdenum anti-oxidant; from 0 wt. % to 1.0 wt. % phenolic anti-oxidant; from 0.1 wt. % to 1.0 wt. % aminic anti-oxidant; from 0 wt. % to 6.0 wt. % dispersant olefin-copolymer; and from 0 to 25 ppm foam inhibitor.

[0022] Preferably, the LEDL of the present invention will contain no sulfur-containing detergent.

[0023] In one embodiment, the hydroxy-aromatic surfactant-based detergent-dispersant additive comprises from 0 to 35% free hydrocarbyl phenol; preferably from 0 to 30% free hydrocarbyl phenol; more preferably from 0 to 20% free hydrocarbyl phenol; most preferably from 0 to 15% free hydrocarbyl phenol.

[0024] The LEDL of the present invention may advantageously comprise a major amount of a base oil of lubricating viscosity and from 0.4 wt. % to 1.0 wt. % ash; from 0.2 wt. % to 0.4 wt. % sulfur; from 0.04 wt. % to 0.08 wt. % phosphorus; and from 2.7 wt. % to 5.5 wt. % of said unsulfurized carboxylate-containing additive. Said LEDL may further comprise from 1.0 wt. % to 4.0 wt. % borated dispersant; and from 0 wt. % to 0.5 wt. % corrosion inhibitor. Most preferably, said LEDL also comprises from 3.0 wt. % to 8.0 wt. % non-borated dispersant; from 0.6 wt. % to 1.4 wt. % calcium-sulfonate; from 0.2 wt. % to 1.1 wt. % zinc dithiophosphate; from 0.1 wt. % to 0.5 wt. % molybdenum anti-oxidant; from 0 wt. % to 1.0 wt. % phenolic anti-oxidant; from 0.1 wt. % to 1.0 wt. % aminic anti-oxidant; from 0 wt. % to 6.0 wt. % dispersant olefin-copolymer; and from 0 to 25 ppm foam inhibitor. Preferably, the sulfur content of said LEDL is from 0.1 wt. % to 0.3 wt. %.

[0025] In one embodiment, the effective corrosion inhibiting amount of an unsulfurized carboxylate-containing hydroxy-aromatic surfactant-based detergent-dispersant additive is prepared by a method comprising: (a) neutralization of hydrocarbyl phenols using an alkaline earth base in the presence of a promoter, to produce a hydrocarbyl phenate; (b) carboxylation of the hydrocarbyl phenate obtained in step (a) using carbon dioxide under carboxylation conditions sufficient to convert at least 20 mole% of the starting hydrocarbyl phenols to hydrocarbyl salicylate; and (c) separation of at least about 10% of the starting hydrocarbyl phenols from the product produced in step (b) to produce said additive, wherein said composition contains: from 0 wt. % to 1.2 wt. % ash; from 0.1 wt. % to 0.5 wt. % sulfur; and from 0.02 wt. % to 0.1 wt. % phosphorus.

[0026] Preferably, said promoter comprises at least one carboxylic acid containing from one to four carbon atoms, and said neutralization step is carried out in the absence of alkali base, in the absence of dialcohol, and in the absence of monoalcohol. The neutralization step is followed by carboxylation of the hydrocarbyl phenate produced in the neutralization step; and separation of the starting hydrocarbyl phenols from the product of the carboxylation step.

[0027] In the above described preparation of the unsulfurized carboxylate-containing hydroxy-aromatic surfactant-based detergent-dispersant additive, the hydrocarbyl phenols may comprise linear and /or branched hydrocarbyl constituents. For example, the hydrocarbyl phenols may be made up entirely of linear hydrocarbyl phenol, entirely of branched hydrocarbyl phenol, or a mixture of both. Preferably, the hydrocarbyl phenols contain up to 85% of linear hydrocarbyl phenol in mixture with at least 15% of branched hydrocarbyl phenol in which the branched hydrocarbyl radical contains at least nine carbon atoms. More preferably, the hydrocarbyl phenols are alkylphenols which contain from 35% to 85% of linear alkylphenol in mixture with from 15% to 65% of branched alkylphenol. The ratio of branched versus linear alkylphenol is given by weight. Preferably, the linear hydrocarbyl radical contains 12 to 40 carbon atoms, more preferably from 18 to 30 carbon atoms, and, if branched hydrocarbyl phenols are present, the branched hydrocarbyl radical contains at least 9 carbon atoms, preferably from 9 to 24 carbon atoms, more preferably 10 to 15 carbon atoms.

[0028] Preferably, the alkaline earth base is selected from the group consisting of calcium oxide, calcium hydroxide, magnesium oxide, and mixtures thereof.

[0029] Preferably, the carboxylic acid is a mixture of formic acid and acetic acid, more preferably a 50/50 by weight mixture of formic and acetic acid.

[0030] Preferably, the neutralization step is carried out at a temperature of at least 200°C, more preferably at least 215°C. The pressure is reduced gradually below atmospheric in order to remove the water of reaction, in the absence of any solvent that may form an azeotrope with water. Preferably, the quantities of reagents used correspond to the following molar ratios:

- (1) alkaline earth base/alkylphenol of from 0.2:1 to 0.7:1, more preferably from 0.3:1 to 0.5:1; and
- (2) carboxylic acid/alkylphenol of from 0.01:1 to 0.5:1, more preferably from 0.03:1 to 0.15:1.

[0031] In one embodiment, the neutralization step is carried out at a temperature of at least 240°C with a gradual reduction in pressure below atmospheric so as to reach a pressure of no more than 7,000 Pa (70 mbars) at 240°C.

[0032] The hydrocarbyl phenate obtained in the neutralization step is carboxylated in order to convert at least 20 mole % of the starting hydrocarbyl phenols to hydrocarbyl salicylate using carbon dioxide under carboxylation conditions. Preferably, at least 22 mole % of the starting hydrocarbyl phenols is converted, and this conversion occurs at a temperature between 180°C and 240°C, under a pressure within the range of from above atmospheric pressure to 15×10^5 Pa (15 bars) for a period of one to eight hours.

[0033] More preferably, the starting hydrocarbyl phenols are alkylphenols and at least 25 mole % of the starting alkylphenols is converted to alkylsalicylate using carbon dioxide at a temperature equal to or greater than 200°C, under a pressure of 4×10^5 Pa (4 bars).

[0034] The hydrocarbyl salicylate produced in the carboxylation step comprises both single-aromatic-ring hydrocarbyl salicylate and double-aromatic-ring hydrocarbyl salicylate. The mole ratio of single-aromatic-ring hydrocarbyl salicylate to double-aromatic-ring hydrocarbyl salicylate is at least 8:1.

[0035] Preferably, the product of the carboxylation step is then filtered to remove any sediment formed in the carboxylation step.

[0036] The product of the carboxylation step is then subjected to a separation procedure such as solvent extraction, distillation, membrane filtration, and the like wherein at least 10% of the starting hydrocarbyl phenols are separated from the product of the carboxylation step. Preferably, at least 30% up to 55% of the starting hydrocarbyl phenols are separated. More preferably, at least 45% to 50% of the starting hydrocarbyl phenols are separated from the product of the carboxylation step.

[0037] Once the starting hydrocarbyl phenols are separated from the product of the carboxylation step, said hydrocarbyl phenols may advantageously be recycled to be used as starting materials in the process of the present invention or in any other process.

[0038] Preferably, the separation step is performed via distillation, more preferably via falling film distillation or short path distillation, most preferably via wiped film evaporator distillation. Said distillation is carried out at a temperature of from 150°C to 250°C and at a pressure of 0.1 to 4 mbar; more preferably from 190°C to 230°C and at 0.5 to 3 mbar; most preferably from 195°C to 225°C and at a pressure of 1 to 2 mbar.

[0039] Prior to its addition to the LEDL composition of the present invention, the unsulfurized, carboxylate-containing hydroxy-aromatic surfactant-based detergent-dispersant additive may advantageously be blended with an effective viscosity improving amount of organic diluent. Preferably, enough diluent is added so that said diluent makes up from 10% to 50% by weight of the blended product. More preferably, said diluent makes up from 20% to 50% by weight of the blended product. Suitable diluents include Group 1 or Group 2 base oils such as 100N base oil; organic solvents such as pentane, heptane, benzene, toluene and the like; and other suitable organic compounds such as hydrocarbyl phenols which may advantageously be recycled from the distillation step of the present invention.

[0040] The unsulfurized, carboxylate-containing hydroxy-aromatic surfactant-based detergent-dispersant additive produced by the above described method has the following composition:

- (a) less than 40% hydrocarbyl phenol,
- (b) 10% to 50% alkaline earth metal hydrocarbyl phenate,
- (c) 15% to 60% alkaline earth metal single-aromatic-ring hydrocarbyl salicylate, and
- (d) 0% to 50% organic diluent.

[0041] Said unsulfurized, carboxylate-containing hydroxy-aromatic surfactant-based detergent-dispersant additive also comprises an alkaline earth metal double-aromatic-ring hydrocarbyl salicylate, but the mole ratio of single-aromatic-ring hydrocarbyl salicylate to double-aromatic-ring hydrocarbyl salicylate will be at least 8:1.

[0042] The LEDL of the present invention may be used as an engine lubricating oil composition containing a major part of lubricating oil, a hydroxy-aromatic surfactant-based detergent-dispersant additive and preferably at least one other additive. Examples of other additives that may be used include metal-containing detergents; ashless dispersants; borated and non-borated dispersants, including ethylene carbonate treated dispersants; low overbased ("LOB"), medium overbased ("MOB"), high overbased ("HOB") and high-high overbased ("HHOB") calcium sulfonates; oxidation inhibitors, rust inhibitors, demulsifiers, extreme pressure agents, friction modifiers, multifunctional additives, viscosity index improvers, pour point depressants, and foam inhibitors.

[0043] In automotive applications, the high temperature deposit control performance, corrosion control and oxidation inhibition performance of a lubricating oil can be improved by adding to the lubricating oil an effective amount of the LEDL composition of the present invention. Accordingly, the corrosion protection in any internal combustion engine may be improved by contacting said engine with the LEDL of the current invention.

DETAILED DESCRIPTION OF THE INVENTION

[0044] In accordance with the broadest aspect described above, the present invention provides a LEDL composition comprising low levels of ash, sulfur and phosphorus. Advantageously, said LEDL contains an unsulfurized, carboxylate-containing hydroxy-aromatic surfactant-based detergent-dispersant additive comprising hydrocarbyl phenol, alkaline earth metal hydrocarbyl phenate, and alkaline earth metal single-aromatic-ring hydrocarbyl salicylate useful for improving BN retention, corrosion performance, bulk oxidation, high temperature deposit control, black sludge control, thermal oxidation stability, and other properties of a lubricating oil.

[0045] Prior to discussing the invention in further detail, the following terms will be defined:

DEFINITIONS

[0046] As used herein the following terms have the following meanings unless expressly stated to the contrary:

The term "hydrocarbyl" means an alkyl or alkenyl group.

EP 1 479 752 B1

The term "metal" means alkali metals, alkaline earth metals, or mixtures thereof.

The term "alkaline earth metal" means calcium, barium, magnesium, strontium, or mixtures thereof.

5 The term "salicylate" means a metal salt of a salicylic acid.

The term "alkaline earth metal single-aromatic-ring hydrocarbyl salicylate" means an alkaline earth metal salt of a hydrocarbyl salicylic acid, wherein there is only one hydrocarbyl salicylic anion per each alkaline earth metal base cation.

10 The term "alkaline earth metal single-aromatic-ring alkylsalicylate" means an alkaline earth metal single-aromatic-ring hydrocarbyl salicylate wherein the hydrocarbyl group is an alkyl group.

15 The term "alkaline earth metal double-aromatic-ring hydrocarbyl salicylate" means an alkaline earth metal salt of a hydrocarbyl salicylic acid, wherein there are two hydrocarbyl salicylic anions per each alkaline earth metal base cation.

The term "alkaline earth metal double-aromatic-ring alkylsalicylate" means an alkaline earth metal double-aromatic-ring hydrocarbyl salicylate wherein the hydrocarbyl groups are alkyl groups.

20 The term "hydrocarbyl phenol" means a phenol having one or more hydrocarbyl substituents; at least one of which has a sufficient number of carbon atoms to impart oil solubility to the phenol.

The term "alkylphenol" means a phenol having one or more alkyl substituents, wherein at least one of the alkyl substituents has a sufficient number of carbon atoms to impart oil solubility to the phenol.

25 The term "phenate" means a metal salt of a phenol.

The term "hydrocarbyl phenate" means a metal salt of a hydrocarbyl phenol.

30 The term "alkaline earth metal hydrocarbyl phenate" means an alkaline earth metal salt of a hydrocarbyl phenol.

The term "alkaline earth metal alkylphenate" means an alkaline earth metal salt of an alkylphenol.

The term "phenate-stearate" means a phenate that has been treated with stearic acid or anhydride or salt thereof.

35 The term "long-chain carboxylic acid" means a carboxylic acid having an alkyl group having an average carbon number of from 13 to 28. The alkyl group may be linear, branched, or mixtures thereof.

40 The term "carboxy-stearate" means an alkaline earth metal single-aromatic-ring hydrocarbyl salicylate that has been treated with a long-chain carboxylic acid, anhydride or salt thereof.

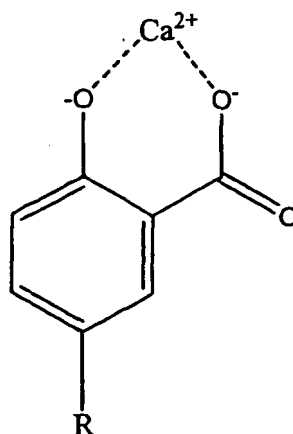
The term "major amount" means at least about 40 % by weight.

45 The term "unsulfurized" means containing less than 0.1 wt % sulfur.

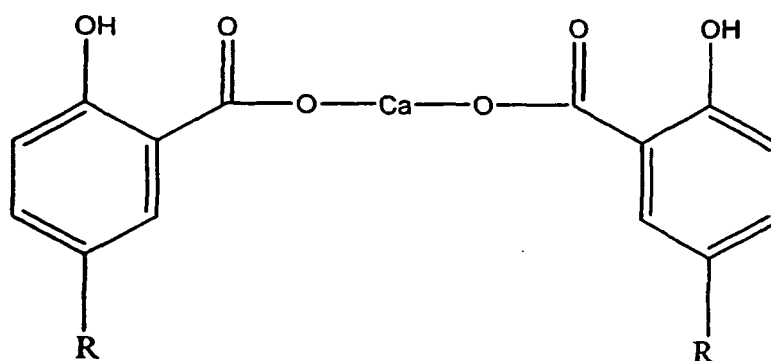
The term "Base Number" or "BN" refers to the amount of base equivalent to milligrams of KOH in one gram of sample. Thus, higher BN numbers reflect more alkaline products, and therefore a greater alkalinity reserve. The BN of a sample can be determined by ASTM Test No. D2896 or any other equivalent procedure.

50 **[0047]** Unless otherwise specified, all percentages are in weight percent.

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single aromatic ring hydrocarbyl salicylate



double aromatic ring hydrocarbyl salicylate

PREPARATION OF AN UNSULFURIZED CARBOXYLATE-CONTAINING HYDROXY-AROMATIC SURFACTANT-BASED DETERGENT-DISPERSANT ADDITIVE

A. NEUTRALIZATION STEP

[0048] In the first step, hydrocarbyl phenols are neutralized in the presence of a promoter. In one embodiment, said hydrocarbyl phenols are neutralized using an alkaline earth metal base in the presence of at least one C_1 to C_4 carboxylic acid. Preferably, this reaction is carried out in the absence of alkali base, and in the absence of dialcohol or monoalcohol.

[0049] The hydrocarbyl phenols may contain up to 100% linear hydrocarbyl groups, up to 100% branched hydrocarbyl groups, or both linear and branched hydrocarbyl groups. Preferably, the linear hydrocarbyl group, if present, is alkyl, and the linear alkyl radical contains 12 to 40 carbon atoms, more preferably 18 to 30 carbon atoms. The branched hydrocarbyl radical, if present, is preferably alkyl and contains at least nine carbon atoms, preferably 9 to 24 carbon atoms, more preferably 10 to 15 carbon atoms. In one embodiment, the hydrocarbyl phenols contain up to 85% of linear hydrocarbyl phenol (preferably at least 35% linear hydrocarbyl phenol) in mixture with at least 15% of branched hydrocarbyl phenol.

[0050] The use of an alkylphenol containing at least 35% of long-chain linear alkylphenol (from 18 to 30 carbon atoms) is particularly attractive because a long linear alkyl chain promotes the compatibility and solubility of the additives in lubricating oils. However, the presence of relatively heavy linear alkyl radicals in the alkylphenols can make the latter less reactive than branched alkylphenols, hence the need to use harsher reaction conditions to bring about their neutralization by an alkaline earth metal base.

[0051] Branched alkylphenols can be obtained by reaction of phenol with a branched olefin, generally originating from propylene. They consist of a mixture of monosubstituted isomers, the great majority of the substituents being in the para

position, very few being in the ortho position, and hardly any in the meta position. That makes them relatively more reactive towards an alkaline earth metal base, since the phenol function is practically devoid of steric hindrance.

[0052] On the other hand, linear alkylphenols can be obtained by reaction of phenol with a linear olefin, generally originating from ethylene. They consist of a mixture of monosubstituted isomers in which the proportion of linear alkyl substituents in the ortho, para, and meta positions is more uniformly distributed. This makes them less reactive towards an alkaline earth metal base since the phenol function is less accessible due to considerable steric hindrance, due to the presence of closer and generally heavier alkyl substituents. Of course, linear alkylphenols may contain alkyl substituents with some branching which increases the amount of para substituents and, resultantly, increases the relative reactivity towards alkaline earth metal bases.

[0053] The alkaline earth metal bases that can be used for carrying out this step include the oxides or hydroxides of calcium, magnesium, barium, or strontium, and particularly of calcium oxide, calcium hydroxide, magnesium oxide, and mixtures thereof. In one embodiment, slaked lime (calcium hydroxide) is preferred.

[0054] The promoter used in this step can be any material that enhances neutralization. For example, the promoter may be a polyhydric alcohol, dialcohol, monoalcohol, ethylene glycol or any carboxylic acid. Preferably, a carboxylic acid is used. More preferably, C₁ to C₄ carboxylic acids are used in this step including, for example, formic, acetic, propionic and butyric acid, and may be used alone or in mixture. Preferably, a mixture of acids is used, most preferably a formic acid/acetic acid mixture. The molar ratio of formic acid/acetic acid should be from 0.2:1 to 100:1, preferably between 0.5:1 and 4:1, and most preferably 1:1. The carboxylic acids act as transfer agents, assisting the transfer of the alkaline earth metal bases from a mineral reagent to an organic reagent.

[0055] The neutralization operation is carried out at a temperature of at least 200°C, preferably at least 215°C, and more preferably at least 240°C. The pressure is reduced gradually below atmospheric in order to distill off the water of reaction. Accordingly the neutralization should be conducted in the absence of any solvent that may form an azeotrope with water. Preferably, the pressure is reduced to no more than 7,000 Pa (70 mbars).

[0056] The quantities of reagents used should correspond to the following molar ratios:

- (1) alkaline earth metal base/ hydrocarbyl phenol of 0.2:1 to 0.7:1, preferably 0.3:1 to 0.5:1; and
- (2) carboxylic acid/ hydrocarbyl phenol of 0.01:1 to 0.5:1, preferably from 0.03:1 to 0.15:1.

[0057] Preferably, at the end of this neutralization step the hydrocarbyl phenate obtained is kept for a period not exceeding fifteen hours at a temperature of at least 215°C and at an absolute pressure of between 5,000 and 10⁵ Pa (between 0.05 and 1.0 bar). More preferably, at the end of this neutralization step the hydrocarbyl phenate obtained is kept for between two and six hours at an absolute pressure of between 10,000 and 20,000 Pa (between 0.1 and 0.2 bar).

[0058] By providing that operations are carried out at a sufficiently high temperature and that the pressure in the reactor is reduced gradually below atmospheric, the neutralization reaction is carried out without the need to add a solvent that forms an azeotrope with the water formed during this reaction.

B. CARBOXYLATION STEP

[0059] The carboxylation step is conducted by simply bubbling carbon dioxide into the reaction medium originating from the preceding neutralization step and is continued until at least 20 mole % of the starting hydrocarbyl phenols is converted to hydrocarbyl salicylate (measured as salicylic acid by potentiometric determination). It must take place under pressure in order to avoid any decarboxylation of the alkylsalicylate that forms.

[0060] Preferably, at least 22 mole % of the starting hydrocarbyl phenols is converted to hydrocarbyl salicylate using carbon dioxide at a temperature of between 180°C and 240°C, under a pressure within the range of from above atmospheric pressure to 15×10⁵ Pa (15 bars) for a period of one to eight hours.

[0061] According to one variant, at least 25 mole % of the starting hydrocarbyl phenols is converted to hydrocarbyl salicylate using carbon dioxide at a temperature equal to or greater than 200°C under a pressure of 4×10⁵ Pa (4 bars).

C. FILTRATION STEP

[0062] The product of the carboxylation step may advantageously be filtered. The purpose of the filtration step is to remove sediments, and particularly crystalline calcium carbonate, which might have been formed during the preceding steps, and which may cause plugging of filters installed in lubricating oil circuits.

D. SEPARATION STEP

[0063] At least 10% of the starting hydrocarbyl phenol is separated from the product of the carboxylation step. Preferably, the separation is accomplished using distillation. More preferably, the distillation is carried out in a wiped film

evaporator at a temperature of from 150°C to 250°C and at a pressure of 0.1 to 4 mbar; more preferably from 190°C to 230°C and at 0.5 to 3 mbar; most preferably from 195°C to 225°C and at a pressure of 1 to 2 mbar. At least 10% of the starting hydrocarbyl phenol is separated. More preferably, at least 30% of the starting hydrocarbyl phenol is separated. Most preferably, up to 55% of the starting hydrocarbyl phenol is separated. The separated hydrocarbyl phenol may then be recycled to be used as starting materials in the novel process or in any other process.

UNSULFURIZED, CARBOXYLATE-CONTAINING HYDROXY-AROMATIC SURFACTANT-BASED DETERGENT-DISPERSANT ADDITIVE

[0064] The unsulfurized, carboxylate-containing hydroxy-aromatic surfactant-based detergent-dispersant additive formed by the above process can be characterized by its unique composition, with much more alkaline earth metal single-aromatic-ring hydrocarbyl salicylate and less hydrocarbyl phenol than produced by other routes. When the hydrocarbyl group is an alkyl group, the unsulfurized, carboxylate-containing additive has the following composition;

- (a) less than 40% alkylphenol,
- (b) from 10% to 50% alkaline earth metal alkylphenate, and
- (c) from 15% to 60% alkaline earth metal single-aromatic-ring alkylsalicylate.

[0065] Unlike alkaline earth metal alkylsalicylates produced by other processes, this unsulfurized, carboxylate-containing additive composition can be characterized by having only minor amounts of an alkaline earth metal double-aromatic-ring alkylsalicylates. The mole ratio of single-aromatic-ring alkylsalicylate to double-aromatic-ring alkylsalicylate is at least 8:1.

CHARACTERIZATION OF THE PRODUCT BY INFRARED SPECTROMETRY

[0066] Out-of-aromatic-ring-plane C-H bending vibrations were used to characterize the unsulfurized carboxylate-containing hydroxy-aromatic surfactant-based detergent-dispersant additive employed in the present invention.

[0067] Infrared spectra of aromatic rings show strong out-of-plane C-H bending transmittance band in the 675-870 cm^{-1} region, the exact frequency depending upon the number and location of substituents. For ortho-disubstituted compounds, transmittance band occurs at 735-770 cm^{-1} . For para-disubstituted compounds, transmittance band occurs at 810-840 cm^{-1} .

[0068] Infrared spectra of reference chemical structures relevant to the present invention indicate that the out-of-plane C-H bending transmittance band occurs at $750 \pm 3 \text{ cm}^{-1}$ for ortho-alkylphenols, at $760 \pm 2 \text{ cm}^{-1}$ for salicylic acid, and at $832 \pm 3 \text{ cm}^{-1}$ for para-alkylphenols.

[0069] Alkaline earth alkylphenates known in the art have infrared out-of-plane C-H bending transmittance bands at $750 \pm 3 \text{ cm}^{-1}$ and at $832 \pm 3 \text{ cm}^{-1}$. Alkaline earth alkylsalicylates known in the art have infrared out-of-plane C-H bending transmittance bands at $763 \pm 3 \text{ cm}^{-1}$ and at $832 \pm 3 \text{ cm}^{-1}$.

[0070] The unsulfurized carboxylate-containing hydroxy-aromatic surfactant-based detergent-dispersant additive employed in the present invention shows essentially no out-of-plane C-H bending vibration at $763 \pm 3 \text{ cm}^{-1}$, even though there is other evidence that alkylsalicylate is present. This particular characteristic has not been fully explained. However, it may be hypothesized that the particular structure of the single aromatic ring alkylsalicylate prevents in some way this out-of-plane C-H bending vibration. In this structure, the carboxylic acid function is engaged in a cyclic structure, and thus may generate increased steric hindrance in the vicinity of the aromatic ring, limiting the free motion of the neighbor hydrogen atom. This hypothesis is supported by the fact that the infrared spectrum of the acidified product (in which the carboxylic acid function is no longer engaged in a cyclic structure and thus can rotate) has an out-of-plane C-H transmittance band at $763 \pm 3 \text{ cm}^{-1}$.

[0071] The unsulfurized carboxylate-containing hydroxy-aromatic surfactant-based detergent-dispersant additive employed in the present invention can thus be characterized by having a ratio of infrared transmittance band of out-of-plane C-H bending at about $763 \pm 3 \text{ cm}^{-1}$ to out-of-plane C-H bending at $832 \pm 3 \text{ cm}^{-1}$ of less than 0.1:1.

[0072] The unsulfurized, carboxylate-containing hydroxy-aromatic surfactant-based detergent-dispersant additive formed by the above method, being non-sulfurized, would provide improved high temperature deposit control performance over sulfurized products while meeting the low sulfur requirements for LEDLs. Being alkali-metal free, this additive can be employed as a detergent-dispersant in applications, such as marine engine oils, where the presence of alkali metals have proven to have harmful effects.

HYDROXY-AROMATIC SURFACTANT-BASED DETERGENT-DISPERSANT ADDITIVES

[0073] Hydroxy-aromatic surfactant-based detergent-dispersant additives are well known in the art. Examples of such

additives include phenates, phenate-carboxylates, salicylates, carboxy-stearates, and the unsulfurized carboxylate-containing additive described above.

PREPARATION OF PHENATES

[0074] The phenates which may be used in the present invention are typically hydrocarbyl substituted phenates in which the hydrocarbyl substituent or substituents of the phenate are preferably one or more alkyl group, either branched or unbranched. Suitable alkyl groups contain from 4 to 50, preferably from 9 to 28 carbon atoms. Particularly suitable alkyl groups are C₁₂ groups derivable from propylene tetramer. The hydrocarbyl substituted phenates are typically sulfurized.

[0075] According to one preferred embodiment of the present invention, overbased sulfurized alkylphenates of alkaline earth metals are prepared by neutralizing a sulfurized alkylphenol with an alkaline earth base in the presence of a dilution oil, a glycol, and halide ions, the glycol being present in the form of a mixture with an alcohol having a boiling point above 150 °C, removing alcohol, glycol, water, and sediment, carbonating the reaction medium with CO₂ in the presence of halide ions, and again removing alcohol, glycol, water, and sediment.

[0076] In another preferred embodiment, an overbased, sulfurized hydrocarbyl phenate is prepared by a process comprising the steps of:

- (a) neutralizing a sulfurized alkylphenol with an alkaline earth base in the presence of a dilution oil, a glycol, and halide ions, the glycol being present in the form of a mixture with an alcohol having a boiling point above 150°C;
- (b) removing alcohol, glycol, and water from the medium, preferably by distillation;
- (c) removing sediment from the medium, preferably by filtration;
- (d) carbonating the resultant medium with CO₂ in the presence of halide ions; and
- (e) removing alcohol, glycol, and water from the medium, preferably by distillation.

[0077] The alkaline earth bases useful in the above process include the oxides and hydroxides of barium, strontium, and calcium, particularly lime. Alcohols with a boiling point above 150°C useful in the process include alcohols of C₆ to C₁₄ such as ethylhexanol, oxoalcohol, decylalcohol, tridecylalcohol; alkoxyalcohols such as 2-butoxyethanol, 2-butoxypropanol; and methyl ethers of dipropylene glycol. The amines useful in the process include polyaminoalkanes, preferably polyaminoethanes, particularly ethylenediamine, and aminoethers, particularly tris(3-oxa-6-amino-hexyl)amine. The glycols useful in the process include alkylene glycols, particularly ethylene glycol. The halide ions employed in the process are preferably Cl⁻ ions which may be added in the form of ammonium chloride or metal chlorides such as calcium chloride or zinc chloride.

[0078] The dilution oils suitable for use in the above process include naphthenic oils and mixed oils and preferably paraffinic oils such as neutral 100 oil. The quantity of dilution oil used is such that the amount of oil in the final product constitutes from about 25% to about 65% by weight of the final product, preferably from about 30% to about 50%.

[0079] The process outlined above is more fully described in US Patent 4,514,313.

PREPARATION OF PHENATE-CARBOXYLATES

[0080] The phenate-carboxylates which may be used in the present invention are typically hydrocarbyl substituted phenate-carboxylates in which the hydrocarbyl substituent or substituents of the phenate are preferably one or more alkyl group, either branched or unbranched. Suitable alkyl groups contain from 4 to 50, preferably from 9 to 28 carbon atoms. Particularly suitable alkyl groups are C₁₂ groups derivable from propylene tetramer. The hydrocarbyl substituted phenate-carboxylates may be sulfurized or unsulfurized.

[0081] The overbased hydrocarbyl phenate-carboxylate is prepared from an overbased hydrocarbyl phenate which has been treated, either before, during, or subsequent to overbasing, with a long-chain carboxylic acid (preferably stearic acid), anhydride or salt thereof. That process comprises contacting a mixture of a hydrocarbyl phenate, at least one solvent, metal hydroxide, aqueous metal chloride, and an alkyl polyhydric alcohol containing from one to five carbon atoms, with carbon dioxide under overbasing reaction conditions. Using an aqueous metal chloride, instead of a solid metal chloride, reduces the viscosity of the product. Preferably, the metals are alkaline earth metals, most preferably calcium. Preferably, the alkyl polyhydric alcohol is ethylene glycol.

[0082] In a preferred embodiment, the overbased hydrocarbyl phenate-carboxylate is produced by overbasing a hydrocarbyl phenate and treating the phenate (before, during, or after overbasing) with a long-chain carboxylic acid (preferably stearic acid), anhydride or salt thereof.

[0083] In the overbasing step, a mixture comprising hydrocarbyl phenate (which can be sulfurized or unsulfurized), at least one solvent, metal hydroxide, aqueous metal chloride, and an alkyl polyhydric alcohol containing from one to five carbon atoms is reacted with carbon dioxide under overbasing reaction conditions. Overbasing reaction conditions

include temperatures of from 250 to 375°F (120 to 191°C) at approximately atmospheric pressure.

[0084] Preferably, the overbased hydrocarbyl phenate is a sulfurized alkylphenate. Preferably, the metal is an alkaline earth metal, more preferably calcium. Preferably, the alkyl polyhydric alcohol is ethylene glycol.

[0085] The carboxylate treatment (treatment with long-chain carboxylic acid, anhydride, or salt thereof) can occur before, during, or after the overbasing step. It is unimportant when the treatment with long-chain carboxylic acid, anhydride, or salt thereof occurs relative to the overbasing step.

[0086] The phenate can be sulfurized or unsulfurized. Preferably, the phenate is sulfurized. If the phenate is sulfurized, the sulfurization step can occur anytime prior to overbasing. More preferably, the phenate is sulfurized before the overbasing step but after the carboxylate treatment.

[0087] The process outlined above is more fully described in US Patent 5,942,476.

PREPARATION OF SALICYLATES

[0088] The preparation of salicylates is well known in the art. Preferred salicylates which may be used in the present invention include medium and high overbased salicylates including salts of polyvalent or monovalent metals, more preferably monovalent, most preferably calcium. As used herein, medium overbased (MOB) is meant to include salicylates with a TBN of about 31 to 170. High overbased (HOB) is meant to include salicylates with a TBN from about 171 to 400. High-high overbased (HHOB) is meant to include salicylates with a TBN over 400.

[0089] In one embodiment, salicylates may be prepared, for instance, starting from phenol, ortho-alkylphenol, or para-alkylphenol, by alkylation, carboxylation and salt formation. The alkylating agent preferably chosen is an olefin or a mixture of olefins with more than 12 carbon atoms to the molecule. Acid-activated clays are suitable catalysts for the alkylation of phenol and ortho- and para- alkylphenol. The amount of catalyst employed is, in general, 1 - 10 wt%, in particular, 3-7 wt%, referred to the sum of the amounts by weight of alkylating agent and phenol to be alkylated. The alkylation may be carried out at temperatures between 100 and 250°C, in particular, between 125 and 225°C.

[0090] The alkylphenols prepared via the phenol or ortho- or para-alkylphenol route may be converted into the corresponding alkylsalicylic acids by techniques well known in the art. For instance, the alkylphenols are converted with the aid of an alcoholic caustic solution into the corresponding alkylphenates and the latter are treated with CO₂ at about 140°C and a pressure of 10 to 30 atmospheres (10.13 to 30.40 bar). From the alkylsalicylates so obtained, the alkylsalicylic acids may be liberated with the aid of, for example, 30% sulfuric acid.

[0091] For the preparation of overbased salicylates, the alkylsalicylic acids may be treated with an excess amount of a metal compound, for instance, calcium in the form of Ca(OH)₂.

[0092] For example, the alkylsalicylic acids may be treated with 4 equivalents of calcium in the form of Ca(OH)₂ with introduction of 1.6 equivalents of CO₂.

[0093] The preparation of medium and overbased salicylates is more fully described in US Patent 4,810,398, and GB Patents 1,146,925; 790,473; and 786,167.

PREPARATION OF CARBOXY-STEARATES

[0094] The carboxy-stearates which may be used in the present invention are typically alkaline earth metal single-aromatic-ring hydrocarbyl salicylates that have been treated with a long-chain carboxylic acid, anhydride or salt thereof.

[0095] The carboxy-stearate is prepared from a mixture of alkaline earth metal single-aromatic-ring salicylate, at least one solvent, and alkaline earth metal hydroxide. The mixture is overbased by contacting the mixture with carbon dioxide in the presence of an alkyl polyhydric alcohol, wherein the alkyl group of the alcohol has from one to five carbon atoms. One such useful alkyl polyhydric alcohol is ethylene glycol.

[0096] The process outlined above is more fully described in US Patent 6,348,438.

BASE OIL OF LUBRICATING VISCOSITY

[0097] The base oil of lubricating viscosity used in such compositions may be mineral oil or synthetic oils of viscosity suitable for use in the crankcase of an internal combustion engine. Crankcase base oils ordinarily have a viscosity of about 1300 cSt (1300 mm²/second) at 0°F (-18°C) to 3 cSt (3 mm²/second) at 210°F (99°C). The base oils may be derived from synthetic or natural sources. Mineral oil for use as the base oil in this invention includes paraffinic, naphthenic and other oils that are ordinarily used in lubricating oil compositions. Synthetic oils include both hydrocarbon synthetic oils and synthetic esters. Useful synthetic hydrocarbon oils include liquid polymers of alpha olefins having the proper viscosity. Especially useful are the hydrogenated liquid oligomers of C₆ to C₁₂ alpha olefins such as 1-decene trimer. Likewise, alkyl benzenes of proper viscosity, such as didodecyl benzene, can be used. Useful synthetic esters include the esters of monocarboxylic acids and polycarboxylic acids, as well as monohydroxy alkanols and polyols. Typical examples are didodecyl adipate, pentaerythritol tetracaprate, di-2-ethylhexyl adipate, dilaurylsebacate, and the like.

Complex esters prepared from mixtures of mono and dicarboxylic acids and mono and dihydroxy alkanols can also be used.

[0098] Blends of mineral oils with synthetic oils are also useful. For example, blends of 10 to 25% hydrogenated 1-decene trimer with 75 to 90% 150 SUS (100°F (38°C)) mineral oil make excellent lubricating oil bases.

[0099] The LEDL of the present invention can be added to Group 1, 2, 3, or 4 base stocks or combinations thereof.

DETERGENTS

[0100] The LEDL of the present invention has been found to provide improved bulk oxidation and corrosion control performance when contacted with an internal combustion engine. Embodiments of the LEDL may contain detergents.

[0101] Detergents help control varnish, ring zone deposits, and rust by keeping insoluble particles in colloidal suspension. Metal-containing (or ash-forming detergents) function both as detergents to control 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 (as measured by ASTM D2896) of from 0 to 10. It is possible to include large amounts of a metal base by reacting an excess of a metal compound such as an oxide or hydroxide with an acidic gas such as carbon dioxide to form an overbased detergent. Such overbased detergents may have a total base number of about 15 to 30 (low overbased ("LOB")); 31 to 170 (medium overbased ("MOB")); 171 to 400 (high overbased ("HOB")); or above 400 (high-high overbased ("HHOB")).

DISPERSANTS

[0102] The LEDLs of this invention may comprise one or more dispersants including nitrogen containing dispersants of the type generally represented by succinimides (e.g., polyisobutylene succinic acid/anhydride (PIBSA)-polyamine having a PIBSA molecular weight of about 700 to 2500). The dispersants may be borated or non-borated, ashless or ash containing. Lubricating oils of this invention may comprise about 1 wt. % to about 12 wt. % or more dispersants.

[0103] Preferred dispersants for this invention comprise one or more dispersants having an average molecular weight (mw) of about 1000 to about 10,000. Dispersants prepared from polyisobutylene (PIB) having a mw of about 1000 to about 5000 are such preferred dispersants.

[0104] A preferred dispersant of this invention may be a one or more succinimides. The term "succinimide" is understood in the art to include many of the amide, imide, etc. species that are also formed by the reaction of a succinic anhydride with an amine and is so used herein. The predominant product, however, is succinimide and this term has been generally accepted as meaning the product of a reaction of an alkenyl- or alkyl-substituted succinic acid or anhydride with a polyamine. Alkenyl or alkyl succinimides are disclosed in numerous references and are well known in the art. Certain fundamental types of succinimides and related materials encompassed by the term of art "succinimide" are taught in U.S. Pat. Nos. 2,992,708; 3,018,250; 3,018,291; 3,024,237; 3,100,673; 3,172,892; 3,219,666; 3,272,746; 3,361,673; 3,381,022; 3,912,764; 4,234,435; 4,612,132; 4,747,965; 5,112,507; 5,241,003; 5,266,186; 5,286,799; 5,319,030; 5,334,321; 5,356,552; 5,716,912.

[0105] This invention may comprise one or more succinimides, which may be either a mono, poly, or bis-succinimide. This invention may comprise lubricating oil involving one or more succinimide dispersants that have or have not been post treated.

[0106] Borated dispersants useful in the present invention may be derived from the reaction product of a polyisobutenylsuccinic anhydride with a polyamine. Preferably, the borated dispersant is derived from polybutenes having a molecular weight of from 1200 to 1400, most preferably about 1300.

[0107] Ethylene carbonate treated, or EC-treated, dispersants useful in the present invention may be derived from the reaction product of a polyisobutenylsuccinic anhydride with a polyamine. The polyisobutene has a number average molecular weight (M_n) of at least 1800. Preferably, the EC-treated dispersant is a polybutene succinimide derived from polybutenes having a molecular weight of from 2000 to 2400. A preferred EC treated succinimide of this invention is described in U.S. Patent Nos. 5,334,321 and 5,356,552.

CORROSION INHIBITORS

[0108] Corrosion inhibitors which may advantageously be used in the LEDL of this invention are, for example, succinimide salts of one or more aromatic dicarboxylic acids, and dispersed aromatic dicarboxylic acid corrosion inhibitors. Preferred aromatic dicarboxylic acids may comprise one or more terephthalic acids.

[0109] Certain corrosion inhibitors, including dispersed aromatic dicarboxylic acid corrosion inhibitors, are described, for example, in U.S. Patent Nos. 3,287,271; 3,692,681; and 3,374,174.

[0110] One embodiment of the dispersed aromatic dicarboxylic acid corrosion inhibitor may be synthesized by reacting about 1100 to about 1500, preferably about 1300 molecular weight polyisobutenyl succinic anhydride (PIBSA) with one or more polyamines, preferably one or more heavy polyamines (HPA) at an amine/PIBSA CMR of about 0.4 to about 0.6, preferably about 0.45. This produces a reaction product that may then be reacted with terephthalic acid.

[0111] Another embodiment of the dispersed aromatic dicarboxylic acid corrosion inhibitor of this invention may be synthesized as follows. One or more PIBSAs may be reacted with one or more polyamines to produce one or more succinimides by heating the mixture, with or without diluent, at a temperature of from about 110°C to about 200°C, preferably about 150°C to about 170°C, for 1 to 20 hours. Heating for about 3 to about 6 hours is preferred. Reactants may be mixed and then heated or heating may occur while the reactants are being mixed. During the heating period, water of the reaction may be removed by any means known in the art. Any PIBSA may be used. This includes thermal PIBSA made from conventional PIB or high reactivity PIB, chlorination PIBSA, a mixture of thermal and chlorination PIBSA, sulfonic acid catalyzed PIBSA, PolyPIBSA, or Terpolymer PIBSA. A mixture of PIBSA and a copolymer may also be used. An amine/PIBSA charge mole ratio (CMR) of about 0.4 to 0.6 may be used. A preferred CMR may be about 0.4 to about 0.5. After heating, the reaction mixture may be cooled to about 110°C to about 150°C, preferably about 130°C to about 135°C. Terephthalic acid may then be added. About 2% to about 5% terephthalic acid, preferably about 2.5% to about 3.5% by weight, based on the succinimide weight may be used. This mixture may then be heated for about 1 to about 10 hours, preferably about 2 to about 4 hours. The mixture may then be filtered. Another embodiment of this invention may comprise one or more corrosion inhibitors synthesized by reacting 1000 molecular weight polyisobutenesuccinic anhydride (PIBSA) with tetraethylenepentamine (TEPA) using an amine/PIBSA charge mole ratio (CMR) of 0.71. This produces a reaction product, which may then be reacted with terephthalic acid to form a dispersed aromatic dicarboxylic acid corrosion inhibitor.

[0112] The preparation of said corrosion inhibitors is further described, for example, in US-A-20030224948 (corresponding to U.S. Patent Application No. 10/367,432, filed February 14, 2003).

WEAR INHIBITORS

[0113] Traditional wear inhibitors may be used in this invention. As their name implies, these agents reduce wear of moving metallic parts. Examples of such agents include, but are not limited to phosphates, phosphites, carbamates, esters, sulfur containing compounds, and molybdenum complexes. The LEDL of this invention comprises one or more wear inhibitors such metal dithiophosphates and metal dithiocarbamates or mixtures thereof. A preferred wear inhibitor for use in this invention comprises zinc dithiophosphate.

OTHER ADDITIVE COMPONENTS

[0114] The following additive components are examples of some components that can be favorably employed in the present invention. These examples of additives are provided to illustrate the present invention, but they are not intended to limit it:

(1) Ashless dispersants: alkenyl succinimides, alkenyl succinimides modified with other organic compounds, and alkenyl succinimides modified with boric acid, alkenyl succinic ester; EC-treated dispersants.

(2) Oxidation inhibitors:

(a) Phenol type oxidation inhibitors: 4,4'-methylene bis(2,6-di-tert-butylphenol), 4,4'-bis(2,6-di-tert-butylphenol), 4,4'-bis(2-methyl-6-tert-butylphenol), 2,2'-methylene bis(4-methyl-6-tert-butylphenol), 4,4'-butylidenebis(3-methyl-6-tert-butylphenol), 4,4'-isopropylidenebis(2,6-di-tert-butylphenol), 2,2'-methylene-bis(4-methyl-6-nonylphenol), 2,2'-isobutylidene-bis(4,6dimethyl-phenol), 2,2'-methylenebis(4-methyl-6-cyclohexylphenol), 2,6-di-tert-butyl-4-methyl-phenol, 2,6-di-tert-butyl-4-ethylphenol, 2,4-dimethyl-6-tert-butyl-phenol, 2,6-di-tert-4-(N,N'-dimethylaminomethylphenol), 4,4'-thiobis(2-methyl-6-tert-butylphenol), 2,2'-thiobis(4-methyl-6-tert-butylphenol), bis(3-methyl-4-hydroxy-5-tert-butylbenzylsulfide, and bis(3,5-di-tert-butyl-4-hydroxybenzyl).

(b) Diphenylamine type oxidation inhibitor: alkylated diphenylamine, phenyl- α -naphthylamine, and alkylated α -naphthylamine.

(c) Other types: metal dithiocarbamate (e.g., zinc dithiocarbamate), molybdenum oxysulfide succinimide complexes, and methylenebis(dibutyl-dithiocarbamate).

(3) Rust inhibitors (Anti-rust agents)

(a) Nonionic polyoxyethylene surface active agents:

polyoxyethylene lauryl ether; polyoxyethylene higher alcohol ether, polyoxyethylene nonylphenyl ether, polyoxyethylene octylphenyl ether, polyoxyethylene octyl stearyl ether, polyoxyethylene oleyl ether, polyoxyethylene sorbitol monostearate, polyoxyethylene sorbitol mono-oleate, and polyethylene glycol monooleate.

(b) Other compounds: stearic acid and other fatty acids, dicarboxylic acids, metal soaps, fatty acid amine salts, metal salts of heavy sulfonic acid, partial carboxylic acid ester of polyhydric alcohol, and phosphoric ester.

(4) Demulsifiers: addition product of alkylphenol and ethyleneoxide, polyoxyethylene alkyl ether, and polyoxyethylene sorbitan ester.

(5) Extreme pressure agents (EP agents): zinc dialkyldithiophosphate (aryl zinc, primary alkyl, and secondary alkyl type), sulfurized oils, diphenyl sulfide, methyl trichlorostearate, chlorinated naphthalene, fluoroalkylpolysiloxane, and lead naphthenate.

(6) Friction modifiers: fatty alcohol, fatty acid, amine, borated ester, and other esters.

(7) Multifunctional additives: sulfurized oxymolybdenum dithiocarbamate, sulfurized oxymolybdenum organo phosphoro dithioate, oxymolybdenum monoglyceride, oxymolybdenum diethylate amide, amine-molybdenum complex compound, and sulfur-containing molybdenum complex compound.

(8) Viscosity index improvers: polymethacrylate type polymers, ethylene-propylene copolymers, styrene-isoprene copolymers, hydrated styrene-isoprene copolymers, polyisobutylene, and dispersant type viscosity index improvers.

(9) Pour point depressants: polymethyl methacrylate.

(10) Foam inhibitors: alkyl methacrylate polymers and dimethyl silicone polymers.

(11) Metal detergents: sulfurized or unsulfurized alkyl or alkenyl phenates, alkyl or alkenyl aromatic sulfonates, calcium sulfonates, sulfurized or unsulfurized metal salts of multihydroxy alkyl or alkenyl aromatic compounds, alkyl or alkenyl hydroxy aromatic sulfonates, sulfurized or unsulfurized alkyl or alkenyl naphthenates, metal salts of alkanolic acids, metal salts of an alkyl or alkenyl multiacid, and chemical and physical mixtures thereof.

LOW EMISSION DIESEL LUBRICATING OIL COMPOSITION

[0115] The LEDL of the present invention is useful for its improved detergency over other engine lubricating oil compositions. Such a lubricating oil composition comprises a major part of a base oil of lubricating viscosity and from 0 wt. % to 1.2 wt. % ash; from 0.1 wt. % to 0.5 wt. % sulfur; and from 0.02 wt. % to 0.1 wt. % phosphorus. Said LEDLs provide improved detergency while at the same time providing compatibility with exhaust gas after-treatment systems.

[0116] In one embodiment, the LEDL would contain:

- (a) a major part of a base oil of lubricating viscosity;
- (b) 0% to 1.2 wt. % ash;
- (c) 0.05% to 0.5 wt. % sulfur;
- (d) 0.02% to 0.1 wt. % phosphorus;
- (e) 1% to 12% of at least one dispersant;
- (f) 0.5% to 1.1% of at least one zinc dithiophosphate;
- (g) 0% to 2.5% of at least one oxidation inhibitor;
- (h) 0% to 1% of at least one foam inhibitor;
- (i) 0% to 10% of at least one viscosity index improver;
- (j) 0% to 0.5% corrosion inhibitor; and

[0117] from 1.8% to 5.5 wt% of the unsulfurized, carboxylate-containing hydroxy-aromatic surfactant-based detergent-dispersant additive of the present invention. It has been found that LEDLs containing said additive provide superior corrosion protection to LEDLs containing commercially available salicylates at constant ash, sulfur and phosphorus levels.

[0118] It has been found that LEDLs of the instant invention may be prepared such that they contain very low sulfur. Very low sulfur is defined to mean about 0.05 wt. % to about 0.3 wt. % sulfur. Surprisingly, very low sulfur LEDLs prepared according to the instant invention provide superior corrosion protection when used in an internal combustion engine.

[0119] In a further embodiment, the LEDL is produced by blending a mixture of the above components. The LEDL produced by that method might have a slightly different composition than the initial mixture, because the components may interact. The components can be blended in any order and can be blended as combinations of components.

EXAMPLES

[0120] The invention will be further illustrated by following examples, which set forth particularly advantageous method

embodiments. While the Examples are provided to illustrate the present invention, they are not intended to limit it.

EXAMPLE 1

PREPARATION OF THE UNSULFURIZED, CARBOXYLATE-CONTAINING HYDROXY-AROMATIC SURFACTANT-BASED DETERGENT-DISPERSANT ADDITIVE

[0121] An intermediate product was prepared according to the procedure given in US Patent 6,162,770, Example 1. Said procedure is reproduced here:

A. Neutralization

[0122] A charge of 875 g of branched dodecylphenol (DDP) having a molecular mass of 270, (i.e. 3.24 moles) and 875 g of linear alkylphenol having a molecular mass of about 390 (i.e. 2.24 moles) was placed in a four-necked 4 liter glass reactor above which was a heat-insulated Vigreux fractionating column. The isomeric molar repartition of para versus ortho alkylphenol was:

DDP: 89% para and 5.5% ortho

Linear alkylphenol: 39% para and 53% ortho.

[0123] The agitator was started up and the reaction mixture was heated to 65°C, at which temperature 158 grams of slaked lime $\text{Ca}(\text{OH})_2$ (i.e. 2.135 moles) and 19 g of a mixture (50/50 by weight) of formic acid and acetic acid were added.

[0124] The reaction medium underwent further heating to 120°C at which temperature the reactor was placed under a nitrogen atmosphere, then heated up to 165°C and then the nitrogen introduction was stopped. Distillation of water commenced at this temperature.

[0125] The temperature was increased to 240° C and the pressure was reduced gradually below atmospheric until an absolute pressure of 5,000 Pa (50 mbars) was obtained.

[0126] The reaction mixture was kept for five hours under the preceding conditions. The reaction mixture was allowed to cool to 180°C, then the vacuum was broken under a nitrogen atmosphere and a sample was taken for analysis.

[0127] The total quantity of distillate obtained was about 120 cm³ ; demixing took place in the lower phase (66 cm³ being water).

B. Carboxylation

[0128] The product obtained in Step (A) was transferred to a 3.6-liter autoclave and heated to 180°C.

[0129] At this temperature, scavenging of the reactor with carbon dioxide (CO₂) was commenced and continued for ten minutes. The amount of CO₂ used in this step was in the order of 20 grams.

[0130] After the temperature had been raised to 200° C, the autoclave was closed, leaving a very small leak, and the introduction of CO₂ was continued so as to maintain a pressure of 3.5×10^5 Pa (3.5 bars) for 5 hours at 200° C. The amount of CO₂ introduced was in the order of 50 grams. After the autoclave had been cooled to 165°C, the pressure was restored to atmospheric (1013 mbar) and the reactor was then purged with nitrogen.

[0131] A total quantity of 1,912 grams of product was recovered prior to filtration. The product was then filtered.

[0132] The above procedure was scaled up to a 6000 gallon (23,000 litre) reactor and used to prepare the intermediate product. The intermediate product was then subjected to the additional step of distillation outlined below.

[0133] Analytical results for the intermediate product from the 6000 gallon (23,000 litre) batch were as follows:

TBN	116 mg KOH/gm
Calcium	4.1 wt%
Salicylic Acid Index(SAI)	40 mg KOH/gm

[0134] SAI is a measure of the quantity of alkylsalicylate formed in the detergent-dispersant. It was determined by acidification of the product by a strong acid (hydrochloric acid) in the presence of diethyl ether, followed by a potentiometric titration on the organic fraction (tetra n-butyl ammonium hydroxide was used as a titration agent). Results are expressed in equivalent mg KOH per gram of product (Base Number unit).

C. Distillation:

[0135] The intermediate product was fed at a rate of 70 kg/hr to a wiped film evaporator (WFE) which had a surface area of 0.39 m². The WFE had an internal condenser and entrainment separator along with a hot oil jacket. The hot oil temperature in the jacket was about 250°C. The pressure within the WFE was 1.3 mbar. The feed temperature to the WFE was 135°C. Final product temperature exiting the WFE was 222°C. The product was cooled to less than 100°C before diluting with 100N base oil. Approximately 47.5 % (by weight) of the feed to the WFE was collected as distillate. The amount of distillate collected may vary from 10% up to about 55% by weight of the feed to the WFE. Depending upon the level of distillation, enough organic diluent is then added to the distilled product to give a manageable viscosity. As the weight percentage of feed collected as distillate increases, the amount of diluent needed to be added to the distilled product in order to give a manageable viscosity increases.

[0136] Analytical results for the distilled product were as follows:

TBN	174 mg KOH/gm
Ca	6.09 wt%
Salicylic Acid Index (SAI)	58
Viscosity at 100°C	705 cSt (705 mm ² /second)
Oil Content (by mass balance)	21.5 wt%

[0137] It is well known in the art that salicylate structures are thermally unstable. As the distilled material had a comparable Salicylic Acid Index to calcium ratio as the feedstock, no decomposition of the salicylate structure occurred even though the feed was exposed to relatively high temperatures. No decomposition occurred as the residence time in the WFE is relatively short. The distillate appearance was clear and slightly yellow which is comparable to the appearance of the starting hydrocarbyl phenols introduced in the neutralization step. The TBN content of the distillate was essentially zero indicating that none of the feedstock to the distillation step carried over into the distillate. The distillate was analyzed by gas chromatography and found to contain approximately 61% branched hydrocarbyl phenol, 39% linear hydrocarbyl phenol, and 6% 100N base oil.

EXAMPLE 2

[0138] The pre-distillation product prepared according to Example 1 was distilled under various conditions in the WFE described above. Typical results for other distillation conditions are shown in Table 1.

Table 1.

	1	2
WFE Conditions:		
Feed Rate (kg/hr)	122	86
Pressure (mbar)	1.44	1.5
Hot Oil Temp (°C)	235	254
Product Temperature Exiting Evaporator (°C)	205	222
Amount of Distillate (wt%) ¹	30	43
Oil in Final Product (wt%)	0	14.5
Product Analytical Results		
TBN (mg KOH/gm)	166	174
Ca (wt%)	5.92	6.2
SAI (mg KOH/gm)	57	59
Viscosity @ 100°C	226	575
(cSt) [mm ² /second]		
Composition of Distillate		
Branched Alkylphenol (wt%)	76	64
Linear Alkylphenol (wt%)	15	27

EP 1 479 752 B1

(continued)

	1	2
100N Base Oil (wt%)	9	9
¹ Based on WFE Feed Rate		

EXAMPLE 3

[0139] Example 1 was repeated except for the following changes:

- a) The WFE had a surface area of 0.78 m²
- b) The feed rate to the WFE was about 135 kg/hr
- c) The final distilled product was diluted with about 36 wt% 100N oil to produce a product with a manageable viscosity. Similar to Example 1, about 46 % (based on weight) of the feed to the evaporator was collected as distillate.

[0140] Analytical results for this product are as follows:

TBN	138 mg KOH/gm
Calcium	4.96 wt%
SAI	47 mg KOH/gm

[0141] Dialysis was performed on about 15 gm of product from Example 3 using a Soxhlet extraction apparatus (pentane solvent) and a Latex membrane condom for about 24 hours to afford a dialysate fraction (the material that passes through the membrane) and a residue fraction (the material left in the latex membrane bag).

[0142] The dialysate fraction from the dialysis procedure was separated into two fractions using silica gel chromatography (0.2 - 0.25 gm on two Silica Gel Cartridges - Waters Part No. 051900) first using 12 ml of hexane to yield Fraction 1 followed by reversing the Cartridges and flushing with 12 ml of 80:20 Ethyl Acetate: Ethanol to afford Fraction 2. Fraction 1 was comprised of diluent oil and Fraction 2 was comprised of free alkylphenols.

[0143] The Fraction 2 obtained from the chromatographic separation procedure was analyzed using supercritical chromatography (SFC) to determine the amount of branched alkylphenol and linear alkylphenol present. Quantification was performed using a calibration curve of known mixtures of branched and linear alkylphenol.

[0144] % SA was determined on the dialysis residue fraction by acidification of the product by a strong acid (hydrochloric acid) in the presence of diethyl ether, followed by a potentiometric titration on the organic fraction (tetra n-butyl ammonium hydroxide was used as a titration agent). This method separates and quantifies the alkyl salicylic acid and the remaining alkylphenol (non-carboxylated alkylphenate). Results were expressed in equivalent mg KOH per gram of product (Base Number unit). % SA was then determined by using the following equation:

$$\% \text{ SA} = 100 * (\text{Alkylsalicylic acid} / (\text{Alkylphenol} + \text{Alkylsalicylic acid}))$$

% Ca in the residue was determined by classical X Ray spectrometry.

[0145] Dialysis results are as follows:

Dialysate	51.1 wt % of starting sample weight
Residue	48.9 wt% of starting sample weight

[0146] Dialysate Composition:

Dodecylphenol	1.0 wt%
Linear Alkylphenol	26.7 wt%
100N Base Oil	72.3 wt%

[0147] Residue Composition:

EP 1 479 752 B1

Calcium	9.3 wt%
TBN	259 mg KOH/gm
SAI	78 mg KOH/gm
% SA	50

[0148] The following composition of the product produced in Example 3 was calculated from the composition of the dialysate and residue fractions:

Total Alkylphenol Content	14.1 wt%
Oil	36.9 wt%
Single Aromatic Ring Alkylsalicylate	24.5 wt%
Calcium Alkylphenate	24.5 wt%

PROCEDURES FOR PERFORMANCE TESTS

[0149] The following Section describes Performance Test Methods referred to in these examples.

Corrosion Control (ASTM D6594-01)

[0150] This is a standard test method for evaluation of corrosiveness of diesel engine oil at 135°C. This test method is used to test diesel engine lubricants to determine their tendency to corrode various metals, specifically alloys of lead and copper commonly used in cam followers and bearings. Four metal specimens of copper, lead, tin, and phosphor bronze are immersed in a measured amount of engine oil. The oil, at an elevated temperature, is blown with air for a period of time. When the test is completed, the copper specimen and the stressed oil are examined to detect corrosion and corrosion products, respectively.

EXAMPLES SHOWING PERFORMANCE ADVANTAGES

[0151] The following Examples illustrate performance advantages demonstrated by the LEDLs of the present invention.

EXAMPLE 4

AUTOMOTIVE PERFORMANCE

[0152] The lubrication oil formulations used in the present example were designed for Low Emission Diesel Lubricants (LEDL) intended for use in Low Emission Diesel Engines and had the following compositions:

Baseline Formulation	A	A	B	B	C	C
Sulfated Ash, %	0.95	0.95	1.0	1.0	1.0	1.0
Sulfur, %	0.10	0.10	0.12	0.12	0.10	0.10
Phosphorus, %	0.05	0.05	0.05	0.05	0.05	0.05
Borated Dispersant	Y	Y	Y	Y	Y	Y
Non-Borated Dispersant	Y	Y	Y	Y	Y	Y
LOB Ca-Sulfonate	N	N	Y	Y	N	N
LOB Salicylate	N	N	N	N	Y	Y
Commercially Available	4.5	N	4.5	N	4.5	N
Salicylate, wt% Unsulfurized Carboxylate-Containing additive prepared according to Example 1, wt%	N	5.0	N	5.0	N	5.0
Secondary ZnDTP	Y	Y	Y	Y	Y	Y
Diphenylamine Anti-Oxidant	Y	Y	Y	Y	Y	Y
Molybdenum Anti-Oxidant	Y	Y	Y	Y	Y	Y
Foam Inhibitor	Y	Y	Y	Y	Y	Y
Olefin Co-polymer Viscosity	Y	Y	Y	Y	Y	Y

EP 1 479 752 B1

(continued)

Baseline Formulation	A	A	B	B	C	C
Index Improver						
Base Oil 1	Y	Y	Y	Y	Y	Y
Base Oil 2	Y	Y	Y	Y	Y	Y
HTCBT*						
Pb, ppm	118	60	140	74	230	108
* High Temperature Corrosion Bench Test						

[0153] Three pairs of LEDL formulations, each pair with the same levels of ash, sulfur and phosphorus, were prepared. For each pair of formulations, an LEDL containing the unsulfurized, carboxylate-containing hydroxy-aromatic surfactant-based detergent-dispersant additive employed in the present invention was compared to an LEDL containing a commercially available salicylate for corrosion performance. In each case, the LEDL of the present invention containing the carboxylate-containing additive displayed superior corrosion control performance. Surprisingly, even at very low sulfur levels, acceptable performance was obtained.

EXAMPLE 5

AUTOMOTIVE PERFORMANCE

[0154] The lubrication oil formulations used in the present example were designed for Low Emission Diesel Lubricants (LEDL) intended for use in Low Emission Diesel Engines and had the following compositions:

Description	A	B	C	D	E
Sulfated Ash, %	0.54	0.86	0.47	0.68	0.90
Sulfur, %	0.18	0.18	0.12	0.12	0.12
Phosphorus, %	0.08	0.08	0.05	0.05	0.05
Borated Dispersant	Y	Y	Y	Y	Y
Non-Borated Dispersant	Y	Y	Y	Y	Y
Co-Detergent	Y	Y	Y	Y	Y
Unsulfurized Carboxylate-Containing additive prepared according to Example 1, wt%	2.0	3.9	1.9	3.2	4.4
Secondary ZnDTP, wt%	1.04	1.04	0.66	0.66	0.66
Diphenylamine Anti-Oxidant	Y	Y	Y	Y	Y
Phenolic Anti-Oxidant	Y	Y	Y	Y	Y
Molybdenum Anti-Oxidant	Y	Y	Y	Y	Y
Corrosion Inhibitor	Y	Y	Y	Y	Y
Foam Inhibitor	Y	Y	Y	Y	Y
OCP VII	Y	Y	Y	Y	Y
Base Oil 1	Y	Y	Y	Y	Y
Base Oil 2	Y	Y	Y	Y	Y
HTCBT*					
Pb, ppm	73	48	62	79	75
* High Temperature Corrosion Bench Test					

[0155] For each LEDL, covering a range of sulfur, phosphorus and ash levels, the LEDL displayed superior corrosion control performance. Said performance is not degraded by decreasing the wt. % ZnDTP. Even at very low sulfur levels, the LEDL of the present invention displayed superior corrosion control performance.

EXAMPLE 6**PREPERATION OF VERY LOW SULFUR LEDL**

5 **[0156]** 3.2 mmol of ZnDTP is combined with the following components:

from 1 wt. % to 4 wt. % borated dispersant;
 from 3 wt. % to 8 wt. % non-borated dispersant;
 from 4 to 8 mmol LOB Ca-Sulfonate;
 10 from 0 wt. % to 0.5 wt. % corrosion inhibitor;
 from 0.1 wt. % to 0.5 wt. % molybdenum anti-oxidant;
 from 0 wt. % to 1 wt. % phenolic anti-oxidant;
 from 0.1 wt. % to 1 wt. % aminic anti-oxidant;
 from 0 wt. % to 6 wt. % olefin-copolymer viscosity index improver;
 15 from 0 to 25 ppm foam inhibitor; and
 from 1.8 wt. % to 5.5 wt. % unsulfurized carboxylate-containing hydroxy-aromatic surfactant-based detergent-dispersant,
 to produce a LEDL containing 0.02 wt. % phosphorus and 0.06 wt. % sulfur.

20 **[0157]** While the present invention has been described with reference to specific embodiments, this application is intended to cover those various changes and substitutions that may be made by those skilled in the art without departing from the scope of the appended claims.

25 **Claims**

1. A low emission diesel lubricant composition comprising:

30 a major amount of a base oil of lubricating viscosity; from 1.8 wt. % to 5.5 wt. % of an unsulfurized, carboxylate-containing hydroxy-aromatic surfactant-based detergent-dispersant additive containing less than 40 wt. % free hydrocarbyl phenol;
 a dispersant; and
 a wear inhibitor,

35 wherein said unsulfurized, carboxylate-containing hydroxy-aromatic surfactant-based detergent-dispersant additive further comprises:

(a) from 10 to 50 wt. % alkaline earth metal hydrocarbyl phenate;
 (b) from 15 to 60 wt. % alkaline earth metal single-aromatic-ring hydrocarbyl salicylate wherein the term "alkaline
 40 earth metal single-aromatic-ring hydrocarbyl salicylate" means an alkaline earth metal salt of a hydrocarbyl salicylic acid, wherein there is only one hydrocarbyl salicylic anion per each alkaline earth metal base cation;
 (c) from 0 wt. % to 50 wt. % organic diluent; and
 (d) alkaline earth metal double-aromatic-ring hydrocarbyl salicylate wherein the term "alkaline earth metal double-aromatic-ring hydrocarbyl salicylate" means an alkaline earth metal salt of a hydrocarbyl salicylic acid,
 45 wherein there are two hydrocarbyl salicylic anions per each alkaline earth metal base cation;

wherein the mole ratio of single-aromatic-ring hydrocarbyl salicylate to double-aromatic-ring hydrocarbyl salicylate is at least 8:1; and

wherein said composition contains:

50 from 0 wt. % to 1.2 wt. % ash;
 from 0.1 wt. % to 0.5 wt. % sulfur; and
 from 0.02 wt. % to 0.1 wt. % phosphorus.

55 **2.** The low emission diesel lubricant composition of Claim 1 wherein said composition contains less than 1.0 wt. % ash;
 less than 0.3 wt. % sulfur; and
 less than 0.08 wt. % phosphorus.

3. The low emission diesel lubricant composition of Claim 1 wherein said composition contains
from 0.4 wt. % to 1.0 wt. % ash;
from 0.05 wt. % to 0.3 wt. % sulfur; and
from 0.02 wt. % to 0.08 wt. % phosphorus.

4. The low emission diesel lubricant composition of Claim 3 wherein said composition contains
from 0.4 wt. % to 1.0 wt. % ash;
from 0.05 wt. % to 0.15 wt. % sulfur; and
from 0.02 wt. % to 0.08 wt. % phosphorus.

5. The low emission diesel lubricant composition according to any one of claims 1 to 4, wherein said composition further comprises a corrosion inhibitor selected from a succinimide salt of one or more aromatic dicarboxylic acids and dispersed aromatic dicarboxylic acid corrosion inhibitors.

6. The low emission diesel lubricant composition of Claim 5 wherein:

said dispersant is a borated dispersant; and
said wear inhibitor is a metal dithiophosphate.

7. The low emission diesel lubricant composition of Claim 6 wherein said composition contains:

from 1.0 wt. % to 4.0 wt. % of said borated dispersant;
from 0.2 wt. % to 1.1 wt. % of said wear inhibitor; and
from 0 wt. % to 0.5 wt. % of said corrosion inhibitor.

8. The low emission diesel lubricant composition of Claim 7 wherein:

said dispersant is a succinimide;
said wear inhibitor is zinc dithiophosphate; and
said corrosion inhibitor is a neutralized terephthalic acid.

9. The low emission diesel lubricant composition of Claim 8 further comprising:

from 3.0 wt. % to 8.0 wt. % non-borated dispersant;
from 0.6 wt. % to 1.4 wt. % calcium-sulfonate;
from 0.1 wt. % to 0.5 wt. % molybdenum anti-oxidant;
from 0 wt. % to 1.0 wt. % phenolic anti-oxidant;
from 0.1 wt. % to 1.0 wt. % aminic anti-oxidant;
from 0 wt. % to 6.0 wt. % dispersant olefin-copolymer; and
from 0 to 25 ppm foam inhibitor.

10. A low emission diesel lubricant composition according to claim 1, wherein the unsulfurized carboxylate-containing additive is prepared by a method comprising:

- (a) neutralization of hydrocarbyl phenols using an alkaline earth base in the presence of a promoter which comprises at least one carboxylic acid containing from one to four carbon atoms, to produce a hydrocarbyl phenate;
(b) carboxylation of the hydrocarbyl phenate obtained in step (a) using carbon dioxide under carboxylation conditions sufficient to convert at least 20 mole% of the starting hydrocarbyl phenols to hydrocarbyl salicylate; and
(c) separation of at least 10 wt. % of the starting hydrocarbyl phenols from the product produced in step (b) to produce said additive,

wherein said composition contains:

from 0 wt. % to 1.2 wt. % ash;
from 0.1 wt. % to 0.5 wt. % sulfur; and
from 0.02 wt. % to 0.1 wt. % phosphorus.

11. The low emission diesel lubricant composition of Claim 10 wherein said composition contains less than 1.0 wt. % ash; less than 0.3 wt. % sulfur; and less than 0.08 wt. % phosphorus.
12. The low emission diesel lubricant composition of Claim 10 wherein said composition contains from 0.4 wt. % to 1.0 wt. % ash; from 0.05 wt. % to 0.3 wt. % sulfur; and from 0.02 wt. % to 0.08 wt. % phosphorus.
13. The low emission diesel lubricant composition of Claim 12 wherein said composition contains from 0.4 wt. % to 1.0 wt. % ash; from 0.05 wt. % to 0.15 wt. % sulfur; and from 0.02 wt. % to 0.08 wt. % phosphorus.
14. The low emission diesel lubricant composition of any one of claims 10 to 13, wherein, in said separation step, at least 30 wt. % of the starting hydrocarbyl phenols is separated from the product produced in step (b) to produce said additive.
15. The low emission diesel lubricant composition of any one of claims 10 to 13, wherein, in said separation step, up to 55 wt% of the starting hydrocarbyl phenols is separated from the product produced in step (b) to produce said additive.
16. The low emission diesel lubricant composition of any one of claims 10 to 13, wherein, in said separation, step 45 wt. % to 50 wt. % of the starting hydrocarbyl phenols is separated from the product produced in step (b) to produce said additive.
17. The low emission diesel lubricant composition of any one of claims 10 to 13, wherein, in said separation step, said starting hydrocarbyl phenols are removed by distillation.
18. The low emission diesel lubricant composition of Claim 17, wherein, in said separation step, at least 30 wt. % of the starting hydrocarbyl phenols is separated from the product produced in step (b) to produce said additive.
19. The low emission diesel lubricant composition of Claim 17, wherein, in said separation step, up to 55 wt. % of the starting hydrocarbyl phenols is separated from the product produced in step (b) to produce said additive.
20. The low emission diesel lubricant composition of Claim 17, wherein, in said separation step, 45 wt. % to 50 wt. % of the starting hydrocarbyl phenols is separated from the product produced in step (b) to produce said additive.
21. The low emission diesel lubricant composition of Claim 17, wherein said distillation is accomplished via falling film distillation, wiped film evaporator distillation, or short path distillation.
22. The low emission diesel lubricant composition of Claim 21, wherein said distillation is carried out at temperatures ranging from 150°C to 250°C and at pressures from 0.1 to 4 mbar.
23. The low emission diesel lubricant composition of Claim 21, wherein said distillation is carried out at temperatures ranging from 190°C to 230°C and at pressures from 0.5 to 3 mbar.
24. The low emission diesel lubricant composition of Claim 21, wherein said distillation is carried out at temperatures ranging from 195°C to 225°C, and at a pressure of 1 to 2 mbar.
25. The low emission diesel lubricant composition of any one of claims 10 to 13, wherein said unsulfurized, carboxylate-containing hydroxy-aromatic surfactant-based detergent-dispersant additive comprises from 10 to 50 wt. % organic diluent.
26. The low emission diesel lubricant composition of claim 25, wherein said unsulfurized, carboxylate-containing hydroxy-aromatic surfactant-based detergent-dispersant additive comprises from 20 to 50 wt. % organic diluent

27. The low emission diesel lubricant composition of any one of claims 10 to 13, wherein, in said neutralization step:

- (a) said neutralization operation is carried out in the presence of at least one carboxylic acid containing from one to four carbon atoms, and in the absence of alkali base, dialcohol, and monoalcohol;
- (b) said neutralization operation is carried out at a temperature of at least 200°C;
- (c) the pressure is reduced gradually below atmospheric in order to remove the water of reaction, in the absence of any solvent that may form an azeotrope with water;
- (d) said hydrocarbyl phenols contain up to 85 wt. % of linear hydrocarbyl phenol in mixture with at least 15 wt. % of branched hydrocarbyl phenol in which the branched hydrocarbyl radical contains at least nine carbon atoms; and
- (e) the quantities of reagents used correspond to the following molar ratios:

- (1) alkaline earth base/hydrocarbyl phenol of 0.2:1 to 0.7:1; and
- (2) carboxylic acid/hydrocarbyl phenol of from 0.01:1 to 0.5:1.

28. The low emission diesel lubricant composition of any one of claims 10 to 13 wherein said composition further comprises a corrosion inhibitor selected from a succinimide salt of one or more aromatic dicarboxylic acids and dispersed aromatic dicarboxylic acid corrosion inhibitors.

29. Use of an unsulfurized, carboxylate-containing hydroxy-aromatic surfactant-based detergent-dispersant additive as defined in claim 1 in a low emission diesel lubricant composition for reducing corrosion, wherein said low emission diesel lubricant composition comprises:

- a major amount of a base oil of lubricating viscosity;
- a dispersant; and
- a wear inhibitor; and

wherein said lubricant composition contains:

- from 0 wt. % to 1.2 wt. % ash;
- from 0.1 wt. % to 0.5 wt. % sulfur; and
- from 0.02 wt. % to 0.1 wt. % phosphorus.

Patentansprüche

1. Schmiermittelzusammensetzung für emissionsarme Dieselmotoren, umfassend

- eine größere Menge Basisöl mit Schmierviskosität;
- von 1,8 Gew.-% bis 5,5 Gew.-% eines nicht sulfurierten, carboxylathaltigen Detergensdispersion-Zusatzmittels auf Basis eines hydroxy-aromatischen Tensids, mit weniger als 40 Gew.-% freiem Hydrocarbylphenol;
- ein Dispergiermittel; und
- einen Verschleißhemmer,

wobei das nicht sulfurierte, carboxylathaltige Detergensdispersion-Zusatzmittel auf Basis eines hydroxy-aromatischen Tensids zudem umfasst

- (a) von 10 bis 50 Gew.-% Alkalierdmetall-Hydrocarbylphenat;
- (b) von 15 bis 60 Gew.-% Alkalierdmetall-Hydrocarbylsalicylat mit einem einzelnen aromatischen Ring, wobei der Begriff "Alkalierdmetall-Hydrocarbylsalicylat mit einem einzelnen aromatischen Ring" ein Alkalierdmetallsalz einer Hydrocarbyl-Salicylsäure bedeutet, wobei nur ein Hydrocarbyl-Salicyl-Anion pro Alkalierdmetall-Basenkation vorliegt;
- (c) von 0 Gew.-% bis 50 Gew.-% organisches Verdünnungsmittel; und
- (d) Alkalierdmetall-Hydrocarbylsalicylat mit doppeltem aromatischen Ring, wobei der Begriff "Alkalierdmetall-Hydrocarbylsalicylat mit doppeltem aromatischen Ring" ein Alkalierdmetallsalz einer Hydrocarbyl-Salicylsäure bedeutet, wobei zwei Hydrocarbyl-Salicyl-Anionen pro Alkalierdmetall-Basenkation vorliegen;

wobei das Molarverhältnis von Alkalierdmetall-Hydrocarbylsalicylat mit einem einzelnen aromatischen Ring zu Al-

kalierdmetall-Hydrocarbylsalicylat mit doppeltem aromatischen Ring mindestens 8:1 ist; und wobei die Zusammensetzung enthält:

von 0 Gew.-% bis 1,2 Gew.-% Asche;
von 0,1 Gew.-% bis 0,5 Gew.-% Schwefel; und
von 0,02 Gew.-% bis 0,1 Gew.-% Phosphor.

2. Schmiermittelzusammensetzung für emissionsarme Dieselmotoren gemäß Anspruch 1, wobei die Zusammensetzung enthält
weniger als 1,0 Gew.-% Asche;
weniger als 0,3 Gew.-% Schwefel; und
weniger als 0,08 Gew.-% Phosphor.
3. Schmiermittelzusammensetzung für emissionsarme Dieselmotoren gemäß Anspruch 1, wobei die Zusammensetzung enthält
von 0,4 Gew.-% bis 1,0 Gew.-% Asche;
von 0,05 Gew.-% bis 0,3 Gew.-% Schwefel; und
von 0,02 Gew.-% bis 0,08 Gew.-% Phosphor.
4. Schmiermittelzusammensetzung für emissionsarme Dieselmotoren gemäß Anspruch 3, wobei die Zusammensetzung enthält
von 0,4 Gew.-% bis 1,0 Gew.-% Asche;
von 0,05 Gew.-% bis 0,15 Gew.-% Schwefel; und
von 0,02 Gew.-% bis 0,08 Gew.-% Phosphor.
5. Schmiermittelzusammensetzung für emissionsarme Dieselmotoren gemäß irgendeinem der Ansprüche 1 bis 4, wobei die Zusammensetzung zudem umfasst einen Korrosionshemmer, ausgewählt aus dem Bernsteinsäureimid-salz von einer oder mehreren aromatischen Dicarboxylsäuren und dispergierten aromatischen Dicarboxylsäure-Korrosionshemmern.
6. Schmiermittelzusammensetzung für emissionsarme Dieselmotoren gemäß Anspruch 5, wobei das Dispergiermittel ein boriiertes Dispergiermittel ist; und der Verschleißhemmer ein Metaldithiophosphat ist.
7. Schmiermittelzusammensetzung für emissionsarme Dieselmotoren gemäß Anspruch 6, wobei die Zusammensetzung enthält
von 1,0 Gew.-% bis 4,0 Gew.-% des boriierten Dispergiermittels;
von 0,2 Gew.-% bis 1,1 Gew.-% des Verschleißhemmers; und
von 0 Gew.-% bis 0,5 Gew.-% des Korrosionshemmers.
8. Schmiermittelzusammensetzung für emissionsarme Dieselmotoren gemäß Anspruch 7, wobei das Dispergiermittel ein Bernsteinsäureimid ist;
der Verschleißhemmer Zinkdithiophosphat ist; und
der Korrosionshemmer eine neutralisierte Terephthalsäure ist.
9. Schmiermittelzusammensetzung für emissionsarme Dieselmotoren gemäß Anspruch 8, zudem umfassend
von 3,0 Gew.-% bis 8,0 Gew.-% nicht boriiertes Dispergiermittel;
von 0,6 Gew.-% bis 1,4 Gew.-% Calciumsulfonat;
von 0,1 Gew.-% bis 0,5 Gew.-% Molybdän-Antioxidans;
von 0 Gew.-% bis 1,0 Gew.-% phenolisches Antioxidans;
von 0,1 Gew.-% bis 1,0 Gew.-% aminisches Antioxidans;
von 0 Gew.-% bis 6,0 Gew.-% dispergierendes Olefin-Copolymer; und
von 0 bis 25 ppm Schaumverhütungsmittel.
10. Schmiermittelzusammensetzung für emissionsarme Dieselmotoren gemäß Anspruch 1, wobei das nicht sulfurierte carboxylathaltige Zusatzmittel hergestellt wird durch ein Verfahren, umfassend

(a) Neutralisation von Hydrocarbylphenolen mit einer Alkalierdbase in Anwesenheit eines Beschleunigers, wel-

cher umfasst mindestens eine Carboxylsäure mit einem bis vier Kohlenstoffatomen, zur Herstellung eines Hydrocarbylphenats;

(b) Carboxylierung des in Schritt (a) erhaltenen Hydrocarbylphenats mit Kohlendioxyd unter Carboxylierungsbedingungen, ausreichend zur Umsetzung von mindestens 20Mol% des anfänglichen Hydrocarbylphenols zu Hydrocarbylsalicylat; und

(c) Abtrennung von mindestens 10 Gew.-% des anfänglichen Hydrocarbylphenols vom in Schritt (b) hergestellten Produkt zur Herstellung des Zusatzmittels,

wobei die Zusammensetzung enthält:

von 0 Gew.-% bis 1,2 Gew.-% Asche;
von 0,1 Gew.-% bis 0,5 Gew.-% Schwefel; und
von 0,02 Gew.-% bis 0,1 Gew.-% Phosphor.

11. Schmiermittelzusammensetzung für emissionsarme Dieselmotoren gemäß Anspruch 10, wobei die Zusammensetzung enthält:

weniger als 1,0 Gew.-% Asche;
weniger als 0,3 Gew.-% Schwefel; und
weniger als 0,08 Gew.-% Phosphor.

12. Schmiermittelzusammensetzung für emissionsarme Dieselmotoren gemäß Anspruch 10, wobei die Zusammensetzung enthält

von 0,4 Gew.-% bis 1,0 Gew.-% Asche;
von 0,05 Gew.-% bis 0,3 Gew.-% Schwefel; und
von 0,02 Gew.-% bis 0,08 Gew.-% Phosphor.

13. Schmiermittelzusammensetzung für emissionsarme Dieselmotoren gemäß Anspruch 12, wobei die Zusammensetzung enthält

von 0,4 Gew.-% bis 1,0 Gew.-% Asche;
von 0,05 Gew.-% bis 0,15 Gew.-% Schwefel; und
von 0,02 Gew.-% bis 0,08 Gew.-% Phosphor.

14. Schmiermittelzusammensetzung für emissionsarme Dieselmotoren gemäß irgendeinem der Ansprüche 10 bis 13, wobei im Abtrennungsschritt mindestens 30 Gew. % der anfänglichen Hydrocarbylphenole vom in Schritt (b) hergestellten Produkt abgetrennt werden zur Herstellung des Zusatzmittels.

15. Schmiermittelzusammensetzung für emissionsarme Dieselmotoren gemäß irgendeinem der Ansprüche 10 bis 13, wobei im Abtrennungsschritt bis zu 55 Gew. % der anfänglichen Hydrocarbylphenole vom in Schritt (b) hergestellten Produkt abgetrennt werden zur Herstellung des Zusatzmittels.

16. Schmiermittelzusammensetzung für emissionsarme Dieselmotoren gemäß irgendeinem der Ansprüche 10 bis 13, wobei im Abtrennungsschritt 45 Gew. % bis 50 Gew.-% der anfänglichen Hydrocarbylphenole vom in Schritt (b) hergestellten Produkt abgetrennt werden zur Herstellung des Zusatzmittels.

17. Schmiermittelzusammensetzung für emissionsarme Dieselmotoren gemäß irgendeinem der Ansprüche 10 bis 13, wobei im Abtrennungsschritt die anfänglichen Hydrocarbylphenole durch Destillation entfernt werden.

18. Schmiermittelzusammensetzung für emissionsarme Dieselmotoren gemäß Anspruch 17, wobei im Abtrennungsschritt mindestens 30 Gew. % der anfänglichen Hydrocarbylphenole vom in Schritt (b) hergestellten Produkt abgetrennt werden zur Herstellung des Zusatzmittels.

19. Schmiermittelzusammensetzung für emissionsarme Dieselmotoren gemäß Anspruch 17, wobei im Abtrennungsschritt bis zu 55 Gew. % der anfänglichen Hydrocarbylphenole vom in Schritt (b) hergestellten Produkt abgetrennt werden zur Herstellung des Zusatzmittels.

20. Schmiermittelzusammensetzung für emissionsarme Dieselmotoren gemäß Anspruch 17, wobei im Abtrennungsschritt 45 Gew. % bis 50 Gew.-% der anfänglichen Hydrocarbylphenole vom in Schritt (b) hergestellten Produkt

abgetrennt werden zur Herstellung des Zusatzmittels.

21. Schmiermittelzusammensetzung für emissionsarme Dieselmotoren gemäß Anspruch 17, wobei die Destillation durchgeführt wird über eine Fallfilmdestillation, Abstreiffilm-Verdampferdestillation oder Kurzwegdestillation.

22. Schmiermittelzusammensetzung für emissionsarme Dieselmotoren gemäß Anspruch 21, wobei die Destillation durchgeführt wird bei Temperaturen im Bereich von 150°C bis 250°C und einem Druck von 0,1 bis 4 mbar.

23. Schmiermittelzusammensetzung für emissionsarme Dieselmotoren gemäß Anspruch 21, wobei die Destillation durchgeführt wird bei Temperaturen im Bereich von 190°C bis 230°C und einem Druck von 0,5 bis 3 mbar.

24. Schmiermittelzusammensetzung für emissionsarme Dieselmotoren gemäß Anspruch 21, wobei die Destillation durchgeführt wird bei Temperaturen im Bereich von 195°C bis 225°C und einem Druck von 1 bis 2 mbar.

25. Schmiermittelzusammensetzung für emissionsarme Dieselmotoren gemäß irgendeinem der Ansprüche 10 bis 13, wobei das nicht sulfurierte, carboxylathaltige Detergensdispersion-Zusatzmittel auf Basis eines hydroxy-aromatischen Tensids von 10 bis 50 Gew.-% organisches Verdünnungsmittel umfasst.

26. Schmiermittelzusammensetzung für emissionsarme Dieselmotoren gemäß Anspruch 25, wobei das nicht sulfurierte, carboxylathaltige Detergensdispersion-Zusatzmittel auf Basis eines hydroxy-aromatischen Tensids von 20 bis 50 Gew.-% organisches Verdünnungsmittel umfasst.

27. Schmiermittelzusammensetzung für emissionsarme Dieselmotoren gemäß irgendeinem der Ansprüche 10 bis 13, wobei im Neutralisationsschritt

(a) die Neutralisation durchgeführt wird in Anwesenheit von mindestens einer Carboxylsäure mit einem bis vier Kohlenstoffatomen, und ein Abwesenheit von Alkalibase, Dialkohol und Monoalkohol;

(b) die Neutralisation bei einer Temperatur von mindestens 200°C durchgeführt wird;

(c) der Druck fortschreitend unter atmosphärischen Druck verringert wird, um Wasser aus der Reaktion zu entfernen, in Abwesenheit von Lösungsmitteln, die mit Wasser ein Azeotrop bilden können;

(d) die Hydrocarbylphenole bis zu 85 Gew.-% lineare Hydrocarbylphenole, vermischt mit mindestens 15 Gew.-% des verzweigten Hydrocarbylphenols, in welchem das verzweigte Hydrocarbylradikal mindestens neun Kohlenstoffatome enthält; und

(e) die Mengen der verwendeten Reagenzien den folgenden Molverhältnissen entsprechen:

(1) Alkalierbase/Hydrocarbylphenol von 0,2:1 bis 0,7:1; und

(2) Carboxylsäure/Hydrocarbylphenol von 0,01:1 bis 0,5:1.

28. Schmiermittelzusammensetzung für emissionsarme Dieselmotoren gemäß irgendeinem der Ansprüche 10 bis 13, wobei die Zusammensetzung zudem umfasst einen Korrosionshemmer, ausgewählt aus einem Bernsteinsäureimidsalz von einer oder mehreren aromatischen Dicarboxylsäuren und dispergierten aromatischen Dicarboxylsäure-Korrosionshemmern.

29. Verwendung eines sulfurierten, carboxylathaltigen Detergensdispersion-Zusatzmittels auf Basis eines hydroxy-aromatischen Tensids wie in Anspruch 1 definiert, in einer Schmiermittelzusammensetzung für emissionsarme Dieselmotoren zur Verringerung von Korrosion, wobei die Schmiermittelzusammensetzung für emissionsarme Dieselmotoren umfasst:

eine größere Menge Basisöl mit Schmierviskosität;

ein Dispergiermittel; und

einen Verschleißhemmer; und

wobei die Schmiermittelzusammensetzung enthält:

von 0 Gew.-% bis 1,2 Gew.-% Asche;

von 0,1 Gew.-% bis 0,5 Gew.-% Schwefel; und

von 0,02 Gew.-% bis 0,1 Gew.-% Phosphor.

Revendications

1. Composition de lubrifiant pour moteur diesel à faibles émissions, comprenant :

une quantité dominante d'une huile de base de viscosité propre à la lubrification ;
1,8 % en poids à 5,5 % en poids d'un additif détergent-dispersant à base d'agent tensioactif hydroxy-aromatique contenant un carboxylate, non sulfuré, contenant moins de 40 % en poids d'hydrocarbylphénol libre ;
un dispersant ; et
un additif anti-usure,
dans laquelle ledit additif détergent-dispersant à base d'agent tensio-actif hydroxy-aromatique contenant un carboxylate, non sulfuré, comprend en outre :

- (a) 10 à 50 % en poids d'un hydrocarbylphénate de métal alcalino-terreux ;
- (b) 15 à 60 % en poids d'un hydrocarbylsalicylate de métal alcalino-terreux, à noyau aromatique unique, l'expression "hydrocarbylsalicylate de métal alcalino-terreux à noyau aromatique unique" désignant un sel de métal alcalino-terreux d'un acide hydrocarbylsalicylique, dans lequel il existe un seul anion hydrocarbylsalicylique pour chaque cation de base de métal alcalino-terreux ;
- (c) 0 % en poids à 50 % en poids d'un diluant organique ; et
- (d) un hydrocarbylsalicylate de métal alcalino-terreux à deux noyaux aromatiques, l'expression "hydrocarbylsalicylate de métal alcalino-terreux à deux noyaux aromatiques" désignant un sel de métal alcalino-terreux d'un acide hydrocarbylsalicylique, dans lequel il existe deux anions hydrocarbylsalicyliques pour chaque cation de base de métal alcalino-terreux" ;

dans laquelle le rapport molaire de l'hydrocarbylsalicylate à noyau aromatique unique à l'hydrocarbylsalicylate à deux noyaux aromatiques est d'au moins 8:1 ; et
ladite composition contenant :

0 % en poids à 1,2 % en poids de cendre ;
0,1 % en poids à 0,5 % en poids de soufre ; et 0,02 % en poids à 0,1 % en poids de phosphore.

2. Composition de lubrifiant pour moteur diesel à faibles émissions suivant la revendication 1, ladite composition contenant :

moins de 1,0 % en poids de cendre ;
moins de 0,3 % en poids de soufre ; et
moins de 0,08 % en poids de phosphore.

3. Composition de lubrifiant pour moteur diesel à faibles émissions suivant la revendication 1, ladite composition contenant :

0,4 % en poids à 1,0 % en poids de cendre ;
0,05 % en poids à 0,3 % en poids de soufre ; et
0,02 % en poids à 0,08 % en poids de phosphore.

4. Composition de lubrifiant pour moteur diesel à faibles émissions suivant la revendication 3, ladite composition contenant :

0,4 % en poids à 1,0 % en poids de cendre ;
0,05 % en poids à 0,15 % en poids de soufre ; et
0,02 % en poids à 0,08 % en poids de phosphore.

5. Composition de lubrifiant pour moteur diesel à faibles émissions suivant l'une quelconque des revendications 1 à 4, ladite composition comprenant en outre un inhibiteur de corrosion choisi entre un sel succinimide d'un ou plusieurs acides dicarboxyliques aromatiques et des inhibiteurs de corrosion dispersés du type acide dicarboxylique aromatique.

6. Composition de lubrifiant pour moteur diesel à faibles émissions suivant la revendication 5, dans laquelle :

ledit dispersant est un dispersant boraté ; et
ledit inhibiteur anti-usure est un dithiophosphate métallique.

7. Composition de lubrifiant pour moteur diesel à faibles émissions suivant la revendication 6, ladite composition contenant :

1,0 % en poids à 4,0 % en poids dudit dispersant boraté ;
0,2 % en poids à 1,1 % en poids dudit additif anti-usure ; et
0 % en poids à 0,5 % en poids dudit inhibiteur de corrosion.

8. Composition de lubrifiant pour moteur diesel à faibles émissions suivant la revendication 7, dans laquelle :

ledit dispersant est un succinimide ;
ledit additif anti-usure est un dithiophosphate de zinc ; et
ledit inhibiteur de corrosion est un acide téréphthalique neutralisé.

9. Composition de lubrifiant pour moteur diesel à faibles émissions suivant la revendication 8, comprenant en outre :

3,0 % en poids à 8,0 % en poids de dispersant non-boraté ;
0,6 % en poids à 1,4 % en poids de sulfonate de calcium ;
0,1 % en poids à 0,5 % en poids d'un anti-oxydant renfermant du molybdène ;
0 % en poids à 1,0 % en poids d'un anti-oxydant phénolique ;
0,1 % en poids à 1,0 % en poids d'un anti-oxydant aminique ;
0 % en poids à 6,0 % en poids d'un copolymère oléfinique dispersant ; et
0 à 25 ppm d'un additif anti-mousse.

10. Composition de lubrifiant pour moteur diesel à faibles émissions suivant la revendication 1, dans laquelle l'additif contenant un carboxylate, non sulfuré, est préparé par un procédé comprenant :

(a) la neutralisation d'hydrocarbylphénols en utilisant une base renfermant un métal alcalino-terreux en présence d'un promoteur qui comprend au moins un acide carboxylique contenant un à quatre atomes de carbone, pour produire un hydrocarbylphénate ;
(b) la carboxylation de l'hydrocarbylphénate obtenu dans l'étape (a) en utilisant du dioxyde de carbone dans des conditions de carboxylation suffisantes pour convertir au moins 20 % en moles des hydrocarbylphénols de départ en hydrocarbylsalicylates ; et
(c) la séparation d'au moins 10 % en poids des hydrocarbylphénols de départ du produit formé dans l'étape (b) pour produire ledit additif,
ladite composition contenant :

0 % en poids à 1,2 % en poids de cendre ;
0,1 % en poids à 0,5 % en poids de soufre ; et 0,02 % en poids à 0,1 % en poids de phosphore.

11. Composition de lubrifiant pour moteur diesel à faibles émissions suivant la revendication 10, ladite composition contenant :

moins de 1,0 % en poids de cendre ;
moins de 0,3 % en poids de soufre ; et
moins de 0,08 % en poids de phosphore.

12. Composition de lubrifiant pour moteur diesel à faibles émissions suivant la revendication 10, ladite composition contenant :

0,4 % en poids à 1,0 % en poids de cendre ;
0,05 % en poids à 0,3 % en poids de soufre ; et
0,02 % en poids à 0,08 % en poids de phosphore.

13. Composition de lubrifiant pour moteur diesel à faibles émissions suivant la revendication 12, ladite composition contenant :

EP 1 479 752 B1

0,4 % en poids à 1,0 % en poids de cendre ;
0,05 % en poids à 0,15 % en poids de soufre ; et
0,02 % en poids à 0,08 % en poids de phosphore.

- 5 **14.** Composition de lubrifiant pour moteur diesel à faibles émissions suivant l'une quelconque des revendications 10 à 13, dans laquelle, dans ladite étape de séparation, une proportion d'au moins 30 % en poids des hydrocarbylphénols de départ est séparée du produit formé dans l'étape (b) pour produire ledit additif.
- 10 **15.** Composition de lubrifiant pour moteur diesel à faibles émissions suivant l'une quelconque des revendications 10 à 13, dans laquelle, dans ladite étape de séparation, une proportion allant jusqu'à 55 % en poids des hydrocarbylphénols de départ est séparée du produit formé dans l'étape (b) pour produire ledit additif.
- 15 **16.** Composition de lubrifiant pour moteur diesel à faibles émissions suivant l'une quelconque des revendications 10 à 13, dans laquelle, dans ladite étape de séparation, 45 % en poids à 50 % en poids des hydrocarbylphénols de départ sont séparés du produit formé dans l'étape (b) pour produire ledit additif.
- 20 **17.** Composition de lubrifiant pour moteur diesel à faibles émissions suivant l'une quelconque des revendications 10 à 13, dans laquelle, dans ladite étape de séparation, lesdits hydrocarbylphénols de départ sont éliminés par distillation.
- 25 **18.** Composition de lubrifiant pour moteur diesel à faibles émissions suivant la revendication 17, dans laquelle, dans ladite étape de séparation, une proportion d'au moins 30 % en poids des hydrocarbylphénols de départ est séparée du produit formé dans l'étape (b) pour produire ledit additif.
- 30 **19.** Composition de lubrifiant pour moteur diesel à faibles émissions suivant la revendication 17, dans laquelle, dans ladite étape de séparation, une proportion allant jusqu'à 55 % en poids des hydrocarbylphénols de départ est séparée du produit formé dans l'étape (b) pour produire ledit additif.
- 35 **20.** Composition de lubrifiant pour moteur diesel à faibles émissions suivant la revendication 17, dans laquelle, dans ladite étape de séparation, 45 % en poids à 50 % en poids des hydrocarbylphénols de départ sont séparés du produit formé dans l'étape (b) pour produire ledit additif.
- 40 **21.** Composition de lubrifiant pour moteur diesel à faibles émissions suivant la revendication 17, dans laquelle ladite distillation est effectuée par distillation à film ruisselant, distillation à évaporateurs à film balayé ou distillation à court trajet.
- 45 **22.** Composition de lubrifiant pour moteur diesel à faibles émissions suivant la revendication 21, dans laquelle ladite distillation est effectuée à des températures comprises dans l'intervalle de 150°C à 250°C et à des pressions de 0,1 à 4 mbar.
- 50 **23.** Composition de lubrifiant pour moteur diesel à faibles émissions suivant la revendication 21, dans laquelle ladite distillation est effectuée à des températures comprises dans l'intervalle de 190°C à 230°C et à des pressions de 0,5 à 3 mbar.
- 55 **24.** Composition de lubrifiant pour moteur diesel à faibles émissions suivant la revendication 21, dans laquelle ladite distillation est effectuée à des températures comprises dans l'intervalle de 195°C à 225°C et à une pression de 1 à 2 mbar.
- 25.** Composition de lubrifiant pour moteur diesel à faibles émissions suivant l'une quelconque des revendications 10 à 13, dans laquelle ledit additif détergent-dispersant à base d'agent tensio-actif hydroxy-aromatique contenant un carboxylate, non sulfuré, comprend 10 à 50 % en poids de diluant organique.
- 26.** Composition de lubrifiant pour moteur diesel à faibles émissions suivant la revendication 25, dans laquelle ledit additif détergent-dispersant à base d'agent tensio-actif hydroxy-aromatique contenant un carboxylate, non sulfuré, comprend 20 à 50 % en poids de diluant organique.
- 27.** Composition de lubrifiant pour moteur diesel à faibles émissions suivant l'une quelconque des revendications 10 à 13, dans laquelle, dans ladite étape de neutralisation :

- (a) ladite opération de neutralisation est effectuée en présence d'au moins un acide carboxylique contenant un à quatre atomes de carbone, et en l'absence de bases renfermant un métal alcalin, de dialcool et de monoalcool ;
 (b) ladite opération de neutralisation est effectuée à une température d'au moins 200°C ;
 (c) la pression est abaissée progressivement au-dessous de la pression atmosphérique afin d'éliminer l'eau de réaction, en l'absence de tout solvant qui peut former un azéotrope avec l'eau ;
 (d) lesdits hydrocarbylphénols contiennent jusqu'à 85 % en poids d'hydrocarbylphénol linéaire en mélange avec au moins 15 % en poids d'hydrocarbylphénol ramifié dans lequel le radical hydrocarbyle ramifié contient au moins neuf atomes de carbone ; et
 (e) les quantités de réactifs utilisées correspondent aux rapports molaires suivantes :

- (1) base renfermant un métal alcalino-terreux/hydrocarbylphénol de 0,2:1 à 0,7:1 ; et
 (2) acide carboxylique/hydrocarbylphénol de 0,01:1 à 0,5:1.

28. Composition de lubrifiant pour moteur diesel à faibles émissions suivant l'une quelconque des revendications 10 à 13, ladite composition comprenant en outre un inhibiteur de corrosion choisi entre un sel succinimide d'un ou plusieurs acides dicarboxyliques aromatiques et des inhibiteurs de corrosion dispersés du type acide dicarboxylique aromatique.

29. Utilisation d'un additif détergent-dispersant à base d'agent tensio-actif hydroxy-aromatique, contenant un carboxylate, non-sulfuré, tel que défini dans la revendication 1, dans une composition de lubrifiant pour moteur diesel à faibles émissions pour la réduction de la corrosion, dans laquelle ladite composition de lubrifiant pour moteur diesel à faibles émissions comprend :

une quantité dominante d'une huile de base de viscosité propre à la lubrification ;
 un dispersant ; et
 un additif anti-usure ; et
 dans laquelle ladite composition de lubrifiant contient :

0 % en poids à 1,2 % en poids de cendre ;
 0,1 % en poids à 0,5 % en poids de soufre ; et
 0,02 % en poids à 0,1 % en poids de phosphore.

REFERENCES CITED IN THE DESCRIPTION

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