(19) **Europäisches Patentamt**
European Patent Office
Office européen des brevets

(11) **EP 1 138 753 A2**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
04.10.2001 Bulletin 2001/40

(21) Application number: **01302619.0**

(22) Date of filing: **21.03.2001**

(51) Int Cl.^{7}: **C10M 163/00**
// (C10M163/00, 129:54, 133:56, 135:18, 137:10, 159:16, 159:20, 159:22, 159:24), C10N10:12, C10N40:26

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE TR
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **31.03.2000 US 540670**

(71) Applicant: **Chevron Oronite Company LLC**
San Ramon, CA 94583-4289 (US)

(72) Inventors:
- **Timar, Joseph, Jr.**
  El Cerrito, California 94530 (US)
- **Shrout, Michael A.**
  Oakley, California 94561 (US)

(74) Representative: **Nash, David Allan et al**
Haseltine Lake & Co.,
Imperial House, 15-19 Kingsway
London WC2B 6UD (GB)

(54) Lubricant composition for air-cooled two-stroke cycle engines

(57) A lubricating oil composition used in air-cooled two-stroke cycle engines having a Mannich detergent and an ashless dispersant, wherein the ratio of the Mannich detergent to ashless dispersant is from 3:1 to 5:1. The detergency additive may also contain at least one of the following compounds: molybdenum, an overbased alkyl oxy benzene sulfonate and an alkylsalicylate. The detergency additive of the present invention provides improved detergency when used in a lubricating oil composition for air-cooled two-stroke cycle engines.

Printed by Jouve, 75001 PARIS (FR)

Description

[0001] The present invention relates to a detergency additive useful in a lubricating oil composition suitable for use in air-cooled two-stroke cycle engines and to lubricating oil compositions containing the detergency additive of the present invention. In another aspect, the present invention relates to a method of improving the detergency in an air-cooled two-stroke cycle engine by lubricating the engine with the lubricating oil composition of the present invention. In still a further aspect, the present invention relates to concentrates of the detergency additive. The detergency additive of the present invention has excellent detergency properties.

BACKGROUND OF THE INVENTION

[0002] Over the past several decades the use of spark ignited two-stroke internal combustion engines has steadily increased. They are presently found in power lawn mowers and other power operated garden equipment, power chain saws, pumps, electrical generators, marine outboard engines, snowmobiles, motorcycles and the like.

[0003] The unique problems and techniques associated with the lubrication of two-stroke cycle engines has led to the recognition by those skilled in the art of two-stroke cycle engine lubricants as a distinct lubricant type. See, for example, U.S. Patents 3,085,975; 3,004,837; and 3,753,905.

[0004] U.S. 4,025,316 to Stover, issued May 24, 1977, discloses polymeric alkyl-hydroxy benzyl N-substituted amines having a high degree of ring formation are derived from the condensation reaction of C_8 -C_{40} aliphatic alkyl substituted hydroxy aromatic, an aldehyde and an amine, wherein the molar ratio of said aromatic to said amine is about 2 to 1, with said aldehyde being present in a molar amount in excess of said aromatic. These novel amines are useful as a detergent and/or antioxidant additive for liquid hydrocarbons, e.g., in lubricating oils for gasoline engines that have a two stroke cycle.

[0005] U.S. 4,088,586 to Wilgus et al., issued May 9, 1978, discloses a new Mannich base, prepared by condensing tetrapropenylphenol, formaldehyde and diethylenetriamine wherein the molar ratio of reactants is 1 mol tetrapropenylphenol to 0.5 to 0.85 mols formaldehyde to at least 0.3 mols of diethylenetriamine, and the calcium salt thereof are useful as dispersant additives for lubricating oils, particularly for use in marine cylinder lubricating oils.

[0006] U.S. 4,200,545 to Clason et al., issued April 29, 1980, discloses combinations of amino phenols, wherein said phenols contain a substantially saturated hydrocarbon substituent of at least 10 aliphatic carbon atoms, and one or more detergent/dispersants selected from the group consisting of (I) neutral or basic metal salts of an organic sulfur acid, phenol or carboxylic acid; (II) hydrocarbyl-substituted amines wherein the hydrocarbyl substituent is substantially aliphatic and contains at least 12 carbon atoms; (III) acylated nitrogen-containing compounds having a substituent of at least 10 aliphatic carbon atoms; and (IV) nitrogen-containing condensates of a phenol, aldehyde and amino compound. Fuels and lubricants containing such combinations as additives are particularly useful in two-cycle (two-stroke) engines.

[0007] U.S. Patent 4,663,063 to Davis, issued May 5, 1987, discloses a functional fluid for a two-cycle engine having base oil and a combination of an alkylated phenol and a polyalkylene polyamine. That patent discloses that metal thiocarbamates are useful as extreme pressure agents.

[0008] U.S. 4,740,321 to Davis et al., issued April 26, 1988, discloses lubricating oils which are useful in two-cycle engines. These oils contain a minor amount of at least one phenolic compound of the general formula: $(R)_a$-AR-$(OH)_b$, or salts thereof, wherein R is a substantially saturated, hydrocarbon-based group of an average of at least 10 aliphatic carbon atoms; a and b are each independently an integer of one up to three times the number of aromatic nuclei present in Ar with the proviso that the sum of a and b does not exceed the unsatisfied valences of Ar; and Ar is a linked polynuclear moiety wherein the bridging linkages are sulfur-containing moieties, having 0 to 3 optional substituents consisting of lower alkyl, lower alkoxyl, methylol or lower hydrocarbon-based substituted methylol, halo and combinations of two or more of said optional substituents.

[0009] WO 91/13950 to Saitor et al., published September 19, 1991, discloses lubricating oils which are utilized in two-stroke engines sometimes produce clogging (gelation) in fuel filters. The gelling is particularly pronounced when an alkali metal or alkaline earth metal containing composition is present in the lubricating oil or the fuel. The present invention deals with this particular problem by introducing a hydrocarbon-soluble or dispersible polycarboxylic acid to the fuel and oil mixture.

[0010] WO 92/21736 to Chamberlin, published December 10, 1992, discloses a lubricant composition for two-cycle engines comprising: a major amount of at least one oil of lubricating viscosity which is free of oils having a viscosity greater than or equal to 100 cSt at 40° C, an amount sufficient to reduce or prevent piston scuffing of a mixture of (A) at least one phenol selected from (A-I) an aminophenol and (A-2) a reaction noduct of a nitrophenol and an amino compound, and (B) at least one ashless dispersant. The compositions may also include up to about 10 % by weight of (C) at least one polyalkene having a number average molecular weight from about 500 to about 2,500. Since lubricant compositions for two-cycle engines are often mixed with fuels before or during combustion. This reference also includes fuel-lubricant mixtures. The above compositions act to control piston scuffing while also contributing to piston lubrication, deposit control, ring stick protection, reduced exhaust port blockage and reduced visible smoke emission.

[0011] U.S. 5,281,346 to Adams et al., issued January 25, 1994, discloses lubricants for two-cycle engines comprising a major amount of at least one oil of lubricating viscosity and a minor amount of at least one metal carboxylate.

[0012] U.S. Patent 5,516,444 to Gaines et al., issued May 14, 1996, discloses a functional fluid for a two-cycle engine having base oil and an acylated nitrogen-containing compound having an oil soluble olefinic substituent and at least one ashless detergent/dispersant. That patent discloses that molybdenum- and molybdenum/sulfur-containing compounds are some of the anti-wear and lubricity agents useful in that invention.

[0013] U.S. Patent 5,688,751 to Cleveland et al., issued November 18, 1997, discloses alkali metal salicylate salts as lubricant additives for two-cycle engines.

SUMMARY OF THE INVENTION

[0014] The present invention provides a detergency additive especially useful in a lubricating oil composition useful in air-cooled two-stroke cycle engines.

[0015] In its broadest embodiment the present invention relates to detergency additive comprising a Mannich detergent and an ashless dispersant wherein the ratio of the Mannich detergent to ashless dispersant is from 3:1 to 5:1. In a further embodiment, the detergency additive may also contain at least one of the following compounds: a molybdenum compound, an overbased alkyl oxy benzene sulfonate, and an alkylsalicylate.

[0016] In another embodiment, the present invention relates to a lubricating oil composition comprising a major amount of at least one base oil of lubricating viscosity and an effective minor amount of a detergency additive of the present invention. Optionally, the lubricating oil composition may further comprise at least a solvent and/or a polyisobutylene.

[0017] The lubricating oil composition can be produced by blending together a major amount of the base oil of lubricating viscosity, an effective minor amount of detergency additive, and, optionally, minor amounts other additives, such as, solvent and polyisobutene. The lubricant composition can be used to improve the detergency of an air-cooled two-stroke cycle engine by supplying the lubricating oil composition to the engine crankcase and operating the engine or by supplying the lubricating oil composition to the fuel and operating the engine.

[0018] The present invention also provides an additive concentrate suitable for mixing with base oil to provide lubricating oils which may be used to lubricate air-cooled two-stroke cycle engines. This additive concentrate has from 5.0 to 15 wt % of an organic diluent and from 85 to 95 wt % of the detergency additive of the present invention.

[0019] Among other factors the present invention provides a low-ash detergency additive that demonstrates superior detergency including dispersancy and lubricity in air-cooled two-stroke cycle engine lubricating or compositions. The lubricating oil composition containing the detergency additive of the present invention keeps air-cooled two-stroke cycle engines clean by preventing ring sticking, piston deposits, plug fouling and exhaust deposits. Other benefits include wear and corrosion prevention.

DETAILED DESCRIPTION OF THE INVENTION

[0020] In its broadest aspect, the present invention involves a detergency additive having excellent detergency properties when used in a lubricating oil composition for air-cooled two-stroke cycle engines. The detergency additive comprises a Mannich detergent and an ashless dispersant wherein the ratio of the Mannich detergent to ashless dispersant is from 3:1 to 5:1. The detergency additive may further contain at least one of the following compounds: a molybdenum compound, an overbased alkyl oxy benzene sulfonate, and an alkylsalicylate.

[0021] Prior to discussing the invention in further detail, the following terms will be defined:

DEFINITIONS

[0022] As used herein the following terms have the following meanings unless expressly stated to the contrary:

[0023] The term "alkylphenol" means a phenol group having one or more alkyl substituents; at least one of which has a sufficient number of carbon atoms to impart oil solubility to the phenol.

[0024] The term "alkaline earth metal" means calcium, barium, magnesium, and strontium.

[0025] The term "alkaline earth alkylsalicylate" means an alkaline earth salt of an alkyl salicylic acid.

[0026] The term "internal olefins," means an olefin wherein the double bond is at the 4- position and higher positions of the alkene, instead of at the 1-, 2-, or 3-position.

[0027] The term "succinimide" is understood in the art to include many of the amide, imide, etc. species which are also formed by the reaction of a succinic anhydride with an amine. 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. Patent Nos. 2,992,708; 3,018,291; 3,024,237; 3,100,673; 3,219,666; 3,172,892; and 3,272,746, the disclosures of which are hereby incorporated by reference.

[0028] The term "polysuccinimide" means a compound that is formed by the reaction of an unsaturated acidic reagent copolymer and an alkene or alkyl succinic acid derivative with an amine.

[0029] The term "polyamine" means a polyamine containing 2 to amine nitrogen atoms and 2 to 40 carbon atoms and includes both acyclic and cyclic polyamines and may be substituted with a variety of substituents so long as the substitution does not significantly adversely affect the deposit control and fuel compatibility properties of the present compositions.

[0030] The term "polyalkylene polyamine" by definition contains at least two amine groups.

[0031] The term "Total Base Number" or "TBN" refers to the amount of base equivalent to milligrams of KOH in one gram of sample. Thus, higher TBN numbers reflect more alkaline products, and therefore a greater alkalinity reserve. The TBN of a sample can be determined by ASTM Test No. D664 or any other equivalent procedure.

[0032] Unless otherwise specified, all percentages are in weight percent and all molecular weights are number average molecular weights.

DETERGENCY ADDITIVE

[0033] The detergency additive of the present invention comprises a Mannich detergent and an ashless dispersant wherein the ratio of the Mannich detergent to ashless dispersant is from 3:1 to 5:1. The detergency additive may further contain at least one of the following compounds: molybdenum, an overbased alkyl oxy benzene sulfonate, and an alkylsalicylate.

Mannich Detergent

[0034] The Mannich base of the present invention may be prepared from a phenol or C_9 to C_{200} alkylphenol, an aldehyde, such as formaldehyde or formaldehyde precursor such as paraformaldehyde, and an amine compound. The amine may be a mono or polyamine and typical compositions are prepared from an alkylamine, such as methylamine or an ethylene amine, such as, diethylene triamine, or tetraethylene pentamine, and the like. The phenolic material may be sulfurized and preferably is dodecylphenol or a C_8 to C_{100} alkylphenol. Typical Mannich bases which can be used in this invention are disclosed in U.S. Patent Nos. 3,368,972; 3,539,663 3,649,229; 4,088,586; 4,157,308; 4,157,309; 4,178,759; and 4,219,430, the disclosures of which are hereby incorporated by reference.

[0035] For example, U.S. Patent 4,088,586 discloses preparing Mannich bases by condensing tetrapropenylphenol, formaldehyde and diethylene triamine wherein the molar ratio of reactants is 1 mol tetrapropenylphenol to 0.5 to 0.85 mols formaldehyde to at least 0.3 mols of diethylene triamine followed by alkaline earth metal salts of the Mannich bases of this invention are particularly useful as lubricating oil additives. Preferred alkaline earth metal salts are calcium and magnesium.

[0036] The alkaline earth metal salts of the Mannich bases are prepared using conventional methods, for example, by treating the Mannich base with an alkaline earth metal hydroxide, such as calcium hydroxide or magnesium methoxide in the presence of a promotor, such as water, ethylene glycol, 1,3-propane diol, 1,4-butane diol, diethylene glycol, butyl cellosolve, propylene glycol, 1,3-butylene glycol, methylcarbitol, diethanol amine, N-methyldiethanol amine, dimethyl formamide, N-methyl acetamide, or dimethyl acetamide. Preferred promotors are water, ethylene glycol and dimethyl acetamide. Most preferred is ethylene glycol. The reaction is carried out at 100°-175° C. After the reaction is completed, the product is stripped at a higher temperature, such as 175°-202° C and at reduced pressure, for example 20 mm Hg, to remove any unreacted low-molecular-weight polyamines, such as ethylene diamine and diethylene triamine, and other volatile components.

[0037] The Mannich bases and the alkaline earth metal salts thereof of this invention provide a high alkalinity value. The alkaline earth metal salts provide a particularly high alkalinity value at a lower ash content than is present in conventional dispersants and acid neutralizers used in lubricating oil additives.

[0038] The detergency additive may comprise from 5.0 to 30 wt % of the Mannich detergent, preferably 15 to 23 wt %, and most preferably 21 to 23 wt %.

Ashless Dispersant

[0039] The ashless dispersant in the present invention is a polyalkylene succinimide. Polyalkylene succinimides are disclosed in numerous references and are well known in the art. Certain fundamental types of succinimides and the related materials encompassed by the term of art "succinimide" are described in U.S. Pat. Nos. 3,219,666; 3,172,892;

and 3,272,746, the disclosures of which are hereby incorporated by reference. The term "succinimide" is understood in the art to include many of the amide, imide, and amidine species which may also be formed. The predominant product however is a 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 nitrogen-containing compound such as a polyalkylene polyamine. Typical polyalkylene polyamines are, for example, ethylene diamine, diethylene triamine, triethylene tetramine, and tetraethylene pentamine.

[0040] The polyalkylene succinimides of the present invention can be prepared by conventional processes, such as disclosed in U.S. Patent No. 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, the disclosures of which are all hereby incorporated by reference in their entirety for all purposes.

[0041] The polyalkylene succinimide additive is an ashless dispersant and can be prepared by reaction of a high molecular weight alkenyl- or alkyl-substituted succinic anhydride and a polyalkylene polyamine having an average of 4 to 10 nitrogen atoms (preferably 5 to 7 nitrogen atoms) per mole. The polyalkylene of the polyalkylene succinimide additive is derived from polyalkylenes having a molecular weight of at least 1,000. Preferably, the polyalkylene succinimide is a polybutene succinimide derived from polybutenes having a molecular weight of from 1,000 to 2,700, more preferably 1,900 to 2,700, and most preferably 2,000 to 2,400. A particularly preferred polyalkylene succinimide additive is derived from a polyalkylene having a molecular weight of 1,300.

[0042] The polyalkylene succinimide additive is prepared by reacting, under reactive conditions, a mixture of a polybutene succinic acid derivative, an unsaturated acidic reagent copolymer of an unsaturated acidic reagent and an olefin, and a polyamine, such as taught in U.S. Patent No. 5,716,912.

[0043] The detergency additive may comprise from 50 to 90 wt % of the ashless dispersant, preferably 73 to 81 wt %, and most preferably 75 to 79 wt %.

[0044] A wide variety of other ashless detergent/dispersants can also be used in the present invention. They are preferably oil-soluble. Typical of such compositions are carboxylic acid amides, hydrocarbyl monoamines, hydrocarbyl polyamines, ashless Mannich bases, succinic esters, phosphoramides, phosphonamides, dispersant viscosity index improvers, and mixtures thereof. These basic nitrogen-containing compounds are described below. Any of the nitrogen-containing compositions may be post-treated using procedures well known in the art so long as the compositions continue to contain basic nitrogen. Post-treatment may be accomplished by contacting the basic nitrogen-containing compound with the post-treating compound(s) concurrently or in any sequence. Suitable post-treating compounds include urea, thiourea, carbon disulfide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, nitriles, epoxides, boron compounds, organic phosphorus compounds, inorganic phosphorus compounds (such as H_3PO_3, H_3PO_4, etc.) or the like, and mixtures thereof. These post-treatments are particularly applicable to succinimides and Mannich base compositions.

Molybdenum Compound

[0045] Suitable molybdenum compounds that can be used in the invention include, for example, molybdenum dithiophosphate (MoDTP) and molybdenum dithiocarbamate (MoDTC). This MoDTP includes molybdenum dialkyl (or diaryl) dithiophosphate such as molybdenum diisopropyldithiophosphate, molybdenum di-(2-ethylhexyl) dithiophosphate and molybdenum di-(nonylphenyl) dithiophosphate. MoDTC includes molybdenum dialkyldithiocarbamate such as molybdenum dibutyldithiocarbamate, molybdenum di-(2-ethylhexyl) dithiocarbamate and molybdenum dilauryldithiocarbamate. Other molybdenum compounds include molybdenum oxydisulfides and Molyvan® 855 (a non-sulfur, non-phosphorus molybdenum compound sold by the R.T. Vanderbilt Company). Particularly preferred molybdenum compounds are molybdenum oxydisulfides.

[0046] The amount of sulfur-containing molybdenum compounds (such as molybdenum dithiophosphates, molybdenum dithiocarbamates, molybdenum oxydisulfides) should be kept low so that the sulfur in the lubricating oil composition will be less than 0.2%.

[0047] The detergency additive may comprise from 0.5 to 10 wt % of the molybdenum compound, preferably 2.0 to 6.0 wt %, and most preferably 3.0 to 5.0 wt %.

The Overbased Alkyl Oxy Benzene Sulfonate

[0048] The lubricating oil has a minor amount of an overbased, alkyl oxy benzene sulfonate having a TBN of at least 200, preferably at least 250, wherein at least 40 wt % of the alkyl group of the sulfonate is attached at the 4- position and higher positions of the alkyl group. The oxy group can be either hydroxy, methoxy, ethoxy, propoxy, butoxy, pentoxy, or hexoxy. Preferably, it is hydroxy.

[0049] Preferably, the alkyl group of the overbased, alkyl oxy benzene sulfonate has from eighteen to thirty.carbon atoms per alkyl group. More preferably, the alkyl group has from twenty to twenty-four carbon atoms per alkyl group.

[0050] The additive of the present invention can be produced by alkylating an oxy benzene with an olefin containing between 40 wt % and 80 wt % internal olefins to produce an alkyl oxy benzene, sulfonating the alkyl oxy benzene to produce an alkyl oxy benzene sulfonic acid; and overbasing the alkyl oxy benzene sulfonic acid to produce the overbased, alkyl oxy benzene sulfonate. An olefin containing between 40 wt % and 80 wt % internal olefins can be formed by isomerizing an alpha olefin using an iron pentacarbonyl catalyst.

[0051] The processes of alkylating an alkyl oxy benzene with an olefin to produce an alkyl oxy benzene, and sulfonating the alkyl oxy benzene to produce an alkyl oxy benzene sulfonic acid are both discussed in detail in U.S. Patent Nos. 5,330,663 and 5,330,664, which have been incorporated by reference for all purposes. Our alkylation and sulfonation processes differ only in the olefins used and reaction time. In our batch alkylation reaction, we need only about six to eight hours. The preferred sulfonation process is a falling film process using a charge mole ratio of sulfur trioxide to alkylphenol of 1.1:1 and a reaction temperature in the range of from 70° to 100° C, followed by immediate neutralization.

[0052] A neutralized slurry of alkyl oxy benzene sulfonic acid is added to a slurry of xylenes, methanol, and calcium hydroxide. The resulting slurry is then carbonated during which a second slurry of alkyl oxy benzene sulfonic acid and a second slurry of xylenes, methanol, and calcium hydroxide are added. After the carbonation, the material is stripped to remove methanol and water. Lube oil is then added and the solids removed. The remainder of the solvents are then stripped off and additional lube oil added to adjust the product to the final base number.

[0053] The detergency additive may comprise from 1.0 to 10 wt % of the overbased alkyl oxy benzene sulfonate, preferably 2.0 to 5.0 wt %, and most preferably 3.0 to 4.0 wt %.

Alkylsalicylate

[0054] The detergency additive of the present invention may further contain an alkyl salicylate. Alkylsalicylates are a class of lubricating oil detergents known to impart improved performance (detergency, water tolerance, thermal stability, antioxidancy) to lubricating oil compositions used for lubrication of internal combustion engines. This class of detergents are well known in the art and their description may be found for example in U.S. Patent 2,197,832; 5,808,145; 5,434,293; and 5,415,792, which are herein incorporated by reference all that they disclose.

[0055] Sulfurized and unsulfurized alkaline earth alkylsalicylate are well known. Such alkylsalicylates are usually double aromatic-ring alkylsalicylates, but single aromatic-ring alkylsalicylates are also known. Preferably, the unsulfurized alkaline earth alkylsalicylate is calcium alkylsalicylate.

a) Preferred Process for Producing Unsulfurized Alkaline Earth Alkylsalicylates

[0056] One preferred process for producing unsulfurized alkaline earth alkylsalicylates can be characterize by its unique composition, with much more alkylphenol and alkaline earth single aromatic-ring alkylsalicylate than produced by other routes. That reaction product has the following composition:

(a) from 40 to 60 wt % alkylphenol,
(b) from 10 to 40 wt % alkaline earth alkylphenate, and
(c) from 20 to 40 wt % alkaline earth single aromatic-ring alkylsalicylate.

[0057] Unlike other processes for producing alkaline earth alkylsalicylates, this reaction product can be characterized by having only minor amounts of an alkaline earth double aromatic-ring alkylsalicylates. The mole ratio of single aromatic-ring alkylsalicylate to double aromatic-ring alkylsalicylate is at least 8:1.

b) Neutralization Step

[0058] In the first step, alkylphenols are neutralized using an alkaline earth base in the presence of at least one C_1 to C_4 carboxylic acid. This reaction is carried out in the absence of alkali base, and in the absence of dialcohol or monoalcohol.

[0059] The alkylphenols contain up to 85 wt % of linear alkylphenol (preferably at least 35 wt % linear alkylphenol) in mixture with at least 15 wt % of branched alkylphenol. Preferably, the linear alkyl radical contains 12 to 40 carbon atoms, more preferably 18 to 30 carbon atoms. The branched alkyl radical contains at least nine carbon atoms, preferably 9 to 24 carbon atoms, more preferably 10 to 15 carbon atoms.

[0060] The use of an alkylphenol containing at least 35 wt % of long 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 makes the latter less reactive than branched alkylphenols, hence the need to use harsher reaction conditions to bring about their neutralization by an alkaline earth base.

[0061] 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 reactive towards an alkaline earth base, since the phenol function is practically devoid of steric hindrance.

[0062] 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 much more uniformly distributed. This makes them much less reactive towards an alkaline earth base since the phenol function is much less accessible due to considerable steric hindrance, due to the presence of closer and generally heavier alkyl substituents.

[0063] The alkaline earth 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.

[0064] The C_1 to C_4 carboxylic acids used in this step include 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 bases from a mineral reagent to an organic reagent.

[0065] 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).

[0066] The quantities of reagents used should correspond to the following molar ratios:

(1) alkaline earth base/alkylphenol of 0.2:1 to 0.7:1, preferably 0.3:1 to 0.5:1; and

(2) carboxylic acid/alkylphenol of 0.01:1 to 0.5:1, preferably from 0.03:1 to 0.15:1.

[0067] Preferably, at the end of this neutralization step the alkylphenate 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 alkylphenate 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).

[0068] 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.

c) Carboxylation Step

[0069] 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 alkylphenate to alkylsalicylate (measured as salicylic acid by potentiometric determination). It must take place under pressure in order to avoid any decarboxylation of the alkylsalicylate that forms.

[0070] Preferably, at least 22 mole% of the starting alkylphenols is converted to alkylsalicylate using carbon dioxide at a temperature of between 180° and 240°C, under a pressure within the range of from above atmospheric pressure to 15 x 105 Pa (15 bars) for a period of one to eight hours.

[0071] According to one variant, 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 x 105 Pa (4 bars).

d) Filtration Step

[0072] 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.

[0073] The detergency additive may comprise from 1.0 to 15 wt % of the alkylsalicylate, preferably 4.0 to 10 wt %, and most preferably 6.0 to 8.0 wt %.

Solvent

[0074] The lubricating oil compositions of the present invention may optionally contain a minor amount of a suitable solvent. The solvent is used just to adjust the viscosity of the finished oil. Suitable solvents include aromatic and dearomatized aliphatic distillate in the 190°-290° C range.

Polyisobutylene

[0075] The lubricating oil compositions of the present invention may optionally contain a polyisobutylene having a molecular weight from 350 to 2,300, preferably about 950. This polyisobutylene may be present in an amount up to 35 wt %, preferably up to 30 wt %, more preferably 25 wt % base of the total weight of the lubricating oil composition. The polyisobutylene acts to improve lubricity and anti-scuff activity of the lubricant.

Other Additives

[0076] The following additive components are examples of some of the 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. Metal Detergents

   Sulfurized or unsulfurized alkyl or alkenyl phenates, alkyl or alkenyl aromatic sulfonates, sulfurized or unsulfurized metal salts of multi-hydroxy alkyl or alkenyl aromatic compounds, alkyl or alkenyl hydroxy aromatic sulfonates, sulfurized or unsulfurized alkyl or alkenyl naphthenates, metal salts of alkanoic acids, metal salts of an alkyl or alkenyl multiacid, and chemical and physical mixtures thereof.

2. Anti-Oxidants

   Anti-oxidants reduce the tendency of mineral oils to deteriorate in service which deterioration is evidenced by the products of oxidation such as sludge and varnish-like deposits on the metal surfaces and by an increase in viscosity. Examples of anti-oxidants useful in the present invention include, but are not limited to, phenol type (phenolic) oxidation inhibitors, such as 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'-butylidene-bis (3-methyl-6-tert-butylphepol), 4,4'-isopropylidene-bis(2,6-di-tert-butylphenol), 2,2'-methylene-bis(4-methyl-6-nonylphenol), 2,2'-isobutylidene-bis(4,6-dimethylphenol), 2,2'-methylene-bis(4-methyl-6-cyclohexylphenol), 2,6-di-tert-butyl-4-methylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,4-dimethyl-6-tert-butyl-phenol, 2,6-di-tert-1-dimethylamino-p-cresol, 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-butylbenzyl)-sulfide, and bis(3,5-di-tert-butyl-4-hydroxybenzyl). Diphenylamine-type oxidation inhibitors include, but are not limited to, alkylated diphenylamine, phenyl-.alpha.-naphthylamine, and alkylated.alpha.-naphthylamine. Other types of oxidation inhibitors include metal dithiocarbamate (e.g., zinc dithiocarbamate), and methylenebis(dibutyldithiocarbamate).

3. Anti-Wear Agents

   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.

4. Rust Inhibitors (Anti-Rust Agents)

   a) Nonionic polyoxyethylene surface active agents: polyoxyethylene lauryl ether, polyoxyethylene higher alcohol ether, polyoxyethylene nonyl phenyl ether, polyoxyethylene octyl phenyl ether, polyoxyethylene octyl stearyl ether, polyoxyethylene oleyl ether, polyoxyethylene sorbitol monostearate, polyoxyethylene sorbitol mono-oleate, and polyethylene glycol mono-oleate.

   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.

5. Demulsifiers

   Addition product of alkylphenol and ethylene oxide, polyoxyethylene alkyl ether, and polyoxyethylene sorbitan ester.

6. Extreme Pressure Agents (EP Agents)
   Zinc dialkyldithiophosphate (primary alkyl, secondary alkyl, and aryl type), sulfurized oils, diphenyl sulfide, methyl trichlorostearate, chlorinated naphthalene, fluoroalkylpolysiloxane, and lead naphthenate.

7. Friction Modifiers
   Fatty alcohol, fatty acid, amine, borated ester, and other esters.

8. Multifunctional Additives
   Sulfurized oxymolybdenum dithiocarbamate, sulfurized oxymolybdenum organo phosphorodithioate, oxymolybdenum monoglyceride, oxymolybdenum diethylate amide, amine-molybdenum complex compound, and sulfur-containing molybdenum complex compound.

9. Viscosity Index Improvers
   Polymethacrylate type polymers, ethylene-propylene copolymers, styrene-isoprene copolymers, hydrated styrene-isoprene copolymers, polyisobutylene, and dispersant type viscosity index improvers.

10. Pour Point Depressants
   Polymethyl methacrylate.

11. Foam Inhibitors
   Alkyl methacrylate polymers and dimethyl silicone polymers.

BASE OIL OF LUBRICATING VISCOSITY

[0077] The base oil of lubricating viscosity used in such compositions may be mineral oils or synthetic oils of viscosity suitable for use in the crankcase of an internal combustion engine. The base oils may be derived from synthetic or natural sources. Mineral oils for use as the base oil in this invention include, for example, paraffinic, naphthenic and other oils that are ordinarily used in lubricating oil compositions. Synthetic oils include, for example, both hydrocarbon synthetic oils and synthetic esters and mixtures thereof having desired viscosity. Useful synthetic hydrocarbon oils include liquid polymers of alpha olefins having the proper viscosity. Especially useful are the hydrogenated liquid oligomers of C_6 to C_{12} 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 mono-hydroxy alkanols and polyols. Typical examples are didodecyl adipate, pentaerythritol tetracaproate, 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. Blends of mineral oils with synthetic oils are also useful.

LUBRICATING OIL COMPOSITION

[0078] The detergency additive of the present invention is useful for imparting greater detergency to an engine lubricating oil composition. Such a lubricating oil composition comprises a major part of base oil of lubricating viscosity and an effective minor amount of the detergency additive.

[0079] In one embodiment, the lubricating oil composition would contain:

(a) a major amount of at least one base oil of lubricating viscosity;

(b) from 1.0 to 10 wt % of the detergency additive of the present invention; and

(c) optionally at least one of the following:

  (1) a minor amount of a solvent; and

  (2) a minor amount of a polyisobutylene.

[0080] The lubricating oil optionally may contain a solvent and/or polyisobutylene, the solvent may be in an amount of 10 to 20 wt %, preferably 15 to 20 wt %, and the polyisobutylene in an amount of 0 to 35 wt %, preferably 25 to 30 wt %.

[0081] The lubricating oil composition of the present invention is useful in a method of lubricating an air-cooled two-stroke cycle engine. In that method, the lubricant composition is supplied to the crankcase of the engine or to the fuel added to the engine, and the engine is operated.

[0082] In a further embodiment, an engine lubricating oil composition is produced by blending a mixture of the above components. The lubricating oil composition produced by that method might have a slightly different composition than the initial mixture, because the components may interact.

[0083] The components can be blended in any order and can be blended as combinations of components. For instance, the Mannich base and ashless dispersant can be blended together prior to being blended with the other components of the mixture, including optionally, a molybdenum compound, an overbased alkyl oxy benzene sulfonate, and an alkylsalicylate. Likewise, the solvent and polyisobutylene can be blended with detergency additive prior to being blended with the base oil.

ADDITIVE CONCENTRATES

[0084] Additive concentrates are also included within the scope of this invention. The concentrates of this invention comprise the compounds or compound mixtures of the present invention, preferably with at least one other additive, as disclosed above. The concentrates contain sufficient organic diluent to make them easy to handle during shipping and storage.

[0085] Preferably, the additive concentrate would comprise from 5.0 to 15% of an organic diluent and 85-95 wt % of the detergency additive of the present invention. Suitable organic diluents that can be used include mineral oil or synthetic oils, as described above in the section entitled "Base Oil of Lubricating Viscosity."

FUEL OILS

[0086] As is well known to those skilled in the art, two-cycle engine lubricating oils are often added directly to the fuel to form a mixture of oil and fuel which is then introduced into the engine cylinder. Such lubricant-fuel oil mixtures are within the scope of this invention. Such lubricant-fuel blends generally contain per 1 part of oil about 15-250 parts fuel, typically they contain 1 part oil to about 25-100 parts fuel.

[0087] In some two-cycle engines, the lubricating oil can be directly injected into the combustion chamber together with the fuel or separated into the fuel just prior to the fuel entering the combustion chamber. The two-cycle lubricants of this invention can be used in this type of engine.

[0088] The fuels used in two-cycle engines are well known to those skilled in the art and usually contain a major portion of a normally liquid fuel such as hydrocarbonaceous petroleum distillate fuel (e.g., motor gasoline as defined by ASTM Specification D-439-73). Such fuels can also contain non-hydrocarbonaceous materials such as alcohols, ethers, organo-nitro compounds and the like (e.g., methanol, ethanol, diethyl ether, methyl ethyl ether, nitromethane). Also within the scope of this invention are liquid fuels derived from vegetable or mineral sources such as corn, alfalfa, shale and coal. Examples of such fuel mixtures are combinations of gasoline and ethanol, diesel fuels, diesel fuels and ether, gasoline and nitromethane, etc. Particularly preferred is gasoline, that is, a mixture of hydrocarbons having as ASTM boiling point of 60°C at the 10% distillation point to about 205°C at the 90% distillation point.

EXAMPLES

[0089] 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.

[0090] The detergency additive of the present invention was evaluated in accordance with the CEC L-79-T-97 test procedure; "3-Hour Detergency Test Procedure for Two-Stroke-Cycle Gasoline Engine Lubricant Evaluation." The procedure is under development by the 2T Engine Oil Subcommittee of Japan Automobile Standards Organization (JASO) and was conducted using the draft procedure released September 9, 1992 at the Seventh International Two-Stroke Oil Specification Meeting.

[0091] The procedure is designed to evaluate the performance of a two-stroke-cycle gasoline lubricant relative to engine cleanliness when tested in a single cylinder engine; Honda SK-50Mm air-cooled engine. Tests are conducted using unleaded gasoline mixed with lubricant to be evaluated at 100:1 fuel oil ratio. The following critical areas are inspected and rated in accordance with JPI-5S-34-91 rating manual:

- Piston Ring Sticking (top and second ring)
- Piston Land Deposits (top and second land)
- Piston Ring Groove Deposits (top and second groove)
- Piston Skirt Deposits
- Piston Undercrown Deposits
- Piston Crown Deposits

- Cylinder Head Deposits

[0092] The Total Actual Merit is calculated as the sum of the ratings referred to above. The higher the number, the better the performance.

[0093] Besides as specified in the examples below, all formulations contained a polyisobutene, mix of heavy and light neutral base oils, and solvent. Test results are presented in Table I.

Example 1

[0094] Formulation I contains 1.12 wt % Mannich detergent, 4.75 wt % ashless dispersant.

Example 2

[0095] Formulation II contains 1.12 wt % Mannich detergent, 3.85 wt % ashless dispersant.

Example 3

[0096] Formulation III contains 1.12 wt % Mannich detergent, 3.85 wt % ashless dispersant, and 0.25 wt % molybdenum compound.

Example 4

[0097] Formulation IV contains 0.80 wt % Mannich detergent, 3.85 wt % ashless dispersant and 0.38 wt % alkylsalicylate.

Example 5

[0098] Formulation V contains 0.80 wt % Mannich detergent, 3.85 wt % ashless dispersant, 0.25 wt % molybdenum compound and 0.38 wt % alkylsalicylate.

Example 6

[0099] Formulation VI contains 0.80 wt % Mannich detergent, 3.85 wt % ashless dispersant, 0.16 wt % overbased alkyl oxy benzenene sulfonate.

Example 7

[0100] Formulation VII contains 0.80 wt % Mannich detergent, 3.85 wt % ashless dispersant, 0.16 wt % overbased alkyl oxy benzene sulfonate and 0.19 wt % alkylsalicylate.

Example 8

[0101] Formulation VII contains 0.80 wt % Mannich detergent, 3.85 wt % ashless dispersant, 0.25 wt % molybdenum compound, 0.16 wt % overbased alkyl oxy benzene sulfonate, and 0.19 wt % alkylsalicylate.

Table I

Formulations, wt %

Components	I	II	III	IV	V	VI	VII	VIII
Mannich Detergent	1.12	1.12	1.12	0.80	0.80	0.80	0.80	0.80
Ashless Dispersant	4.75	3.85	3.85	3.85	3.85	3.85	3.85	3.85
Molybdenum Compound			0.25		0.25			0.25
Overbased Alkyl Oxy Benzene Sulfonate						0.16	0.16	0.16
Alkylsalicylate				0.38	0.38		0.19	0.19
Total Actual Merit	72.8	73.7	78.0	75.9	79.5	74.9	78.3	78.3

Claims

1. A detergency additive suitable for lubricating oil compositions used in air-cooled two-stroke cycle engines comprising:

    a) a Mannich detergent;

    b) an ashless dispersant;
    wherein the ratio of the Mannich detergent to ashless dispersant is from 3:1 to 5:1; and

    c) at least one of the following compounds:

        1) a molybdenum compound;
        2) an overbased alkyl oxy benzene sulfonate; and
        3) an alkylsalicylate.

2. A detergency additive according to Claim 1, wherein said Mannich detergent is a condensation product of tetrapropenylphenol, formaldehyde, and diethylene triamine.

3. A detergency additive according to Claim 2, wherein said Mannich detergent is a calcium salt of said condensation product.

4. A detergency additive according to Claim 1, wherein said ashless dispersant is a polyalkylene succinimide derived from a reaction product of an alkenyl- or alkyl-substituted succinic acid or anhydride and a polyalkylene polyamine.

5. A detergency additive according to Claim 1, wherein said molybdenum compound is a molybdenum oxydisulfide

6. A detergency additive according to Claim 1, wherein said overbased alkyl oxy benzene sulfonate has a TBN of at least 200, wherein between 40 wt % and 80 wt % of the alkyl group is attached at the 4-position and higher positions of the alkyl group, and wherein the oxy is selected from the group consisting of hydroxy, methoxy, ethoxy, propoxy, butoxy, pentoxy, and hexoxy.

7. A detergency additive according to Claim 6, wherein said overbased alkyl oxybenzene sulfonate has a TBN of at least 250, wherein 45 wt % and 70 wt % of the alkyl group is attached at the 4-position and higher position of the alkyl group, and wherein the oxy group is hydroxy.

8. A detergency additive according to Claim 1, wherein said alkylsalicylate is an unsulfurized alkaline earth alkylsalicylate.

9. A detergency additive according to Claim 8, wherein said unsulfurized alkaline earth alkylsalicylate is calcium alkylsalicylate.

10. A lubricating oil composition suitable for air-cooled two-stroke cycle engines comprising:

a) a major amount of at least one base oil of lubricating viscosity;

b) from 1.0 to 10 wt % of a detergency additive according to Claim 1; and

c) optionally, at least one of the following:

1) a minor amount of a solvent; and

2) a minor amount of a polyisobutene.

11. A method of producing a lubricating oil composition suitable for air-cooled two-stroke cycle engines comprising blending the following components together:

a) a major amount of at least one base oil of lubricating viscosity;

b) from 1.0 to 10 wt % of a detergency additive according to Claim 1; and

c) optionally, at least one of the following:

1) minor amount of a solvent; and

2) a minor amount of a polyisobutylene.

12. A lubricating oil composition according to Claim 11, wherein said lubricating oil composition optionally contains a polyisobutylene.

13. A method of improving the detergency of an air-cooled two-stroke cycle engine, comprising supplying the lubricating oil composition according to Claim 11 the crankcase of said engine and operating said engine.

14. A method of improving the detergency of an air-cooled two-stroke cycle engine, comprising supplying the lubricating oil composition according to Claim 11 to the fuel of said engine and operating said engine.

15. A detergency additive concentrate suitable for air-cooled two-stroke cycle engines comprising:

a) from 5.0 to 15% of an organic diluent,

b) from 85 to 95 wt % of the detergency additive according to Claim 1.