

DIESEL ENGINE OILS

FIELD OF INVENTION

The present invention relates to lubricating oil compositions. More specifically, it relates to lubricating oil compositions for use in railroad diesel engines or inland marine engines.

BACKGROUND OF THE INVENTION

Lead bearing corrosion in locomotive engines has been a concern for original equipment manufacturers (OEMs). Total Base Number (TBN) retention has also been a technical challenge. Historically, railroad engine oils (RREO) are non-zinc containing formulations because of the silver bearings which were used in some locomotive engines. Without the benefit of zinc dialkyl dithiophosphate, the proper detergent mixture has been the key factor in control of TBN retention and lead corrosion.

In March 2008, the Environmental Protection Agency (EPA) finalized a three-part program that will dramatically reduce emissions from diesel locomotives of all types -- line-haul, switch, and passenger rail. The rule will decrease particulate matter (PM) emissions from these engines by as much as 90 percent and NOx emissions by as much as 80 percent when fully implemented. This final rule sets new emission standards for existing locomotives when they are remanufactured. The rule also sets Tier 3 emission standards for newly-built locomotives, provisions for clean switch locomotives, and idle reduction requirements for new and remanufactured locomotives. Finally, the rule establishes long-term, Tier 4, standards for newly-built engines based on the application of high-efficiency catalytic aftertreatment technology, beginning in 2015.

Due to new EPA emission requirements and the introduction of ultra low sulfur diesel (ULSD) fuel, there will be a move to low SAPS railroad engine oils. As in heavy duty diesel oils for truck engines, there will be a decrease in TBN as well as a reduction in sulfur levels. Traditionally RREOs were 13 – 17 TBN oils. The TBN will likely be lowered to 8-11 TBN due to these changes. Balancing reductions in TBN and sulfur with long standing concerns about TBN retention and lead corrosion will require a different formulation. It has been found that when TBN levels were lowered, but the components were not changed, TBN retention and lead corrosion levels suffered. A problem exists of maintaining or improving lead corrosion and TBN retention when TBN in the oils and sulfur are decreased in RREOs.

- 5 It has been discovered that formulations containing salicylate detergent in addition to the traditional components showed decreased levels of lead corrosion and better TBN retention.

Prior Art

- 10 Research Disclosure No. RD0493012 teaches the use of salicylate detergents and supplementary antioxidants for improved lead corrosion in low sulfated ash, phosphorus and sulfur heavy-duty diesel formulations.

- Tomomi et al, JP 3925978 teaches a composition which comprises lubricating base oil, (a)perbasic
15 alkali earth metal salicylate, (b)perbasic alkali earth metal phenate and (c)bis-type alkenyl succinimide, bis-type alkyl succinimide or their boron adducts.

- Locke, EP 1256619 teaches a lubricating oil composition comprising (A) an oil of lubricating
viscosity, in a major amount, and added thereto, (B) a detergent composition comprising one or more
20 metal detergents which comprises metal salts of organic acids, in a minor amount, wherein the detergent composition comprises more than 50 mole % of a metal salt of an aromatic carboxylic acid, based on the moles of the metal salts of organic acids in the detergent composition, and (C) one or more co-additives, in a minor amount; wherein the total amounts of phosphorus and sulfur derived from (B) or (C) or both (B) and (C) are less than 0.1 mass % of phosphorus and at most 0.5 mass % of
25 sulfur, based on the mass of the oil composition.

- Shaw, U.S. Published Patent Application 2006/0052254 teaches an oil composition, which contains a salicylate, having sulfur (up to 0.3 wt%), phosphorus (up to 0.08 wt%), sulfated ash (up to 0.80 wt%),
30 comprises a mixture of an oil of lubricating viscosity (a); and an overbased alkali or alkaline earth metal alkyl salicylate lubricating oil detergent (b) having salicylate soap (20 - 25 wt%).

- Reiff, U.S. Patent No. 2,197,832 teaches a mineral oil composition which incorporates a small quantity of a multifunctional compound selected from that group of class of metalorganic compounds which is referred to as the oil-soluble or oil-miscible metal salts of alkyl-substituted hydroxyaromatic
35 carboxylic acids.

- Yagishita, U.S. Patent No. 7,563,751 teaches a lubricating oil composition comprising a base oil having a sulfur content adjusted to 0.1 wt% or less, and at least one of two different alkali or alkali earth metal salicylate mixtures.

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- 5 Yasushi, Japanese Patent No., JP 2007217607 teaches a diesel engine oil which contains mineral oil and/or synthetic oil as base oil, salicylate type cleaning agent (1-8 mass%) and diphenylamine derivative (0.005-0.03 mass%) as additive.

SUMMARY OF THE INVENTION

- 10 One embodiment of the present invention is directed to alubricating oil additive composition comprising
- a. a first carboxylate detergent having a TBN of the actives of greater than about 200 to about 400;
 - b. a second carboxylate detergent having a TBN of the actives of greater than about 60
 - 15 to about 200; and
 - c. at least one polyalkenyl succinimide.

One embodiment of the present invention is directed to a lubricating oil composition comprising

- a. a major amount of oil of lubricating viscosity;
- 20 b. a first carboxylate detergent having a TBN of the actives of greater than about 200 to about 400;
- c. second carboxylate detergent having a TBN of the actives of greater than about 60 to about 200; and
- d. at least one polyalkenyl succinimide.

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One embodiment of the present invention is directed to a method for operating a diesel locomotive engine comprising lubricating said diesel locomotive engine with a lubricating oil composition comprising

- a. a major amount of an oil of lubricating viscosity; and
- 30 b. a first carboxylate detergent having a TBN of the actives of greater than about 200 to about 400;
- c. a second carboxylate detergent having a TBN of the actives of greater than about 60 to about 200; and
- d. at least one polyalkenyl succinimide.

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One embodiment of the present invention is directed to a method for operating an inland marine engine comprising lubricating said inland marine engine with a lubricating oil composition comprising

- a. a major amount of an oil of lubricating viscosity; and

- 5 b. a first carboxylate detergent having a TBN of the actives of greater than about 200 to about 400;
- c. a second carboxylate detergent having a TBN of the actives of greater than about 60 to about 200; and
- d. at least one polyalkenyl succinimide.

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One embodiment of the present invention is directed to a method of improving TBN retention comprising lubricating an engine with a lubricating oil composition having

1. a major amount of an oil of lubricating viscosity;
2. a first carboxylate detergent having a TBN of the actives of greater than about 200 to about 15 400;
3. a second carboxylate detergent having a TBN of the actives of greater than about 60 to about 200; and
4. at least one polyalkenyl succinimide.

20 Detailed Description of the Invention

Definitions

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

The term "alkyl" refers to both straight- and branched-chain alkyl groups.

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The term "metal" refers to alkali metals, alkaline earth metals, transition metals or mixtures thereof.

The term "Metal to Substrate ratio" refers to the ratio of the total equivalents of the metal to the equivalents of the substrate. An overbased sulphonate detergent typically has a metal ratio of 12.5:1 to 30 40:1, in one aspect 13.5:1 to 40:1, in another aspect 14.5:1 to 40:1, in yet another aspect 15.5:1 to 40:1 and in yet another aspect 16.5:1 to 40:1.

Total Base Number (TBN or BN) numbers reflect more alkaline products and therefore a greater alkalinity reserve. The TBN of a sample can be determined by ASTM Test No. D2896 or any other 35 equivalent procedure. In general terms, TBN is the neutralization capacity of one gram of the lubricating composition expressed as a number equal to the mg of potassium hydroxide providing the equivalent neutralization. Thus, a TBN of 10 means that one gram of the composition has a neutralization capacity equal to 10 mg of potassium hydroxide. TBN of the actives should be measured.

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The term "low overbased" or "LOB" refers to an overbased detergent having a low TBN of the actives of about 0 to about 60.

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The term "medium overbased" or "MOB" refers to an overbased detergent having a medium TBN of the actives of greater than about 60 to about 200.

The term "high overbased" or "HOB" refers to an overbased detergent having a high TBN of the actives of greater than about 200 to about 400.

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Lubricating Oil Additive Composition

The lubricating oil additive composition of the present invention comprises a first carboxylate detergent having a TBN of from about 60 to about 200 TBN; a second carboxylate detergent having a TBN of from about 200 to about 400 TBN and a polyalkenyl succinimide. Other additives may be employed in the lubricating oil additive composition.

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Carboxylate Detergent

In one embodiment, a first carboxylate detergent and a second carboxylate detergent are employed in the lubricating oil additive composition.

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Typically, the carboxylate detergents are prepared according methods that are well known in the art, including, but not limited to, the processes described in U.S. Patent Publication No. 2007/0105730 and U.S. Patent Publication No. 2007/0027043.

In one embodiment, the first carboxylate detergent is a single-ring carboxylate.

Single-Ring Carboxylate

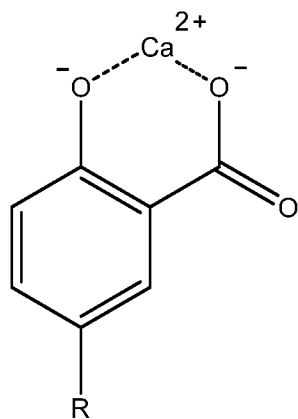
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One of the carboxylate detergents that may be used in the lubricating oil additive composition is a single-ring carboxylate having a Total Base Number (TBN) of the actives of greater than about 60 to about 200.

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The single carboxylate has the following structure:



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wherein R is a linear hydrocarbyl group, a branched hydrocarbyl group or mixtures thereof.

Preferably, R is a linear hydrocarbyl group. More preferably, R is an alkyl group having from 12 to 40 carbon atoms.

15 The single-ring carboxylate is prepared according to the following method.

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 C₁ to C₄ carboxylic acid. Preferably, this reaction is carried out in the absence
20 of alkali base, and in the absence of dialcohol or monoalcohol.

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,
25 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.

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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

5 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.

Branched alkylphenols can be obtained by reaction of phenol with a branched olefin, generally
10 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.

15 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
20 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.

The alkaline earth metal bases that can be used for carrying out this step include the oxides or
25 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.

The promoter used in this step can be any material that enhances neutralization. For example, the
30 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,
35 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.

The neutralization operation is carried out at a temperature of at least 200°C, preferably at least
40 215°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

- 5 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).

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
10 acid/hydrocarbyl phenol of 0.01:1 to 0.5:1, preferably from 0.03:1 to 0.15:1.

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 10,000 Pa (between 0.05 and 1.0 bar). More preferably, at the end of this neutralization
15 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).

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
20 the need to add a solvent that forms an azeotrope with the water formed during this reaction.

B. Carboxylation Step

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
25 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.

30 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 15×10^5 Pa (15 bars) for a period of one to eight hours.

35 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 4×10^5 Pa (4 bars).

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C. Filtration Step

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

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 about 150°C to about 250°C and at a pressure of about 0.1 to about 4 mbar; more preferably from about 190°C to about 230°C and at about 0.5 to about 3 mbar; most preferably from about 195°C to about 225°C and at a pressure of about 1 to about 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 Additive

The unsulfurized, carboxylate-containing additive formed by the present 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 (b) from 15% to 60% alkaline earth metal single-aromatic-ring alkylsalicylate.

Unlike alkaline earth metal alkylsalicylates produced by other process, 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.

5 Characterization of the Product by Infrared Spectrometry

Out-of-aromatic-ring-plane C--H bending vibrations were used to characterize the unsulfurized carboxylate-containing additive of the present invention. 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
10 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} .

Infrared spectra of reference chemical structures relevant to the present invention indicate that the out-
15 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.

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
20 out-of-plane C--H bending transmittance bands at $763\pm 3 \text{ cm}^{-1}$ and at $832\pm 3 \text{ cm}^{-1}$.

The unsulfurized carboxylate-containing additive of 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
25 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
30 engaged in a cyclic structure and thus can rotate) has an out-of-plane C--H transmittance band at $763\pm 3 \text{ cm}^{-1}$.

The unsulfurized carboxylate-containing additive of 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
35 out-of-plane C--H bending at $832\pm 3 \text{ cm}^{-1}$ of less than 0.1:1.

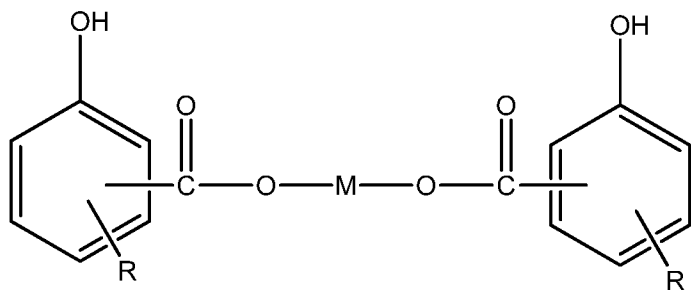
The unsulfurized, carboxylate-containing additive formed by this method, being non-sulfurized, would provide improved high temperature deposit control performance over sulfurized products. Being alkali-metal free, this additive can be employed as a detergent-dispersant in applications, such
40 as marine engine oils, where the presence of alkali metals have proven to have harmful effects.

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Additional Carboxylate Additives

The second carboxylate detergent may be prepared according the following process.

- 10 The overbased alkaline earth metal alkylhydroxybenzoate (i.e., carboxylate detergent) of the present invention will typically have a structure as shown below as Formula (I).



- 15 wherein R is a linear aliphatic group, branched aliphatic group or a mixture of linear and branched aliphatic groups. Preferably, R is an alkyl or alkenyl group. More preferably, R is an alkyl group.

M is an alkaline earth metal selected of the group consisting of calcium, barium, magnesium, strontium. Calcium and magnesium are the preferred alkaline earth metal. Calcium is more preferred.

- 20 When R is a linear aliphatic group, the linear alkyl group typically comprises from about 12 to 40 carbon atoms, more preferably from about 18 to 30 carbon atoms.

- When R is a branched aliphatic group, the branched alkyl group typically comprises at least 9 carbon atoms, preferably from about 9 to 40 carbon atoms, more preferably from about 9 to 24 carbon atoms
25 and most preferably from about 10 to 18 carbon atoms. Such branched aliphatic groups are preferably derived from an oligomer of propylene or butene.

- R can also represent a mixture of linear or branched aliphatic groups. Preferably, R represents a mixture of linear alkyl containing from about 20 to 30 carbon atoms and branched alkyl containing
30 about 12 carbon atoms.

- When R represents a mixture of aliphatic groups, the alkaline-earth metal alkylhydroxybenzoic acid employed in the present invention may contain a mixture of linear groups, a mixture of branched groups, or a mixture of linear and branched groups. Thus, R can be a mixture of linear aliphatic
35 groups, preferably alkyl; for example, an alkyl group selected from the group consisting of C₁₄-C₁₆,

5 C₁₆-C₁₈, C₁₈-C₂₀, C₂₀-C₂₂, C₂₀-C₂₄ and C₂₀-C₂₈ alkyl and mixtures thereof and derived from normal alpha olefins. Advantageously, these mixtures include at least 95 mole %, preferably 98 mole % of alkyl groups and originating from the polymerization of ethylene.

10 The alkaline earth metal alkylhydroxybenzoates (i.e., carboxylates) of the present invention wherein R represents a mixture of alkyl groups, can be prepared from linear alpha olefin cuts, such as those marketed by Chevron Phillips Chemical Company under the names Normal Alpha Olefin C₂₆-C₂₈ or Normal Alpha Olefin C₂₀-C₂₄, by British Petroleum under the name C₂₀-C₂₆ Olefin, by Shell Chimie under the name SHOP C₂₀-C₂₂, or mixtures of these cuts or olefins from these companies having from about 20 to 28 carbon atoms.

15 The --COOM group of Formula (I) can be in the ortho, meta or para position with respect to the hydroxyl group.

20 The alkaline earth metal alkylhydroxybenzoates of the present invention can be any mixture of alkaline-earth metal alkylhydroxybenzoic acid having the --COOM group in the ortho, meta or para position.

The alkaline earth metal alkylhydroxybenzoates of the present invention are generally soluble in oil as characterized by the following test.

25 A mixture of a 600 Neutral diluent oil and the alkylhydroxybenzoate at a content of 10 wt % with respect to the total weight of the mixture is centrifuged at a temperature of 60°C and for 30 minutes, the centrifugation being carried out under the conditions stipulated by the standard ASTM D2273 (it should be noted that centrifugation is carried out without dilution, i.e. without adding solvent);
30 immediately after centrifugation, the volume of the deposit which forms is determined; if the deposit is less than 0.05% v/v (volume of the deposit with respect to the volume of the mixture), the product is considered as soluble in oil.

35 Advantageously, the TBN of the high overbased alkaline earth metal alkylhydroxybenzoate of the present invention is greater than 250, preferably from about 250 to 450 and more preferably from about 300 to 400 and will generally have less than 3 volume %, preferably less than 2 volume % and more preferably less than 1 volume % crude sediment. For the middle overbased alkaline earth metal alkylhydroxybenzoate of the present invention, the TBN is from about 100 to 250, preferably from about 140 to 230 and will generally have less than 1 volume %, preferably less than 0.5 volume %
40 crude sediment.

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Process

In the first embodiment of the present invention, the process for preparing the overbased alkaline earth metal alkylhydroxybenzoate involves overbasing the alkaline earth metal alkylhydroxybenzoate or a mixture of alkaline earth metal alkylhydroxybenzoate and up to 50 mole % of alkylphenol, based on the total mixture of alkylhydroxybenzoate and alkylphenol, with a molar excess of alkaline earth metal base and at least one acidic overbasing material in presence of at least one carboxylic acid having from one to four carbon atoms and a solvent selected from the group consisting of aromatic hydrocarbons, aliphatic hydrocarbons, monoalcohols, and mixtures thereof.

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Overbasing of the alkaline earth metal alkylhydroxybenzoate or mixture of alkaline earth metal alkylhydroxybenzoate and alkylphenol may be carried out by any method known by a person skilled in the art to produce overbased alkaline earth metal alkylhydroxybenzoates. However, it has been surprisingly discovered that the addition of a small quantity of C₁-C₄ carboxylic acid at this step decreases the crude sediment obtained at the end of overbasing step by a factor of at least 3.

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The C₁-C₄ carboxylic acids used in the neutralization step include formic acid, acetic acid, propionic acid, and butyric acid, which may be used alone or in mixture. It is preferable to use mixtures of such acids as, for example, formic acid:acetic acid, in a molar ratio of formic acid:acetic acid of from about 0.1:1 to 100:1, preferably from about 0.5:1 to 4:1, more preferably from about 0.5:1 to 2:1, and most preferably about 1:1.

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Generally, the overbasing reaction is carried out in a reactor in the presence of alkylhydroxybenzoic acid from about 10 wt % to 70 wt %, alkylphenol from about 1 wt % to 30 wt %, diluent oil from about 0 wt % to 40 wt %, an aromatic solvent from about 20 wt % to 60 wt %. The reaction mixture is agitated. The alkaline earth metal associated with an aromatic solvent, a monoalcohol and carbon dioxide are added to the reaction while maintaining the temperature between about 20°C and 80°C.

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The degree of overbasing may be controlled by the quantity of the alkaline earth metal, carbon dioxide and the reactants added to the reaction mixture and the reaction conditions used during the carbonation process.

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The weight ratios of reagents used (methanol, xylene, slaked lime and CO₂) will correspond to the following weight ratios: Xylene:slaked lime from about 1.5:1 to 7:1, preferably from about 2:1 to 4:1. Methanol:slaked lime from about 0.25:1 to 4:1, preferably from about 0.4:1 to 1.2:1. Carbon

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5 dioxide:slaked lime from a molar ratio about 0.5:1 to 1.3:1, preferably from about 0.7:1 to 1.0:1. C₁-C₄ carboxylic acid:alkylhydroxybenzoic acid a molar ratio from about 0.02:1 to 1.5:1, preferably from about 0.1:1 to 0.7:1.

Lime is added as a slurry, i.e., as a pre-mixture of lime, methanol, xylene, and CO.sub.2 is introduced
10 over a period of 1 hour to 4 hours, at a temperature between about 20°C and 65°C.

The quantity of lime and CO.sub.2 are adjusted in order to obtain a high overbased material (TBN>250) and crude sediment in the range of 0.4 to 3 volume %, preferably in the range of 0.6 to 1.8 volume %, without any deterioration of the performance. With the omission of C₁-C₄ carboxylic
15 acid, it is not able to reach this low level of crude sediment. Typically, crude sediment without a C₁-C₄ carboxylic acid will range from about 4 to 8 volume %.

For a middle overbased material (TBN from about 100 to 250), the quantity of lime and CO₂ are adjusted in order to obtain a crude sediment in the range of 0.2 to 1 volume %. The crude sediment
20 without the use of C₁-C₄ carboxylic acid will range from about 0.8 to 3 volume %.

In a second embodiment of the present invention, the overbased alkaline earth metal alkylhydroxybenzoate may be prepared by the following steps:

25 A. Formation of the Alkali Metal Base Alkylphenate:

In the first step, alkylphenols are neutralized using an alkali metal base preferably in the presence of a light solvent, such as toluene, xylene isomers, light alkylbenzene or the like, to form the alkali metal base alkylphenate. In one embodiment, the solvent forms an azeotrope with water. In another
30 embodiment, the solvent may also be a mono-alcohol such as 2-ethylhexanol. In this case, the 2-ethylhexanol is eliminated by distillation before carboxylation. The objective with the solvent is to facilitate the elimination of water.

The hydrocarbyl phenols may contain up to 100 wt % linear hydrocarbyl groups, up to 100 wt %
35 branched hydrocarbyl groups, or both linear and branched hydrocarbyl groups. Preferably, the linear hydrocarbyl group, if present, is alkyl, and the linear alkyl group contains from about 12 to 40 carbon atoms, more preferably from about 18 to 30 carbon atoms. The branched hydrocarbyl group, if present, is preferably alkyl and contains at least 9 carbon atoms, preferably from about 9 to 40 carbon atoms, more preferably from about 9 to 24 carbon atoms and most preferably from about 10 to 18
40 carbon atoms. In one embodiment, the hydrocarbyl phenols contain up to 85 wt % of linear

5 hydrocarbyl phenol (preferably at least 35 wt % linear hydrocarbyl phenol) in mixture with at least 15 wt % of branched hydrocarbyl phenol. In one embodiment, the hydrocarbyl phenols are 100% linear alkylphenols.

The use of an alkylphenol containing up to at least 35 wt % of long linear alkylphenol (from about 18
10 to 30 carbon atoms) is particularly attractive because a long linear alkyl chain promotes the compatibility and solubility of the additives in lubricating oils.

Branched alkylphenols can be obtained by reaction of phenol with a branched olefin, generally originating from propylene.

15 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.

On the other hand, linear alkylphenols can be obtained by reaction of phenol with a linear olefin,
20 generally originating from ethylene. They consist of a mixture of monosubstituted isomers in which the proportion of linear alkyl substituents in the ortho, meta, and para positions is much more uniformly distributed. Of course, linear alkylphenols may contain alkyl substituents with some branching which increases the amount of para substituents and, resultantly may increase the relative reactivity towards alkali metal bases.

25 The alkali metal bases that can be used for carrying out this step include the oxides or hydroxides of lithium, sodium or potassium. In a preferred embodiment, potassium hydroxide is preferred. In another preferred embodiment, sodium hydroxide is preferred.

30 An objective of this step is to have an alkylphenate having less than 2000 ppm, preferably less than 1000 ppm and more preferably less than 500 ppm of water.

In this regard, the first step is carried out at a temperature high enough to eliminate water. In one
35 embodiment, the product is put under a slight vacuum in order to require a lower reaction temperature.

In one embodiment, xylene is used as a solvent and the reaction conducted at a temperature between 130°C and 155°C, under an absolute pressure of 800 mbar (8×10^4 Pa).

40 In another embodiment, 2-ethylhexanol is used as solvent. As the boiling point of 2-ethylhexanol

5 (184°C) is significantly higher than xylene (140°C), the reaction is conducted at a temperature of at least 150°C.

The pressure is reduced gradually below atmospheric in order to complete the distillation of water reaction. Preferably, the pressure is reduced to no more than 70 mbar (7×10^3 Pa).

10

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 formation of the alkali metal base alkylphenate is carried out without the need to add a solvent and forms an azeotrope with the water formed during this reaction. For instance, temperature is heated up to 200°C and then the pressure is reduced gradually below atmospheric. Preferably the pressure is reduced to no more than 70 mbar (7×10^3 Pa).

15

Elimination of water is done over a period of at least 1 hour, preferably at least 3 hours.

20

The quantities of reagents used should correspond to the following molar ratios: alkali metal base:alkylphenol from about 0.5:1 to 1.2:1, preferably from about 0.9:1 to 1.05:1 solvent:alkylphenol (wt:wt) from about 0.1:1 to 5:1, preferably from about 0.3:1 to 3:1

B. Carboxylation:

25

This carboxylation step is conducted by simply bubbling carbon dioxide (CO_2) into the reaction medium originating from the preceding neutralization step and is continued until at least 50 mole % of the starting alkylphenol has been converted to alkylhydroxybenzoic acid (measured as hydroxybenzoic acid by potentiometric determination).

30

At least 50 mole %, preferably 75 mole %, and more preferably 85 mole %, of the starting alkylphenol is converted to alkylhydroxylbenzoate using carbon dioxide at a temperature between about 110°C and 200°C under a pressure within the range of from about atmospheric to 15 bar (15×10^5 Pa), preferably from 1 bar (1×10^5 Pa) to 5 bar (5×10^5 Pa), for a period between about 1 and 8 hours.

35

In one variant with potassium salt, temperature is preferably between about 125°C and 165°C and more preferably between 130°C and 155°C, and the pressure is from about atmospheric to 15 bar (15×10^5 Pa), preferably from about atmospheric to 4 bar (4×10^5 Pa).

40

5 In another variant with sodium salt, temperature is directionally lower preferably between from about 110°C and 155°C. More preferably from about 120°C and 140°C and the pressure from about 1 bar to 20 bar (1×10^5 to 20×10^5 Pa), preferably from 3 bar to 15 bar (3×10^5 to 15×10^5 Pa).

The carboxylation is usually carried out, diluted in a solvent such as hydrocarbons or alkylate, e.g.,
10 benzene, toluene, xylene and the like. In this case, the weight ratio of solvent:hydroxybenzoate is from about 0.1:1 to 5:1, preferably from about 0.3:1 to 3:1.

In another variant, no solvent is used. In this case, carboxylation is conducted in the presence of diluent oil in order to avoid a too viscous material.

15 The weight ratio of diluent oil:alkylhydroxybenzoate is form about 0.1:1 to 2:1, preferably from about 0.2:1 to 1:1, and more preferably from about 0.2:1 to 0.5:1.

C. Acidification:

20 The objective of this step is to acidify the alkylhydroxybenzoate salt diluted in the solvent to give an alkylhydroxybenzoic acid. Any acid stronger than alkylhydroxybenzoic acid could be utilized. Usually hydrochloric acid or aqueous sulfuric acid is utilized.

25 Acidification step is conducted with an H^+ equivalent excess of acid versus potassium hydroxide of at least 5 H^+ equivalent %, preferably 10 H^+ equivalent % and more preferably 20 H^+ equivalent %, the acidification is complete.

In one embodiment, sulfuric acid is used. It is diluted to about 5 volume % to 50 volume %, preferably 10 volume % to 30 volume %. The quantity of sulfuric acid used versus hydroxybenzoate (salicylate), on a per mole of hydroxybenzoate basis, is at least 0.525 mole, preferably 0.55 mole and more preferably 0.6 mole of sulfuric acid.

35 The acidification reaction is carried out under agitation or with any suitable mixing system at a temperature from about room temperature to 95°C, preferably from about 50°C to 70°C, over a period linked with the efficiency of the mixing. For example, when a stirred reactor is utilized and the period is from about 15 minutes to 300 minutes, preferably from about 60 minutes to 180 minutes. When a static mixer is utilized, the period may be shorter.

40 At the end of this period time, the agitation is stopped in order to allow good phase separation before

5 the aqueous phase was separated. After phase separation is complete, the organic phase is then neutralized, overbased, centrifugated to eliminate impurities and distilled to eliminate solvent. The water phase is treated as a waste material. In one embodiment, the organic phase is sent through a coalescer to decrease the level of residual water and water-soluble impurities such as sulfuric acid and potassium sulfate as a consequence.

10 D. Contact with Carboxylic Acid:

The alkylhydroxybenzoic acid in step C is contacted with at least one carboxylic acid having from about one to four carbon atoms.

15 E. Neutralization:

The mixture of alkylhydroxybenzoic acid and the at least one carboxylic acid from step D is neutralized with an alkaline earth metal base and at least one solvent selected from the group
20 consisting of aromatic hydrocarbons, aliphatic hydrocarbons monoalcohols, and mixtures thereof to form an alkaline earth metal alkylhydroxylbenzoate and at least one alkaline earth metal carboxylic acid salt.

F. Overbasing:

25 Overbasing of the mixture of alkylhydroxybenzoic acid and alkylphenol may be carried out by any method known by a person skilled in the art to produce alkylhydroxybenzoates. However, it has been surprisingly discovered that the addition of a small quantity of C₁-C₄ carboxylic acid at this step decreases the crude sediment obtained at the end of overbasing step by a factor of at least 3.

30 The C₁-C₄ carboxylic acids used in the neutralization step include formic acid, acetic acid, propionic acid, and butyric acid, which may be used alone or in mixture. It is preferable to use mixtures of such acids as, for example, formic acid:acetic acid, in a molar ratio of formic acid:acetic acid of from about 0.1:1 to 100:1, preferably from about 0.5:1 to 4:1, and more preferably from about 0.5:1 to 2:1.

35 Generally, the overbasing reaction is carried out in a reactor in the presence of alkylhydroxybenzoic acid from about 10 wt % to 70 wt %, alkylphenol from about 1 wt % to 30 wt %, diluent oil from about 0 wt % to 40 wt %, an aromatic solvent from about 20 wt % to 60 wt %. The reaction mixture is agitated. The alkaline earth metal associated with an aromatic solvent, a monoalcohol and carbon
40 dioxide are added to the reaction while maintaining the temperature between about 20°C and 80°C.

5

The degree of overbasing may be controlled by the quantity of the alkaline earth metal, carbon dioxide and the reactants added to the reaction mixture and the reaction conditions used during the carbonation process.

- 10 The weight ratios of reagents used (methanol, xylene, slaked lime and CO₂) will correspond to the following weight ratios: Xylene:slaked lime from about 1.5:1 to 7:1, preferably from about 2:1 to 4:1. Methanol:slaked lime from about 0.25:1 to 4:1, preferably from about 0.4:1 to 1.2:1. Carbon dioxide:slaked lime from a molar ratio about 0.5:1 to 1.3:1, preferably from about 0.7:1 to 1.0:1. C₁-C₄ carboxylic acid:alkylhydroxybenzoic acid a molar ratio from about 0.02:1 to 1.5:1, preferably from
15 about 0.1:1 to 0.7:1.

Lime is added as a slurry, i.e., as a pre-mixture of lime, methanol, xylene, and CO₂ is introduced over a period of 1 hour to 4 hours, at a temperature between about 20°C and 65°C.

- 20 The quantity of lime and CO₂ are adjusted in order to obtain a high overbased material (TBN >250) and crude sediment in the range of 0.4 to 3 volume %, preferably in the range of 0.6 to 1.8 volume %, without any deterioration of the performance. With the omission of C₁-C₄ carboxylic acid, it is not able to reach this low level of crude sediment. Typically, crude sediment without a C₁-C₄ carboxylic acid will range from about 4 to 8 volume %.

25

For a middle overbased material (TBN from about 100 to 250), the quantity of lime and CO₂ are adjusted in order to obtain a crude sediment in the range of 0.2 to 1 volume %. The crude sediment without the use of C₁-C₄ carboxylic acid will range from about 0.8 to 3 volume %.

- 30 In the third embodiment of the present invention, the overbased alkaline earth metal alkylhydroxybenzoate may be obtained by a process having steps A through C above followed by:

D. Neutralization:

- 35 The mixture of alkylhydroxybenzoic acid from step C is neutralized with a molar excess of an alkaline earth metal base and at least one solvent selected from the group consisting of aromatic hydrocarbons, aliphatic hydrocarbons, monoalcohols, and mixtures thereof to form an alkaline earth metal alkylhydroxybenzoate.

5

E. Contact with Carboxylic Acid:

The alkaline earth metal alkylhydroxybenzoate and alkaline earth metal base formed in step D is contacted with at least one carboxylic acid having from about one to four carbon atoms to form a mixture of alkaline earth metal alkylhydroxybenzoate and at least one alkaline earth metal carboxylate.

F. Overbasing:

The alkaline earth metal alkylhydroxybenzoate is then overbased according to the description provided above.

Optionally, predistillation, centrifugation and distillation may also be utilized to remove solvent and crude sediment. Water, methanol and a portion of the xylene may be eliminated by heating between about 110°C to 134°C. This may be followed by centrifugation to eliminated unreacted lime. Finally, xylene may be eliminated by heating under vacuum in order to reach a flash point of at least about 160°C as determined with the Pensky-Martens Closed Cup (PMCC) Tester described in ASTM D93.

In one embodiment, the lubricating oil additive composition comprises at least one polyalkenyl succinimide that is prepared according the process described in U.S. Patent No. 5,821,905, U.S. Patent No. 5,334,321 and U.S. Patent No.,5,356,552 which are herein incorporated by reference and by other methods that are well known in the art.

The lubricating oil additive composition may also comprise other additives described below. These additional components can be blended in any order and can be blended as combinations of components.

Other Additive Components

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

A. Metal Detergents

Sulfurized or unsulfurized alkyl or alkenyl phenates, sulfonates derived from synthetic or natural feedstocks, carboxylates, salicylates, phenalates, 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.

B. 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. Antioxidants may include, but are not limited to, such anti-oxidants as 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-butyl phenol), 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-1-4-methylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,4-dimethyl-6-tert-butyl-phenol, 2,6-di-tert-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(dibutylidithiocarbamate). The anti-oxidant is generally incorporated into an oil in an amount of about 0 to about 10 wt %, preferably 0.05 to about 3.0 wt %, per total amount of the engine oil.

C. Anti-Wear/Extreme Pressure 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, molybdenum complexes, zinc dialkyldithiophosphate (primary alkyl, secondary alkyl, and aryl type), sulfurized oils, sulfurized isobutylene, sulfurized polybutene, diphenyl sulfide, methyl trichlorostearate, chlorinated naphthalene, fluoroalkylpolysiloxane, and lead naphthenate.

D. Rust Inhibitors (Anti-rust Agents)

- 1) 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,

- 5 polyoxyethylene sorbitol monostearate, polyoxyethylene sorbitol monooleate, and polyethylene glycol monooleate.
- 2) 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.

10

E. Demulsifiers

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

15 F. Friction Modifiers

Fatty alcohols, 1,2-diols, borated 1,2-diols, fatty acids, amines, fatty acid amides, borated esters, and other esters.

G. Multifunctional Additives

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

H. Viscosity Index Improvers or Thickeners

- 25 Polymethacrylate type polymers, ethylene-propylene copolymers, styrene-isoprene copolymers, hydrogenated styrene-isoprene copolymers, polyisobutylene, and dispersant type viscosity index improvers.

I. Pour Point Depressants

- 30 Polymethyl methacrylate.

J. Foam Inhibitors

Alkyl methacrylate polymers and dimethyl silicone polymers.

35 K. Metal Deactivators

Disalicylidene propylenediamine, triazole derivatives, mercaptobenzothiazoles, thiadiazole derivatives, and mercaptobenzimidazoles.

5 L. Dispersants

Alkenyl succinimides, alkenyl succinimides modified with other organic compounds, alkenyl succinimides modified by post-treatment with ethylene carbonate or boric acid, esters of polyalcohols and polyisobutenyl succinic anhydride, phenate-salicylates and their post-treated analogs, alkali metal or mixed alkali metal, alkaline earth metal borates, dispersions of hydrated alkali metal borates, 10 dispersions of alkaline-earth metal borates, polyamide ashless dispersants and the like or mixtures of such dispersants. Preferably, the alkenyl succinimide is a polyalkenyl succinimide. More preferably, a polyisobutenyl succinimide, wherein the polyisobutentyl group has a molecular weight of from about 1000 to about 2300. The alkenyl succinimide is prepared according methods that are well known in the art.

15

Lubricating Oil Composition

In one embodiment, the invention is directed to a lubricating oil composition comprising the lubricating oil additive composition that was described herein above and an oil of lubricating viscosity.

20

Oil of Lubricating Viscosity

The lubricating oil additive composition described above is generally added to a base oil that is sufficient to lubricate moving parts, for example internal combustion engines, gears, and transmissions. Typically, the lubricating oil composition of the present invention comprises a major 25 amount of an oil of lubricating viscosity and a minor amount of the lubricating oil additive composition.

30

The base oil employed may be any of a wide variety of oils of lubricating viscosity. The base oil of lubricating viscosity used in such compositions may be mineral oils or synthetic oils. A base oil having a viscosity of at least 2.5 cSt at 40°C and a pour point below 20°C, preferably at or below 0°C, is desirable. The base oils may be derived from synthetic or natural sources.

35

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 the desired viscosity. Hydrocarbon synthetic oils may include, for example, oils prepared from the polymerization of ethylene, polyalphaolefin or PAO oils, or oils prepared from hydrocarbon synthesis procedures using carbon monoxide and hydrogen gases such as in a Fisher-Tropsch process. Useful synthetic hydrocarbon oils include liquid polymers of alpha olefins having the proper viscosity. Especially

5 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 mono-hydroxy alkanols and polyols. Typical examples are didodecyl adipate, pentaerythritol tetracaprate, di-2-ethylhexyl adipate, dilaurylsebacate, and the like. Complex esters prepared from mixtures of
10 mono and dicarboxylic acids and mono and dihydroxy alkanols can also be used. Blends of mineral oils with synthetic oils are also useful.

Thus, the base oil can be a refined paraffin type base oil, a refined naphthenic base oil, or a synthetic hydrocarbon or non-hydrocarbon oil of lubricating viscosity. The base oil can also be a mixture of
15 mineral and synthetic oils.

Additive Packages

In another embodiment, the invention is directed to additive concentrates for engine oils that contain a first carboxylate detergent, a second carboxylate detergent and a polyalkenyl succinimide. In
20 another embodiment, the invention is directed to additive concentrates for engine oils that contain a first carboxylate detergent having a TBN of from about 60 to about 200 TBN, a second carboxylate detergent having a TBN of from about 200 to about 400 TBN, and a polyalkenyl succinimide. The lubricating oil additive composition, which is described herein above, concentrate may be provided as an additive package or concentrate which will be incorporated into a substantially inert, normally
25 liquid organic diluent such as, for example, mineral oil, naphtha, benzene, toluene or xylene to form an additive concentrate. These concentrates usually contain from about 1% to about 99% by weight, and in one embodiment about 10% to about 90% by weight of such diluent. Typically, a neutral oil having a viscosity of about 4 to about 8.5 cSt at 100°C. and preferably about 4 to about 6 cSt at 100°C. will be used as the diluent, though synthetic oils, as well as other organic liquids which are
30 compatible with the additives and finished lubricating oil can also be used.

One embodiment of the invention is directed to a method for operating a diesel locomotive engine comprising lubricating a diesel locomotive engine with a lubricating oil composition comprising a major amount of an oil of lubricating viscosity and the lubricating oil additive package described
35 hereinabove, which contains a first carboxylate detergent, a second carboxylate detergent and a polyalkenyl succinimide.

One embodiment of the invention is directed to a method for operating an inland marine engine comprising lubricating an inland marine engine with a lubricating oil composition comprising a major amount of an oil of lubricating viscosity and the lubricating oil additive package described

5 hereinabove which contains a first carboxylate detergent, a second carboxylate detergent and a polyalkenyl succinimide.

One embodiment of the invention is directed to a method of improving TBN retention wherein the lubricating oil composition comprises a major amount of an oil of lubricating viscosity and the lubricating oil additive package described hereinabove which contains a first carboxylate detergent, a
10 second carboxylate detergent and a polyalkenyl succinimide.

Examples

Base Lubricating Oil Composition

15 A lubricating oil composition was prepared by blending a polyisobutenyl succinimide, wherein the polyisobutenyl group has a molecular weight of 2300, a 263 TBN oil concentrate of a phenate detergent, a 114 TBN oil concentrate of a phenate detergent, a calcium salt of a Mannich base alkylphenol, at least one antioxidant, a foam inhibitor, and a Group I base oil.

Comparative Examples 1-8 were comprised primarily of the Base Lubricating Oil Composition (see
20 Table 1). Examples 1-7 (Examples of the Invention) comprised the Base Lubricating Oil Composition and at least two carboxylate detergents –a 350 TBN oil concentrate of a carboxylate detergent and a 150 TBN oil concentrate of a carboxylate detergent (See Table 2).

Each of the comparative oils was tested in the B2-7 which is otherwise known as the Union Pacific Oxidation Test. This test method is described below.

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30

35

5 B2-7 Test/ Union Pacific Oxidation Test

The B2-7 test is an oxidation test with the following conditions:

	U.P. Oxidation (B2)
Temp	149 C (300F)
Duration	96 hr
Coupons	Cu, Fe, Pb
Flow	oxygen
Replenishing oil	At 48 hr (50 mL) 72 hr (50 mL)
Comments	Trend data of TBN, AN, pH and Pb ppm

10

According to the B2-7 test, the oil to be tested is heated at 300° F for 96 hours with bubbling oxygen. Copper, iron and lead coupons are suspended in the oil. Fifty milliliter samples are taken at 48, 72 and 96 hours. The samples at 48 and 72 hours are replenished with fresh oil. The oil test samples are evaluated for base number, acid number, pH and lead.

Table 1. – Comparative Examples

Oil number	Comp 1	Comp 2	Comp 3	Comp 4	Comp 5	Comp 6	Comp 7	Comp 8
Dispersants								
Ethylene Carbonate treated Succinimide Dispersant (wt%)	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.000
HOB Detergents								
263 TBN phenate (mmol)	(22.00)	(22.00)	(22.00)	(22.00)	(30.00)	(30.00)	(30.00)	(30.00)
114 TBN phenate (mmol)	(30.00)	(30.00)	(30.00)	(30.00)	(22.00)	(22.00)	(22.00)	(22.00)
350 TBN carboxylate								
150 TBN ¹ carboxylate								
Mannich Base (wt%)	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
Antioxidants								
Diphenylamine (wt%)	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Hindered Phenol (wt%)	0.00	1.00	2.00	3.00	0.00	1.00	2.00	3.00
Molybdenum Oxsulfide (wt%)	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
Foam								

¹ Prepared according to U.S. Published Patent Application No. 2007/0027043

Inhibitors								
Foam Inhibitor	3ppm	3ppm	3ppm	3ppm	3ppm	3ppm	3ppm	3ppm
B. Oils								
EXXON 150N (wt% of total base oil)	5	5	5	5	5	5	5	5
EXXON 600N (wt% of total base oil)	95	95	95	95	95	95	95	95
B2 Test Results								
TBN decrease (mg/KOH)	5.88	5.47	5.16	5.33	5.11	5.5	5.34	5.06
Pb (ppm)	545	578	647	464	406	925	334	331

Table 2 – Examples of the Invention

Oil number	Ex 1	Ex 2	Ex 3	Ex 4	Ex 5	Ex 6	Ex 7
Dispersants							
Succinimide Ethylene Carbonate treated Succinimide Dispersant (wt%)	3.000	3.000	3.000	3.000	3.000	3.000	3.000
HOB Detergents							
350 TBN carboxylate (mmol)	(22.00)	(22.00)	(22.00)	(30.00)	(30.00)	(30.00)	(30.00)
150 TBN carboxylate ² (mmol)	(30.00)	(30.00)	(30.00)	(22.00)	(22.00)	(22.00)	(22.00)
Mannich Base (wt%)	3.000	3.000	3.000	3.000	3.000	3.000	3.000
Antioxidants							
Diphenylamine (wt%)	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Hindered Phenol (wt%)	1.00	2.00	3.00	0.00	1.00	2.00	3.00
Molybdenum Oxysulfide (wt%)	0.20	0.20	0.20	0.20	0.20	0.20	0.20
Foam Inhibitors							
Foam Inhibitor	3ppm	3ppm	3ppm	3ppm	3ppm	3ppm	3ppm

² Prepared according to U.S. Published Patent Application No. 2007/0027043

B. Oils							
EXXON 150N (wt% of total base oil)	5	5	5	5	5	5	5
EXXON 600N (wt% of total base oil)	95	95	95	95	95	95	95
B2 Test Results							
TBN decrease (mg/KOH)	2.94	3.28	3.01	3.57	2.78	3.43	3.54
Pb (ppm)	40	10	26	24	19	28	41

The samples in the comparative examples (Comparative Examples 1-8) and samples in the examples of the invention (Examples 1-7) were evaluated for Total Base Number (TBN) decrease and lead corrosion which is measured as parts per million of lead found in the oil (i.e., pb ppm).

Higher numbers for TBN decrease indicate greater depletion of the base in the oil and are considered less favorable. Similarly, higher numbers for pb (ppm) indicate greater lead corrosion and are considered less favorable. An oil for extended use in a locomotive diesel engine will ideally retain TBN and not show corrosion against lead.

B2-7 Results

Based upon the results of the test it is evident that the lubricating oil compositions of the invention Examples 1-7 exhibit lower numbers for TBN decrease, thus indicating that the base in the lubricating oil is not depleted as much as in the Comparative Examples. In particular, when Examples 1-7 are compared to Comparative Examples 1-8, TBN decrease has improved by more than or equal to 30%.

Additionally, lead corrosion has decreased in the samples of the oils that are Examples 1-7. The amount of lead corrosion is low, especially when compared to the lead corrosion results of the oils that are Comparative Examples 1-8. Specifically, the lead corrosion measurements of Examples 1-7 (of the invention) show lead measurements that 10-15% of the measurements for the Comparative Examples.

The lubricating oil compositions, comprising at least two carboxylate detergents, show a significant improvement with regard to both TBN retention and lead corrosion over oils which do not contain the carboxylates employed in the present invention.

WHAT IS CLAIMED IS:

1. A lubricating oil additive composition comprising
 - a. a first carboxylate detergent having a TBN of the actives of greater than about 200 to about 400;
 - b. a second carboxylate detergent having a TBN of the actives of greater than about 60 to about 200; and
 - c. at least one polyalkenyl succinimide.
2. The lubricating oil additive composition of Claim 1 wherein the polyalkenyl succinimide is a polyisobutenyl succinimide.
3. A lubricating oil composition comprising
 - a. a major amount of oil of lubricating viscosity;
 - b. a first carboxylate detergent having a TBN of the actives of greater than about 200 to about 400;
 - c. a second carboxylate detergent having a TBN of the actives of greater than about 60 to about 200; and
 - d. at least one polyalkenyl succinimide.
4. The lubricating oil composition of Claim 3 wherein the lubricating oil composition is used as a railroad engine oil.
5. A method for operating a diesel locomotive engine comprising lubricating said diesel locomotive engine with a lubricating oil composition comprising
 - a. a major amount of an oil of lubricating viscosity; and
 - b. a first carboxylate detergent having a TBN of the actives of greater than about 200 to about 400;
 - c. a second carboxylate detergent having a TBN of the actives of greater than about 60 to about 200; and
 - d. at least one polyalkenyl succinimide.

6. A method for operating an inland marine engine comprising lubricating said inland marine engine with a lubricating oil composition comprising
 - a. a major amount of an oil of lubricating viscosity; and
 - b. a first carboxylate detergent having a TBN of the actives of greater than about 200 to about 400;
 - c. a second carboxylate detergent having a TBN of the actives of greater than about 60 to about 200; and
 - d. at least one polyalkenyl succinimide.
7. A method of improving TBN retention comprising lubricating an engine with a lubricating oil composition having
 - a. a major amount of an oil of lubricating viscosity;
 - b. a first carboxylate detergent having a TBN of the actives of greater than about 200 to about 400;
 - c. a second carboxylate detergent having a TBN of the actives of greater than about 60 to about 200; and
 - d. at least one polyalkenyl succinimide.