A lubricant additive composition comprising (a) a carboxylated detergent-dispersant obtained by (i) neutralizing alkylphenols using an alkaline earth base in the presence of at least one carboxylic acid that contains from one to four carbon atoms but in the absence of alkali base, dialcohol, and monoalcohol, forming an intermediate product, then (ii) carboxylating the intermediate product using carbon dioxide so that at least 20 mole percent of the original alkylphenol starting material has been converted to single aromatic-ring hydrocarbyl salicylate; and (b) an overbased, non-sulfonate-containing detergent such as, for instance, a hydrocarbyl phenate-carboxylate; a medium overbased salicylate having a total base number of about 50 to 170; a high overbased salicylate having a total base number greater than 170; or an overbased sulfurized hydrocarbyl phenate of alkaline earth metals; and combinations and mixtures thereof. Also provided for are additive packages and finished lubricating oil compositions comprising the same. The compositions of this invention reduce sludge and contaminant formation, especially in low and medium speed diesel engines and in marine diesel engines.
CARBOXYLATED DETECTING-DISPERSANT-CONTAINING COMPOSITIONS HAVING IMPROVED PROPERTIES IN LUBRICATION OILS

FIELD OF THE INVENTION

This invention is directed, in part, to novel lubricant additive compositions comprising an unsulfurized, alkali metal-free, carboxylated detergent-dispersant, as well as additive packages and finished oil compositions comprising the same. The compositions, which combine the carboxylated detergent-dispersant with overbased, non-sulfonate-containing detergents, exhibit increased control of deposits in internal combustion engines, especially diesel engines, and most especially heavy marine and powerplant diesel engines compared to conventional compositions. This invention is also directed, in part, to methods for preparing novel additive compositions including the carboxylated detergent-dispersant and overbased non-sulfonate-containing detergents.

REFERENCES

The following references are cited in this application as superscript numbers:


All of the above references are herein incorporated by reference in their entirety to the same extent as if each individual publication or patent was specifically and individually indicated to be incorporated by reference in its entirety.

STATE OF THE ART

Contamination of lubricating oils, particularly for lubrication of internal combustion engines operating under severe conditions such as high blow-by gases or for engines operating on poor quality fuels is a recognized problem in the industry. Lubricating oils contaminated with unburned residues lead to black paint deposits in piston undercrows, as well as deposits and dirt in cam boxes and crankcases, in diesel engines. The deposit and contamination problems occur with four stroke and two stroke engines.

Marine engines and power plant diesels typically operate on residual bunker fuel with high sulfur and asphaltene content. Such fuels may contaminate lubricating oils either by leakage of the raw fuel or through blow-by gases entering the crankcase and causing dirt and deposits. Contamination of lubricating oil in such a way makes the engine and oil highly prone toward forming deposits, often called black sludge or black paint. Such sludge, in turn, causes numerous mechanical and cosmetic problems including sticky deposits, undercrown deposits, and fuel pump plunger sticking.

Railroad engines and automotive engines are also prone to sludge deposits under typical conditions of operation which can cause decreased oil life or degradation in engine performance.

A key lubricating oil additive component used for controlling engine oil sludge is calcium carbonate alkyl salicylates. These components are widely used in the marine lubricant product area owing to their ability to control sludge and their excellent oxidation control performance. Salicylates are also finding increasing use in the product line areas of automotive, railroad and industrial oils. The references disclose various compositions either using phenates or using salicylates, that attempt to address the contamination issues.

A main difficulty with salicylate technology is the complexity of salicylate synthesis and the resulting high cost of manufacturing such materials. The current salicylate synthesis technology is based on the Kolbe-Schmidt reaction, which works best for alkali metal (Li, Na, K, Rb or Cs) salts of phenol. However, these salts are not desirable in the final lubricant additive so they must be removed by an aqueous process, and residual water is an undesirable contaminant as it collects acids which can corrode engine parts. Alternatively, with calcium salts of phenol the yields of salicylate are lowered such that the resulting products contain a lower content of salicylate than what might be desired.

Additives and their methods of manufacture have been disclosed 1, 2, 5, 6 for use in various lubricating oil compositions.

In view of the above, improvements in the ability of lubricating oil compositions to resist and reduce contamination and its adverse effects on engines are highly desirable.

SUMMARY OF THE INVENTION

This invention is directed to the novel and unexpected discovery that compositions including a carboxylated detergent-dispersant together with overbased non-sulfonate-containing detergents are highly effective in controlling the contamination of engines.

In addition, this invention is directed to the novel and unexpected discovery that the carboxylated detergent-dispersant has beneficial characteristics of both phenates and salicylates, thus obtaining the benefits of both types of
compounds, especially for diesel use, but without the difficulty, complexity, and expense of synthesis of salicylate compounds as described above. This invention is further directed to the novel and unexpected discovery that the carboxylated detergent-dispersant may be substituted on a 1:1 mass percentage basis for salicylates used in combination with other additives in lubricant additive compositions with increased performance characteristics but without the difficulty, complexity, and expense of synthesis of salicylate compounds.

[0019] Accordingly, in one of its composition aspects, this invention is directed to a lubricant additive composition comprising (a) a carboxylated detergent-dispersant obtained by (i) neutralizing alklyphenols using an alkylalane earth base in the presence of at least one carboxylic acid that contains from one to four carbon atoms but in the absence of alkali base, dialcohol, and monoaolcohol, forming an intermediate product, then (ii) carboxylating the intermediate product using carbon dioxide so that at least 20 mole percent of the original alklyphenol starting material has been converted to single aromatic-ring hydrocarbyl salicylate; and (b) at least one overbased, non-sulfonate-containing detergent.

[0020] Another aspect of the invention is directed to said lubricant additive compositions wherein the overbased, non-sulfonate-containing detergent is (a) a phenate, preferably a sulfurized hydrocarbyl phenate, more preferably sulfurized hydrocarbyl phenates of alkaline earth metals, most especially sulfurized hydrocarbyl phenates of alkaline earth metals wherein said alkaline earth metal is calcium; (b) a phenate-carboxylate, preferably a hydrocarbyl phenate-carboxylate, more preferably a hydrocarbyl phenate-stearate; (c) a salicylate, preferably a medium or high overbased salicylate; or (d) mixtures and combinations thereof.

[0021] Yet another aspect of the invention is directed to lubricant additive compositions comprising (a) a carboxylated detergent-dispersant obtained by (i) neutralizing alklyphenols using an alkylalane earth base in the presence of at least one carboxylic acid that contains from one to four carbon atoms but in the absence of alkali base, dialcohol, and monoaolcohol, forming an intermediate product, then (ii) carboxylating the intermediate product using carbon dioxide so that at least 20 mole percent of the original alklyphenol starting material has been converted to single aromatic-ring hydrocarbyl salicylate; and (b) at least one additive selected from the group consisting of (i) a hydrocarbyl phenate-carboxylate, wherein the mass ratio of carboxylated detergent-dispersant to hydrocarbyl phenate-carboxylate is from 0.5:1 to 6:1, preferably 0.75:1 to 3:1, more preferably 1.1:1 to 1.5:1; (ii) a medium overbased salicylate having a total base number of about 50 to 170, preferably 100 to 165, more preferably 120 to 160; (iii) a high overbased salicylate having a total base number greater than 170, preferably greater than 200, more preferably greater than 250; (iv) an overbased sulfurized hydrocarbyl phenate of alkaline earth metals, wherein the mass ratio of carboxylated detergent-dispersant to overbased sulfurized hydrocarbyl phenate is from 0.5:1 to 6:1, preferably 0.67:1 to 3:1, more preferably 0.75:1 to 2:1; and (v) combinations and mixtures thereof.

[0022] It has also been discovered that when the carboxylated detergent-dispersant is used with high or medium overbased salicylates, control of deposits is greatly increased. Furthermore, compositions including the combination of carboxylated detergent-dispersant and hydrocarbyl phenate-carboxylate alone, exhibit an unexpected increase in control of contaminants without the presence of the more expensive overbased sulfurized hydrocarbyl phenate of alkaline earth metals.

[0023] Another aspect of this invention is directed to additive packages or concentrates comprising compositions of sufficient quantities of carboxylated detergent-dispersant; overbased hydrocarbyl phenate-carboxylate; medium overbased salicylate; high overbased salicylate; and overbased sulfurized hydrocarbyl phenate of alkaline earth metals described above so as to have a TBN of greater than 170. Such additive packages or concentrates can be added in effective amounts to an oil of lubricating viscosity to form a finished oil composition having a TBN of from 0.1 to 100, preferably from 5 to 80, most preferably from 20 to 60. Accordingly, the finished oil compositions of this invention contain the additive packages as described above upon further blending with an oil of lubricating viscosity.

DETAILED DESCRIPTION OF THE INVENTION

[0024] In its broadest aspect, the present invention involves a carboxylated detergent-dispersant useful for improving the detergency power of an overbased non-sulfonate-containing detergent additive in a lubricating oil.

[0025] Prior to discussing the invention in further detail, the following terms will be defined:

[0026] Definitions

[0027] As used herein the following terms have the following meanings unless expressly stated to the contrary:

[0028] The term “hydrocarbyl” means an alkyl or alkenyl group. The term “metal” means alkali metals, alkaline earth metals, or mixtures thereof.

[0029] The term “sulfonate” means a hydrocarbon in which a hydrogen atom has been replaced with the —SO$_3$X group, where X is a metallic ion or alkyl radical.

[0030] The term “alkaline earth metal” means calcium, barium, magnesium, strontium, or mixtures thereof.

[0031] The term “hydrocarbyl phenol” means a phenol group having one or more hydrocarbyl substituents; at least one of which has a sufficient number of carbon atoms to impart oil solubility to the phenol.

[0032] The term “alkylphenol” means a phenol group having one or more alkyl substituents, wherein at least one of the alkyl substituents has a sufficient number of carbon atoms to impart oil solubility to the phenol.

[0033] The term “phenate” means a metal salt of a phenol.

[0034] The term “hydrocarbyl phenate” means a metal salt of a hydrocarbyl phenol.

[0035] The term “alkaline earth metal alkylphenate” means an alkaline earth metal salt of an alkylphenol.

[0036] The term “long-chain carboxylic acid” means a carboxylic acid having an alkyl group having an average carbon number of from 13 to 28. The alkyl group may be linear, branched, or mixtures thereof.
The term “stearic acid” means a long-chain carboxylic acid, wherein the carbon number of the acid is predominately 18.

The term “phenate-carboxylate” means a phenate that has been treated with a long-chain carboxylic acid, or anhydride or salt thereof.

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

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

The term “alkaline earth metal single aromatic-ring alkysalicylate” means an alkaline earth metal single aromatic-ring hydrocarbyl salicylate wherein the hydrocarbyl group is an alkyl group.

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

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

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

Accordingly, in one of its composition aspects, this invention is directed to a lubricating oil composition containing (a) an overbased phenate, and (b) a carboxylated detergent-dispersant obtained by (i) neutralizing alklyphenols using an alkaline earth base in the presence of at least one carboxylic acid that contains from one to four carbon atoms but in the absence of alkali base, dialcohol, and monoalkohol, forming an intermediate product, then (ii) carboxylating the intermediate product using carbon dioxide so that at least 20 mole percent of the original alklyphenol starting material has been converted to single aromatic-ring hydrocarbyl salicylate. Preferably, the overbased phenate is a hydrocarbyl substituted phenate, more preferably a sulfurized hydrocarbyl phenate of alkaline earth metals, most preferably a sulfurized hydrocarbyl calcium phenate.

Where the carboxylated detergent-dispersant is used together with an overbased phenate, the ratio of the mass percentages of carboxylated detergent-dispersant to phenate in the finished lubricating oil will be in the range of from 0.5:1 to 6:1, preferably from 0.67:1 to 3:1, and more preferably from 0.75:1 to 2:1. Methods of producing overbased phenates are described in U.S. Pat. No. 4,514,313, which is incorporated by reference into this application.

In another of its composition aspects, this invention is directed to a lubricating oil composition containing (a) an overbased phenate-carboxylate, and (b) a carboxylated detergent-dispersant obtained by (i) neutralizing alklyphenols using an alkaline earth base in the presence of at least one carboxylic acid that contains from one to four carbon atoms but in the absence of alkali base, dialcohol, and monoalkohol, forming an intermediate product, then (ii) carboxylating the intermediate product using carbon dioxide so that at least 20 mole percent of the original alklyphenol starting material has been converted to single aromatic-ring hydrocarbyl salicylate. Preferably, the overbased phenate-carboxylate is a hydrocarbyl substituted phenate-carboxylate, more preferably a hydrocarbyl phenate-stearate.

Where the carboxylated detergent-dispersant is used together with an overbased phenate-carboxylate, the ratio of the mass percentages of carboxylated detergent-dispersant to phenate-carboxylate in the finished lubricating oil will be in the range of from 0.5:1 to 6:1, preferably, from 0.75:1 to 3:1, and more preferably from 1:1 to 1.5:1. Methods for producing phenate-carboxylate are disclosed in References 1 and 2, and in U.S. Pat. Nos. 5,433,871 and 5,942,476 which are also incorporated by reference into this application.

The present invention has also been discovered to reduce the deposition of sludge and other contaminants where the carboxylated detergent-dispersant is used in combination with high overbased salicylate additives having base numbers above 170, preferably above 200, and more preferably above 250. The effect of the carboxylated detergent-dispersant on deposit and contamination control is seen where the mass ratio of carboxylated detergent-dispersant to high overbased salicylate is from 0.25:1 to 2:1, preferably from 0.4:1 to 1.5:1, most preferably from 0.75:1 to 1:3:1, and optionally where the carboxylated detergent-dispersant is used to replace the high overbased salicylate on a 1:1 basis.

Medium overbased salicylates having base numbers in the range of about 50 to about 170, preferably from about 100 to about 165, and more preferably from about 120 to 160, may be present where the mass ratio of carboxylated detergent-dispersant to medium overbased salicylate is from 0.25:1 to 2:1, preferably from 0.4:1 to 1.5:1, most preferably from 0.75:1 to 1:3:1, and optionally where the carboxylated detergent-dispersant is used to replace the medium overbased salicylate on a 1:1 basis.

Methods for producing high and medium overbased salicylates are well known to the art, and appear, for example, in U.S. Pat. No. 4,810,398, and GB Patents 1,146,925; 790,473; and 786,167 which are incorporated by reference into this application.

The carboxylated detergent-dispersant, overbased phenate-carboxylates, medium and high overbased salicylates, and overbased phenates will be added to lubricating oils in quantities sufficient to achieve the desired base number for the final oil composition. On a weight percent basis, the weight percent of these components in the final lubricating oil in which they are used will typically range from about 2 weight percent for low base number lubricating oils, to 30 weight percent for higher base number lubricating oils.
I. Preparation of the Carboxylated Detergent-Dispersant

A. Neutralization Step

In the first step, hydrocarbyl phenols are neutralized using an alkaline earth metal base in the presence of at least one C1 to C4 carboxylic acid. This reaction is carried out in the absence of alkali base, and in the absence of dialcohol or mono alcohol.

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. Preferably, the hydrocarbyl group is alkyl, and the linear alkyl radical contains 12 to 40 carbon atoms, more preferably 18 to 30 carbon atoms. The branched hydrocarbyl radical is preferably alkyl and contains at least nine carbon atoms, preferably 9 to 24 carbon atoms, more preferably 10 to 15 carbon atoms.

The use of an alkylphenol containing at least 35% 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 metal base.

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 metal base, since the phenol function is practically devoid of steric hindrance.

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 metal 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.

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

The C1 to C4 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 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 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 mbar).

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

1) alkaline earth metal 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.

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).

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

B. Carboxylation Step

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 is converted to single aromatic-ring hydrocarbyl salicylate (measured as salicylic acid by potentiometric determination). It must take place under pressure in order to avoid any decarboxylation of the single aromatic-ring hydrocarbyl salicylate that forms.

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

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

C. Carboxylated Detergent-Dispersant Product

The carboxylated detergent-dispersant formed by this method can be characterized by its unique composition, with much more hydrocarbyl phenol and alkaline earth metal single aromatic-ring hydrocarbyl salicylate than produced by other routes. When the hydrocarbyl group is an
alkyl group, that detergent-dispersant has the following composition;

(a) from 40% to 60% alkylphenol,

(b) from 10% to 40% alkaline earth metal alkylphenate, and

(c) from 20% to 40% alkaline earth metal single aromatic-ring alkylsalicylate.

The preceding process is more fully described in U.S. Pat. No. 6,162,770, which is incorporated by reference into this application.

Unlike alkaline earth alkylsalicylates produced by other process, this detergent-dispersant composition can be characterized by having only minor amounts of an alkaline earth double aromatic-ring alkylsalicylates. The molar ratio of single aromatic-ring alkylsalicylate to double aromatic-ring alkylsalicylate is at least 8:1.

Preferably, the BN of the detergent-dispersant should be from 100 to 150, more preferably from 110 to 130.

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

The carboxylated detergent-dispersant formed by the process described above has been found to provide improved high temperature deposit control performance when combined with overbased, non-sulfonate containing detergents.

Detergents help control varnish, ring zone deposits, and rust by keeping insoluble particles in colloidal suspension. Metal-containing (or ash-forming detergents) function both as detergents to control deposits, and as acid neutralizers or rust inhibitors, thereby reducing wear and corrosion and extending engine life. Detergents generally comprise a polar head with a long hydrophobic tail; with the polar head comprising a metal salt of an organic compound. The salts may contain a substantially stoichiometric amount of the metal in which case they are usually described as normal or neutral salts, and would typically have a total base number (as measured by ASTM D2896) of from 0 to 10. It is possible to include large amounts of a metal base by reacting an excess of a metal compound such as an oxide or hydroxide with an acidic gas such as carbon dioxide to form an overbased detergent. Such overbased detergents may have a total base number of 15 to 30 (low overbased), or typically 50 to 170 (medium overbased), or optionally above 170 (high overbased). Detergents that may be used include overbased phenates and sulfurized phenates; overbased phenate-carboxylates; and medium and high overbased salicylates. Suitable metals include the alkali or alkaline earth metals, e.g., sodium, potassium, lithium, calcium, and magnesium. The most commonly used metals are calcium and magnesium, which may both be present in detergents used in a lubricant.

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

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

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

(a) neutralizing a sulfurized alkylphenol with an alkaline earth base in the presence of a dilution oil, a glycol, and halide ions, the glycol being present in the form of a mixture with an alcohol having a boiling point above 150° C.;

(b) removing alcohol, glycol, and water from the medium, preferably by distillation;

(c) removing sediment from the medium, preferably by filtration;

(d) carbonating the resultant medium with CO2 in the presence of halide ions; and

(e) removing alcohol, glycol, and water from the medium, preferably by distillation.

The alkaline earth bases useful in the above process include the oxides and hydroxides of barium, strontium, and calcium, particularly lime. Alcohols with a boiling point above 150° C. useful in the process include alcohols of C n to C 5, such as ethylhexanol, oxoalcohol, decylalcohol, tridecylalcohol; alkoxylalkohols such as 2-butoxyethanol, 2-butoxypropanol; and methyl ethers of dipropylene glycol. The amines useful in the process include polyamines, preferably polyvinylamines, particularly ethylenediamine, and aminooethers, particularly tris(3-oxa-6-amino-hexyl)amine. The glycols useful in the process include alkylene glycols, particularly ethylene glycol. The halide ions employed in the process are preferably Cl- ions which may be added in the form of ammonium chloride or metal chlorides such as calcium chloride or zinc chloride.

The dilution oils suitable for use in the above process include naphthenic oils and mixed oils and preferably paraffinic oils such as neutral 100 oil. The quantity of dilution oil used is such that the amount of oil in the final product constitutes from about 25% to about 65% by weight of the final product, preferably from about 30% to about 50%.
The process outlined above is more fully described in U.S. Pat. No. 4,514,313, which is incorporated by reference into this application.

IV. Preparation of Overbased Phenate-Carboxylates

The phenate-carboxylates used in the present invention are typically hydrocarbyl substituted phenate-carboxylates in which the hydrocarbyl substituent or substituents of the phenate are preferably one or more alkyl group, either branched or unbranched. Suitable alkyl groups contain from 4 to 50, preferably from 9 to 28 carbon atoms. Particularly suitable alkyl groups are C₃₋₁₂ groups derivable from propylene tetramer. The hydrocarbyl substituted phenate-carboxylates may be sulfurized or unsulfurized.

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

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

In the overbasing step, a mixture comprising hydrocarbyl phenate (which can be sulfurized or unsulfurized), at least one solvent, metal hydroxide, aqueous metal chloride, and an alkyl polyhydric alcohol containing from one to five carbon atoms is reacted with carbon dioxide under overbasing reaction conditions. Overbasing reaction conditions include temperatures of from 250 to 375°F at approximately atmospheric pressure.

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

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

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

The process outlined above is more fully described in U.S. Pat. No. 5,942,476, which is incorporated by reference into this application.

The preparation of medium and high overbased salicylates is well known in the art. Preferred salicylates include salts of polyvalent or monovalent metals, more preferably monovalent, most preferably calcium. As used herein, medium overbased is meant to include salicylates with a TBN of about 50 to 170. High overbased is meant to include salicylates with a TBN over 170.

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

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

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

For example, the alkylsalicylic acids may be treated with 4 equivalents of calcium in the form of Ca(OH)₂ with introduction of 1.6 equivalents of CO₂. The preparation of medium and overbased salicylates is more fully described in U.S. Pat. No. 4,810,398, and GB Patents 1,146,925; 790,473; and 786,167, which are incorporated by reference into this application.

The additive packages, concentrates, and lubricant compositions of this invention can further employ additives conventionally used in lubricating oil compositions for engines, and especially for low or medium speed diesel engines, and most especially for marine and powerplant diesel engines. Conventional additives include detergents, foam inhibitors, extreme pressure and antiwear agents, rust inhibitors, antioxidants, and similar materials.

Base Oil of Lubricating Viscosity

The lubricating oil, or base oil, used in such compositions may be mineral oil or synthetic oils of viscosity suitable for use in the crankcase of an internal combustion engine, such as gasoline engines and diesel engines, which include marine engines. Lubricating oils ordinarily have a viscosity of about 4 cSt to 32 cSt at 100°C. The lubricating oils may be derived from synthetic or natural sources. Mineral oil for use as the base oil in this invention includes paraffinic, naphthenic and other oils that are ordinarily used in lubricating oil compositions. Synthetic oils include both hydrocarbon synthetic oils and synthetic esters. Useful syn-
thetic hydrocarbon oils include liquid polymers of alpha olefins having the proper viscosity. Especially useful are the hydrogenated liquid oligomers of C₈ to C₁₂ alpha olefins such as 1-decene trimer. Likewise, alkyl benzenes of proper viscosity, such as didodecyl benzene, can be used. Useful synthetic esters include the esters of monocarboxylic acids and polycarboxylic acids, as well as monohydroxy alkanols and polyols. Typical examples are didodecyl adipate, pentacyrtritol tetracaprate, di-2-ethylhexyl adipate, dilaurylsebacate and the like. Complex esters prepared from mixtures of mono and dicarboxylic acids and mono and dihydroxy alkanols can also be used.

[0114] Blends of mineral oils with synthetic oils are also useful. For example, blends of 10 to 25% hydrogenated 1-trimer with 75 to 90% SUS 100°F viscosities of mineral oil gives an excellent lubricating oil base.

[0115] The oil may be suitable for lubrication without adjusting its viscosity, or viscosity may be adjusted by adding more or less viscous oils, such as bright stock. The lubricating oil base will typically comprise greater than 70% and typically over 80% by weight of the actual composition used in the engine for lubrication.

[0116] Lubricating oils for slow and medium speed diesel engines will typically be contaminated with a fuel oil that has a residual oil content. The fuel oil is typically a diesel fuel. Fuels oils can be divided into two main categories or groups—distillates and heavy fuels. Distillates consist of one or more distilled fractions. Heavy fuels are fuels that comprise at least a portion of the residual oil that remains after distillation fractions are separated from unrefined oil. The composition of the residual oil will vary with the composition of the pre-distillation starting oil, usually crude oil, and will vary with the distillation conditions. Residual oil is of a high molecular weight and high boiling point. Heavy oils can also include heavy distillates. The present invention is especially effective where the contaminant in the lubricating oil composition is heavy fuel. Heavy fuel is typical present in the lubricating oil base at from 0.1 to 10 wt%, often 0.3 to 5 wt%, and more frequently 0.5-3 wt%.

[0117] Other Additive Components

[0118] The following additive components are examples of some components that can be favorably employed in the compositions of the present invention. These examples of additives are provided to illustrate the present invention, but they are not intended to limit it:

[0119] (1) Metal detergents: sulfurized or unsulfurized alkyl or alkenyl phenates, sulfurized or unsulfurized metal salts of multi-hydroxy alkyl or alkenyl aromatic compounds, 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.

[0120] (2) Ashless dispersants: alkyl succinimides, alkenyl succinimides modified with other organic compounds, and alkenyl succinimides modified with boric acid, alkenyl succinimide ester.

[0121] (3) Oxidation inhibitors

[0122] (a) Phenol type oxidation inhibitors: 4,4'-methylen bis (2,6-di-t-butylphenol), 4,4'-bis(2,6-di-t-tert-butylphenol), 2,2'-methylene bis (4-methyl-6-t-butylphenol), 4,4'-butylidenedebis(3-methyl-6-t-butylphenol), 4,4'-isopropylidenedebis(2,6-di-t-butylphenol), 2,2'-methylenebis(4-methyl-6-nonylphenol), 2,2'-isobutyldenedebis(4,6-dimethylphenol), 2,2'-methylenebis(4-methyl-6-cyclohexylphenol), 2,6-di-t-butyl-4-methylphenol, 2,6-di-t-butyl-4-ethylphenol, 2,4-dimethyl-6-t-butylphenol, 2,6-di-t-butyl-4-(N,N-dimethylaminomethylphenol), 4,4'-diobis(2-methyl-6-t-butylphenol), 2,2'-diobis(4-methyl-6-t-butylphenol), bis(3-methyl-4-hydroxy-5-t-butylbenzyl)sulfide, and bis (3,5-di-t-butyl-4-hydroxybenzyl).

[0123] (b) Diphenylamine type oxidation inhibitor: alkylated diphenylamine, phenyl-o-naphthylamine, and alkylated-α-naphthylamine.

[0124] (c) Other types: metal dithiocarbamate (e.g., zinc dithiocarbamate), and methylenebis (dibutylthiuramdisulfide).

[0125] (d) Rust inhibitors (Anti-rust agents)

[0126] (a) Nonionic polyoxyethylene surface active agents: polyoxyethylene lauryl ether, polyoxyethylene higher alcohol ether, polyoxyethylene nonylphenyl ether, polyoxyethylene octylphenyl ether, polyoxyethylene octyl stearyl ether, polyoxyethylene oleyl ether, polyoxyethylene sorbitol monostearate, polyoxyethylene sorbitol mono-oleate, and polyethyleneglycol monoleate.

[0127] (b) Other compounds: stearic acid and other fatty acids, dicarboxylic acids, metal soaps, fatty acid amine salts, metal salts of high sulfuric acid, partial carboxylic acid ester of polyhydric alcohol, and phosphoric ester.


[0130] (7) Friction modifiers: fatty alcohol, fatty acid, amine, borated ester, and other esters.


[0132] (9) Viscosity index improvers: polyalkylacrylate type polymers, ethylene-propylene copolymers, styrene-isoprene copolymers, hydrogenated styrene-isoprene copolymers, polyisobutylene, and dispersant type viscosity index improvers.
Pour point depressants: polymethyl methacrylate.

Foam Inhibitors: alkyl methacrylate polymers and dimethyl silicone polymers.

Additive Concentrates

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. From 20% to 80% of the concentrate is organic diluent. Suitable organic diluents which can be used include mineral oil or synthetic oils, as described above in the section entitled “Base Oil of Lubricating Viscosity.”

Engine Lubricating Oil Composition

The compositions of the present invention are especially suited for use in high TBN lubricating oils that are suitable for use in low or medium speed diesel engines, especially marine and power plant diesel engines. Those lubricating oils typically comprise a fuel oil. Such a lubricating oil composition comprises a major part of a base oil of lubricating viscosity and an effective amount of the compositions of the present invention.

The present invention provides a method for significantly reducing deposition in low and medium speed diesel engines, comprising, lubricating the moving parts of the engine with a lubricating oil composition suitable for use in such an engine, the lubricating oil comprising a fuel oil with a residual oil content characterized in that the lubricating oil composition further comprises (a) a carboxylated detergent-dispersant obtained by (i) neutralizing alkylphenols using an alkaline earth base in the presence of at least one carboxylic acid that contains from one to four carbon atoms but in the absence of alkali base, dialcohol, and monoalcohol, forming an intermediate product, then (ii) carboxylating the intermediate product using carbon dioxide so that at least 20 mole percent of the original alkylphenol starting material has been converted to single aromatic-ring hydrocarboxyl salicylate; and (b) at least one overbased, non-sulfonate-containing detergent.

PREFERABLY, the overbased, non-sulfonate-containing detergent of the method above is (a) a phenate, preferably a sulfonated hydrocarboxyl phenate, more preferably sulfonated hydrocarboxyl phenates of alkaline earth metals, most especially sulfonated hydrocarboxyl phenates of alkaline earth metals wherein said alkaline earth metal is calcium; (b) a phenate-carboxylate, preferably a hydrocarboxyl phenate-carboxylate, more preferably a hydrocarboxyl phenate-carboxylate, (c) a salicylate, preferably a medium or high overbased salicylate; or (d) mixtures and combinations thereof.

The finished lubricating oil compositions of the present invention will have a TBN in the range of 0.1 to 100 mg KOH/g, preferably from 5 to 80, more preferably from 20 to 60. Where the composition is to be used in a 4-stroke trunk piston engine, the TBN is preferably in the range of 5-70, more preferably 5-60 mg KOH/g. Where it is to be used in a 2-stroke cross-head engine, and particularly for the crankcase, the TBN is preferably 0.1-15 more preferably 1 to 10 mg KOH/g.

The lubricating oil composition will typically be a monograde lubricant having an SAE grade of from SAE 10 to SAE 50, more typically SAE 30 to SAE 40 oil. Multigrade oils can be used with the present invention.

EXAMPLES

The invention will be further illustrated by the 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.

As used herein, the following abbreviations have the following meanings. If not defined, the abbreviation will have its art recognized meaning.

Total Base Number (TBN) and Base Number (BN): TBN’s and BN’s of the test compositions were measured by ASTM method D2896. The base number contribution of individual components can be calculated based on the mass percents.

KHT test is a lubrication industry bench test that measures the detergency and thermal and oxidative stability of a lubricating oil. Detergency and thermal and oxidative stability are three performance areas that are generally accepted in the industry as being essential to satisfactory overall performance of a lubricating oil. In performing the KHT test, the oil is pumped upwards through a glass tube that is placed inside an oven at a certain temperature. Air is introduced in the oil stream before the oil enters the glass tube, and flows upward (cocurrent) with the oil. Evaluations of Marine Trunk Piston Engine Oils (TPEOs) are often conducted at temperatures between 300-330 Degrees Celsius. The test result is determined by comparing the amount of lacquer deposited on the glass test tube to a rating scale ranging from 1.0 (very black) to 10.0 (perfectly clean). The result is determined in multiples of 0.5. At a certain temperature the oil becomes so poor that it the tube is blocked. (Blockage is deposition below a 1.0 result, in which case the lacquer is very thick and dark but still allows fluid flow, although at a rate that is completely unsatisfactory for a useable oil).

The KHT test differs from the ISOT test in that ISOT looks at bulk oxidation and degradation only, while KHT looks at detergency as well. Furthermore, ISOT is more sensitive to alkylphenols.

Mass Percent (m %) gives the mass percent of the component in the finished lubricating oil. Mass percent is approximately the same as weight percent, as is well known in science, and the two terms are frequently used interchangeably. Total m % is the mass percent of all additives listed in the lubricating oil composition tested.

Medium Over Based (MOB), having a base number of from 50 to 170.

High Over Based (HOB), having a base number above 170.

High Viscosity Index (HVI), refers to base stocks commercially available.

Society for Automotive Engineers (SAE), SAE 30 and similar designations refer to the SAE grades for lubricating oils.
The formulations include other components as described above that are used in the lubricating oils tested.

The examples reported in the tables below compare the carboxylated detergent-dispersant-containing compositions with standard salicylate-containing and other compositions using the following components:

I. Carboxylated Detergent-Dispersant

The carboxylated detergent-dispersant was prepared as follows:

A. Neutralization

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

DPP: 89% para and 5.5% ortho

Linear alkylphenol: 39% para and 53% ortho.

The agitator was started up and the reaction mixture was heated to 65°C, at which temperature 158 grams of slaked lime Ca(OH)2 (i.e. 2.135 moles) and 19 g of a mixture (50/50 by weight) of formic acid and acetic acid were added. The reaction medium underwent further heating to 120°C at which temperature the reactor was placed under a nitrogen atmosphere, then heated up to 165°C and then the nitrogen introduction was stopped. Distillation of water commenced at this temperature.

The temperature was increased to 240°C and the pressure was reduced gradually below atmospheric until an absolute pressure of 5,000 Pa (50 mbars) was obtained. The reaction mixture was kept for five hours under the preceding conditions. The reaction mixture was allowed to cool to 180°C, then the vacuum was broken under a nitrogen atmosphere and a sample was taken for analysis. The total quantity of distillate obtained was about 120 cm3; demixing took place in the lower phase (66 cm3 being water).

B. Carboxylation

The product obtained in Step (A) was transferred to a 3.6-liter autoclave and heated to 180°C. At this temperature, scavenging of the reactor with carbon dioxide (CO2) was commenced and continued for ten minutes. The amount of CO2 used in this step was in the order of 20 grams.

After the temperature had been raised to 200°C, the autoclave was closed, leaving a very small leak, and the introduction of CO2 was continued so as to maintain a pressure of 3.5×105 Pa (3.5 bars) for 5 hours at 200°C. The amount of CO2 introduced was in the order of 50 grams. After the autoclave had been cooled to 165°C, the pressure was restored to atmospheric and the reactor was then purged with nitrogen.

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

II. Phenate

The sulfurized alkylphenate was prepared as follows:

(A) Sulfurization, Dehydration, and Neutralization

A reaction vessel is charged with the following under constant stirring:

(d) calcium chloride, zinc chloride or ammonium chloride; and

dilution oil.

The vessel is heated to 160°C, and a mixture of ethylene glycol and ethylhexanol is slowly added over a period of 80 minutes under a slightly reduced pressure of about 960×10^2 Pa.

The reaction medium is then allowed to stand for 1 hour at 165°C, under a slightly reduced pressure of about 930×10^2 Pa and a distillate, D1, is collected.

(B) Carbonation

Carbonation is carried out for 100 minutes at a temperature of from about 165°C, to about 175°C, at atmospheric pressure. The remaining dilution oil is then added.

(C) Removal of Alcohol, Glycol, and Water

Alcohol, glycol, and water are distilled off by heating at 190°C, for 1 hour while gradually applying a vacuum until the pressure reaches 66.5×10^2 Pa.

Stripping with nitrogen is then carried out for 1 hour at 190°C, and a distillate, D2, is collected.

(D) Removal of Sediment

The product medium is then filtered to remove sediment.

III. Phenate-Stearate

The phenate-stearate was prepared as follows:

To a 1 gallon stainless steel reactor was charged:

| 903 grams | 100 Neutral oil, |
| 0.5 ml | Antifoam, |
| 1415 grams | Decyl alcohol, |
| 158 grams | Ethylene glycol, |
| 642 grams | Lime, |
| 1126 grams | Dodecylphosphate, |
| 722 grams | Molen stearic acid, |
| 34 grams | Solid calcium chloride dihydrate |

at approximately room temperature (nominally 75°F). This mixture was heated to 150°F over approximately fifteen minutes with agitation. When the reactor reached 150°F, an additional 642 grams of lime was added to the
reactor. The reactor was then sealed, placed under slight vacuum (13.7 psia) and heated to 300°F over approximately one hour. When the reactor reached 290°F, 187 grams of molten sulfur were charged via a valved port on the reactor. When the reactor reached 300°F, 113 grams of ethylene glycol were added over 1.5 hours at approximately 1.26 grams/minute. As soon as this ethylene glycol charge was started, the temperature of the reactor was heated to 360°F over approximately 1.5 hours. When the reactor reached 350°F, the vacuum was increased to atmospheric pressure (14.7 psia) and was held at 350°F while 28 grams of CO₂ was added over thirty minutes at approximately 0.93 grams/minute. Immediately after starting this CO₂ addition, 180 grams of ethylene glycol was added over three hours at approximately 1.0 grams/minute. When this charge of CO₂ was completed, an additional 406 grams of CO₂ was added over three hours at approximately 2.26 grams/minute. When this CO₂ addition was complete, the pressure in the reactor was reduced to between 0.5 and 1.0 psia over 15 minutes and then the reactor was heated to 400°F over thirty minutes. The reactor was held at 400°F and 0.6 psia for thirty minutes. The pressure in the reactor was then increased to atmospheric pressure with nitrogen and the reactor allowed to cool to approximately room temperature. The contents of the reactor were drained to yield 2916 grams of crude product with a TBN of 426. This material was diluted with 100N oil and vacuum filtered with the aid of filter aid to afford a product with 383 TBN, CO₂ content of 10.9%, and viscosity of 496 cSt at 100°F.

Several different types of lubricating oil compositions were tested, with various base oils, SAE grades, base numbers, and compositions.

<table>
<thead>
<tr>
<th>TABLE 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>40 BN, SAE 40, Marine TPEOs made with Esso HVI basestocks (Esso 600 Neutral, Esso 150 Neutral, Esso 150 BS)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Example:</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Components</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbonylated detergent-dispersant</td>
<td>16.26</td>
<td></td>
</tr>
<tr>
<td>MOB Salicylate</td>
<td>—</td>
<td>16.37</td>
</tr>
<tr>
<td>Phenate</td>
<td>7.93</td>
<td>5.59</td>
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<tr>
<td>Dispersant</td>
<td>2.00</td>
<td>2.00</td>
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<tr>
<td>Zn Dithiophosphate</td>
<td>0.47</td>
<td>0.47</td>
</tr>
<tr>
<td>Foam Inhibitor</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Total m%</td>
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</tr>
<tr>
<td>Test Results:</td>
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</tr>
<tr>
<td>KHT @ 310 C Rating</td>
<td>9.0</td>
<td>7.5</td>
</tr>
<tr>
<td>KHT @ 320 C Rating</td>
<td>8.5</td>
<td>6.5</td>
</tr>
<tr>
<td>KHT @ 330 C Rating</td>
<td>7.5</td>
<td>Blocked</td>
</tr>
</tbody>
</table>

Examples 3 and 4 compare carbonylated detergent-dispersant/phenate-stearate to MOB salicylate/phenate-stearate additives. Examples 5 and 6 compare carbonylated detergent-dispersant/phenate to MOB salicylate/phenate additives.

<table>
<thead>
<tr>
<th>TABLE 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>40 BN, SAE 40, Marine TPEOs made with Esso HVI basestocks (Esso 600 Neutral, Esso 150 Neutral, Esso 150 BS)</td>
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</tbody>
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<table>
<thead>
<tr>
<th>Example:</th>
<th>3</th>
<th>4</th>
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<th>M %</th>
<th>6</th>
<th>M %</th>
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<tbody>
<tr>
<td>Components</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbonylated detergent-dispersant</td>
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<td>8.13</td>
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<td></td>
<td></td>
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<tr>
<td>MOB Salicylate</td>
<td>—</td>
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<tr>
<td>Phenate</td>
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<td></td>
<td></td>
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<tr>
<td>Phenate-Stearate</td>
<td>7.56</td>
<td>6.85</td>
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<td>Dispersant</td>
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<td>0.98</td>
<td>0.98</td>
<td>0.98</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn Dithiophosphate</td>
<td>0.47</td>
<td>0.47</td>
<td>0.47</td>
<td>0.47</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Foam Inhibitor</td>
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<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
<td></td>
<td></td>
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<tr>
<td>Total m%</td>
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<td>16.43</td>
<td>21.52</td>
<td>20.37</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Test results:</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KHT @ 310 C Rating</td>
<td>9.0</td>
<td>7.5–8.0</td>
<td>7.5</td>
<td>7.0–7.5</td>
<td></td>
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</tr>
<tr>
<td>KHT @ 320 C Rating</td>
<td>8.0</td>
<td>Blocked</td>
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<td>4.5</td>
<td></td>
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<tr>
<td>KHT @ 330 C Rating</td>
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<td>Blocked</td>
<td>6.0</td>
<td>Blocked</td>
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</table>

Examples 7 and 8 compare carbonylated detergent-dispersant/phenate-stearate to MOB salicylate/phenate-stearate additives. Examples 9 and 10 compare carbonylated detergent-dispersant/phenate to MOB salicylate/phenate additives.
### Table 3

<table>
<thead>
<tr>
<th>Example:</th>
<th>m%</th>
<th>m%</th>
<th>m%</th>
<th>m%</th>
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<tbody>
<tr>
<td>Components</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carboxylated detergent-dispersant</td>
<td>12.20</td>
<td>12.20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MOB Salicylate</td>
<td>6.30</td>
<td>5.21</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenate-Stearate</td>
<td>0.98</td>
<td>0.98</td>
<td>0.98</td>
<td>0.98</td>
</tr>
<tr>
<td>Dispersant</td>
<td>0.47</td>
<td>0.47</td>
<td>0.47</td>
<td>0.47</td>
</tr>
<tr>
<td>Foam Inhibitor</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
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<tr>
<td>Total m%:</td>
<td>19.99</td>
<td>18.90</td>
<td>23.61</td>
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<tr>
<td>Test results:</td>
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</tr>
<tr>
<td>KHT @ 310 C Rating</td>
<td>8.5</td>
<td>8.0</td>
<td>8.0</td>
<td>7.0</td>
</tr>
<tr>
<td>KHT @ 320 C Rating</td>
<td>8.5</td>
<td>Blocked</td>
<td>8.0</td>
<td>6.0</td>
</tr>
<tr>
<td>KHT @ 330 C Rating</td>
<td>6.5</td>
<td>Blocked</td>
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</tr>
</tbody>
</table>

### Table 5

<table>
<thead>
<tr>
<th>Example:</th>
<th>m%</th>
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<th>m%</th>
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</thead>
<tbody>
<tr>
<td>Components</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Carboxylated detergent-dispersant</td>
<td>12.20</td>
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<td>6.10</td>
</tr>
<tr>
<td>MOB Salicylate</td>
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<td>Zn Dithiophosphate</td>
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<td>0.47</td>
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<tr>
<td>Foam Inhibitor</td>
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<td>Total m%:</td>
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<tr>
<td>KHT @ 310 C Rating</td>
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<td>6.5-7.0</td>
<td>8.0</td>
</tr>
<tr>
<td>KHT @ 320 C Rating</td>
<td>7.5-8.0</td>
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</tr>
</tbody>
</table>

TABLE 7-continued

<table>
<thead>
<tr>
<th>BN, SAE 30, Marine TPEOs made with Exxon HVI basestocks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example:</td>
</tr>
<tr>
<td>m%</td>
</tr>
<tr>
<td>Phenate-Stearate</td>
</tr>
<tr>
<td>Dispersant</td>
</tr>
<tr>
<td>Zn Dithiophosphate</td>
</tr>
<tr>
<td>Foam Inhibitor</td>
</tr>
<tr>
<td>Total m%:</td>
</tr>
</tbody>
</table>
Test results:
KHT @ 310 C Rating | 6.0 | 2.5 | 5.0 | 2.5 |
KHT @ 320 C Rating | 1.0 | Blocked | 1.0 | Blocked |
KHT @ 330 C Rating | Blocked | Blocked | Blocked | Blocked |


TABLE 8

<table>
<thead>
<tr>
<th>40 BN, SAE 30, Marine TPEOs made with Esso HVI basestocks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example:</td>
</tr>
<tr>
<td>m%</td>
</tr>
<tr>
<td>Components</td>
</tr>
<tr>
<td>Carboxylated detergent-dispersant</td>
</tr>
<tr>
<td>MOB Salicylate</td>
</tr>
<tr>
<td>Phenate-Stearate</td>
</tr>
<tr>
<td>Dispersant</td>
</tr>
<tr>
<td>Zn Dithiophosphate</td>
</tr>
<tr>
<td>Foam Inhibitor</td>
</tr>
<tr>
<td>Total m%:</td>
</tr>
</tbody>
</table>
Test results:
KHT @ 310 C Rating | 9.0 |
KHT @ 320 C Rating | 7.0–7.5 |
KHT @ 330 C Rating | Blocked |

[0203] Examples 27 and 28 compare carboxylated detergent-dispersant/phenate-stearate to MOB salicylate/phenate-stearate mixtures.

TABLE 9

<table>
<thead>
<tr>
<th>55 BN, SAE 40, Marine TPEOs made with Esso HVI basestocks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example:</td>
</tr>
<tr>
<td>m%</td>
</tr>
<tr>
<td>Components</td>
</tr>
<tr>
<td>Carboxylated detergent-dispersant</td>
</tr>
<tr>
<td>MOB Salicylate</td>
</tr>
<tr>
<td>Phenate-Stearate</td>
</tr>
</tbody>
</table>

[0204] Examples 29 and 30 compare carboxylated detergent-dispersant/phenate-stearate to MOB salicylate/phenate-stearate mixtures.

TABLE 10

<table>
<thead>
<tr>
<th>30 BN, SAE 30, Marine TPEOs made with Esso HVI basestocks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example:</td>
</tr>
<tr>
<td>m%</td>
</tr>
<tr>
<td>Components</td>
</tr>
<tr>
<td>Carboxylated detergent-dispersant</td>
</tr>
<tr>
<td>MOB Salicylate</td>
</tr>
<tr>
<td>Phenate-Stearate</td>
</tr>
<tr>
<td>Dispersant</td>
</tr>
<tr>
<td>Zn Dithiophosphate</td>
</tr>
<tr>
<td>Foam Inhibitor</td>
</tr>
<tr>
<td>Total m%:</td>
</tr>
</tbody>
</table>
Test results:
KHT @ 310 C Rating | 9.0 |
KHT @ 320 C Rating | 8.0 |
KHT @ 330 C Rating | Blocked |

[0205] From the foregoing description, various modifications and changes in the above-described invention will occur to those skilled in the art. All such modifications coming within the scope of the appended claims are intended to be included therein.

What is claimed is:

1. A lubricant additive composition comprising:

(a) a carboxylated detergent-dispersant obtained by:

(i) neutralizing alkylphenols using an alkaline earth base in the presence of at least one carboxylic acid that contains from one to four carbon atoms but in the absence of alkaline base, dialcohol, and monocalcohol, forming an intermediate product; and

(ii) carboxylating the intermediate product using carbon dioxide so that at least 20 mole percent of the original alkylphenol starting material has been converted to alkaline earth metal single aromatic-ring hydrocarbyl salicylate; and,
(b) at least one overbased, non-sulfonate-containing detergent.

2. The lubricant additive composition according to claim 1 wherein said overbased, non-sulfonate-containing detergent is selected from the group consisting of:

(a) phenates;
(b) phenate-carboxylates;
(c) salicylates;
and mixtures and combinations thereof.

3. The lubricant additive composition according to claim 1 wherein said overbased, non-sulfonate-containing detergent is selected from the group consisting of:

(a) sulfurized hydrocarbyl phenates;
(b) hydrocarbyl phenate-carboxylates;
(c) medium overbased salicylates;
(d) high overbased salicylates;
and mixtures and combinations thereof.

4. The lubricant additive composition according to claim 1 wherein said overbased, non-sulfonate-containing detergent is selected from the group consisting of:

(a) sulfurized hydrocarbyl phenates of alkaline earth metals;
(b) hydrocarbyl phenate-stearetes;
(c) medium overbased salicylates;
(d) high overbased salicylates;
and mixtures and combinations thereof.

5. The lubricant additive composition according to claim 1 wherein said alkaline earth metal is calcium.

6. A lubricant additive composition comprising:

(a) a carboxylated detergent-dispersant obtained by:

(i) neutralizing alklyphenols using an alkaline earth base in the presence of at least one carboxylic acid that contains from one to four carbon atoms but in the absence of alkali base, dialcohol, and monoalcohol, forming an intermediate product; and
(ii) carboxylating the intermediate product using carbon dioxide so that at least 20 mole percent of the original alklyphenol starting material has been converted to alkaline earth metal single aromatic-ring hydrocarbyl salicylate; and,

(b) at least one additive selected from the group consisting of:

(i) an overbased sulfurized hydrocarbyl phenate of alkaline earth metals;
(ii) an overbased hydrocarbyl phenate-carboxylate;
(iii) a medium overbased salicylate having a total base number of about 50 to 170;
(iv) a high overbased salicylate having a total base number greater than 170;
and combinations and mixtures thereof.

7. The composition of claim 6 wherein the mass ratio of carboxylated detergent-dispersant to overbased sulfurized hydrocarbyl phenate is from 0.5:1 to 6:1.

8. The composition of claim 7 wherein the mass ratio of carboxylated detergent-dispersant to overbased sulfurized hydrocarbyl phenate is from 0.67:1 to 3:1.

9. The composition of claim 8 wherein the mass ratio of carboxylated detergent-dispersant to overbased sulfurized hydrocarbyl phenate is from 0.75:1 to 2:1.

10. The composition of claim 6 wherein the phenate-carboxylate is a phenate-stearete.

11. The composition of claim 6 wherein the mass ratio of carboxylated detergent-dispersant to overbased hydrocarbyl phenate-carboxylate is from 0.5:1 to 6:1.

12. The composition of claim 11 wherein the mass ratio of carboxylated detergent-dispersant to overbased hydrocarbyl phenate-carboxylate is from 0.75:1 to 3:1.

13. The composition of claim 12 wherein the mass ratio of carboxylated detergent-dispersant to overbased hydrocarbyl phenate-carboxylate is from 1.1:1 to 1.5:1.

14. The composition of claim 6 wherein the medium overbased salicylate has a base number in the range of 50 to 170.

15. The composition of claim 14 wherein the medium overbased salicylate has a base number in the range of 100 to 165.

16. The composition of claim 15 wherein the medium overbased salicylate has a base number in the range of 120 to 160.

17. The composition of claim 6 wherein the high overbased salicylate has a base number above 170.

18. The composition of claim 17 wherein the high overbased salicylate has a base number above 200.

19. The composition of claim 18 wherein the high overbased salicylate has a base number above 250.

20. The composition of claim 6 wherein the alkaline earth metal of the overbased sulfurized hydrocarbyl phenate of alkaline earth metals is calcium.

21. A lubricating oil composition comprising:

(a) an oil of lubricating viscosity;

(b) a carboxylated detergent-dispersant obtained by:

(i) neutralizing alklyphenols using an alkaline earth base in the presence of at least one carboxylic acid that contains from one to four carbon atoms but in the absence of alkali base, dialcohol, and monoalcohol, forming an intermediate product; and
(ii) carboxylating the intermediate product using carbon dioxide so that at least 20 mole percent of the original alklyphenol starting material has been converted to alkaline earth metal single aromatic-ring hydrocarbyl salicylate; and,

(c) at least one overbased, non-sulfonate-containing detergent.

22. A lubricating oil composition comprising:

(a) an oil of lubricating viscosity;

(b) a carboxylated detergent-dispersant obtained by:

(i) neutralizing alklyphenols using an alkaline earth base in the presence of at least one carboxylic acid that contains from one to four carbon atoms but in the absence of alkali base, dialcohol, and monoalcohol, forming an intermediate product; and

(ii) carboxylating the intermediate product using carbon dioxide so that at least 20 mole percent of the original alklyphenol starting material has been converted to alkaline earth metal single aromatic-ring hydrocarbyl salicylate; and,
the absence of alkali base, dialcohol, and monoalcohol, forming an intermediate product; and

(ii) carboxylating the intermediate product using carbon dioxide so that at least 20 mole percent of the original alkylphenol starting material has been converted to alkaline earth metal single aromatic-ring hydrocarbaryl salicylate; and,

(c) at least one additive selected from the group consisting of:

(i) an overbased sulfurized hydrocarbaryl phenate of alkaline earth metals;
(ii) an overbased hydrocarbaryl phenate-carboxylate;
(iii) a medium overbased salicylate having a total base number of about 50 to 170;
(iv) a high overbased salicylate having a total base number greater than 170;

and combinations and mixtures thereof.

23. The composition of claim 22 wherein the phenate-carboxylate is a phenate-stearate.

24. An additive package comprising:

(a) from about 10 to 75 mass percent of the composition according to claim 1; and

(b) from about 25 to 90 mass percent of one or more of additives selected from the group consisting of ashless dispersants, detergents, sulfurized hydrocarbons, dialkyl hydrogen phosphates, zinc dithiophosphates, dialkyl hydrogen phosphates, pentaerythritol monooleate, 2,5-dimercapto thiadiazole, benzotriazole, foam inhibitors, and imidazolines; wherein the mass percent of each component is based on the total mass of the composition.

25. An additive package comprising:

(a) from about 10 to 75 mass percent of the composition according to claim 6; and

(b) from about 25 to 90 mass percent of one or more of additives selected from the group consisting of ashless dispersants, detergents, sulfurized hydrocarbons, dialkyl hydrogen phosphates, zinc dithiophosphates, dialkyl hydrogen phosphates, pentaerythritol monooleate, 2,5-dimercapto thiadiazole, benzotriazole, foam inhibitors, and imidazolines; wherein the mass percent of each component is based on the total mass of the composition.

26. A method of improving the detergent and dispersant properties of lubricating oils, comprising adding to said oils an effective detergent amount of the additive composition of claim 1.

27. A method of improving the detergent and dispersant properties of lubricating oils, comprising adding to said oils an effective detergent amount of the additive composition of claim 6.