

METHOD FOR IMPROVING ELASTOMER COMPATIBILITY

5 The present invention relates to a method of improving elastomer seal compatibility and dispersancy in an internal combustion engine. More particularly, the present invention relates to a method comprising contacting elastomer seals in an internal combustion engine with a lubricating oil composition having improved elastomer seal compatibility. Moreover, the present invention relates to the use of a lubricating oil composition able to
10 render nitrogen-containing dispersants contained in lubricating oils compatible with elastomer seals used in internal combustion engines.

BACKGROUND OF THE INVENTION

15 It is known to employ nitrogen-containing dispersants and/or detergents in the formulation of crankcase lubricating oil compositions. Many of the known dispersant/detergent compounds are based on the reaction of an alkenylsuccinic acid or anhydride with an amine or polyamine to produce an alkenylsuccinimide or an alkenylsuccinamic acid as determined by selected
20 conditions of reaction.

A continuing problem in the art of lubrication is to provide lubricating oil compositions which satisfy the demands imposed upon them by the original equipment manufacturers. One such requirement is that lubricants not
25 contribute to premature deterioration of seals, clutch face plates or other parts made from elastomers such as fluoro, acrylic, silicone, nitrile and the like. Elastomers are increasingly being used in fabricating the flexible seals which are used in internal combustion engines. These seals are used, for example, to prevent leakage of lubricants at the point where moving parts, such as a
30 crankshaft, leave the engine. Any substantial leakage of lubricant from the engine is obviously undesirable. Unfortunately, elastomer seals are subject to discoloration and mechanical deterioration when used in engines which are lubricated with lubricating oils containing polyamine dispersants, i.e., nitrogen-containing dispersants. The polyamine dispersants interact with the elastomer
35 seals, causing the seals to swell and to lose mechanical and dimensional integrity. The rate of attack of the elastomer seals by a polyamine dispersant

appears to be directly proportional to the concentration of polyamine dispersant and to the operating temperature of the engine. As the engine operating temperature rises, the rate of decomposition of the seal rises proportionately. As interaction of the dispersant with the seal continues, the mechanical strength and dimensional integrity of the seal increasingly deteriorates until the seal fails to prevent the leakage of lubricant from the engine.

Accordingly, qualification tests have been established whereby the effect of a lubricant composition on seal-type materials is measured under a particular set of controlled laboratory bench test conditions. Contemporary test methods for evaluating elastomer compatibility of lubricants and functional fluids include, but not limited to, the Volkswagen PV 3344 Elastomer Compatibility Test, the ACEA Oil-Elastomer Seal Test (CEC L-39-T-87), the DaimlerChrysler Oil-Elastomer Seal Test (VDA 675301-"Closed Test Cup") and the API CI-4 Elastomer test.

Generally, known succinimides useful as dispersants and/or detergents are not always compatible with elastomer seals when present in lubricating oil compositions at concentration levels necessary to be effective in controlling engine deposits. Of the nitrogenated components normally used in lubricants, bis-succinimides with dispersant action have proved particularly critical towards elastomers, either when used alone or in combination with, for example, viscosity index improvement polymers of dispersant action containing nitrogenated monomers. In this respect, both these classes of additive contain strongly basic amino groups (primary and/or secondary and/or tertiary).

The literature describes various processes which can be used to overcome the aforesaid drawback. Many known process involve post-treating various nitrogen-containing dispersants with various substances to reduce reactivity with elastomer seals.

U.S. Patent No. 4,379,064 teaches mild oxidation of nitrogenated dispersants to make the dispersant unreactive towards fluoroelastomers. However, the

process results in an excessive decrease (50-90%) in the initial TBN (Total Base Number).

5 U.S. Patent No. 4,873,009 is also concerned, in part, with the use of succinimides as lube oil additives. This patent teaches in Col. 2, lines 28 et seq. that lube additives prepared from "long chain aliphatic polyamines", i.e., succinimides, "are excellent lube oil additives". It teaches such succinimides are "inferior to additives where the alkylene polyamine is hydroxyalkylated" (Col. 2, lines 31-32). Such hydroxyalkylated polyamine- based succinimides, 10 however, "have the drawback that they tend to attack engine seals particularly those of the fluorocarbon polymer type" (Col. 2, lines 35-37). This patent solves the fluoroelastomer seal compatibility problem by directly borating the hydroxylated polyamine-based succinimide.

15 Furthermore, U.S. Patent No. 4,873,009 teaches it would be desirable for the additive to have a relatively high concentration of N-hydroxyalkyl moieties because the more N-hydroxyalkyl substituents, the cleaner the engine. However, it also teaches that the more amino groups in the polyamine, the greater the degradation of fluoroelastomer seal, and that alkylene amines containing more than 2 amino groups cannot be utilized (Col. 2, lines 50-62). 20

U.S. Patent No. 4,940,552 relates to polyamine dispersants passivated toward fluorohydrocarbon compositions. The dispersants described comprise the reaction product of a Mannich polyamine dispersant with an amount of 25 maleic anhydride sufficient to reduce the reactivity with fluorohydrocarbons of the dispersant.

U.S. Patent No. 5,356,552 teaches succinimide additives post-treated with a cyclic carbonate having fluoroelastomer seal compatibility and for 30 concentration levels at which fluoroelastomer seal compatibility is achieved, possess improved dispersancy and/or detergency.

U.S. Patent No. 6,124,247 teaches that dispersants of mono-succinimides or bis-succinimides are even more effective if their relative basic nitrogen 35 content is high, i.e. insofar as the number of nitrogen atoms of the polyamine is larger than the number of succinic anhydride groups substituted by a

polyisobutenyl group. However, the higher the basic nitrogen content of these dispersants, the more they favor the attack of the fluoroelastomer seal used in modern engines, because the basic nitrogen tends to reach with the acidic hydrogen atoms of this type of seal, and this attack results in the formation of cracks in the elastomer surface and the loss of other physical properties sought in this type of material. The patent provides that by using lubricating oil compositions containing a dispersant of mono-succinimide or bis-succinimide type, post-treated or not, in combination with a borated glycerol ester, one obtains a composition compatible with fluorocarbon elastomers.

U.S. Patent No. 6,162,770 teaches a process for preparing an unsulfurized, alkali metal-free, detergent-dispersant composition having from 40% to 60% alkylphenol, from 10% to 40% alkaline earth alkylphenate, and from 20% to 40% alkaline earth single aromatic-ring alkylsalicylate. This composition may have an alkaline earth double aromatic-ring alkylsalicylate as long as the mole ratio of single-ring alkylsalicylate to double aromatic-ring alkylsalicylate is at least 8:1. This composition may be produced by the three-step process involving neutralization of alkylphenols, carboxylation of the resulting alkylphenate, and filtration of the product of the carboxylation step. The detergent-dispersant produced by the method can be used in an engine lubricating composition to improve antioxidant properties, high temperature deposit control, and black sludge control. The patent does not mention that the detergent-dispersant produced provides improved elastomer seal compatibility.

Clearly, a need exists to provide highly effective nitrogen-containing dispersants which provide dispersancy to the lubricating oil while at the same time not causing the deterioration of elastomer seals, such as, for example, fluoro, acrylic, silicone, nitrile and the like, and the associated leak of lubricant.

SUMMARY OF THE INVENTION

The present invention provides a method of improving elastomer seal compatibility and dispersancy in an internal combustion engine, said method comprising contacting the elastomer seal in the internal combustion engine

with a lubricating oil composition comprising:

- a) a major amount of a base oil of lubricating viscosity;
- b) 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; 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
- c) a nitrogen-containing dispersant.

The nitrogen-containing dispersant employed in the lubricating oil composition of the present invention is an ashless dispersant such as an alkenyl succinimide, an alkenyl succinic anhydride, an alkenyl succinate ester, and the like, or mixtures of such dispersants.

Alkenyl succinimides are preferred. Bis-succinimides are more preferred.

In an alternative embodiment, the present invention is directed to the use of a certain carboxylated detergent-dispersant to improve the elastomer seal compatibility in a lubricating oil composition containing a basic nitrogen-containing dispersant in an internal combustion engine.

Among other factors, the present invention is based on the discovery that a certain carboxylated detergent-dispersant improves elastomer seal compatibility of lubricating oil compositions containing nitrogen-containing dispersants.

DETAILED DESCRIPTION OF THE INVENTION

5 In its broadest aspect, the present invention relates to a method of improving elastomer seal compatibility and dispersancy in an internal combustion engine. More particularly, the present invention relates to a method comprising contacting elastomer seals in an internal combustion engine with a lubricating oil composition having improved elastomer seal compatibility.

DEFINITIONS

10 Prior to discussing the present invention in detail, the following terms will have the following meanings unless expressly stated to the contrary.

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

20 The term "alkaline earth metal" means calcium, barium, magnesium, strontium, potassium, sodium, and lithium.

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

25 The term "alkaline earth alkylsalicylate" means an alkaline earth metal salt of an alkyl salicylic acid.

30 The term "alkaline earth single aromatic-ring alkylsalicylate" means an alkaline earth alkylsalicylate having only one alkyl salicylic anion per each alkaline earth metal base cation. Thus one mole of alkaline earth single aromatic-ring alkylsalicylate will contain one mole of aromatic ring and one mole of alkaline earth base cation. Thus, a calcium single aromatic-ring alkylsalicylate would have one aromatic ring for each calcium ion.

35

5 The term "alkaline earth double aromatic-ring alkylsalicylate" means an alkaline earth alkylsalicylate having two alkyl salicylic anions per each alkaline earth metal base cation. Thus one mole of alkaline earth double aromatic-ring alkylsalicylate will contain two moles of aromatic rings and one mole of alkaline earth base cation. Thus, a calcium double aromatic-ring alkylsalicylate would have two aromatic rings for each calcium ion.

10 The term "succinimide" is understood in the art to include many of the amide, imide, etc. species which are also formed by the reaction of a succinic anhydride with an amine and is so used herein. The predominant product, however, is succinimide and this term has been generally accepted as meaning the product of a reaction of an alkenyl- or alkylsubstituted succinic acid or anhydride with a polyamine.

15 The term "Total Base Number" or "TBN" refers to the amount of base equivalent to milligrams of KOH in 1 gram of sample. Thus, higher TBN numbers reflect more alkaline products and therefore a greater alkalinity reserve. The TBN of a sample can be determined by ASTM D 2896 or any other equivalent procedure.

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

25

BASE OIL OF LUBRICATING VISCOSITY

30 The base oil of lubricating viscosity of the present invention may be mineral oils or synthetic oils. A base oil having a viscosity of at least about 2.5 cSt at about 40°C and a pour point below about 20°C, preferably at or below 0°C is desirable. The base oils may be derived from synthetic or natural sources. Mineral oils for use as the base oil in this invention include, for example, paraffinic, naphthenic and other oils that are ordinarily used in lubricating oil compositions. Synthetic oils include, for example, both hydrocarbon synthetic oils and synthetic esters and mixtures thereof having the desired viscosity.

35

Hydrocarbon synthetic oils may include, for example, oils prepared from the polymerization of alpha olefins, i.e., polyalphaolefin or PAO, or 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 useful are the hydrogenated liquid oligomers of about C₆ to about 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 mono and dicarboxylic acids and mono and dihydroxy alkanols can also be used. Blends of mineral oils with synthetic oils are also useful.

CARBOXYLATED DETERGENT-DISPERSANT ADDITIVE

The lubricating oil composition of the present invention comprises a carboxylated detergent-dispersant additive (also referred to herein as "carboxylate" or "carboxylated detergent") made by the following process.

A. Neutralization Step

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

The alkylphenols contain up to 98% of linear alkylphenol (preferably up to 35% linear alkylphenol) in mixture with up to 15% of branched alkylphenol. Preferably, the linear alkyl radical contains about 12 to about 40 carbon atoms, more preferably about 18 to about 30 carbon atoms. The branched alkyl radical contains at least nine carbon atoms, preferably about 9 to about 24 carbon atoms, more preferably about 10 to about 15 carbon atoms.

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

10 Branched alkylphenols can be obtained by reaction of phenol with a branched olefin, generally originating from propylene. They consist of a mixture of monosubstituted isomers, the great majority of the substituents being in the para position, very few being in the ortho position, and hardly any in the meta position. That makes them relatively reactive towards an alkaline earth base, since the phenol function is practically devoid of steric hindrance.

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

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

30 The C₁ to about 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.

35 The molar ratio of formic acid/acetic acid should be from about 0.2:1 to about 100:1, preferably between about 0.5:1 and about 4:1, and most preferably

1:1. The carboxylic acids act as transfer agents, assisting the transfer of the alkaline earth bases from a mineral reagent to an organic reagent.

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

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

(2) carboxylic acid/alkylphenol of about 0.01:1 to about 0.5:1, preferably from about 0.03:1 to about 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 to alkylsalicylate (measured as salicylic acid by potentiometric determination). It must take place under pressure in order to avoid any decarboxylation of the alkylsalicylate that forms.

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

5

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

10

The product of the carboxylation step is then 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.

15

The carboxylated detergent-dispersant formed by this process can be characterized by its unique composition, with much more alkylphenol and alkaline earth metal single aromatic-ring hydrocarbyl salicylate than produced by other routes. The reaction product will typically have the following composition:

20

- a) from about 1 % to about 40 % alkylphenol,
- b) from about 10 % to about 40 % alkaline earth metal alkylphenate, and
- c) from about 30 % to about 70 % alkaline earth metal single aromatic-ring alkylsalicylate.

25

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

30

Unlike alkaline earth alkylsalicylates produced by other processes, this detergent-dispersant composition can be characterized by having only minor amounts of an alkaline earth double aromatic-ring alkylsalicylates. The mole ratio of single aromatic-ring alkylsalicylate to double aromatic-ring

35

alkylsalicylate is at least 8:1.

Preferably, the TBN of the detergent-dispersant should be from about 100 to about 250, more preferably from about 150 to about 200.

5 In the lubricating oil composition employed in the present invention, the carboxylated detergent-dispersant will typically range from about 0.5 to about 15 wt %, preferably from about 1 to about 12 wt % and more preferably about 1 to about 8 wt %, based on the weight of the total lubricating oil composition.

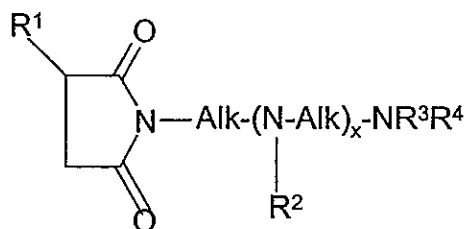
10 NITROGEN-CONTAINING DISPERSANT

The nitrogen-containing dispersant employed in the lubricating oil composition of the present invention is an ashless dispersant such as an alkenyl or alkyl succinimide, an alkenyl or alkyl succinic anhydride, an alkenyl or alkyl succinate ester, and the like, or mixtures of such dispersants.

Ashless dispersants are broadly divided into several groups. One such group is directed to copolymers which contain a carboxylate ester with one or more additional polar function, including amine, amide, imine, imide, hydroxyl carboxyl, and the like. These products can be prepared by copolymerization of long chain alkyl acrylates or methacrylates with monomers of the above function. Such groups include alkyl methacrylate-vinyl pyrrolidinone copolymers, alkyl methacrylate-dialkylaminoethyl methacrylate copolymers and the like. Additionally, high molecular weight amides and polyamides or esters and polyesters such as tetraethylene pentamine, polyvinyl polyesterates and other polystearamides may be employed. Preferred dispersants are N-substituted long chain alkenyl succinimides.

Alkenyl succinimides are usually derived from the reaction of alkenyl succinic acid or anhydride and alkylene polyamines. These compounds are generally considered to have the formula:

35



5

wherein R^1 is a substantially hydrocarbon radical having a molecular weight from about 400 to about 3000, that is, R^1 is a hydrocarbyl radical, preferably an alkenyl radical, containing about 30 to about 200 carbon atoms; Alk is an alkylene radical of about 2 to about 10, preferably about 2 to about 6, carbon atoms, R^2 , R^3 , and R^4 are selected from a C_1 to about C_4 alkyl or alkoxy or hydrogen, preferably hydrogen, and x is an integer from 0 to about 10, preferably 0 to about 3. The actual reaction product of alkylene succinic acid or anhydride and alkylene polyamine will comprise the mixture of compounds including succinamic acids and succinimides. However, it is customary to designate this reaction product as a succinimide of the described formula, since this will be a principal component of the mixture. See, for example, U.S. Patent Nos. 3,202,678; 3,024,237; and 3,172,892, the descriptions of which are incorporated herein by way of reference. Reduction of the alkenyl substituted succinic anhydride produces the corresponding alkyl derivative. The mono alkenyl succinimide and bis alkenyl succinimide produced may depend on the charge mole ratio of polyamine to succinic groups and the particular polyamine used. Charge mole ratios of polyamine to succinic groups of about 1:1 may produce predominately mono alkenyl succinimide. Charge mole ratios of polyamine to succinic group of about 1:2 may produce predominately bis alkenyl succinimide.

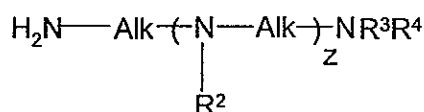
30

Particularly, advantageous results with the method of the present invention are obtained when the alkenyl or alkyl succinimide is a mono- or bis-succinimide prepared from a succinic anhydride substituted by polyisobutene of a polyalkylene polyamine as discussed in further detail below. Bis-succinimides are preferred.

35

These N-substituted alkenyl succinimides can be prepared by reacting maleic anhydride with an olefinic hydrocarbon followed by reacting the resulting alkenyl succinic anhydride with the alkylene polyamine. The R¹ radical of the above formula, that is, the alkenyl radical, is preferably derived from a polymer prepared from an olefin monomer containing from about 2 to about 5 carbon atoms. Thus, the alkenyl radical is obtained by polymerizing an olefin containing from about 2 to about 5 carbon atoms to form a hydrocarbon having a molecular weight ranging from about 400 to about 3,000. Such olefin monomers are exemplified by ethylene, propylene, 1-butene, 2-butene, isobutene, and mixtures thereof.

The preferred polyalkylene amines used to prepare the succinimides are of the formula:



wherein z is an integer of from 0 to about 10 and Alk, R², R³, and R⁴ are as defined above.

The alkylene amines include principally methylene amines, ethylene amines, butylene amines, propylene amines, pentylene amines, hexylene amines, heptylene amines, octylene amines, other polymethylene amines and also the cyclic and the higher homologs of such amines as piperazine and amino alkyl-substituted piperazines. They are exemplified specifically by ethylene diamine, triethylene tetraamine, propylene diamine, decamethyl diamine, octamethylene diamine, diheptamethylene triamine, tripropylene tetraamine, tetraethylene pentamine, trimethylene diamine, pentaethylene hexamine, ditrimethylene triamine, 2-heptyl-3-(2-aminopropyl)-imidazoline, 4-methyl imidazoline, N,N-dimethyl-1,3-propane diamine, 1,3-bis(2-aminoethyl)imidazoline, 1-(2-aminopropyl)-piperazine, 1,4-bis(2-

aminoethyl)piperazine and 2-methyl-1-(2-aminobutyl)piperazine. Higher homologs such as are obtained by condensing two or more of the above-illustrated alkylene amines likewise are useful.

5 The ethylene amines are especially useful. They are described in some detail under the heading "Ethylene Amines" in Encyclopedia of Chemical Technology, Kirk-Othmer, Vol. 5, pp. 898-905 (Interscience Publishers, New York, 1950).

10 The term "ethylene amine" is used in a generic sense to denote a class of polyamines conforming for the most part to the structure:



15

wherein a is an integer from 1 to about 10.

Thus, it includes, for example, ethylene diamine, diethylene triamine,
20 triethylene tetraamine, tetraethylene pentamine, pentaethylene hexamine, and the like.

Also included within the term "alkenyl succinimides" are post-treated succinimides such as post-treatment processes involving ethylene carbonate
25 and boric acid disclosed by Wollenberg, et al., U.S. Patent No. 4,612,132; Wollenberg, et al., U.S. Patent No. 4,746,446; and the like as well as other post-treatment processes each of which are incorporated herein by reference in its entirety.

30

Preferably, the nitrogen-containing dispersant is a polyalkylene succinimide, preferably a polyisobutylene succinimide. More preferably, the nitrogen-containing dispersant is a polyisobutylene bis-succinimide. The nitrogen-
35 containing dispersant employed in the present invention will be present in

sufficient quantity to impart the desired dispersant properties to the lubricating oil composition in order to prevent the deposit of contaminants formed in oil during operation of the internal combustion engine. In general, in the lubricating oil composition, the nitrogen-containing dispersant will typically
5 range from about 2 to about 13 wt %, preferably from about 4 to about 8 wt % and more preferably about 6 to about 7.5 wt %, based on the weight of the total lubricating oil composition.

10 OTHER ADDITIVES

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

1. Metal detergents: sulfurized or unsulfurized alkyl or alkenyl phenates, alkyl or alkenyl aromatic sulfonates, sulfurized or unsulfurized metal
20 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 alkanolic acids, metal salts of an alkyl or alkenyl multiacid, and chemical and physical mixtures thereof.
2. Anti-oxidants: Anti-oxidants reduce the tendency of mineral oils to
25 deteriorate in service which deterioration is evidenced by the products of oxidation such as sludge and varnish-like deposits on the metal surfaces and by an increase in viscosity. Examples of anti-oxidants
30 useful in the present invention include, but are not limited to, phenol type (phenolic) oxidation inhibitors, such as 4,4'-methylene-bis(2,6-di-tert-butylphenol), 4,4'-bis(2,6-di-tert-butylphenol), 4,4'-bis(2-methyl-6-tert-butylphenol), 2,2'-methylene-bis(4-methyl-6-tert-butylphenol),
35 4,4'-butylidene-bis(3-methyl-6-tert-butylphenol), 4,4'-isopropylidene-

- bis(2,6-di-tert-butylphenol), 2,2'-methylene-bis(4-methyl-6-nonylphenol), 2,2'-isobutylidene-bis(4,6-dimethylphenol), 2,2'-methylene-bis(4-methyl-6-cyclohexylphenol), 2,6-di-tert-butyl-4-methylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,4-dimethyl-6-tert-butylphenol, 2,6-di-tert-butyl-4-dimethylamino-p-cresol, 2,6-di-tert-butyl-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). Other types of oxidation inhibitors include metal dithiocarbamate (e.g., zinc dithiocarbamate), and methylenebis(dibutyldithiocarbamate).
3. Anti-wear agents: As their name implies, these agents reduce wear of moving metallic parts. Examples of such agents include, but are not limited to, phosphates, phosphites, carbamates, esters, sulfur containing compounds, and molybdenum complexes.
4. Rust inhibitors (Anti-rust agents)
- a) Nonionic polyoxyethylene surface active agents: polyoxyethylene lauryl ether, polyoxyethylene higher alcohol ether, polyoxyethylene nonyl phenyl ether, polyoxyethylene octyl phenyl ether, polyoxyethylene octyl stearyl ether, polyoxyethylene oleyl ether, polyoxyethylene sorbitol monostearate, polyoxyethylene sorbitol mono-oleate, and polyethylene glycol mono-oleate.
- b) Other compounds: stearic acid and other fatty acids, dicarboxylic acids, metal soaps, fatty acid amine salts, metal salts of heavy sulfonic acid, partial carboxylic acid ester of polyhydric alcohol, and phosphoric ester.

5. Demulsifiers: addition product of alkylphenol and ethylene oxide, polyoxyethylene alkyl ether, and polyoxyethylene sorbitan ester.
6. Extreme pressure agents (EP agents): zinc dialkyldithiophosphate (primary alkyl, secondary alkyl, and aryl type), sulfurized oils, diphenyl sulfide, methyl trichlorostearate, chlorinated naphthalene, fluoroalkylpolysiloxane, and lead naphthenate.
7. Friction modifiers: fatty alcohol, fatty acid, amine, borated ester, and other esters.
8. Multifunctional additives: sulfurized oxymolybdenum dithiocarbamate, sulfurized oxymolybdenum organo phosphorodithioate, oxymolybdenum monoglyceride, oxymolybdenum diethylate amide, amine-molybdenum complex compound, and sulfur-containing molybdenum complex compound.
9. Viscosity index improvers: polymethacrylate type polymers, ethylene-propylene copolymers, styrene-isoprene copolymers, hydrated styrene-isoprene copolymers, polyisobutylene, and dispersant type viscosity index improvers.
10. Pour point depressants: polymethyl methacrylate.
11. Foam inhibitors: alkyl methacrylate polymers and dimethyl silicone polymers.

EXAMPLES

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

EXAMPLE 1

CARBOXYLATED DETERGENT-DISPERSANT

5 A carboxylated detergent-dispersant was prepared as follows:

A. Neutralization:

10 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 distribution of para versus ortho alkylphenol was:

15

DDP: 89% para and 5.5% ortho

Linear alkylphenol: 39% para and 53% ortho.

20 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
25 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.

30 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
35 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:

5 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.

10 After the temperature had been raised to 200°C, the autoclave was closed, leaving a very small leak, and the introduction of CO₂ was continued so as to maintain a pressure of 3.5×10^5 Pa (3.5 bars) for 5 hours at 200°C. The amount of CO₂ introduced was in the order of 50 grams. After the autoclave
15 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.
20 The product was then filtered.

EXAMPLE 2

25 The present invention was evaluated for compatibility with elastomer seals in a bench test (PV 3344) by suspending a fluorocarbon test piece (AK 6) in an oil-based solution heated to 150 °C. for 282 hours, the oil being renewed every 92 hours, then by measuring the variation in the physical properties of the sample, in particular the tensile strength break (TSB) and the elongation
30 at break (ELB), in accordance with procedure DIN 53504, by observing whether any cracks had formed at 100% elongation. The passing test criteria included the following: no evidence of crack development; a tensile strength break greater than 8N/mm² and an elongation at break greater than 160%. This test procedure will be designated above and later simply as the "VW
35 Bench Test".

The formulation tested comprised a polyisobutenyl (PIB) bis-succinimide (the PIB having a molecular weight of 2300 and the bis-succinimide having been post-treated with ethylene carbonate)(6.5 wt %), low overbased (LOB) calcium sulfonate (0.68 wt %), carboxylated detergent, prepared in the manner described in Example 1, (2.45 wt %), high overbased (HOB) calcium alkylphenate (1.13 wt %), zinc dithiophosphate (0.69 wt %), a molybdenum-based anti-oxidant (0.05 wt %), a diphenylamine-based antioxidant (0.3 wt %), a friction modifier (0.25 wt %), a foam inhibitor (0.0025 wt %), a pour point depressant (0.15 wt %), a viscosity index improver (6.4 wt %), and a base oil of lubricating viscosity (80.8 wt %).

COMPARATIVE EXAMPLE A

Comparative Example A was conducted as described in Example 2 except that 1.97 wt % of a commercial medium overbased (MOB) calcium phenate was substituted for the carboxylate and 0.5 wt % of the friction modifier was used instead of 0.25 wt %.

The results of the Example 2 and Comparative Example A are presented below in Table 1.

Table 1.

Volkswagen PV 3344 Seal Test

Test	VW EAM Acrylate Seals	VW ACM Acrylate Seals	VW AK-6 Fluoroelastomer Seals	Result
	Tensile Strength, % (Limit $\geq$ -40)	Elongation, % (Limit $\geq$ -40)	Cracks in Seal (Limit: None)	
Example 2	-36	-31.4	None	Pass
Comparative Example A	-48.3	-45.1	Cracks	Fail

The results in Table 1 indicate that the detergent-dispersant employed in the present invention enables you to pass the seal tests whereas a comparable commercial detergent, on an equal molar basis, fails these tests. Example 2 showed no seal cracks and were well within the passing limits of the Volkswagen VW seal test.

EXAMPLE 3

The evaluation of Oil-Elastomer Compatibility, either by CEC-L-39-T-97 plus DaimlerChrysler requirement for AEM or by complete DaimlerChrysler requirements plus CEC elastomer RE3, is aimed at determining the degree of compatibility of lubricating oils and cured elastomers used in the automotive industry. Elastomer test pieces are immersed in the test oil for a given period of time and a given temperature. The size, the volume, the hardness, and the stress-strain properties are determined before and after immersion. The compatibility of the oil and the elastomer is estimated by the change in these characteristics.

The materials and test temperatures are provided in the following Table A. Immersion duration 168 hours (7 days), in fresh oil with no elastomer pre-aging.

Table A.

Material Designation	General Elastomer Type	Test Temperature
CEC RE 1 or DC FPM	Fluoro-elastomer	150 °C
CEC RE 2 or DC FPM	Acrylic	150 °C
CEC RE 3	Silicone	150 °C
CEC RE 4 or DC NBR	Nitrile	100 °C
DC AEM	Vamac	150 °C

The formulations tested and their results are presented in Table 2.

Table 2.

CEC-L-39-T-97 or DaimlerChrysler Seal Test

5	Component	Weight % of Component ^a			Test Limit
		Formulation 1	Formulation 2	Formulation 3	
10	Borated Bis-Succinimide	1.5	2.5	3	
	Ethylene-Carbonated Bis-Succinimide	5.0	5.0	5.0	
15	Carboxylate	4.72	4.72	4.72	
		Test Results			
	Tensile Strength	-37.7	-40	-45	-45
20	Elongation	-36.1	-36	-41	-50
	Hardness	2.7	2	3	-5/+5
	Volume	0.9	0.6	0.6	0/+5
25		Pass	Pass	Borderline Pass	

^aOther components: Phenate-salicylate (0.69 wt %), Zinc dithiophosphate (1.03 wt %), Molybdenum-based anti-oxidant (0.17 wt %), Foam inhibitor (0.0025 wt %), Viscosity index improver (5.55 wt %), and a base oil of lubricating viscosity (80.7 wt %).

EXAMPLE 4

The test in Example 3 was repeated with a lubricating oil composition containing the carboxylated detergent-dispersant (Formulation 4) employed in

the present invention and compared with a lubricating oil composition containing a comparable commercially available detergent (Formulation 5) without the detergent-dispersant. The results are shown in Table 3.

Table 3.

CEC-L-39-T-97 or DaimlerChrysler Seal Test

Component	Weight % of Component ^a		Test Limit
	Formulation 4	Formulation 5	
Ethylene-Carbonated Bis-Succinimide	8	8	
Carboxylate	4.8	-	
Commercial Detergent	0.69	2.83	
	Test Results		
Tensile Strength (%)	-40.7	-48.6	-45
Elongation	-40.3	-45.7	-50
Hardness	3.3	2.6	-5/+5
Volume 0.8	0.4	0/+5	
	Pass	Fail	

^aOther components: Zinc dithiophosphate (1.0 wt %), Molybdenum-based anti-oxidant (0.17 wt %), Foam inhibitor (0.0025 wt %), Viscosity index improver (5.55 wt %), and a base oil of lubricating viscosity (79 wt %).

The results in Table 3 indicate that in a direct comparison between

carboxylate and a commercial detergent, seal compatibility can be maintained with the carboxylate (Formulation 4). Comparatively, in Formulation 5 containing no carboxylate and with a commercial detergent, the seal compatibility is lost.

5

The overall conclusion in the above examples clearly indicates that elastomer compatability can be maintained at high dispersant levels. Switching to conventional detergent technology with identical dispersant levels will result in failure.

10

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

15

20

25

30

35

CLAIMS:

- 5 1. A method of improving elastomer seal compatibility and dispersancy in an internal combustion engine, said method comprising contacting the elastomer seal in the internal combustion engine with a lubricating oil composition comprising:
- 10 a) a major amount of a base oil of lubricating viscosity;
- 15 b) 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; and
- 20 (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
- 25 c) a nitrogen-containing dispersant.
- 30 2. The method according to Claim 1, wherein the nitrogen-containing dispersant is selected from the group consisting of an alkenyl succinimide, an alkenyl succinic anhydride, an alkenyl succinate ester, or mixtures thereof.
- 35 3. The method according to Claim 2, wherein the nitrogen-containing dispersant is an alkenyl succinimide.

4. The method according to Claim 3, wherein the alkenyl succinimide is a polyalkylene succinimide.
- 5 5. The method according to Claim 4, wherein the polyalkylene succinimide is a polyisobutenyl succinimide.
6. The method according to Claim 5, wherein the polyalkylene
10 succinimide is a polyisobutenyl bis-succinimide.
7. The method according to Claim 1, wherein the carboxylated detergent-dispersant is present in the lubricating oil composition from about 0.5
15 to about 15 wt %, based on the weight of the total lubricating oil composition.
8. The method according to Claim 7, wherein the carboxylated detergent-dispersant is present in the lubricating oil composition from about 1 to
20 about 12 wt %, based on the weight of the total lubricating oil composition.
9. The method according to Claim 8, wherein the carboxylated detergent-dispersant is present in the lubricating oil composition from about 1 to
25 about 8 wt %, based on the weight of the total lubricating oil composition.
- 30 10. The method according to Claim 1, wherein the nitrogen-containing dispersant is present in the lubricating oil composition from about 2 to about 13 wt %, based on the weight of the total lubricating oil composition.

35

11. The method according to Claim 10, wherein the nitrogen-containing dispersant is present in the lubricating oil composition from about 4 to about 8 wt %, based on the weight of the total lubricating oil composition.

5

12. The method according to Claim 11, wherein the nitrogen-containing dispersant is present in the lubricating oil composition from about 6 to about 7.5 wt %, based on the weight of the total lubricating oil composition.

10

15

20

25

30

35