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(54) **LUBRICATING OIL ADDITIVE  
COMPRISING EC-TREATED SUCCINIMIDE,  
BORATED DISPERSANT AND CORROSION  
INHIBITOR**

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(57) **ABSTRACT**

An additive formulation comprising one or more ec-treated dispersants, borated dispersants, and a dispersed aromatic dicarboxylic acid corrosion inhibitor; a dispersant inhibitor package comprising one or more ec-treated dispersants, borated dispersants, and a dispersed aromatic dicarboxylic acid corrosion inhibitor; a lubricating oil comprising said dispersant inhibitor package; and a method for lubricating engines.

**LUBRICATING OIL ADDITIVE COMPRISING  
EC-TREATED SUCCINIMIDE, BORATED  
DISPERSANT AND CORROSION INHIBITOR**

[0001] This application claims the benefit of priority from U.S. Provisional Application No. 60/356,699, filed Feb. 14, 2002.

**FIELD OF THE INVENTION**

[0002] This invention includes an additive formulation comprising one or more ethylene carbonate (EC) treated polyalkene succinimides and one or more borated polyalkene with a specific dispersed aromatic dicarboxylic acid corrosion inhibitor; a lubricating oil comprising this additive formulation, an oil of lubricating viscosity and any other additives typically used in the lubricating oil industry.

[0003] The lubricating oil of this invention may be used in any engine but they are particularly advantageous for lubricating internal combustion engines, and even more particularly useful in heavy-duty diesel engines. The lubricating oil of this invention lowers wear in engines. It is particularly useful to lower bearing wear and valve train wears. The lubricating oil of this invention also prevents deposits, disperses soot, and provides excellent high temperature performance.

**BACKGROUND OF THE INVENTION**

[0004] New diesel engines are equipped with Exhaust Gas Recirculation (EGR). EGR introduces NO<sub>x</sub> in the intake stream of the engine. In the presence of water and at lower temperature, acids may be formed which may condensate in the intake system. These acids lower the TBN of the crankcase lubricant and may ultimately cause an increase in bearing corrosion. The use of the corrosion inhibitor and the use of a borated dispersant result in improved bearing corrosion control.

**SUMMARY OF THE INVENTION**

[0005] It has now been discovered that the combination of one or more EC-treated polyalkene succinimides and one or more borated polyalkene succinimides with a specific dispersed aromatic dicarboxylic acid corrosion inhibitor provides decreased wear in engines. It is particularly useful to lower bearing wear and valve train wears. The lubricating oil of this invention also prevents deposits, disperses soot, and provides excellent high temperature performance.

[0006] Accordingly, the present invention comprises:

[0007] A lubricating oil additive composition comprising:

[0008] (a) one or more ethylene carbonate-treated succinimides;

[0009] (b) one or more borated succinimides, and

[0010] (c) one or more dispersed aromatic dicarboxylic acid corrosion inhibitors which are succinimide salts of one or more aromatic dicarboxylic acids.

[0011] The present invention further provides:

[0012] A lubricating oil composition comprising a major amount of an oil of lubricating viscosity and a lubricating oil additive composition comprising:

[0013] (a) one or more ethylene carbonate treated succinimides,

[0014] (b) one or more borated succinimides, and

[0015] (c) one or more dispersed aromatic dicarboxylic acid corrosion inhibitors which are succinimide salts of one or more aromatic dicarboxylic acids.

[0016] The present invention also provides a method for lubricating an internal combustion engine comprising contacting the engine with the lubricating oil composition of the present invention.

[0017] The present invention additionally provides a method for reducing bearing corrosion in a diesel engine which comprises operating the engine with the lubricating oil composition of the present invention.

[0018] Among other factors, the present invention is based on the surprising discovery that the unique combination of one or more EC-treated polyalkene succinimides and one or more borated polyalkene succinimides with a specific dispersed aromatic dicarboxylic acid corrosion inhibitor provides decreased wear in engines.

**DESCRIPTION OF THE INVENTION**

[0019] This invention includes an additive formulation comprising one or more combinations of one or more ethylene carbonate (EC) treated dispersants and one or more borated dispersants with one or more dispersed aromatic dicarboxylic acid corrosion inhibitors, a lubricating oil comprising this additive formulation, an oil of lubricating viscosity and other additives typically used in the lubricating oil industry.

[0020] I. EC-treated Dispersant and Borated Dispersant Combination

[0021] The combination of one or more EC-treated dispersants and one or more borated dispersants of this invention is described in U.S. Pat. No. 5,861,363; this patent is incorporated herein by reference in its entirety. The additive formulation of this invention further comprises one or more dispersed aromatic dicarboxylic acid corrosion inhibitors.

[0022] The EC-treated Dispersant and Borated Dispersant Combination of the present invention comprises from 10% to 50% of a borated dispersant derived from a lower molecular weight polyalkylene and from 50% to 90% of an EC-treated dispersant derived from a higher molecular weight polyalkylene. Unless otherwise specified, all percents (%) are weight percents (wt. %).

[0023] Preferably, the EC-treated Dispersant and Borated Dispersant Combination of this invention comprises from 20% to 40% borated dispersant and from 60% to 80% EC-treated dispersant.

[0024] The individual dispersants used in the EC-treated Dispersant and Borated Dispersant Combination of this invention may be prepared by conventional processes, such as those disclosed in U.S. Pat. Nos. 2,992,708; 3,018,250; 3,018,291; 3,024,237; 3,100,673; 3,172,892; 3,219,666; 3,272,746; 3,361,673; 3,381,022; 3,912,764; 4,234,435; 4,612,132; 4,747,965; 5,112,507; 5,241,003; 5,266,186; 5,286,799; 5,319,030; 5,334,321; 5,356,552; and 5,716,912, the disclosures of which are all hereby incorporated by reference in their entirety for all purposes.

[0025] The EC-treated Dispersant and Borated Dispersant Combination of this invention may be prepared by physically mixing the borated dispersant and the EC-treated dispersants. The EC-treated Dispersant and Borated Dispersant Combination may have a slightly different composition than the initial mixture, because the components may interact.

#### [0026] I. (A). Borated Dispersant

[0027] The EC-treated Dispersant and Borated Dispersant Combination comprises from 10% to 50%, preferably from 20% to 40%, of a borated dispersant derived from the reaction product of a polyisobutenylsuccinic anhydride with a polyamine. Preferably, the borated dispersant is derived from polybutenes having a molecular weight of from 1200 to 1400, most preferably about 1300.

[0028] The additive package of this invention may comprise greater than 0% to about 40%, preferably from 5% to 30%, and more preferably from 10% to 20% of a borated dispersant.

#### [0029] I. (B). EC-Treated Dispersant

[0030] The EC-treated Dispersant and Borated Dispersant Combination comprises from 50% to 90%, preferably from 60% to 80%, of an EC-treated dispersant derived from the reaction product of a polyisobutenylsuccinic anhydride with a polyamine. The polyisobutene has a number average molecular weight ( $M_n$ ) of at least 1800. Preferably, the EC-treated dispersant is a polybutene succinimide derived from polybutenes having a molecular weight of from 2000 to 2400. The EC-treated succinimide of this invention is described in U.S. Pat. Nos. 5,334,321 and 5,356,552. It is not a mixture of a polybutene succinic acid derivative, a copolymer and a polyamine such as taught in U.S. Pat. No. 5,716,912.

[0031] The additive package of this invention may comprise from about 10% to about 80%, preferably from about 20% to about 60%, and more preferably from about 30% to about 50% of an EC-treated dispersant derived from the reaction product of a polyisobutenylsuccinic anhydride with a polyamine.

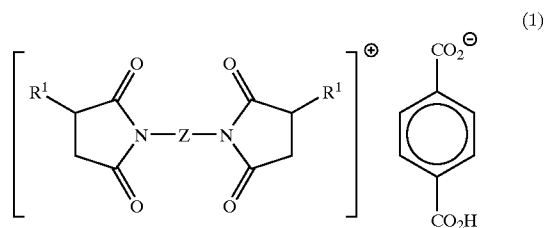
#### [0032] II. Dispersed Aromatic Dicarboxylic Acid Corrosion Inhibitor

[0033] The dispersed aromatic dicarboxylic acid corrosion inhibitors of this invention are succinimide salts of one or more aromatic dicarboxylic acids. Preferred aromatic dicarboxylic acids may comprise one or more terephthalic acids.

[0034] Certain embodiments of the dispersed aromatic dicarboxylic acid corrosion inhibitor of this invention are

described in U.S. Pat. Nos. 3,287,271; 3,692,681; and 3,374,174, all of which are incorporated herein in their entirety. Certain embodiments of the dispersed aromatic dicarboxylic acid corrosion inhibitors of this invention comprise one or more succinimide salts of Terephthalic Acid.

[0035] One embodiment of the dispersed aromatic dicarboxylic acid corrosion inhibitor of this invention may comprise one or more dispersed aromatic dicarboxylic acid corrosion inhibitors having the general formula:



[0036] where  $R^1$  is one or more polyisobutenyl groups with a number average molecular weight of about 1100-1500, and Z is one or more protonated poly amino radical having from about 3 to about 7 nitrogen atoms, more preferably from about 4 to about 5 nitrogen atoms and about 8 to about 20 carbon atoms.

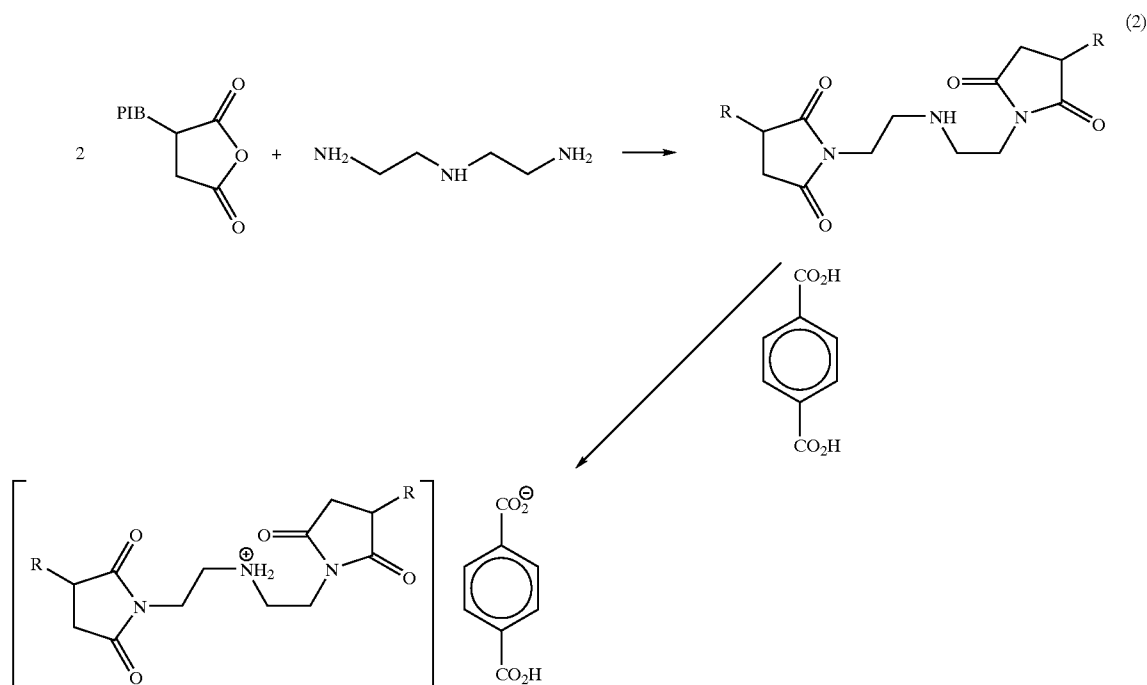
[0037] The dispersed aromatic dicarboxylic acid corrosion inhibitors of this invention inhibit lead corrosion better than other known lead corrosion inhibitors. Another embodiment of this invention may comprise a combination of one or more of the dispersed aromatic dicarboxylic acid corrosion inhibitors described herein.

#### [0038] III. Dispersed Aromatic Dicarboxylic Acid Corrosion Inhibitor Synthesis

[0039] The dispersed aromatic dicarboxylic acid corrosion inhibitors of this invention may be synthesized as described in U.S. Pat. Nos. 3,287,271; 3,692,681; and 3,374,174, all of which are incorporated herein in their entirety.

[0040] One embodiment of the dispersed aromatic dicarboxylic acid corrosion inhibitor of this invention may be synthesized by reacting about 1100 to about 1500, preferably about 1300 molecular weight polyisobutenyl succinic anhydride (PIBSA) with one or more polyamines, preferably one or more heavy polyamines (HPA) at an amine/PIBSA CMR of about 0.4 to about 0.6, preferably about 0.45. This produces a reaction product that may then be reacted with terephthalic acid.

[0041] Another embodiment of the dispersed aromatic dicarboxylic acid corrosion inhibitor of this invention may be synthesized by the reaction of PIBSA with polyamine and terephthalic acid shown in formula (2). Diethylenetriamine (DETA) may be used as the polyamine in this reaction. Any polyamine may be used.



[0042] Another embodiment of the dispersed aromatic dicarboxylic acid corrosion inhibitor of this invention may be synthesized as follows. One or more PIBSAs may be reacted with one or more polyamines to produce one or more succinimides by heating the mixture, with or without diluent, at a temperature of from about 110° C. to about 200° C., preferably about 150° C. to about 170° C., for 1 to 20 hours. Heating for about 3 to about 6 hours is preferred. Reactants may be mixed and then heated or heating may occur while the reactants are being mixed. During the heating period, water of the reaction may be removed by any means known in the art. Any PIBSA may be used. This includes thermal PIBSA made from conventional PIB or high reactivity PIB, chlorination PIBSA, a mixture of thermal and chlorination PIBSA, sulfonic acid catalyzed PIBSA, PolyPIBSA, or Terpolymer PIBSA. A mixture of PIBSA and a copolymer may also be used. An amine/PIBSA charge mole ratio (CMR) of about 0.4 to 0.6 may be used. A preferred CMR may be about 0.4 to about 0.5. After heating, the reaction mixture may be cooled to about 110° C. to about 150° C., preferably about 130° C. to about 135° C. Terephthalic acid may then be added. About 2% to about 5% terephthalic acid, preferably about 2.5% to about 3.5% by weight, based on the succinimide weight may be used. This mixture may then be heated for about 1 to about 10 hours, preferably about 2 to about 4 hours. The mixture may then be filtered.

[0043] Another embodiment of this invention may comprise one or more corrosion inhibitors synthesized by reacting 1000 molecular weight polyisobutenesuccinic anhydride (PIBSA) with tetraethylenepentamine (TEPA) using an amine/PIBSA charge mole ratio (CMR) of 0.71. This produces a reaction product, which may then be reacted with terephthalic acid to form a dispersed aromatic dicarboxylic acid corrosion inhibitor.

[0044] Another embodiment of this invention may comprise combining one or more of the dispersed aromatic dicarboxylic acid corrosion inhibitors of this invention.

[0045] IV. The Dispersant Inhibitor Package of this Invention and Method of Preparation

[0046] Another embodiment of this invention may comprise a Dispersant Inhibitor Package that comprises one or more borated dispersants comprising EC-treated dispersants, borated dispersants, one or more corrosion inhibitors, and any other additives traditionally used in lubricating oils. The components of the DI-Package may be combined in any order and heated to about 80° F. to about 200° F., preferably to about 145° F. to about 155° F., with agitation until all components are mixed. The components may either be mixed together while heating or mixed together and then heated to these temperatures. The DI-Package may be blended with viscosity improver additives and added to lubricating oil or the viscosity improver additives may be added to the oil separately or added to the DI-Package with the other DI-Package components. The DI-Package may comprise greater than 0% to about 30% of one or more borated dispersants, preferably about 10% to about 20%; about 10% to about 80% EC-treated dispersants, preferably about 20% to about 60%; and greater than 0% to about 5%, preferably about 0.5% to about 3% of one or more dispersed aromatic dicarboxylic acid corrosion inhibitors and any other additives traditionally used in lubricating oils. The percentages in the previous sentence are weight percentages of the DI-Package.

[0047] IV. Additional Additive Components

[0048] The following additive components are examples of some of the components that may be favorably employed

in some embodiments of this invention. These examples of additives are provided to illustrate this invention, but they are not intended to limit it.

**[0049] A. Antioxidants**

**[0050]** Embodiments of this invention may include but are not limited to such antioxidants as phenol type (phenolic) oxidation inhibitors, such as 4,4'-methylene-bis(2,6-di-tert-butylphenol), 4,4'-bis(2,6-di-tert-butylphenol), 4,4'-bis(2-methyl-6-tert-butylphenol), 2,2'-methylene-bis(4-methyl-6-tert-butylphenol), 4,4'-butylidene-bis(3-methyl-6-tert-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-butyl-phenol, 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). Diphenylamine-type oxidation inhibitors include, but are not limited to, alkylated diphenylamine, phenyl- $\alpha$ -naphthylamine, and alkylated- $\alpha$ -naphthylamine. Other types of oxidation inhibitors include metal dithiocarbamate (e.g., zinc dithiocarbamate), and methylenebis (dibutyldithiocarbamate).

**[0051] B. Wear Inhibitors**

**[0052]** Embodiments of this invention may comprise traditional wear inhibitors. 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.

**[0053] C. Rust Inhibitors (Anti-Rust Agents)**

**[0054]** Embodiments of this invention may comprise traditional rust inhibitors including, but not limited to:

**[0055]** 1. Nonionic polyoxyethylene surface active agents: polyoxyethylene lauryl ether, polyoxyethylene higher alcohol ether, polyoxyethylene nonyl phenyl ether, polyoxyethylene octyl phenyl ether, polyoxyethylene octyl stearyl ether, polyoxyethylene oleyl ether, polyoxyethylene sorbitol monostearate, polyoxyethylene sorbitol mono-oleate, and polyethylene glycol mono-oleate; and

**[0056]** 2. Other compounds: stearic acid and other fatty acids, dicarboxylic acids, metal soaps, fatty acid amine salts, metal salts of heavy sulfonic acid, partial carboxylic acid ester of polyhydric alcohol, and phosphoric ester.

**[0057] D. Demulsifiers**

**[0058]** Embodiments of this invention may comprise traditional demulsifiers including but not limited to addition products of alkylphenol and ethylene oxide, polyoxyethylene alkyl ether, and polyoxyethylene sorbitan ester.

**[0059] E. Extreme Pressure Agents (EP Agents)**

**[0060]** Embodiments of this invention may comprise traditional EP Agents including but not limited to EP Agents that may be used include Zinc dialkyldithiophosphate (pri-

mary alkyl, secondary alkyl, and aryl type), sulfurized oils, diphenyl sulfide, methyl trichlorostearate, chlorinated naphthalene, fluoroalkylpolysiloxane, and lead naphthenate.

**[0061] F. Friction Modifiers**

**[0062]** Embodiments of this invention may comprise traditional friction modifiers including but not limited to fatty alcohol, fatty acid, amine, borated ester, and other esters.

**[0063] G. Multifunctional Additives**

**[0064]** Embodiments of this invention may comprise traditional multifunctional additives including but not limited to sulfurized oxymolybdenum dithiocarbamate, sulfurized oxymolybdenum organo phosphorodithioate, oxymolybdenum monoglyceride, oxymolybdenum diethylate amide, amine-molybdenum complex compound, and sulfur-containing molybdenum complex compound may be used.

**[0065] H. Viscosity Index Improvers**

**[0066]** Embodiments of this invention may comprise traditional viscosity index improvers including but not limited to polymethacrylate type polymers, ethylene-propylene copolymers, styrene-isoprene copolymers, hydrated styrene-isoprene copolymers, polyisobutylene, and dispersant type viscosity index improvers may be used.

**[0067] I. Pour Point Depressants**

**[0068]** Embodiments of this invention may comprise traditional pour point depressants including but not limited to polymethyl methacrylate may be used.

**[0069] J. Foam Inhibitors**

**[0070]** Embodiments of this invention may comprise traditional foam inhibitors including but not limited to alkyl methacrylate polymers and dimethyl silicone polymers may be used.

**[0071] V. Lubricating Oil of This Invention**

**[0072]** One embodiment of this invention is a lubricating oil comprising a major amount of one or more oils of lubricating viscosity and one or more of the dispersed aromatic dicarboxylic acid corrosion inhibitors of this invention. The corrosion inhibitor of this invention may be added to the lubricating oil separately or as part of the additive package of this invention.

**[0073]** One embodiment of this invention is a lubricating oil comprising a major amount of one or more oils of lubricating viscosity and one or more of the DI-Packages of this invention. The DI-Package this invention may be added to the lubricating oil as a package or the components of the DI-Package of this invention may be added separately and in any order.

**[0074]** The oil of lubricating viscosity used in such embodiments may be mineral oils or synthetic oils. A base oil having a viscosity of at least 2.5 cSt at 40° C. and a pour point below 20° C., preferably at or below 0° C. is desirable. The base oils may be derived from synthetic or natural sources. Mineral oils for use as the base oil in this invention include, for example, paraffinic, naphthenic and other oils that are ordinarily used in lubricating oil compositions. Synthetic oils include, for example, both hydrocarbon synthetic oils and synthetic esters and mixtures thereof having the desired viscosity. Hydrocarbon synthetic oils may

include, for example, oils prepared from the polymerization of ethylene, 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 C<sub>6</sub> to C<sub>12</sub> 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. The components of the lubricating oil may be combined while heating to a temperature from about 80° F. to about 200° F., preferably about 145° F. to about 155° F. with agitation until all components are mixed. The components of the lubricating oil of this invention may either be mixed together while heating or mixed together and then heated to these temperatures.

**[0075]** An embodiment of this invention may comprise a lubricating oil that comprises an oil of lubricating viscosity and the Dispersant Inhibitor Package of this invention. The Dispersant Inhibitor Package of this invention may be added to an oil of lubricating viscosity in any manner and the individual components of the Dispersant Inhibitor Package may be combined with an oil of lubricating viscosity separately or as a Dispersant Inhibitor Package. Additional additives generally known in the lubricating oil industry may also be added individually or in combination with the additive formulation of this invention.

**[0076]** An embodiment of this invention may comprise lubricating oil compositions having a major amount of a base oil of lubricating viscosity, the EC-treated Dispersant and Borated Dispersant Combination of this invention (about 1% to about 20%, preferably about 3% to about 10%), the dispersed aromatic dicarboxylic acid corrosion inhibitor of this invention (greater than 0% to about 1%, preferably about 0.05% to about 0.3%, most preferably about 0.1% to about 0.2%).

**[0077]** Another embodiment of this invention may additionally comprise one or more of the following: detergent (greater than about 1% to about 10%, preferably about 2% to about 5%, most preferably about 3% to about 4%), zinc dithiophosphate (greater than 0% to about 3%, preferably about 0.5% to about 2.5%, most preferred about 1% to about 2%), oxidation inhibitor (greater than 0% to about 3%, preferably greater than 0% to about 1%, most preferred 0.2% to about 0.8%), foam inhibitor (greater than 0% to about 1%), and viscosity index improver (greater than 0% to about 20%). Any zinc dithiophosphate may be used, but a preferred zinc dithiophosphate may comprise one or more secondary zinc dithiophosphates. The percentages in this lubricating oil section are weight percent of the finished lubricating oil.

**[0078]** Another embodiment of this invention comprises one or more Lubricating Oil Compositions, wherein the ratio of EC-treated succinimide to one or more borated succinimide is between about 100 to about 1 and about 10 to about 1.

**[0079]** VI. Methods of Lubricating Engine Embodiments of This Invention

**[0080]** Another embodiment of this invention may comprise a method for reducing bearing corrosion in one or more diesel engines equipped with exhaust gas recirculation resulting in increased levels of nitration of the lubricating oil used to lubricate the engine.

**[0081]** Another embodiment of this invention may comprise a method for lubricating one or more engines comprising contacting the engine with one or more lubricating oils of this invention.

**[0082]** Another embodiment of this invention may comprise a method for lubricating one or more internal combustion engines comprising contacting the engine with one or more lubricating oils of this invention.

**[0083]** Another embodiment of this invention may comprise a method for lubricating one or more heavy-duty diesel engines comprising contacting the engine with one or more lubricating oils of this invention.

**[0084]** The following examples are included to demonstrate preferred embodiments of the invention. It should be appreciated by those of skill in the art that the techniques disclosed in the examples that follow may represent techniques discovered by the inventor to function well in the practice of the invention, and thus may be considered to constitute preferred modes for its practice. However, those of skill in the art should, in light of the present disclosure, appreciate that many changes may be made in the specific embodiments that are disclosed and still obtain a like or similar result without departing from the spirit and scope of the invention.

#### EXAMPLES

**[0085]** The examples describe experiments performed using Corrosion Inhibitors 1, 2 and 3 and Samples A through K. The corrosion inhibition performance of these samples has been evaluated in a number of bench and engine tests, which will be discussed in the various examples. Some of the samples contain non-EC-treated dispersant in addition to the EC-treated dispersant (a) and the borated dispersant (c).

**[0086]** Corrosion Inhibitor 1 was prepared by adding 400 g of 1000 molecular weight PIBSA (saponification number 67.1 mg KOH/g sample, 0.24 mole) to an apparatus comprising a 1L three neck flask equipped with a mechanical stirrer, Dean Stark trap, condenser and nitrogen inlet. This was heated to 70° C. and to this was added 32.2 g tetraethylene pentamine (TEPA), 0.17 mole, as the temperature was heated to 160° C. The amine/PIBSA CMR was 0.71. This product was heated at 160° C. for 3 hours. To 387.75 g of this product, we added 156.9 g diluent oil and to this was added at 132° C. 20.95 g terephthalic acid (0.126 mole). This was stirred for 3 hours at 132° C. The product was then filtered.

**[0087]** Corrosion Inhibitor 2 was prepared by adding 400 g of 1000 molecular weight PIBSA (saponification number 67.1 mg KOH/g sample, 0.24 mole) to an apparatus comprising a 1L three neck flask equipped with a mechanical stirrer, Dean Stark trap, condenser and nitrogen inlet. This was heated to 70° C. and to this was added 32.2 g of a mixture of 20% DETA and 80% HPA, 0.17 mole, as the

temperature was heated to 160° C. The amine/PIBSA CMR was 0.71. This product was heated at 160° C for 3 hours. To 387.75 g of this product, we added 156.9 g diluent oil and to this was added at 132° C. 20.95 g terephthalic acid (0.126 mole). This was stirred for 3 hours at 132° C. The product was then filtered.

**[0088]** Corrosion Inhibitor 3 was prepared by following the general procedure from corrosion inhibitor 1 and then 16834 g of a succinimide made from 1300 molecular weight PIBSA with HPA using a CMR of 0.45 was mixed with 4218 g diluent oil and reacted with 780 g of terephthalic acid. The product after filtration had 1.85% nitrogen, TAN=29 mg KOH/g sample, TBN=43.7 mg KOH/g sample, and a viscosity @100° C. of 596 cSt.

**[0089]** Sample A was prepared by combining about 7.0% EC-treated dispersant (a), about 2.0% borated dispersant (c), about 0.855% LOB Sulfonate, about 2.709% Ca-Phenate, about 2.075% wear inhibitor, 1.25% anti-oxidant, about 5 mg/kg foam inhibitor, and Group 1 base oil. Sample A was prepared by combining the components at 140° F. with agitation until all components were mixed.

**[0090]** Sample B was prepared by combining about 7.0% EC-treated dispersant (a), about 2.0% borated dispersant (c), about 0.855% LOB Sulfonate, about 2.709% Ca-Phenate, about 2.075% wear inhibitor, 1.25% anti-oxidant, about 5 mg/kg foam inhibitor, about 0.25% Corrosion Inhibitor 1 and Group 1 base oil. Sample B was prepared by combining the components at 140° F. with agitation until all components were mixed.

**[0091]** Sample C was prepared by combining about 7.0% EC-treated dispersant (a), about 2.0% borated dispersant (c), about 0.855% LOB Sulfonate, about 2.709% Ca-Phenate, about 2.075% wear inhibitor, 1.25% anti-oxidant, about 5 mg/kg foam inhibitor, about 0.5% Corrosion Inhibitor 1 and Group 1 base oil. Sample C was prepared by combining the components at 140° F. with agitation until all components were mixed.

**[0092]** Sample D was prepared by combining about 6.0% EC-treated dispersant (a), about 1.0% non-EC-treated dispersant, about 0.6% borated dispersant (c), about 0.684% LOB Sulfonate, about 2.924% Ca-Phenate, about 1.826% wear inhibitor, 0.57% anti-oxidant, about 5 mg/kg foam inhibitor, and Group 1 base oil. Sample D was prepared by combining the components at 140° F. with agitation until all components were mixed.

**[0093]** Sample E was prepared by combining about 6.0% EC-treated dispersant (a), about 1.0% non-EC-treated dispersant, about 0.6% borated dispersant (c), about 0.684% LOB Sulfonate, about 2.924% Ca-Phenate, about 1.826% wear inhibitor, 0.57% anti-oxidant, about 5 mg/kg foam inhibitor, about 0.10 Corrosion Inhibitor 2 and Group 1 base oil. Sample E was prepared by combining the components at 140° F. with agitation until all components were mixed.

**[0094]** Sample F was prepared by combining about 6.0% EC-treated dispersant (a), about 1.0% non-EC-treated dispersant, about 0.6% borated dispersant (c), about 0.684% LOB Sulfonate, about 2.924% Ca-Phenate, about 1.826% wear inhibitor, 0.57% anti-oxidant, about 5 mg/kg foam inhibitor, about 0.20 Corrosion Inhibitor 2 and Group 1 base oil. Sample F was prepared by combining the components at 140° F. with agitation until all components were mixed.

**[0095]** Sample G was prepared by combining about 6.0% EC-treated dispersant (a), about 1.0% non-EC-treated dispersant, about 0.6% borated dispersant (c), about 0.684% LOB Sulfonate, about 2.924% Ca-Phenate, about 1.826% wear inhibitor, 0.57% anti-oxidant, about 5 mg/kg foam inhibitor, about 0.40% Corrosion Inhibitor 2 and Group 1 base oil. Sample G was prepared by combining the components at 140° F. with agitation until all components were mixed.

**[0096]** Sample H was prepared by combining about 6.0% EC-treated dispersant (a), about 1.0% non-EC-treated dispersant, about 0.6% borated dispersant (c), about 0.684% LOB Sulfonate, about 2.924% Ca-Phenate, about 1.826% wear inhibitor, 0.57% anti-oxidant, about 5 mg/kg foam inhibitor, about 0.10% Corrosion Inhibitor 3 and Group 1 base oil. Sample H was prepared by combining the components at 140° F. with agitation until all components were mixed.

**[0097]** Sample I was prepared by combining about 6.0% EC-treated dispersant (a), about 1.0% non-EC-treated dispersant, about 0.6% borated dispersant (c), about 0.684% LOB Sulfonate, about 2.924% Ca-Phenate, about 1.826% wear inhibitor, 0.57% anti-oxidant, about 5 mg/kg foam inhibitor, about 0.20% Corrosion Inhibitor 3 and Group 1 base oil. Sample I was prepared by combining the components at 140° F. with agitation until all components were mixed.

**[0098]** Sample J was prepared by combining about 6.0% EC-treated dispersant (a), about 1.0% non-EC-treated dispersant, about 0.6% borated dispersant (c), about 0.684% LOB Sulfonate, about 2.924% Ca-Phenate, about 1.826% wear inhibitor, 0.57% anti-oxidant, about 5 mg/kg foam inhibitor, about 0.30% Corrosion Inhibitor 3 and Group 1 base oil. Sample J was prepared by combining the components at 140° F. with agitation until all components were mixed.

**[0099]** Sample K was prepared by combining about 6.0% EC-treated dispersant (a), about 1.0% non-EC-treated dispersant, about 0.6% borated dispersant (c), about 0.684% LOB Sulfonate, about 2.924% Ca-Phenate, about 1.826% wear inhibitor, 0.57% anti-oxidant, about 5 mg/kg foam inhibitor, about 0.40% Corrosion Inhibitor 3 and Group 1 base oil. Sample K was prepared by combining the components at 140° F. with agitation until all components were mixed.

#### Example 1

**[0100]** Bearing Corrosion Evaluation in Engine Test

**[0101]** The Mack T-10 engine test has been developed by the American Society for Testing and Materials (ASTM). The test is part of the API lubricant specification for diesel engines, CI-4, and measures piston ring, cylinder liner, and bearing wear. Bearing wear in this test is the result of corrosion of the copper-lead surface of the bearings. The conventional approach to bearing protection is the neutralization of acidic contaminants responsible for bearing corrosion. Neutralization capability is provided by detergents and the base reserve during the test is monitored by the Total Base Number (TBN). The capability of an oil to protect the bearing material from corrosion is evaluated by determining the amount of lead (Pb) found in oil samples taken from the

engine at regular intervals during the test and at the end of the test. This determination of the Pb-content is done using an ICP analysis. Lower Pb-contents indicate better corrosion protection.

[0102] Samples A and C were tested in the Mack T-10 engine test. Results are presented in Table 1. The results demonstrate that both samples show TBN depletion to the point where corrosion becomes a concern. In the case of Sample A, the Pb-content increases gradually over the course of the test and increases exponentially toward the end on the test indicating that the corrosion is out of control. Sample C, which contains Corrosion Inhibitor 1, shows TBN depletion and a gradual increase in Pb-content over the duration of the test but did not show any exponential increase in Pb toward the end of the test.

TABLE 1

<u>Bearing Corrosion Engine Test Results</u>				
Test Time, h	Sample A		Sample C	
	TBN, mg/g KOH	Pb-Content, mg/kg	TBN, mg/g KOH	Pb-Content, mg/kg
0	8.01	1	8.08	1
50	4.43	2	4.24	2
100	2.80	4	2.28	7
150	1.93	7	1.18	17
200	1.21	13	0.51	24
250	0.51	33	0.11	34
275	0.62	65	0.25	38
300	0.05	88	0.05	43

## Example 2

## [0103] Bearing Corrosion Bench Test Evaluation

[0104] Samples A through C were evaluated in a bearing corrosion bench test. This bench test has been designed to mimic the Mack T-10 engine test where the wear phase is preceded by a lubricant degradation phase where the oil sees significant TBN depletion as a result of contamination with condensed acids. In the bearing corrosion bench test, a sample of the candidate oil was contaminated with H<sub>2</sub>SO<sub>4</sub>. The contaminated sample was exposed to an elevated temperature for about 20 hours while NO<sub>2</sub> in air was pumped through the sample. Three metal coupons (Cu, Pb and Fe) were submersed in the sample during the test. At the end of the test, the amount of Pb in the oil sample was determined using the ICP.

[0105] Samples A, B and C were evaluated in the bearing corrosion bench test and the Pb-content of the oil at the end of the test was measured. The results are shown in Table 2.

TABLE 2

<u>Bearing Corrosion Bench Test Results</u>			
	Sample A	Sample B	Sample C
Corrosion Inhibitor 1 Treat Rate, %	0.00	0.25	0.50
Used Oil Pb-Content, mg/kg	217	119	51

## Example 3

## [0106] Bearing Corrosion Evaluation in Bench Test

[0107] Samples D through G were evaluated in the bearing corrosion bench test. This bench test has been described in Example 2. The results are shown in Table 3.

TABLE 3

<u>Bearing Corrosion Bench Test Results</u>				
	Sample D	Sample E	Sample F	Sample G
Corrosion Inhibitor 2 Treat Rate, %	0.00	0.10	0.20	0.40
Used Oil Pb-Content, mg/kg	164	73	77	66

## Example 4

## [0108] Bearing Corrosion Evaluation in Bench Test

[0109] Samples H through K were evaluated in the bearing corrosion bench test, and compared with Sample D. This bench test has been described in Example 2. The results are shown in Table 4.

TABLE 4

<u>Bearing Corrosion Bench Test Results Using Corrosion Inhibitors of This Invention</u>					
	Sample D	Sample H	Sample I	Sample J	Sample K
Corrosion Inhibitor 3 Treat Rate, %	0.00	0.10	0.20	0.30	0.40
Used Oil Pb-Content, mg/kg	164	79	73	70	42

What is claimed is:

1. A lubricating oil additive composition comprising:
  - (a) one or more ethylene carbonate-treated succinimides;
  - (b) one or more borated succinimides, and
  - (c) one or more dispersed aromatic dicarboxylic acid corrosion inhibitors which are succinimide salts of one or more aromatic dicarboxylic acids.
2. The lubricating oil additive composition of claim 1, wherein the corrosion inhibitors are one of more succinimide salts of terephthalic acid.
3. The lubricating oil additive composition of claim 2, wherein the succinimide salts of terephthalic acid are polyisobutenyl succinimide salts.
4. The lubricating oil additive composition of claim 1, wherein the ethylene carbonate-treated succinimide is a polybutene succinimide derived from the reaction product of a polyisobutenyl succinic anhydride with a polyamine.
5. The lubricating oil additive composition of claim 4, wherein the ethylene carbonate-treated succinimide is derived from polybutenes having a molecular weight of from at least 1800.
6. The lubricating oil additive composition of claim 1, wherein the borated succinimide is derived from the reaction product of a polyisobutenyl succinic anhydride with a polyamine.



7. The lubricating oil additive composition of claim 6, wherein the borated succinimide is derived from polybutenes having a molecular weight of from 1200 to 1400.

8. A lubricating oil composition comprising a major amount of an oil of lubricating viscosity and a lubricating oil additive composition comprising:

- (a) one or more ethylene carbonate treated succinimides,
- (b) one or more borated succinimides, and
- (c) one or more dispersed aromatic dicarboxylic acid corrosion inhibitors which are succinimide salts of one or more aromatic dicarboxylic acids.

9. A method for lubricating an internal combustion engine comprising contacting the engine with a lubricating oil composition of claim 8.

10. The method of claim 9, wherein the internal combustion engine is a heavy duty diesel engine.

11. A method for reducing bearing corrosion in a diesel engine which comprises operating the engine with a lubricating oil composition of claim 8.

\* \* \* \* \*