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JUNG et al.(10) **Pub. No.: US 2014/0338253 A1**(43) **Pub. Date: Nov. 20, 2014**(54) **FUEL ADDITIVE COMPOSITION**(71) Applicant: **BASF SE**, Ludwigshafen (DE)(72) Inventors: **Alfred K. JUNG**, Carmel, NY (US);
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14, 2013.**Publication Classification**(51) **Int. Cl.**
C10L 1/232 (2006.01)(52) **U.S. Cl.**CPC **C10L 1/232** (2013.01)USPC **44/347**(57) **ABSTRACT**

A fuel additive composition includes a polyalkenylsuccinimide, a mono or polyfunctional polyisobutene amine, and a carrier oil selected from the group of mineral oils, polyethers, polyetheramines, esters, and combinations thereof. The polyalkenylsuccinimide includes the reaction product of a hydrocarbyl dicarboxylic acid producing reaction intermediate and a nucleophilic reactant. The hydrocarbyl dicarboxylic acid producing reaction intermediate includes the reaction product of a polyolefin comprising C₂ to C₁₈ olefin units and having a number average molecular weight (M_n) of about 500 to 5,000 g/mol and a C₄ to C₁₀ monounsaturated acid reactant. The hydrocarbyl dicarboxylic acid producing reaction intermediate includes from 0.5 to 10 dicarboxylic acid producing moieties per molecule of the polyolefin. The nucleophilic reactant is selected from the group of amines, alcohols, amino alcohols, and combinations thereof.

FUEL ADDITIVE COMPOSITION

FIELD OF THE DISCLOSURE

[0001] The present disclosure generally relates to a fuel additive composition for improving the fuel economy of engines and reducing deposits within these engines. The fuel additive composition includes a polyalkenylsuccinimide, a polyisobutene amine, and a carrier oil.

DESCRIPTION OF THE RELATED ART

[0002] Modern vehicles include sophisticated combustion engines, which optimize combustion, emissions, performance, durability, and fuel economy. Fuel additive compositions (e.g. gasoline performance packages), which include fuel economy and additional fuel additives, such as detergents, can be added to fuel to further optimize combustion, emissions, performance, durability, and fuel economy of such engines.

[0003] These engines typically include one or more pistons which are located inside a cylinder. Fuel and air is introduced into the cylinder and ignited to move the piston and power the engine. Fuel economy additives reduce friction between the piston and the cylinder and thus reduce fuel consumption and improve the fuel economy of the engine.

[0004] Fuel additive compositions may include fuel additives such as the reaction products of a carbonic acid or a derivative thereof and a polyalcohol and/or alkanol amine, and fatty acid amides and propoxylated fatty acid amides. Fuel additive compositions may also include various fuel additives such as polyalkene amines and polyalkenylsuccinimides. Fuel additive compositions may further include various carrier oils known in the art, including mineral oils and synthetic oils.

[0005] However, fuel additive compositions comprising fuel additives such as those set forth above, e.g. polyalkenylsuccinimide, etc., are generally immiscible with one another. As such, fuel additive compositions that include such fuel additives can often be non-homogeneous and non-pumpable or may even form precipitates, separate into two phases, and/or solidify over various times and at various temperatures.

[0006] Because it is technically and commercially desirable that such fuel additive compositions be homogeneous and pumpable over a broad range of temperatures, even at temperatures as low as $-20^{\circ}\text{C}.$, solubilizers have been used to improve miscibility of additives and the homogeneity of fuel additive compositions formed therefrom. However, these solubilizers are costly and do not typically contribute to performance improvement of engines. In some cases these solubilizers can even cause negative side effects such as poor seal compatibility, oil dilution, and higher levels of combustion chamber deposits. Such deposits can cause enrichment of fuel to air ratios in engines which result in increased hydrocarbon and carbon monoxide emissions, driving problems such as rough idling and frequent stalling, reduced fuel economy, and decreased engine life.

[0007] As such, there remains an opportunity to develop improved fuel additives which are miscible with additional fuel additives, and also an opportunity to develop fuel additive compositions formed with the improved fuel additives that are stable over a broad range of temperatures and conditions and that improve fuel economy of internal combustion engines.

SUMMARY OF THE DISCLOSURE AND ADVANTAGES

[0008] In some aspects, a fuel additive composition includes a polyalkenylsuccinimide, a mono or polyfunctional polyisobutene amine, and a carrier oil selected from the group of mineral oils, polyethers, polyetheramines, esters, and combinations thereof. The polyalkenylsuccinimide itself includes the reaction product of a hydrocarbyl dicarboxylic acid producing reaction intermediate and a nucleophilic reactant. The hydrocarbyl dicarboxylic acid producing reaction intermediate includes the reaction product of a polyolefin comprising C_2 to C_{18} olefin units and having a number average molecular weight (M_n) of about 500 to 5,000 g/mol and a C_4 to C_{10} monounsaturated acid reactant. The hydrocarbyl dicarboxylic acid producing reaction intermediate includes from 0.5 to 10 dicarboxylic acid producing moieties per molecule of the polyolefin. The nucleophilic reactant is selected from the group of amines, alcohols, amino alcohols, and combinations thereof.

[0009] The polyalkenylsuccinimide improves the fuel economy of internal combustion engines when added to fuel yet is miscible with the polyisobutene amine and the carrier oil included in the fuel additive compositions. As such, the fuel additive compositions possess excellent storage stability and remain homogenous over a wide range of times and temperatures and do not require inclusion of a solubilizer. Further, the fuel additive compositions can be added to fuel in minimal amounts to improve fuel economy and reduce engine deposits and emissions.

DETAILED DESCRIPTION OF THE DISCLOSURE

[0010] In some aspects, the present disclosure provides fuel additive compositions ("compositions"). The compositions include: (A) a polyalkenylsuccinimide, (B) a mono or polyfunctional polyisobutene amine, and (C) a carrier oil. The compositions can be used in fuels, such as diesel fuels, gasoline, kerosene or middle distillates, and heating oil, and can also be used as an additive in lubricants. The compositions can be used as a fully formulated fuel additive composition, which can be added to fuel to reduce fuel consumption and thus improve fuel economy of an internal combustion engine. As a fuel additive, the compositions also reduce deposits in carburetors, fuel intake systems, and engines, reduce emissions, and improve engine performance.

The Polyalkenylsuccinimide (A)

[0011] In some embodiments, the polyalkenylsuccinimide (A) includes the reaction product of: (1) a hydrocarbyl dicarboxylic acid producing reaction intermediate and (2) a nucleophilic reactant.

The Hydrocarbyl Dicarboxylic Acid Producing Reaction Intermediate (A.1)

[0012] In some embodiments, the reaction intermediate (A.1) includes the reaction product of: (A.1.a) a polyolefin comprising C_2 to C_{18} olefin units and having a number average molecular weight (M_n) of about 500 to 5,000 g/mol and (A.1.b) a C_4 to C_{10} monounsaturated acid reactant. The polyolefin (A.1.a) and the C_4 to C_{10} monounsaturated acid reac-

tant (A.1.b) can be reacted by way of various reaction mechanisms under various conditions to form the reaction intermediate (A.1).

[0013] For example, the reaction intermediate (A.1) can be formed via an “ene” reaction by heating a mixture of the polyolefin (A.1.a) and the C_4 to C_{10} monounsaturated acid reactant (A.1.b). In such an “ene” reaction, the polyolefin (A.1.a) undergoes an addition of the C_4 to C_{10} monounsaturated acid reactant (A.1.b) at a double bond. As another example, the polyolefin (A.1.a) can be first halogenated, for example, chlorinated or brominated with from 1 to 8, alternatively from 3 to 7, weight % chlorine or bromine, based on the weight of polyolefin (A.1.a). By passing the chlorine or bromine through the polyolefin (A.1.a) at a temperature of from 60 to 160, alternatively from 110 to 130, ° C. for from 0.5 to 10, alternatively from 1 to 7, hours to form a halogenated polyolefin. The halogenated polyolefin is then reacted with the C_4 to C_{10} monounsaturated acid reactant (A.1.b) at a temperature of from 100 to 250, alternatively from 180 to 235, ° C. for a time of from 0.5 to 10, alternatively from 3 to 8, hours, to form the reaction intermediate (A.1).

[0014] The hydrocarbyl dicarboxylic acid producing reaction intermediate (A.1) can include a polyolefin substituted with dicarboxylic acid producing moieties. Specifically, the reaction intermediate (A.1) is, for example, an acid, an anhydride, or ester which includes a long chain hydrocarbon (polyolefin (A.1.a)) substituted with an average of from 0.5 to 10.0, alternatively from 0.5 to 5, alternatively from 0.7 to 2.0, alternatively from 0.7 to 1.7, alternatively from 0.9 to 1.7, mol of the C_4 to C_{10} monounsaturated acid reactant (A.1.b), i.e., dicarboxylic acid producing moieties, per mol of polyolefin (A.1.a). In one embodiment, the reaction intermediate (A.1) is a polyalkenylsuccinic anhydride, e.g. a polyisobutenylsuccinic anhydride. These functionality ratios of dicarboxylic acid producing moieties to polyolefin, e.g. 1.2 to 2.0, etc., are based upon the total amount of polyolefin (A.1.a) that is present in the resulting product formed in the aforementioned reactions.

The Polyolefin (A.1.a)

[0015] The polyolefin (A.1.a) of the subject disclosure includes C_2 to C_{18} , alternatively C_2 to C_{10} , alternatively C_2 to C_8 , alternatively C_2 to C_6 , olefin units. Non-limiting examples of olefin units include ethylene, propylene, butylene, isobutylene, pentene, octene-1, and styrene. In some embodiments, the polyolefin (A.1.a) is a polyalkene. The polyolefin (A.1.a) can be homopolymer, such as polyisobutylene, or copolymer of two or more of different olefin units. Non-limiting examples of copolymers which can be used to form the polyolefin (A.1.a) include ethylene and propylene, butylene and isobutylene, propylene and isobutylene. Additional non-limiting examples of copolymers include copolymers that include a minor molar amount of olefin units, e.g. 1 to 10 mol %, are C_4 to C_{18} non-conjugated diolefin units such as a copolymer of isobutylene and butadiene or a copolymer of ethylene, propylene, and 1,4-hexadiene.

[0016] The polyolefin (A.1.a) can be linear or branched. In some embodiments, the polyolefin (A.1.a) has a number average molecular weight (M_n) of from 500 to 5,000, alternatively from 750 to 4,000, alternatively from 1,000 to 3,000, alternatively from 1,000 to 2,000, g/mol.

[0017] The polyolefin (A.1.a) can be saturated or unsaturated. One non-limiting example of the polyolefin (A.1.a) which is saturated is an ethylene-propylene copolymer made

by a Ziegler-Natta synthesis using hydrogen as a moderator to control molecular weight. In some embodiments, the polyolefin (A.1.a) is unsaturated. In some embodiments, the polyolefin (A.1.a) includes a terminal double bond.

[0018] To this end, in one embodiment, the polyolefin (A.1.a) is a first reactive polyisobutene. The first reactive polyisobutene is a highly reactive polyisobutene which has a high content of terminal ethylenic double bonds. Terminal double bonds are alpha-olefinic double bonds, e.g. vinylidene double bonds. The first reactive polyisobutene can have a content of terminal double bonds of greater than 50, alternatively greater than 70, alternatively greater than 75, alternatively greater than 80, alternatively greater than 85, mol %. The first reactive polyisobutene can have a uniform polymer backbone which includes greater than 85, alternatively greater than 90, alternatively greater than 95, % by weight of isobutene units.

[0019] The first reactive polyisobutene can have a number average molecular weight (M_n) of from 500 to 5,000, alternatively from 800 to 4,000, alternatively from 800 to 3,000, alternatively from 800 to 2,000, g/mol. The dispersity D (M_w/M_n), i.e., the quotient of the weight average molecular weight M_w divided M_n , of the first reactive polyisobutene is less than 7, alternatively less than 3, alternatively from 1.05 to 7. In some embodiments, the dispersity D (M_w/M_n) of the first reactive polyisobutene is less than 3. In some embodiments, the first reactive polyisobutene has a dispersity of less than 2.0 for M_n less than or equal to 2,000, and a dispersity of less than 1.5 for M_n less than or equal to 1,000. In some embodiments, the first reactive polyisobutene is free of organic and inorganic bases, water, alcohols, ethers, acids and peroxides.

[0020] Suitable non-limiting examples of the first reactive polyisobutene are commercially available from BASF SE under the GLISSOPAL® brand of polyisobutenes.

The C_4 to C_{10} Monounsaturated Acid Reactant (A.1.b)

[0021] The C_4 to C_{10} monounsaturated acid reactant (A.1.b) reacts with the polyolefin (A.1.a) to form the reaction intermediate (A.1). The C_4 to C_{10} monounsaturated acid reactant (A.1.b) can be an alpha or beta unsaturated C_4 to C_{10} dicarboxylic acid, anhydride or ester thereof. Non-limiting examples of the C_4 to C_{10} monounsaturated acid reactant (A.1.b) include fumaric acid, itaconic acid, maleic acid, maleic anhydride, chloromaleic acid, dimethyl fumarate, chloromaleic anhydride, and combinations thereof.

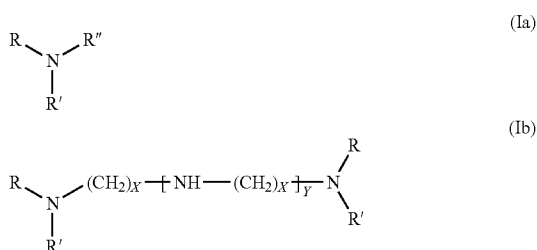
[0022] In one embodiment, the C_4 to C_{10} monounsaturated acid reactant (A.1.b) is selected from the group of maleic acid, maleic anhydride, functional derivatives thereof, and combinations thereof. As used in the above sentence, the term functional derivative describes derivatives of maleic acid or maleic anhydride which react with the polyolefin (A.1.a) to form the same or a comparable result or product, i.e., the reaction intermediate (A.1). In the case of maleic acid, functional derivatives include, for example, monoalkyl maleates, dialkyl maleates, maleyl dichloride, maleyl dibromide, maleic acid monoalkyl ester monochloride, or maleic acid monoalkyl ester monobromide. The alcohol components, in the case of the maleates are, for example, lower alkyl radicals of, for example, 1 to 6, in particular 1 to 4, carbon atoms, for example methyl or ethyl. In some embodiments, the C_4 to C_{10} monounsaturated acid reactant (A.1.b) is maleic anhydride. In one embodiment, maleic anhydride is reacted with the first reactive polyisobutene to form the reaction intermediate (A.1) comprising polyisobutenylsuccinic anhydride.

The Nucleophilic Reactant (A.2)

[0023] As set forth above, the polyalkenylsuccinimide (A) includes the reaction product of the hydrocarbyl dicarboxylic acid producing reaction intermediate (A.1) and the nucleophilic reactant (A.2). In some embodiments, the polyalkenylsuccinimide (A) is formed via a neutralization reaction of the nucleophilic reactant (A.2) with the hydrocarbyl dicarboxylic acid producing reaction intermediate (A.1). The nucleophilic reactant (A.2) can be selected from the group of amines, alcohols, amino alcohols, and combinations thereof.

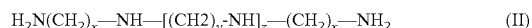
[0024] The nucleophilic reactant (A.2) can be a monoamine, an oligoamine or a polyamine. Since tertiary amines are generally unreactive with anhydrides, it is desirable to have at least one primary or secondary amine group on the amine.

[0025] The nucleophilic reactant (A.2) can include an amine having Formula Ia or Ib immediately below:



wherein R, R', and R'' are independently selected from the group consisting of hydrogen, C₁ to C₂₅ straight or branched chain alkyl radicals, C₁ to C₁₂ alkoxy C₂ to C₆ alkylene radicals, C₂ to C₁₂ hydroxy amino alkylene radicals, and C₁ to C₁₂ alkylamino C₂ to C₆ alkylene radicals; each X can be the same or a different number of from 2 to 6, alternatively from 2 to 4; and Y is a number from 0 to 10, alternatively from 2 to 7, alternatively from 3 to 7.

[0026] In some embodiments, the nucleophilic reactant (A.2) includes an amine having Formula II:



where x and y are each independently an integer from 1 to 5, alternatively from 2 to 4, and z is an integer from 0 to 8, or mixtures thereof.

[0027] The nucleophilic reactant (A.2) can include an alkylene polyamine, such as a methylenepolyamine, ethylenepolyamine, butylenepolyamine, propylenepolyamine and pentylenepolyamine. In various embodiments, the alkylene polyamine from 2 to 40, alternatively from 2 to 20, alternatively from 2 to 12, alternatively from 2 to 6, total carbon atoms and from 1 to 12, alternatively from 2 to 12, alternatively from 2 to 9, alternatively from 3 to 9, nitrogen atoms per molecule. To form the polyalkenylsuccinimide (A) of such embodiments, from 0.1 to 3.0, alternatively from 0.1 to 2.0, alternatively from 0.2 to 1.0, alternatively from 0.2 to 0.6, mol of succinic moieties can be reacted per equivalent of the nucleophilic reactant (A.2), e.g. amine, to form the polyalkenylsuccinimide (A).

[0028] The nucleophilic reactant (A.2) can also include a polyoxyalkylene polyamine, e.g. polyoxyalkylene amines, polyoxyalkylene diamines, and polyoxyalkylene triamines which have a number average molecular weight (M_n) of from 200 to about 4000, alternatively from 400 to 2000, g/mol. Non-limiting examples of polyoxyalkylene polyamines

include the polyoxyethylene, polyoxypropylene diamines, and the polyoxypropylene triamines having a number average molecular weight (M_n) of from 200 to 2000 g/mol.

[0029] The nucleophilic reactant (A.2) can also include a hydrocarbyl amine or a hydrocarbyl amine which includes other functional groups, e.g. hydroxy groups, alkoxy groups, amide groups, nitriles, imidazoline groups, etc. For example, in one embodiment, the nucleophilic reactant (A.2) includes a hydrocarbyl amine with from 1 to 6, alternatively from 1 to 3, hydroxy groups. Such amines are capable of reacting with the acid or anhydride groups of the reaction intermediate (A.1) via their amine functional groups or the other functional groups (described immediately above). Specific, non-limiting examples of the nucleophilic reactant (A.2) include hydroxyamines such as 2-amino-1-butanol, 2-amino-2-methyl-1-propanol, p-(beta-hydroxyethyl)-aniline, 2-amino-1-propanol, 3-amino-1-propanol, 2-amino-2-methyl-1,3-propanediol, 2-amino-2-ethyl-1,3-propanediol, N-(beta-hydroxy-propyl)-N'-(beta-amino-ethyl)-piperazine, tris(hydroxy-methyl)amino-methane (also known as trimethylol-aminomethane), 2-amino-1-butanol, ethanolamine, beta-(beta-hydroxyethoxy)-ethylamine, and the like.

[0030] The nucleophilic reactant (A.2) can also include an unsaturated alcohol such as allyl alcohol, cin-namyl alcohol, propargyl alcohol, 1-cyclohexane-3-ol, and oleyl alcohol. Still other classes of the alcohols capable of yielding the polyalkenylsuccinimide (A) of this disclosure include ether-alcohols and amino-alcohols, e.g. the oxy-alkylene, oxy-arylene-, amino-alkylene-, and amino-arylene-substituted alcohols having one or more oxy-alkylene, amino-alkylene or amino-arylene oxy-arylene radicals exemplified by N,N,N',N'-tetrahydroxy-trimethylene diamine, and ether-alcohols having up to about 150 oxy-alkylene radicals in which the alkylene radical includes from 1 to about 8 carbon atoms.

[0031] Additional non-limiting examples of the nucleophilic reactant (A.2) include alicyclic diamines such as 1,4-di(aminomethyl)cyclo-hexane, and heterocyclic nitrogen compounds such as imidazolines, and N-aminoalkyl piperazines. Specific, non-limiting examples of such amines include 2-pentadecyl imidazoline, N-(2-aminoethyl) piperazine, combinations thereof.

[0032] In one embodiment, the nucleophilic reactant (A.2) includes a polyamine selected from the group of ethylenediamine, triethylenetetramine, propylenediamine, trimethylenediamine, tripropylenetetramine, tetraethylenepentamine, hexaethylenepentamine, pentaethylenhexamine, and combinations thereof. In this embodiment, the nucleophilic reactant (A.2) can be the reaction product of ethylene dichloride and ammonia or the reaction product of an ethyleneimine with a ring-opening agent, for example water or ammonia.

[0033] In another embodiment, the nucleophilic reactant (A.2) includes an ethylene polyamine, such as diethylene triamine, triethylene tetramine, tetraethylene pentamine and pentaethylene hexamine. In this embodiment, the ethylene polyamine can be the reaction product of an alkylene chloride with ammonia or an ethylene imine with ammonia. These reactions result in a mixture of alkylene polyamines, including cyclic products such as piperazines.

[0034] Combinations of the various types and embodiments and examples of the nucleophilic reactant (A.2) referenced above can be reacted with the reaction intermediate (A.1) to form the polyalkenylsuccinimide (A).

The Polyalkenylsuccinimide (A)

[0035] The polyalkenylsuccinimide (A) of the subject disclosure is broadly defined herein to include polyalkenylsuccinimides (e.g. polyisobutenylsuccinimides), diesters of succinic acids or acidic esters (e.g. partially esterified succinic acids), and also partially esterified polyhydric alcohols or phenols, e.g. esters having free alcohols or phenolic hydroxyl radicals.

[0036] The polyalkenylsuccinimide (A) can be, or include a polyisobutenylsuccinimide which includes monosuccinimides and bissuccinimides. A ratio of monosuccinimides to bissuccinimides in the polyisobutenylsuccinimide can be influenced, for example, by the varying the molar ratio of the reaction intermediate (A.1), e.g. polyisobutenylsuccinic anhydride, to the nucleophilic reactant (A.2), e.g. amine, reacted to form the polyalkenylsuccinimide (A), e.g. polyisobutenylsuccinimide. The larger the molar amount of the reaction intermediate (A.1), e.g. polyisobutenylsuccinic anhydride in relation to the nucleophilic reactant (A.2), e.g. amine, the larger the resulting amounts of monosuccinimide, and vice versa. In order to obtain a higher proportion of monosuccinimide, a molar ratio of the reaction intermediate (A.1), e.g. polyisobutenylsuccinic anhydride, to the nucleophilic reactant (A.2), e.g. amine, of from 0.7 to 1.3, alternatively from 0.9 to 1.1, can be employed. In order to obtain a higher proportion of bissuccinimide, a molar ratio of the reaction intermediate (A.1), e.g. polyisobutenylsuccinic anhydride, to the nucleophilic reactant (A.2), e.g. amine, of from 3 to 18, alternatively from 2.3 to 1.9, is can be employed. A polyalkenylsuccinimide (A), e.g. polyisobutenylsuccinimide, having a higher monosuccinimide content is particularly suitable as an additive for fuels (diesel fuel, heating oil, gasoline fuel), while a polyalkenylsuccinimide (A), e.g. polyisobutenylsuccinimide, having a higher content of bissuccinimides is particularly suitable as an additive for lubricants.

[0037] To form the polyalkenylsuccinimide (A), the nucleophilic reactant (A.2), e.g. amines described above, can be reacted with the reaction intermediate (A.1), e.g. alkenylsuccinic anhydride, by heating an oil solution including 5 to 95 weight % of the reaction intermediate (A.1) to a temperature of from 100 to 200, alternatively from 125 to 175, °C., for a time of from 0.5 to 10, alternatively 1 to 6 hours to remove any residual water and adding the nucleophilic reactant (A.2). The step of heating the reaction intermediate (A.1) can facilitate formation of imides or mixtures of imides and amides, rather than amides and salts. The reaction ratios of the reaction intermediate (A.1) to equivalents of amine as well as the other nucleophilic reactants (A.2) described herein can vary considerably, depending upon the reactants and type of bonds formed. In some embodiments, from 0.1 to 2.0, alternatively from 0.1 to 2.0, alternatively from 0.2 to 0.6, mol of dicarboxylic acid moiety content (e.g. grafted maleic anhydride content) is used, per equivalent of nucleophilic reactant (A.2), e.g. amine. For example, about 0.8 mol of a pentamine (having two primary amino groups and 5 equivalents of nitrogen per molecule) can be used to form a mixture of amides and imides, the product formed by reacting one mol of olefin with sufficient maleic anhydride to add 1.6 mol of succinic anhydride groups per mol of olefin, i.e., the pentamine can be used in an amount sufficient to provide about 0.4 mol (that is 1.6/(0.8×5) mol) of succinic anhydride moiety per nitrogen equivalent of the amine.

[0038] In one embodiment, the polyalkenylsuccinimide (A) is formed from polyisobutylene substituted with succinic

anhydride groups and reacted with polyethylene amines, e.g. tetraethylene pentamine, pentaethylene hexamine, polyoxyethylene and polyoxy-propylene amines, e.g. polyoxypropylene diamine, trimethylolaminomethane and pentaerythritol, and combinations thereof. As one example, the polyalkenylsuccinimide (A) can be formed by reacting a polyisobutene substituted with succinic anhydride groups with a hydroxy compound, e.g. pentaerythritol, a polyoxyalkylene polyamine, e.g. polyoxypropylene diamine, and a polyalkylene polyamine, e.g. polyethylene diamine and tetraethylene pentamine.

[0039] In another embodiment, the polyalkenylsuccinimide (A) includes the reaction product of a polyisobutenylsuccinic anhydride, a first amine, and an alcohol. In this embodiment, the polyisobutenylsuccinic anhydride, the first amine, and the alcohol are reacted at a temperature of from 50 to 200, alternatively 80 to 180, alternatively 80 to 160, alternatively 100 to 160, °C. to form the polyisobutenylsuccinimide.

[0040] The first amine can have the following formula:



where x and y are each independently an integer from 1 to 5, alternatively from 2 to 4, and z is an integer from 0 to 8, or mixtures thereof.

[0041] The alcohol is selected from the group consisting of monohydric alcohols of the formula R^4OH , where R^4 is straight-chain or branched, cyclic or branched cyclic alkyl of 1 to 16 carbon atoms, and combinations thereof. In many embodiments, the alcohol is a monohydric alcohol, but polyhydric alcohol is also suitable. The alcohol is can be a monohydric alcohol of the formula R^4OH , where R^4 is straight-chain or branched, cyclic or branched cyclic alkyl of 1 to 16, alternatively 6 to 16, carbon atoms.

[0042] Specific, non-limiting examples of the alcohol include methanol, ethanol, n-propanol, isopropanol, cyclopropylcarbinol, n-butanol, sec-butanol, isobutanol, tert-butanol, 2-hydroxymethylfuran, amyl alcohol, isoamyl alcohol, vinylcarbinol, cyclohexanol, n-hexanol, 4-methyl-2-pentanol, 2-ethylbutyl alcohol, sec-capryl alcohol, 2-ethylhexanol, n-decanol, lauryl alcohol, isocetyl alcohol and mixtures thereof. In one embodiment, the alcohol is 2-ethylhexanol. Additional specific, non-limiting examples of the alcohol include phenol, naphthol, (o,p)-alkylphenols, e.g. di-tert-butylphenol, and salicylic acid.

[0043] The molar ratio of the polyisobutenylsuccinic anhydride to the alcohol can vary. It is not necessary to use stoichiometric amounts of the alcohol, and even comparatively small molar amounts of the alcohol can be sufficient to form the polyisobutenylsuccinimide. A example molar ratio of the polyisobutenylsuccinic anhydride to alcohol is from 10 to 0.5, alternatively from 4 to 0.8.

[0044] In this embodiment, the polyisobutenylsuccinic anhydride can be first reacted with the alcohol, then reacted with the first amine to form the polyisobutenylsuccinimide. More specifically, the polyisobutenylsuccinic anhydride can be first reacted with the alcohol to form a second reaction intermediate comprising a monoester of polyisobutenylsuccinic acid, which is then reacted with the first amine. In this embodiment, the polyisobutenylsuccinic anhydride and the alcohol are combined in a reaction vessel. After the polyisobutenylsuccinic anhydride and the alcohol react, the first amine can be introduced into the reaction vessel. After the reaction, any alcohol, which is either unreacted or cleaved, can be removed in a conventional manner.

[0045] In an embodiment, the second reaction intermediate includes the reaction product of (1) the first reactive polyisobutene having a molecular weight M_n of from 500 to 5,000 g/mol and a content of terminal double bonds of greater than 50, alternatively greater than 70, mol %, (2) maleic anhydride, and (3) the alcohol selected from the group consisting of monohydric alcohols of the formula R^4OH , where R^4 is straight-chain or branched, cyclic or branched cyclic alkyl of 1 to 16 carbon atoms.

[0046] The second reaction intermediate which is formed during the formation of the polyisobutenylsuccinimide can, if desired, also be isolated. The reaction intermediate is not only useful in the formation of the polyalkenylsuccinimide (A) but, alone or in combination with other additives, can also be used as additives for fuels or lubricants.

[0047] Alternatively in this embodiment, isolation of the second reaction intermediate is not necessary. That is, the polyisobutenylsuccinic anhydride, the first amine and the alcohol are reacted simultaneously, i.e., in a single step to form the polyisobutenylsuccinimide. After the reaction, any alcohol, which is either unreacted or cleaved, can be removed in a conventional manner.

[0048] In another embodiment, the polyalkenylsuccinimide (A) can be the reaction product of (1) the first reactive polyisobutene having a molecular weight (M_n) of from 500 to 5,000 g/mol and a content of terminal double bonds of greater than 50, alternatively greater than 75, mol %, (2) maleic anhydride, and (3) the first amine (A.2) having the formula:

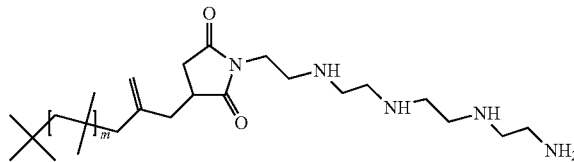


where x and y are each independently an integer from 1 to 5, alternatively from 2 to 4, and z is an integer from 0 to 8, or mixtures thereof.

[0049] In another embodiment, the polyalkenylsuccinimide (A) includes the reaction product of (1) the first reactive polyisobutene having a number average molecular weight (M_n) of from 500 to 5,000 g/mol and a content of terminal double bonds of greater than 50, alternatively greater than 70, mol %, (2) maleic anhydride, and (3) a linear, branched, cyclic or cyclic branched alkylenepolyamine having 1 to 10, alternatively 2 to 4, carbon atoms in each alkylene group and 1 to 12, alternatively 2 to 12, alternatively 2 to 9, alternatively 3 to 9, nitrogen atoms, of which at least one nitrogen atom is present as a primary amino group, or mixtures thereof, including less than 30% by weight, based on the total weight of the product, of the corresponding polyisobutenylsuccinimide.

[0050] In another embodiment, the polyalkenylsuccinimide (A) includes the reaction product of the reaction intermediate (A.1), e.g. polyisobutenylsuccinic anhydride, and the nucleophilic reactant (A.2) comprising a C_2 to C_{40} , alternatively C_2 to C_{20} , alternatively C_2 to C_{12} polyalkylene polyamine which includes from 2 to 12, alternatively 2 to 9, alternatively 3 to 9, nitrogen atoms per molecule an amine. To form the polyalkenylsuccinimide (A), e.g. polyisobutenylsuccinimide, of this embodiment, 0.1 to 3.0, alternatively 0.2 to 1.0, alternatively 0.2 to 0.6, mol of succinic moieties are reacted per equivalent of the nucleophilic reactant (A.2), e.g. amine, to form the polyalkenylsuccinimide (A).

[0051] In some embodiments, the polyalkenylsuccinimide (A) has the following structure:



wherein m is an integer of from 2 to 80, alternatively from 2 to 40, alternatively from 2 to 20, alternatively from 6 to 16.

[0052] In some embodiments, the polyalkenylsuccinimide (A) of the subject disclosure includes a minimal amount of corresponding amides (polyisobutenylsuccinimide or polyisobutenylsuccinic acid monoamide). More specifically, the polyalkenylsuccinimide (A) can include less than 30, alternatively less than 25, alternatively less than 20, alternatively less than 15, % by weight corresponding amides, based on the total weight of the polyalkenylsuccinimide (A), of the corresponding amides. In addition, the polyalkenylsuccinimide (A) can include no ester fractions, even when the polyalkenylsuccinimide (A) includes the reaction product of the reaction intermediate (A.1), the nucleophilic reactant (A.2), and the alcohol (A.3) and the reaction with the alcohol (A.3) is carried out in an intermediate stage. Increased purity (minimal corresponding amides/amide bi-products and lack of ester fractions) of the polyalkenylsuccinimide (A) can be attributed to the process by which the polyalkenylsuccinimide (A) is formed.

[0053] In some embodiments the polyalkenylsuccinimide (A) has a number average molecular weight (M_n) of greater than 500, alternatively greater than 800, alternatively greater than 1,000, alternatively from 500 to 5,000, alternatively from 750 to 5,000, alternatively from 1,000 to 4,000, alternatively from 1,000 to 3,000, g/mol. The higher molecular weight (e.g. $M_n > 1,000$ g/mol) polyalkenylsuccinimide (A) reduces fuel consumption in internal combustion engines when added to the fuel combusted. That is, the polyalkenylsuccinimide (A) is an effective fuel economy additive. In contrast, it is thought that lower molecular weight (e.g. M_n 300 to 500 g/mol) molecules do not reduce fuel consumption in internal combustion engines when added to the fuel combusted. In some embodiments, a hydrophobic moiety of such molecules known in the art is typically derived from synthetic or natural mono or oligo fatty acids with a chain length of typically C_{12} to C_{20} . In contrast, polyalkenylsuccinimide (A), as is described above, can be formed from the first reactive polyisobutene having a chain length of C_{40} to C_{400} , alternatively from C_{40} to C_{200} and a number average molecular weight (M_n) of from 500 to 5,000 g/mol.

[0054] The compositions can be added to fuel in an amount such that the polyalkenylsuccinimide (A) can be present in the fuel in an amount of from 10 to 500, alternatively from 20 to 200, alternatively from 25 to 75, mg/kg of fuel. Further, the polyalkenylsuccinimide (A) can be present in the compositions in an amount of from 1 to 75, alternatively 1 to 50, alternatively 5 to 40, alternatively 4 to 40, alternatively 6 to 45, alternatively 2 to 20, alternatively 4 to 15, alternatively from 5 to 12, alternatively from 15 to 45, alternatively from 20 to 35, parts by weight per 100 parts by weight of the composition.

The Polyisobutene Amine (B)

[0055] Referring back, in some embodiments, the compositions also include the polyisobutene amine (B). The polyisobutene amine (B) as described herein includes mono and polyfunctional polyisobutene amines. In some embodiments, the polyisobutene amine (B) includes the reaction product of (B.1) a second polyolefin and (B.2) a second amine.

The Second Polyolefin (B.1)

[0056] The second polyolefin (B.1) of the subject disclosure includes C_2 to C_{18} , alternatively C_2 to C_{10} , alternatively C_2 to C_5 , olefin units. Non-limiting examples of olefin units include ethylene, propylene, butylene, isobutylene, pentene, octene-1, and styrene. In some embodiments, the second polyolefin (B.1) is a polyalkene. The second polyolefin (B.1) can be homopolymer, such as polyisobutylene, or copolymer of two or more of different olefin units. Non-limiting examples of copolymers which can be used to form the second polyolefin (B.1) include ethylene and propylene, butylene and isobutylene, propylene and isobutylene. Additional non-limiting examples of copolymers include copolymers that include a minor molar amount of olefin units, e.g. 1 to 10 mol %, are C_4 to C_{18} non-conjugated diolefin units such as a copolymer of isobutylene and butadiene or a copolymer of ethylene, propylene, and 1,4-hexadiene.

[0057] The second polyolefin (B.1) can be linear or branched. In some embodiments, the second polyolefin (B.1) has a number average molecular weight (M_n) of from 500 to 5,000, alternatively from 750 to 4,000, alternatively from 1,000 to 3,000, alternatively from 1,000 to 2,000, g/mol.

[0058] In some embodiments, the second polyolefin (B.1) is unsaturated. In some embodiments, the second polyolefin (B.1) includes a terminal double bond.

[0059] To this end, in one embodiment, the second polyolefin (B.1) is a second reactive polyisobutene. The second reactive polyisobutene can be a highly reactive polyisobutene which has a high content of terminal ethylenic double bonds. In some embodiments, the second reactive polyisobutene has a content of terminal double bonds of greater than 50, alternatively greater than 70, alternatively greater than 75, alternatively greater than 80, alternatively greater than 85, mol %. The second reactive polyisobutene can have a uniform polymer backbone which includes greater than 85, alternatively greater than 90, alternatively greater than 95, % by weight of isobutene units.

[0060] In some embodiments, the second reactive polyisobutene has a number average molecular weight (M_n) of from 500 to 5,000, alternatively from 750 to 4,000, alternatively from 1,000 to 3,000, alternatively from 1,000 to 2,000, g/mol. The dispersity D (M_w/M_n), i.e., the quotient of the weight average molecular weight M_w divided M_n , of the second reactive polyisobutene is less than 7, alternatively from 1.05 to 7. In one embodiment, the dispersity D (M_w/M_n) of the second reactive polyisobutene is less than 3. In some embodiments, a second reactive polyisobutene has a dispersity of less than 2.0 for M_n less than or equal to 2,000, and a dispersity of less than 1.5 for M_n less than or equal to 1,000. In some embodiments, the second reactive polyisobutene is free of organic and inorganic bases, water, alcohols, ethers, acids and peroxides.

[0061] Suitable non-limiting examples of the second reactive polyisobutene are commercially available from BASF SE under the GLISSOPAL® brand of polyisobutenes.

The Second Amine (B.2)

[0062] As described above, the second polyolefin (B.1) reacts with the second amine (B.2) to form the polyisobutene amine (B). In some embodiments, the second amine (B.2) has the following formula:



wherein R^1 and R^2 are each independently H, a C_1 - C_{18} -alkyl, C_2 - C_{18} -alkenyl, C_4 - C_{18} -cycloalkyl, C_1 - C_{18} -alkylaryl, hydroxy- C_1 - C_{18} -alkyl, poly(oxyalkyl), polyalkylene polyamine, a polyalkylene amine radical, a polyalkylene imine radical; or, together with the nitrogen atom to which they are bonded, form a heterocyclic ring.

[0063] Non-limiting examples of C_1 - C_{18} -alkyl radicals include straight-chain or branched radicals having from 1 to 18 carbon atoms such as methyl, ethyl, iso- or n-propyl, n-, iso-, sec- or tert-butyl, n- or isopentyl; and also n-hexyl, n-heptyl, n-octyl, n-nonyl, n-decyl, n-undecyl, n-tridecyl, n-tetradecyl, n-pentadecyl and n-hexadecyl and n-octadecyl, and also the mono- or polybranched analogs thereof; and also corresponding radicals in which the hydrocarbon chain has one or more ether bridges.

[0064] Non-limiting examples of C_2 - C_{18} -alkenyl radicals include the mono- or polyunsaturated, alternatively mono- or diunsaturated analogs of the above-mentioned alkyl radicals having from 2 to 18 carbon atoms, in which the double bonds can be in any position in the hydrocarbon chain.

[0065] Non-limiting examples of C_4 - C_{18} -cycloalkyl radicals includes cyclobutyl, cyclopentyl and cyclohexyl, and also the analogs thereof substituted by from 1 to 3 C_1 - C_4 -alkyl radicals; the C_1 - C_4 -alkyl radicals are, for example, selected from methyl, ethyl, iso- or n-propyl, n-, iso-, sec- or tert-butyl.

[0066] Non-limiting examples of C_1 - C_{18} -alkylaryl radicals include the C_1 - C_{18} -alkyl group is as defined above and the aryl group is derived from a monocyclic or bicyclic fused or nonfused 4- to 7-membered, in particular 6-membered aromatic or heteroaromatic group such as phenyl, pyridyl, naphthyl and biphenyl.

[0067] Non-limiting examples of C_2 - C_{18} -alkenylaryl radicals include radicals where the C_2 - C_{18} -alkenyl group is as defined above and the aryl group is as defined above. Non-limiting examples of hydroxy- C_1 - C_{18} -alkyl radical include the analogs of the above C_1 - C_{18} -alkyl radicals which have been mono- or polyhydroxylated, alternatively monohydroxylated, in particular monohydroxylated in the terminal position; for example 2-hydroxyethyl and 3-hydroxypropyl.

[0068] Non-limiting examples of a poly(oxyalkyl) radical, e.g. that can be hydroxylated, include radicals which are obtainable by alkoxylation of the nitrogen atom with from 2 to 10 C_1 - C_4 -alkoxy groups in which individual carbon atoms can include hydroxyl groups. Exemplary alkoxy groups include methoxy, ethoxy and n-propoxy groups.

[0069] Non-limiting examples of a polyalkylene polyamine radical include radicals of the formula:



where m is an integer from 0 to 5, Z is H or a C_1 - C_6 -alkyl. The C_1 - C_6 -alkyl represents radicals such as methyl, ethyl, iso- or n-propyl, n-, iso-, sec- or tert-butyl, n- or isopentyl, and also n-hexyl, and C_1 - C_6 -alkylene represents the corresponding bridged analogs of these radicals.

[0070] Non-limiting examples of the polyalkylene imine radical include radicals comprising from 1 to 10 C_1 - C_4 -alky-

lene imine groups, in particular ethylene imine groups. Examples of a heterocyclic ring include an optionally substituted 5- to 7-membered heterocyclic ring which is optionally substituted by from one to three C₁-C₄-alkyl radicals and optionally bears one further ring heteroatom such as O or N.

[0071] Non-limiting examples of compounds of the formula HNR^1R^2 include: ammonia primary amines such as methylamine, ethylamine, n-propylamine, isopropylamine, n-butylamine, isobutylamine, sec-butylamine, tert-butylamine, pentylamine, hexylamine, cyclopentylamine and cyclohexylamine; and also primary amines of the formula $\text{CH}_3\text{—O—C}_2\text{H}_4\text{—NH}_2$, $\text{C}_2\text{H}_5\text{—O—C}_2\text{H}_4\text{—NH}_2$, $\text{CH}_3\text{—O—C}_3\text{H}_6\text{—NH}_2$, $\text{C}_2\text{H}_5\text{—O—C}_3\text{H}_6\text{—NH}_2$, $\text{n-C}_4\text{H}_9\text{—O—C}_4\text{H}_8\text{—NH}_2$, $\text{HO—C}_2\text{H}_4\text{—NH}_2$, $\text{HO—C}_3\text{H}_6\text{—NH}_2$ and $\text{HO—C}_4\text{H}_8\text{—NH}_2$; secondary amines, for example dimethylamine, diethylamine, methylethylamine, di-n-propylamine, diisopropylamine, diisobutylamine, di-sec-butylamine, di-tert-butylamine, dipentylamine, dihexylamine, dicyclopentylamine, dicyclohexylamine and diphenylamine; and also secondary amines of the formula $(\text{CH}_3\text{—O—C}_2\text{H}_4)_2\text{NH}$, $(\text{C}_2\text{H}_5\text{—O—C}_2\text{H}_4)_2\text{NH}$, $(\text{CH}_3\text{—O—C}_3\text{H}_6)_2\text{NH}$, $(\text{C}_2\text{H}_5\text{—O—C}_3\text{H}_6)_2\text{NH}$, $(\text{n-C}_4\text{H}_9\text{—O—C}_4\text{H}_8)_2\text{NH}$, $(\text{HO—C}_2\text{H}_4)_2\text{NH}$, $(\text{HO—C}_3\text{H}_6)_2\text{NH}$ and $(\text{HO—C}_4\text{H}_8)_2\text{NH}$; heterocyclic amines such as pyrrolidine, piperidine, morpholine and piperazine, and also their substituted derivatives such as N—C₁-C₆-alkylpiperazines and dimethylmorpholine. polyamines, for example C₁-C₄-alkylenediamines, di-C₁-C₄-alkylenetriamines, tri-C₁-C₄-alkylenetetramines and higher analogs; polyethylene imines, alternatively oligoethylene imines, consisting of from 1 to 10, alternatively from 2 to 6 ethylene imine units. Non-limiting examples of polyamines and polyimines are n-propylenediamine, 1,4-butanediamine, 1,6-hexanediamine, diethylenetriamine, triethylenetetramine and polyethylene imines, and also their alkylation products, for example 3-(dimethylamino)-n-propylamine, N,N-dimethylethylenediamine, N,N-diethylethylenediamine and N,N,N',N'-tetramethyldiethylenetriamine. Ethylenediamine is yet another non-limiting example.

The Polyisobutene Amine (B)

[0072] The mono or polyfunctional polyisobutene amine (B) can be formed via various reactions under various reaction conditions.

[0073] For example, in one embodiment, the mono or polyfunctional polyisobutene amine (B) includes the reaction product of a halogenated hydrocarbon, e.g. halogenated polyisobutene, and the second amine described above. More specifically, the halogen atoms of the hydrocarbon chain are replaced by a polyamine group, while a hydrogen halide is formed. The hydrogen halide can then be removed in any suitable way, for example, as a salt with excess polyamine. The reaction between halogenated hydrocarbon and the second amine can be effected at elevated temperature in the presence of a solvent, e.g. a solvent having a boiling point of at least 160° C.

[0074] As another example, the polyisobutene amine (B) can be formed via alkylation of aliphatic polyamines. For example, the second amine, e.g. a polyamine, can be reacted with an alkyl or alkenyl halide. The formation of the alkylated polyamine is accompanied by the formation of hydrogen halide, which is removed, for example, as a salt of the starting polyamine which is present in excess.

[0075] As yet another example, a polyalkene having a terminal double bond whose beta carbon atoms carries a methyl

group, e.g. the second reactive polyisobutene, can be chlorinated with a theoretical quantity of chlorine to yield an alpha-polyisobutyl allyl chloride and beta-polyisobutyl methallyl chloride, while hydrochloric acid is split off. During chlorination, side reactions also produce a quantity of dichloro compound. The second amine, e.g. a polyamine, is then alkylated with the chlorination compounds obtained to form polyisobutene amine (B). For example, the first reactive polyisobutylene is treated with chlorine in an inert solvent at room temperature and the resulting polyisobutenyl chloride is converted with tetraethylenepentamine into monoisobutenyltetraethylepentamine or diisobutenyltetraethylepentamine.

[0076] In another embodiment, the polyisobutene amine (B) includes the reaction product of the second reactive polyisobutene, a second amine having the following formula;



[0077] wherein R² and R³ are each independently H, a C₁-C₁₈-alkyl, C₂-C₁₈-alkenyl, C₄-C₁₈-cycloalkyl, C₁-C₁₈-alkylaryl, hydroxy-C₁-C₁₈-alkyl, poly(oxyalkyl), polyalkylene polyamine or a polyalkylene amine radical; or, together with the nitrogen atom to which they are bonded, form a heterocyclic ring.

[0078] For example, the mono or polyfunctional polyisobutene amine (B) includes a reaction product formed via hydroformylation of the second reactive polyisobutene to form an oxo intermediate and subsequent reductive amination of the oxo intermediate in the presence of ammonia.

[0079] Specifically, the polyisobutene amine (B) can be formed via hydroformylation of an appropriate polyalkene, e.g. the second reactive polyisobutene, with a rhodium or cobalt catalyst in the presence of CO and H₂ at a temperature of from 80 to 200° C. and CO/H₂ pressures of up to 600 bar and then subjecting the oxo product to a Mannich reaction or amination under hydrogenating conditions. The amination reaction can be carried out at 80 to 200° C. and pressures of equal to or less than 600, alternatively from 80 to 300, bar.

[0080] In this formation process, it is advantageous to use a suitable, inert solvent in order to reduce the viscosity of the reaction mixture. Non-limiting examples of such solvents include aliphatic, cycloaliphatic, and aromatic hydrocarbons having low sulfur content. In one embodiment, an aliphatic solvent which is free of sulfur compounds and include less than 1% of aromatics is used. Such solvents have the advantage that, at high amination temperatures, no heat of hydrogenation is liberated and no hydrogen is consumed. In the amination and hydroformulation reaction, the solvent content can be from 0 to 70% by weight, depending on the viscosity of the polymer and of the solvent.

[0081] In this formation process, polybutene conversions of 80 to 90% can readily be achieved. In one embodiment, the second reactive polybutene comprising equal to or greater than 80% by weight isobutene and having a number average molecular weight (M_n) of from 300 to 5000, alternatively from 500 to 2500, g/mol is used. In this embodiment, the second reactive polybutene has a mean degree of polymerization P of from 10 to 100 and a content E of double bonds which are capable of reacting with maleic anhydride is from 60 to 90%. A value E of 100% corresponds to the calculated theoretical value where each molecule of the butene or isobutene polymer includes one reactive double bond of this type. The value is calculated for a reaction of polyisobutene with maleic anhydride in a weight ratio of 5:1, the stirred mixture being heated for 4 hours at 200° C.

[0082] Independent of how the polyisobutene amine (B) is formed, the polyisobutene amine (B) of the compositions has excellent low temperature properties, e.g. a low cloud point, a low pour point, and is stable when stored at low temperatures. Further, the polyisobutene amine (B) can function as a detergent in internal combustion engines when added to the fuel combusted.

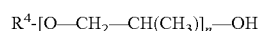
[0083] To this end, the compositions can be added to fuel in an amount such that the polyisobutene amine (B) can be present in the fuel in an amount of from 20 to 2,000, alternatively from 50 to 1,000, alternatively from 100 to 500, mg/kg of fuel. Further, the polyisobutene amine (B) can be present in the compositions in an amount of from 5 to 70, alternatively from 10 to 60, alternatively from 10 to 40, alternatively from 30 to 60, alternatively from 5 to 35, alternatively from 15 to 25, parts by weight per 100 parts by weight of the composition.

The Carrier Oil (C)

[0084] Referring back, the compositions also include the carrier oil (C). One or more different carrier oils can be added to the compositions, i.e., the carrier oil (C) can include a mixture of one or more different types of carrier oil. The carrier oil (C) can include mineral carrier oil, synthetic carrier oil, and combinations thereof. The carrier oil (C) can include one or more different carrier oils selected from the group of mineral oils, polyethers, polyetheramines, and esters. The compositions can include any carrier oil known in the art, including those carrier oils not specifically described herein.

[0085] As is set forth above, the compositions can include one or more mineral carrier oils. Non-limiting examples of mineral carrier oils include fractions obtained in mineral oil processing, such as kerosine or naphtha, or brightstock or base oils. Non-limiting examples of suitable mineral carrier oils include naphthenic or paraffinic mineral oils having a viscosity of from 2 to 25 mm²/s at 100° C.

[0086] As is set forth above, the compositions can include one or more polyether carrier oils. Non-limiting examples of polyether carrier oils include polyalkylene oxides having a number average molecular weight (M_n) of equal to or greater than 500 g/mol and propoxylates. Generally, the polyalkylene oxide carrier oils are formed by polymerizing one or more alkylene oxides, such as ethylene oxide (EO), propylene oxide (PO), and/or butylene oxide (BO) with an initiator in the presence of a catalyst. The initiator used to form the polyalkylene oxide can be an alkanol, an alkanediol, an amine, or an alkylphenol. For example, the initiator can be 1,6-hexanediol, 1,8-octanediol, 2-ethylhexanol, 2-propylhexanol, isotridecanol, isononylphenol, isodecylphenol, and/or isotridecylamine. The polyalkylene oxides can be linear or branched and can have a random, repeating, or block structure. One non-limiting example of a suitable polyether carrier oil is a polyalkylene oxide formed from 50, alternatively from 8 to 30, mol of propylene oxide or butylene oxide or of a mixture thereof, per initiator molecule. Another non-limiting example of a suitable polyether carrier oil is a propoxylate having the following formula:

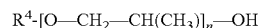


wherein n is an integer of from 14 to 17, and R⁴ is straight-chain or branched C₈-C₁₈-alkyl or C₈-C₁₈-alkenyl.

[0087] As is set forth above, the compositions can include one or more polyetheramine carrier oils. Non-limiting examples of polyetheramine carrier oils include polyetheramines based on EO, PO, and/or BO and ammonia or primary or secondary mono- or polyamines having a number average molecular weight (M_n) of equal to or greater than 500 g/mol. Such polyetheramines can be prepared from polyethers by an amination reaction wherein the terminal hydroxyl group is replaced by an amino group with elimination of water.

[0088] As is set forth above, the compositions can include one or more esters of mono- or polycarboxylic acids with alkanols or polyols carrier oils. Non-limiting examples of such ester carrier oils include esters of mono- or polycarboxylic acids with alkanols or polyols having a minimum viscosity of 2 mm²/s at 100° C., aliphatic or aromatic mono- or polycarboxylic acids, and C₆ to C₂₄ ester alcohols or ester polyols, adipates, phthalates, isophthalates, terephthalates, and trimellitates of isooctanol, isononanol, isodecanol and of isotridecanol.

[0089] In some embodiments, the compositions include a propoxylate carrier oil having the following formula:



wherein n is an integer of from 8 to 35, alternatively from 14 to 17, and R⁴ is straight-chain or branched C₈-C₁₈-alkyl or C₈-C₁₈-alkenyl.

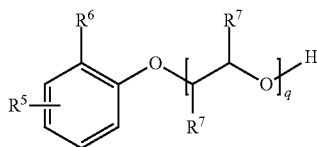
[0090] In one embodiment, R⁴ is straight-chain or branched alkyl of 10 to 16 carbon atoms, or mixtures thereof. In another embodiment, R⁴ is alkyl of 12 to 14 carbon atoms or is a mixture of such alkyl radicals. In yet another embodiment, R⁴ has 13 carbon atoms.

[0091] In one embodiment, n is an integer from 12 to 18. In another embodiment, n is an integer from 14 to 17. In yet another embodiment, n is an integer from 14 to 16. In still yet another embodiment, n is 15. Of course, the above numerical data for n is an average value since many preparation methods produce a mixture of compounds with varying molecular weight distribution.

[0092] In one embodiment, the propoxylate carrier oil has the formula above wherein n is an integer from 14 to 16, alternatively 15, and R⁴ is a branched C₁₃-alcohol, in particular C₁₃-monoalcohol. Branched C₁₃-alcohols can be obtainable by oligomerization of C₂-C₆-olefins, in particular C₃- or C₄-olefins, and subsequent hydroformylation.

[0093] The propoxylate carrier oil of this embodiment is prepared by reacting an alcohol, as an initiator molecule, with propylene oxide in the presence of an alkali, e.g. sodium hydroxide solution, potassium hydroxide solution, sodium methylate, potassium methylate, or another alkali metal alkoxide, at from 120 to 160, alternatively from 130 to 160, ° C., to give the desired adducts. After alkoxylation is complete, the propoxylate carrier oil is freed from the catalyst, for example by treatment with magnesium silicate. In one embodiment, the propoxylate carrier oil is propoxylated isotridecanol.

[0094] In another embodiment, the compositions include a dialkylphenol-initiated propoxylate carrier oil having the following formula:



where R^5 and R^6 independently of one another are each branched or straight-chain C_6 to C_{30} alkyl groups, one of the two radicals R^7 is methyl and the other is hydrogen and q is from 1 to 100. This embodiment can also include a monoalkylphenol-initiated propoxylate carrier oil, this propoxylate carrier oil represented by the formula above with the proviso that R^6 is omitted.

[0095] In general, any mixture of the carrier oils described above can be included in the carrier oil (C) of the compositions. To this end, in another embodiment, the carrier oil (C) includes a mixture of polyether carrier oil and ester carrier oil.

[0096] Suitable polyether carrier oils include polyalkylene oxides having a number average molecular weight (M_n) of equal to or greater than 500 g/mol. The polyalkylene oxides of this embodiment can be formed from initiators such as aliphatic and aromatic mono-, di- or polyalcohols or even amines or amides and alkylphenols. The polyalkylene oxides of this embodiment can be formed from alkylene oxides such as EO, PO, and BO, but it is also possible to use higher oxides for forming these polyalkylene oxides.

[0097] Suitable esters carrier oils include esters of aliphatic or aromatic mono- or polycarboxylic acids with long-chain alcohols, polyol esters (based for example on neopentyl glycol, pentaerythritol or trimethylolpropane with corresponding monocarboxylic acids) and oligomer or polymer esters, for example those based on dicarboxylic acid, a polyol and a monoalcohol, and esters of aromatic di-, tri- and tetracarboxylic acids with long-chain aliphatic alcohols composed solely of carbon, hydrogen and oxygen, the total number of carbon atoms of the esters being 22 or more and the molecular weight being from 370 to 1500, alternatively from 414 to 1200, g/mol. Suitable esters can have a minimum viscosity of $2 \text{ mm}^2/\text{s}$ at 100°C . In one embodiment, the ester is an adipate, phthalate, isophthalate, terephthalate and trimellitate of isooctanol, isononanol, isodecanol and isotridecanol, and combinations thereof.

[0098] The carrier oil (C) functions to carry the components ((A), (B), etc.) of the compositions and can also function to reduce deposits in the region of the intake valves of an engine. To this end, the compositions can be added to fuel in an amount such that the carrier oil (C) is typically added to the fuel in an amount of from 10 to 2,000, alternatively, from 20 to 1,000, alternatively from 50 to 500, mg/kg of fuel. Further, the carrier oil (C) can be present in the compositions in an amount of from 2 to 94, alternatively from 2 to 80, alternatively from 5 to 60, alternatively from 10 to 30, alternatively from 12 to 18, alternatively from 5 to 15, alternatively from 2 to 20, parts by weight per 100 parts by weight of the composition.

Additives

[0099] The compositions can include one or more additives, differing from components (A) and (B) and (C) described above, selected from the group of detergents, lubricity additives, corrosion inhibitors, antioxidants, demulsifiers, metal deactivators, dehazers, markers, solvents, cet-

ane number improvers, antifoams, solubilizers, deodorants, dehazers, and other additives. The compositions can include, but do not require solubilizers. Solubilizers are materials, known in the art, which improve miscibility of the components included in the fuel additive compositions and thus improve the homogeneity of the fuel additive compositions.

Detergents

[0100] One or more detergents, differing from components (A) and (B) described above, can be added to the compositions. Suitable examples include detergents, other than the polyisobutene amine (B), which have detergent action and/or have valve seat wear-inhibiting action. Suitable, non-limiting examples of the one or more detergents include neutral metal sulphonates, phenates and salicylates, and combinations thereof, which are described below.

[0101] One suitable detergent is a compound having at least one hydrophobic hydrocarbon radical having a number average molecular weight (M_n) of from 85 to 20,000 and at least one polar moiety selected from: (a) mono- or polyamino groups having up to 6 nitrogen atoms, of which at least one nitrogen atom has basic properties; (b) nitro groups which can be in combination with hydroxyl groups; (c) hydroxyl groups in combination with mono- or polyamino groups, in which at least one nitrogen atom has basic properties; (d) carboxyl groups or their alkali metal or their alkaline earth metal salts; (e) sulfonic acid groups or their alkali metal or alkaline earth metal salts; (f) polyoxy- C_2 - to $-C_4$ -alkylene groups which are terminated by hydroxyl groups, mono- or polyamino groups, in which at least one nitrogen atom has basic properties, or by carbamate groups; (g) carboxylic ester groups; and/or (h) moieties obtained by Mannich reaction of substituted phenols with aldehydes and mono- or polyamines.

[0102] The hydrophobic hydrocarbon radical in the aforementioned detergents that improves the solubility of the compositions in the fuel can have a number average molecular weight (M_n) of from 85 to 20,000, alternatively from 113 to 5,000, alternatively from 300 to 5,000. Example hydrophobic hydrocarbon radicals, especially in conjunction with the polar moieties (a), (c), (h) and (i), include polypropenyl, polybutenyl and polyisobutenyl radical each having number average molecular weight (M_n) of from 300 to 5,000, alternatively from 500 to 2,500, alternatively from 700 to 2,300, g/mol.

[0103] Detergents comprising mono- or polyamino groups (a) can be polyalkenemono- or polyalkenepolyamines based on polypropene or conventional, i.e., having predominantly internal double bonds, polybutene or polyisobutene having number average molecular weight (M_n) from 300 to 5,000. When polybutene or polyisobutene having predominantly internal double bonds (usually in the beta and gamma position) are used as starting materials in the preparation of the detergents, a possible preparative route is by chlorination and subsequent amination or by oxidation of the double bond with air or ozone to give the carbonyl or carboxyl compound and subsequent amination under reductive (hydrogenating) conditions. The amines used for the amination can be, for example, ammonia, monoamines or polyamines, such as dimethylaminopropylamine, ethylenediamine, diethylenetriamine, triethylenetetramine or tetraethylenepentamine.

[0104] Detergents comprising monoamino groups (a) can also be the hydrogenation products of the reaction products of polyisobutenes having an average degree of polymerization P of from 5 to 100 with nitrogen oxides or mixtures of nitrogen

oxides and oxygen. Detergents comprising monoamino groups (a) can also be compounds obtainable from polyisobutene epoxides by reaction with amines and subsequent dehydration and reduction of the amino alcohols.

[0105] Detergents comprising nitro groups (b) which can be in combination with hydroxyl groups, can be reaction products of polyisobutenes having an average degree of polymerization P of from 5 to 100 or from 10 to 100 with nitrogen oxides or mixtures of nitrogen oxides and oxygen. These reaction products are generally mixtures of pure nitropolyisobutenes (e.g. alpha,beta-dinitropolyisobutene) and mixed hydroxynitropolyisobutenes (e.g. alpha-nitro-beta-hydroxypolyisobutene).

[0106] Detergents comprising hydroxyl groups in combination with mono- or polyamino groups (c) can be reaction products of polyisobutene epoxides obtainable from polyisobutene having terminal double bonds and number average molecular weight (M_n) from 300 to 5,000, with ammonia or mono- or polyamines.

[0107] Detergents comprising carboxyl groups or their alkali metal or alkaline earth metal salts (d) can be copolymers of C_2 to C_{40} olefins with maleic anhydride which have a total molar mass of from 500 to 20,000 and of whose carboxyl groups some or all have been converted to the alkali metal or alkaline earth metal salts and any remainder of the carboxyl groups has been reacted with alcohols or amines. Such detergents can prevent valve seat wear and can be used in combination with the polyisobutene amine (B).

[0108] Detergents comprising sulfonic acid groups or their alkali metal or alkaline earth metal salts (e) can be alkali metal or alkaline earth metal salts of an alkyl sulfosuccinate. Such detergents also can prevent valve seat wear and can be used in combination with the polyisobutene amine (B).

[0109] Detergents comprising polyoxy- C_2 - C_4 -alkylene moieties (f) can be polyethers or polyether amines which are obtainable by reaction of C_2 - to C_{60} -alkanols, C_6 - to C_{30} -alkanediols, mono- or di- C_2 - C_{30} -alkylamines, C_1 - C_{30} -alkylcyclohexanols or C_1 - C_{30} -alkylphenols with from 1 to 30 mol of ethylene oxide and/or propylene oxide and/or butylene oxide per hydroxyl group or amino group and, in the case of the polyether amines, by subsequent reductive amination with ammonia, monoamines or polyamines. In the case of polyethers, such products can also have carrier oil properties. Examples of these detergents include tridecanol butoxylates, isotridecanol butoxylates, isononylphenol butoxylates and polyisobutenol butoxylates and propoxylates and also the corresponding reaction products with ammonia.

[0110] Detergents comprising carboxylic ester groups (g) can be esters of mono-, di- or tricarboxylic acids with long-chain alkanols or polyols, in particular those having a minimum viscosity of 2 mm²/s at 100° C. The mono-, di- or tricarboxylic acids used can be aliphatic or aromatic acids, and particularly suitable ester alcohols or ester polyols are long-chain representatives having, for example, from 6 to 24 carbon atoms. Example esters include adipates, phthalates, isophthalates, terephthalates and trimellitates of isooctanol, of isononanol, of isodecanol and of isotridecanol. Such products can also have carrier oil properties.

[0111] Detergents comprising moieties obtained by Mannich reaction of substituted phenols with aldehydes and mono- or polyamines (h) can be reaction products of polyisobutene-substituted phenols with formaldehyde and mono-

or polyamines such as ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine or dimethylaminopropylamine.

Lubricity Additives

[0112] One or more lubricity additives can also be added to the compositions. Non-limiting examples of lubricity additives include certain carboxylic acids or fatty acids, alkenylsuccinic esters, bis(hydroxyalkyl) fatty amines, hydroxyacetamides or castor oil. The aforementioned carboxylic acids or fatty acids can be present as monomer and/or dimeric species.

Corrosion Inhibitors

[0113] One or more corrosion inhibitors can also be included in the compositions. Non-limiting examples of corrosion inhibitors include ammonium salts of organic carboxylic acids, which tend to form films. Heterocyclic aromatics can also be included as corrosion inhibitors for nonferrous metals. Amines for reducing the pH can also be included with corrosion inhibitors.

Antioxidants

[0114] One or more antioxidants or stabilizers can also be included in the compositions. Non-limiting examples of antioxidants or stabilizers include amines, such as para-phenylenediamine, dicyclohexylamine, morpholine or derivatives of these amines, phenolic antioxidants, such as 2,4-di-tert-butylphenol or 3,5-di-tert-butyl-4-hydroxyphenylpropionic acid and derivatives thereof.

[0115] Non-limiting examples of antioxidants include alkylated monophenols, for example 2,6-di-tert-butyl-4-methylphenol, 2-tert-butyl-4,6-dimethylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,6-di-tert-butyl-4-n-butylphenol, 2,6-di-tert-butyl-4-isobutylphenol, 2,6-dicyclopentyl-4-methylphenol, 2-(α -methylcyclohexyl)-4,6-dimethylphenol, 2,6-dioctadecyl-4-methylphenol, 2,4,6-tricyclohexylphenol, 2,6-di-tert-butyl-4-methoxymethylphenol, 2,6-dinonyl-4-methylphenol, 2,4-dimethyl-6-(1'-methylundec-1'-yl)phenol, 2,4-dimethyl-6-(1'-methylheptadec-1'-yl)phenol, 2,4-dimethyl-6-(1'-methyltridec-1'-yl)phenol, and combinations thereof.

[0116] Other non-limiting examples of suitable antioxidants include alkylthiomethylphenols, for example 2,4-dioctylthiomethyl-6-tert-butylphenol, 2,4-dioctylthiomethyl-6-methylphenol, 2,4-dioctylthiomethyl-6-ethylphenol, 2,6-didodecylthiomethyl-4-nonylphenol, and combinations thereof; hydroquinones and alkylated hydroquinones, for example 2,6-di-tert-butyl-4-methoxyphenol, 2,5-di-tert-butylhydroquinone, 2,5-di-tert-amylhydroquinone, 2,6-diphenyl-4-octadecyloxyphenol, 2,6-di-tert-butylhydroquinone, 2,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyphenyl stearate, bis-(3,5-di-tert-butyl-4-hydroxyphenyl) adipate, and combinations thereof; hydroxylated thiobiphenyl ethers, for example 2,2'-thiobis(6-tert-butyl-4-methylphenol), 2,2'-thiobis(4-octylphenol), 4,4'-thiobis(6-tert-butyl-3-methylphenol), 4,4'-thiobis(6-tert-butyl-2-methylphenol), 4,4'-thiobis(3,6-di-*i*-sec-amylphenol), 4,4'-bis-(2,6-dimethyl-4-hydroxyphenyl)disulfide, and combinations thereof; alkylidenebisphenols, for example 2,2'-methylenebis(6-tert-butyl-4-methylphenol), 2,2'-methylenebis(6-tert-butyl-4-ethylphenol), 2,2'-methylenebis[4-methyl-6-(α -methylcyclohexyl)]

phenol], 2,2'-methylenebis(4-methyl-6-cyclohexylphenol), 2,2'-methylenebis(6-nonyl-4-methylphenol), 2,2'-methylenebis(4,6-di-tert-butylphenol), 2,2'-ethylidenebis(4,6-di-tert-butylphenol), 2,2'-ethylidenebis(6-tert-butyl-4-isobutylphenol), 2,2'-methylenebis[6-(α,α -methylbenzyl)-4-nonylphenol], 2,2'-methylenebis[6-(α,α -dimethylbenzyl)-4-nonylphenol], 4,4'-methylenebis(2,6-di-tert-butylphenol), 4,4'-methylenebis(6-tert-butyl-2-methylphenol), 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 2,6-bis(3-tert-butyl-5-methyl-2-hydroxybenzyl)-4-methylphenol, 1,1,3-tris(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)-3-n-dodecylmercapto butane, ethylene glycol bis[3,3-bis(3'-tert-butyl-4'-hydroxyphenyl)butyrate], bis(3-tert-butyl-4-hydroxy-5-methyl-phenyl)dicyclopentadiene, bis[2-(3'-tert-butyl-2'-hydroxy-5'-methylbenzyl)-6-tert-butyl-4-methylphenyl]terephthalate, 1,1-bis-(3,5-dimethyl-2-hydroxyphenyl)butane, 2,2-bis-(3,5-di-tert-butyl-4-hydroxyphenyl)propane, 2,2-bis-(5-tert-butyl-4-hydroxy-2-methylphenyl)-4-n-dodecylmercaptobutane, 1,1,5,5-tetra-(5-tert-butyl-4-hydroxy-2-methyl phenyl)pentane, and combinations thereof can be utilized as antioxidants; O-, N- and S-benzyl compounds, for example 3,5,3',5'-tetra-tert-butyl-4,4'-dihydroxydibenzyl ether, octadecyl-4-hydroxy-3,5-dimethylbenzylmercaptoacetate, tris-(3,5-di-tert-butyl-4-hydroxybenzyl)amine, bis(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)dithiol terephthalate, bis(3,5-di-tert-butyl-4-hydroxybenzyl)sulfide, isooctyl-3,5-di-tert-butyl-4-hydroxybenzylmercaptoacetate, and combinations thereof; hydroxybenzylated malonates, for example dioctadecyl-2,2-bis-(3,5-di-tert-butyl-2-hydroxybenzyl)-malonate, di-octadecyl-2-(3-tert-butyl-4-hydroxy-5-methylbenzyl)-malonate, di-dodecylmercaptoethyl-2,2-bis-(3,5-di-tert-butyl-4-hydroxybenzyl)malonate, bis[4-(1,1,3,3-tetramethylbutyl)phenyl]-2,2-bis(3,5-di-tert-butyl-4-hydroxybenzyl)malonate, and combinations thereof; triazine compounds, for example 2,4-bis(octylmercapto)-6-(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,3,5-triazine, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,2,3-triazine, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)isocyanurate, 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl 2,4,6-tris(3,5-di-tert-butyl-4-hydroxyphenylethyl)-1,3,5-triazine, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxyphenyl propionyl)-hexahydro-1,3,5-triazine, 1,3,5-tris(3,5-dicyclohexyl-4-hydroxybenzyl)isocyanurate, and combinations thereof; aromatic hydroxybenzyl compounds, for example 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene, 1,4-bis(3,5-di-tert-butyl-4-hydroxybenzyl)-2,3,5,6-tetramethylbenzene, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)phenol, and combinations thereof; benzylphosphonates, for example dimethyl-2,5-di-tert-butyl-4-hydroxybenzylphosphonate, diethyl-3,5-di-tert-butyl-4-hydroxybenzylphosphonate, dioctadecyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonate, dioctadecyl-5-tert-butyl-4-hydroxy 3-methylbenzylphosphonate, the calcium salt of the monoethyl ester of 3,5-di-tert-butyl-4-hydroxybenzylphosphonic acid, and combinations thereof; acylaminophenols, for example 4-hydroxylauranilide, 4-hydroxystearanilide, octyl N-(3,5-di-tert-butyl-4-hydroxyphenyl)carbamate; esters of [3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethyl-

ene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl) isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane, and combinations thereof; esters of β -(5-tert-butyl-4-hydroxy-3-methylphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl) isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane, and combinations thereof; esters of β -(3,5-dicyclohexyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl) isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane, and combinations thereof; compounds including nitrogen, such as amides of [3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid e.g. N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hexamethylenediamine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)trimethylenediamine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hydrazine; aminic compounds such as N,N'-diisopropyl-p-phenylenediamine, N,N'-di-sec-butyl-p-phenylenediamine, N,N'-bis(1,4-dimethylpentyl)-p-phenylenediamine, N,N'-bis(1-ethyl-3-methylpentyl)-p-phenylenediamine, N,N'-bis(1-methylheptyl)-p-phenylenediamine, N,N'-dicyclohexyl-p-phenylenediamine, N,N'-diphenyl-p-phenylenediamine, N,N'-bis(2-naphthyl)-p-phenylenediamine, N-isopropyl-N'-phenyl-p-phenylenediamine, N-(1,3-dimethyl-butyl)-N'-phenyl-p-phenylenediamine, N-(1-methylheptyl)-N'-phenyl-p-phenylenediamine, N-cyclohexyl-N'-phenyl-p-phenylenediamine, 4-(p-toluene-sulfamoyl)diphenylamine, N,N'-dimethyl-N,N'-di-sec-butyl-p-phenylenediamine, diphenylamine, N-allyldiphenylamine, 4-isopropoxydiphenylamine, N-phenyl-1-naphthylamine, N-phenyl-2-naphthylamine, octylated diphenylamine, for example p,p'-di-tert-octyldiphenylamine, 4-n-butylaminophenol, 4-butyrylaminophenol, 4-nonanoylaminophenol, 4-dodecanoylaminophenol, 4-octadecanoylaminophenol, bis(4-methoxyphenyl)amine, 2,6-di-tert-butyl-4-dimethylamino methylphenol, 2,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylmethane, N,N,N',N'-tetramethyl-4,4'-diaminodiphenylmethane, 1,2-bis[(2-methyl-phenyl)amino]ethane, 1,2-bis(phenylamino)propane, (o-tolyl)biguanide, bis[4-(1',3'-dimethylbutyl)phenyl]amine, tert-octylated N-phenyl-1-naphthylamine, a

mixture of mono- and dialkylated tert-butyl/tert-octyldiphenylamines, a mixture of mono- and dialkylated isopropyl/isohexyldiphenylamines, mixtures of mono- and dialkylated tert-butyl diphenylamines, 2,3-dihydro-3,3-dimethyl-4H-1,4-benzothiazine, phenothiazine, N-allylphenothiazine, N,N,N',N'-tetraphenyl-1,4-diaminobut-2-ene, N,N-bis(2,2,6,6-tetramethylpiperid-4-yl)-hexamethylenediamine, bis(2,2,6,6-tetramethyl piperid-4-yl)sebacate, 2,2,6,6-tetramethylpiperidin-4-one and 2,2,6,6-tetramethyl piperidin-4-ol, and combinations thereof; aliphatic or aromatic phosphites, esters of thiodipropionic acid or of thiodiacetic acid, or salts of dithiocarbamic or dithiophosphoric acid, 2,2,12,12-tetramethyl-5,9-dihydroxy-3,7,11-trithiatridecane and 2,2,15,15-tetramethyl-5,12-dihydroxy-3,7,10,14-tetrathiahexadecane, and combinations thereof; and sulfurized fatty esters, sulfurized fats and sulfurized olefins, and combinations thereof.

Demulsifiers

[0117] One or more demulsifiers can also be included in the compositions. Although a single demulsifier can be included in the compositions, more than one demulsifier can be included in the compositions. Each demulsifier can include one or more solvents which facilitate dispersion of the demulsifier in the compositions. As such, the one or more demulsifiers and one or more solvents included therewith are collectively referred to herein as (D) a demulsifier package. When added to the compositions, the demulsifier package (D) prevents the fuel, additivated with the compositions, from forming an emulsion with water. Specifically, when water and the additivated fuel are mixed, the demulsifier package (D) increases the rate at which water and additivated fuel separate into layers, decreases the amount of water in the fuel layer, decreases the amount of non-aqueous components in the water, and prevents the formation of an emulsion layer. The properties imparted by the demulsifier package (D) on the additivated fuel are collectively referred to as the demulsification properties of the demulsifier package (D).

[0118] ASTM Test Method D 1094-07 and ExxonMobil Analytical Method AM-S 529-08 can be used to test the demulsification properties of the demulsifier package (D). In such tests, the compositions, including the demulsifier package (D), is mixed with fuel to form additivated fuel. In turn, the additivated fuel is mixed with water and tested in accordance with methods such as those set forth above to determine the extent to which the additivated fuel and water emulsify.

[0119] As is set forth in the background, fuel additive compositions including polyalkenylsuccinimides and other additives can phase separate over time, especially at lower temperatures (e.g. temperatures below 23° C.). ExxonMobil Analytical Method FWI-013 can be used to test the storage stability (i.e. the homogeneity and resistance to phase separation) of the compositions. The compositions disclosed herein are homogenous and resistant to phase separation when stored “neat”, i.e., not in additivated fuel. Although demulsifiers can provide demulsification properties to additivated fuel, demulsifiers can also cause phase separation of the compositions over time or upon exposure to lower temperatures. The demulsifier package (D) used with the compositions disclosed herein provides the compositions with robust demulsification properties, and does not cause phase separation of the compositions during storage.

[0120] The demulsifier package (D) can include a demulsifier selected from salts of fatty acids, alkylamino carboxylic

acids, organo sulfur compounds (e.g. sulfonic acids, alkylaryl sulfonate), polyetherols, and combinations thereof. The demulsifier package (D) can include any combination of demulsifiers selected from the chemical genera set forth in the previous sentence, and can include more than one chemical species from each chemical genus.

[0121] Polyetherols include the reaction product of a base molecule (also known as an initiator) and an alkylene oxide, in a chemical reaction known as alkoxylation. The base molecule is selected to impart certain physical properties to the polyetherol, for example, a base molecule including N or a cyclic hydrocarbon can be used to form the polyetherol. The alkylene oxide can be selected from the group of EO, PO, BO, and combinations thereof. Alkoxylation enables control of hydrophilic-lipophilic balance value (“HLB value”), M_n , and various other properties of the resulting polyetherol. Alkoxylation can be carried out to form polyetherols having a “block” structure (block polyetherols) and/or a “random” structure. In some embodiments, the polyetherol can have a heteric structure. For example, the polyetherol can have a totally heteric (or random) EO, PO structure. As another example, the polyetherol can have heteric, but uniform blocks, e.g. blocks comprising EO and blocks comprising PO. As yet another example, the polyetherol can have heteric blocks and uniform blocks, e.g. blocks comprising all EO and blocks comprising random EO, PO. As such, the base molecule and the type and amount of alkylene oxide used for alkoxylation the base molecule can be varied to achieve certain properties, such as calculated HLB value and M_n , which improve the demulsification properties of the particular demulsifier in the compositions in additivated fuel.

[0122] The demulsifier package (D) can include a polyetherol demulsifier selected from alkoxyated butyl, amyl, and nonyl phenol resins, alkoxyated alkyl phenol formaldehyde resins, alkoxyated epoxy resins, alkoxyated polyethyleneimines, oxyalkylated alkyl phenols, amine alkoxyates, EO polyetherols (e.g. nonylphenol ethoxylate), PO polyetherols, EO/PO block polyetherols, and combinations thereof. The polyetherol can be a block copolymer, a random copolymer, or a hybrid thereof. In one embodiment, the demulsifier package (D) includes a combination of the exemplary polyetherols set forth above.

[0123] As set forth above, the demulsifier package (D) can also include one or more organo sulfur compounds. Specific, non-limiting examples of suitable organo sulfur compounds include sulfonic acids, alkylaryl sulfonates, and combinations thereof. Specific, non-limiting examples of suitable sulfonic acids include dodecyl benzene sulfonic acid and other alkylbenzene sulfonic acids. In one embodiment, the demulsifier package (D) includes a sulfonic acid.

[0124] In some embodiments, the demulsifier package (D) includes less than 2,000, alternatively less than 1,500, alternatively from 100 to 1,000, ppm of sulfur. Accordingly, in various embodiments, the demulsifier package (D), when used in the compositions set forth herein, delivers an amount of sulfur to fuel which is less than an amount which can be detected by instruments and test methods commonly used to detect sulfur content in additivated fuel.

[0125] In one embodiment, the demulsifier package (D) is substantially free of sulfur. “Substantially free” as used herein in relation to the demulsifier package (D) being substantially free of sulfur means that the demulsifier package (D) includes sulfur containing compounds in an amount less than about 25, alternatively less than about 10, alternatively less than 5,

alternatively less than about 1, alternatively less than about 0.5, alternatively less than about 0.2, alternatively less than about 0.15, alternatively 0 parts by weight, based on 100 parts by weight of the demulsifier package (D). Alternatively, in one embodiment, the demulsifier package (D) contributes less than 50, alternatively less than 25, alternatively less than 1.5, alternatively less than 1, alternatively less than 0.5, alternatively less than 0.2, alternatively less than 0.1, alternatively less than 0.05, alternatively less than 0.01, mg of sulfur/kg of fuel at the treat rates set forth herein.

[0126] The compositions can be added to fuel in an amount such that the demulsifier (or demulsifier package (D)) can be present in the fuel in an amount of from 0.5 to 500, alternatively from 0.5 to 200, alternatively from 0.5 to 100, alternatively from 0.5 to 50, alternatively from 1 to 25, mg/kg of fuel. Further, the demulsifier package (D) can be present in the compositions in an amount of less than 5, alternatively less than 4, alternatively less than 3, alternatively less than 2.5, alternatively less than 2, alternatively less than 1.5, alternatively less than 1, alternatively less than 0.8, alternatively from 0.1 to 5, alternatively from 0.2 to 2.5, alternatively from 0.2 to 2, alternatively from 0.2 to 1, alternatively from 0.2 to 2, alternatively from 0.2 to 0.8, parts by weight per 100 parts by weight of the composition.

Metal Deactivators

[0127] One or more metal deactivators can also be included in the compositions. Non-limiting examples of the one or more metal deactivators include benzotriazoles and derivatives thereof, for example 4- or 5-alkylbenzotriazoles (e.g. triazole) and derivatives thereof, 4,5,6,7-tetrahydrobenzotriazole and 5,5'-methylenebisbenzotriazole; Mannich bases of benzotriazole or triazole, e.g. 1-[bis(2-ethylhexyl)aminomethyl]triazole and 1-[bis(2-ethylhexyl)aminomethyl]benzotriazole; and alkoxyalkylbenzotriazoles such as 1-(nonyloxymethyl)benzotriazole, 1-(1-butoxyethyl)benzotriazole and 1-(1-cyclohexyloxybutyl)triazole, and combinations thereof.

[0128] Additional non-limiting examples of the one or more metal deactivators include 1,2,4-triazoles and derivatives thereof, for example 3-alkyl(or aryl)-1,2,4-triazoles, and Mannich bases of 1,2,4-triazoles, such as 1-[bis(2-ethylhexyl)aminomethyl]-1,2,4-triazole; alkoxyalkyl-1,2,4-triazoles such as 1-(1-butoxyethyl)-1,2,4-triazole; and acylated 3-amino-1,2,4-triazoles, imidazole derivatives, for example 4,4'-methylenebis(2-undecyl-5-methylimidazole) and bis[(N-methyl)imidazol-2-yl]carbinol octyl ether, and combinations thereof.

[0129] Further non-limiting examples of the one or more metal deactivators include sulfur-containing heterocyclic compounds, for example 2-mercaptobenzothiazole, 2,5-dimercapto-1,3,4-thiadiazole and derivatives thereof; and 3,5-bis[di(2-ethylhexyl)aminomethyl]-1,3,4-thiadiazolin-2-one, and combinations thereof. Even further non-limiting examples of the one or more metal deactivators include amino compounds, for example salicylidenepropylenediamine, salicylaminoguanidine and salts thereof, and combinations thereof.

Dehazers

[0130] One or more dehazers can also be included in the compositions. Non-limiting examples of dehazers include alkoxyated phenol-formaldehyde condensates.

Markers

[0131] One or more markers can also be included in the compositions. The marker can be used to color the compositions and/or for traceability. Markers can also allow for the quantitative analysis of additivated fuel at the refinery, on the roadside, or in the laboratory. That is, markers can allow for a determination of the amount of composition included in the additivated fuel.

Solvents

[0132] One or more solvents can also be included in the compositions. The solvents used in the compositions can be inert stable oleophilic (i.e., dissolves in fuel) organic solvents boiling in the range of about 65° C. to 205° C. For example, an aliphatic or an aromatic hydrocarbon solvent is used, such as benzene, toluene, xylene or higher-boiling aromatics or aromatic thinners. Aliphatic alcohols of about 3 to 8 carbon atoms, such as isopropanol, isobutylcarbinol, n-butanol, 2-ethylhexanol, and the like, in combination with hydrocarbon solvents, are also suitable for use in the compositions.

The Compositions

[0133] The compositions are not particularly limited in this disclosure so long as it includes the polyalkenylsuccinimide (A), the polyisobutene amine (B), and the carrier oil (C).

[0134] In various embodiments, the compositions consist essentially of, or consist of, the polyalkenylsuccinimide (A), the polyisobutene amine (B), and the carrier oil (C). In embodiments that consist essentially of the polyalkenylsuccinimide (A), the polyisobutene amine (B), and the carrier oil (C), the compositions are typically free of materials or material compounds that affect the basic properties of the compositions including, but not limited to, additional solubilizers.

[0135] In various embodiments, the compositions consist essentially of, or consists of, the polyalkenylsuccinimide (A), the polyisobutene amine (B), the carrier oil (C), the demulsifier package (D), and solvent. In embodiments that consist essentially of the polyalkenylsuccinimide (A), the polyisobutene amine (B), the carrier oil (C), the demulsifier package (D), and solvent, the compositions are free of other materials or material compounds that affect the basic properties of the compositions.

[0136] In various other embodiments, the compositions are substantially free of sulfur. "Substantially free" as used herein in relation to the compositions being substantially free of sulfur means that the compositions includes sulfur containing compounds in an amount less than about 5, alternatively less than about 4, alternatively less than about 3, alternatively less than about 2, alternatively less than about 1, alternatively less than about 0.5, alternatively less than about 0.25, alternatively 0 parts by weight, based on 100 parts by weight of the composition.

[0137] Sulfur limits in fuels in many regions of the globe are less than 30, less than 20, or even less than 10 ppm (mg/kg fuel) sulfur. Generally, sulfur limits in fuels are moving towards less than 10 ppm sulfur across the globe. In some embodiments, the compositions deliver an amount of sulfur to the fuel which is less than an amount which can be detected by instruments and test methods commonly used to detect sulfur content in fuel. In various embodiments, the compositions deliver no more sulfur to the fuel than an amount which would "round up" the sulfur content of the unadditivated fuel to the nearest ppm limit. In some embodiments, the compo-

sitions contribute less than 50, alternatively less than 25, alternatively less than 1.5, alternatively less than 1, alternatively less than 0.5, alternatively less than 0.2, alternatively less than 0.1, alternatively less than 0.05, alternatively less than 0.01, mg of sulfur/kg of fuel at the treat rates set forth herein.

[0138] In some embodiments, the compositions include 1 to 75 parts by weight of the polyalkenylsuccinimide (A), 15 to 25 parts by weight of the polyisobutene amine (B), 5 to 70 parts by weight of the carrier oil (C), 2 to 94 parts by weight solvents, and less than 5 parts by weight of the demulsifier package (D), based on 100 parts by weight of the composition.

[0139] In other embodiments, the compositions include 20 to 35 parts by weight of the polyalkenylsuccinimide (A), 15 to 25 parts by weight of the polyisobutene amine (B), 5 to 15 parts by weight of the carrier oil (C), 28 to 55 parts by weight solvents, less than 5 parts by weight of the demulsifier package (D), and less than 0.5 parts by weight of the marker, based on 100 parts by weight of the composition.

[0140] In other embodiments, the compositions include 4 to 15 parts by weight of the polyalkenylsuccinimide (A), 30 to 60 parts by weight of the polyisobutene amine (B), 12-18 parts by weight of the carrier oil (C), 16 to 20 parts by weight solvents, 0.35 to 0.5 parts by weight corrosion inhibitors, 0.5 to 3.5 parts by weight dehazers, and 0.5 to 1.5 parts by weight marker, based on 100 parts by weight of the composition. In one embodiment, the compositions include the polyalkenylsuccinimide (A) in an amount of about 6 parts by weight, the polyisobutene amine (B) in an amount of about 34.67 parts by weight, and the carrier oil (C) in an amount of about 15 parts by weight, each based on the total weight of the composition.

[0141] The subject disclosure also includes a method of forming the compositions comprising the step of mixing the components, e.g. mixing a polyalkenylsuccinimide (A), a polyisobutene amine (B), a carrier oil (C), and a demulsifier package (D), and solvents and other additives. In various embodiments, the step of mixing is conducted with no particular order of addition. For example, all of the components can be mixed in a single, simultaneous step to form the compositions. In other embodiments, the step of mixing is conducted with an order of addition. For example, in one embodiment, the fatty alcohol solvent, the demulsifier package (D), and the marker are mixed together. Then, the aromatic solvent is added to the mixture and mixed in, the polyisobutene amine (B) is added to the mixture and mixed in, and the carrier oil (C) is added to the mixture and mixed in. Finally, the polyisobutenylsuccinimide (A) is added to the mixture and mixed in to form the compositions.

[0142] The composition can be used as an additive in fuels, such as diesel fuel, gasoline fuel, heating oil, and kerosene or middle distillates. When the compositions are used as an additive in diesel fuel, they can be used in any effective amount, alternatively in an amount of from 10 to 10,000, alternatively from 10 to 5,000, alternatively from 50 to 1,000, mg/kg of diesel fuel. When the compositions are used as an additive in gasoline fuel, they can be used in any effective amount, alternatively in an amount of from 10 to 10,000, alternatively from 10 to 5,000, alternatively from 50 to 2,000, mg/kg of gasoline fuel. When the compositions are used as an additive in heating oil, they can be used in any effective amount, alternatively in an amount of from 10 to 1,000, alternatively from 50 to 500, mg/kg of heating oil.

[0143] The subject disclosure also includes a method of improving the fuel economy of an internal combustion engine. The method includes the step of adding the compositions to fuel. The compositions can be added to fuel in the amounts set forth in the preceding paragraph. For example, in one embodiment of the method, 10 to 10,000 mg of the compositions is added per kg of fuel.

[0144] The subject disclosure also includes a fuel including the compositions. The compositions can be included in the fuel in the amounts set forth above. For example, one kg of the fuel can include 10 to 10,000 mg of the composition.

[0145] The following examples are meant to illustrate the disclosure and are not to be viewed in any way as limiting to the scope of the disclosure.

EXAMPLES

[0146] A polyisobutenylsuccinimide is formed in accordance with the instant disclosure. Specifically, the polyisobutenylsuccinimide is the reaction product of (1) a polyisobutene having a chain length of C₄₀ to C₂₀₀ and an average molecular weight (M_n) of greater than 1,000 g/mol and a content of terminal double bonds of greater than 75 mol %, (2) maleic anhydride, and (3) tetraethylenepentamine wherein each mol of polyisobutene is functionalized with 1 to 2 moles of maleic anhydride.

[0147] The polyisobutenylsuccinimide was added to fuel and the additivated fuel was tested to determine fuel economy in accordance with the US Federal Test Procedure—Highway Fuel Economy Test (U.S. Environmental Protection Agency Test Protocol, C.F.R. Title 40, Part 600, Subpart B) for five different automobiles. Standard U.S. regular unleaded gasoline was used in the testing. For each automobile, fuel consumption was determined first with unadditivated fuel and then with additivated fuel formed with a dosage of 190 mg/kg. The results of the fuel economy testing are set forth in Table 1 below.

TABLE 1

Vehicle Model	Model Year	Engine	Fuel Economy Improvement (%)
Dodge Caravan	2008	3.3 L V-6	2.50
Mercury Marquis	2007	4.6 L V-8	0.69
Chevrolet Uplander	2008	3.9 L V-6	1.14
Dodge Journey	2009	3.5 L V-6	3.61
Dodge Caravan	2008	3.8 L V-6	3.57
Base Fuel: Unadditivated U.S. regular unleaded gasoline			
Additive: PIBSI (100%) based on GLISSOPAL ® 1000, MSA, and TEPA			
Dosage of Additivated Fuel: 190 mg/kg			
Crankcase Oil: 10W-30			
Test protocol: U.S. Environmental Protection Agency Test Protocol, C.F.R. Title 40, Part 600, Subpart B			

Note:

Fuel economy determined by carbon balance.

[0148] Referring now to Table 1, use of the polyisobutenylsuccinimide in the additivated fuel resulted in an average fuel savings of 2.3% for the five automobiles tested. Further, the fuel economy benefit of the polyisobutenylsuccinimide is even more astonishing since it demonstrates almost no activity in any type of High Frequency Reciprocating Rig (HFRR) testing and, as is set forth below with Example 1, is miscible with additional fuel additives.

[0149] Example 1 is a fuel additive composition which includes the polyisobutenylsuccinimide and is in accordance

with the instant disclosure. Comparative Examples 1 and 2 are fuel additive compositions which include fuel economy additives known in the art. Specifically, the fuel additive composition of Comparative Example 1 includes a fatty acid amide and the fuel additive composition of Comparative Example 2 includes a propoxylated fatty acid amide. The fuel additive compositions of Example 1 and Comparative Examples 1 and 2 are set forth in Table 2 below. The amounts set forth in Table 2 are parts by weight based on 100 parts by weight of the fuel additive composition.

[0150] Further, the fuel additive compositions of Example 1 and Comparative Examples 1 and 2 were stored at -20°C . for 6 weeks and then examined for any evidence of phase separation. The phase separation test results are also set forth in Table 2 below.

TABLE 2

	Example 1	Comparative Example 1	Comparative Example 2
Polyisobutenylsuccinimide (according to the subject disclosure)	11.1	—	—
Fatty Acid Amide (according to WO 2009/050256)	—	11.1	—
Propoxylated Fatty Acid Amide (according to WO 2010/005720)	—	—	11.1
Polyisobutene Amine (according to the subject disclosure)	10.9	10.9	10.9
Propoxylate Carrier Oil (according to the subject disclosure)	26.7	26.7	26.7
Paraffinic Solvent	5.8	5.8	5.8
Aromatic Solvent	45.5	45.5	45.5
Total	100.0	100.0	100.0
Phase Separation Test Results (After 6 weeks of storage at -20°C .)	One clear phase - pass	Two phases - failure	Two phases - failure

[0151] Referring now to Table 2, the fuel additive composition of Example 1, which includes the polyisobutenylsuccinimide, the polyisobutene amine, and the propoxylate carrier oil, remains clear and in a single phase even after 6 weeks of storage at -20°C . However, the fuel additive compositions of Comparative Examples 1 and 2 form separate phases after 6 weeks of storage at -20°C .

[0152] Example 2 is a fuel additive composition in accordance with the instant disclosure which includes the polyisobutenylsuccinimide, the polyisobutene amine, the polyether carrier oil, and a demulsifier package. The fuel additive composition of Example 2 is set forth in Table 3 below. To form the fuel additive composition of Example 2, the fatty alcohol solvent, the demulsifier components, and the marker are mixed together. Then, the aromatic solvent was added to the mixture and mixed in, the polyisobutene amine was added to the mixture and mixed in, and the polyether carrier oil was added to the mixture and mixed in. Finally, the polyisobutenylsuccinimide was added to the mixture and mixed in to form the fuel additive composition of Example 2.

TABLE 3

Generic Name	Example 2		
	% by weight (based on 100 parts by weight of the fuel additive composition)	Additivated Fuel (PPM)	Ratio (Demulsifier Component: PIBSI, by wt.)
Polyisobutenylsuccinimide	20-35%	130-303 ppm	—
Polyisobutene Amine	15-25%	97-217 ppm	—
Polyether Carrier Oil	5-15%	32-130 ppm	—
Marker	<0.5%	<5 ppm	—
First Demulsifier Component	<3%	<26 ppm	<1:8
Second Demulsifier Component	<1%	<9 ppm	<1:14
Third Demulsifier Component	<2%	<17 ppm	<0.13
Fatty Alcohol Solvent	8-10%	52-104 ppm	—
Aromatic Solvent	20-45%	130-390 ppm	—

[0153] Fuel additivated with the fuel additive composition of Example 2 was tested in accordance with ASTM D 1094-07. The test method of ASTM D 1094-07 determines the miscibility of components in additivated gasoline with water and the effect of these components on volume change and on the fuel-water interface. In this test method, a sample of fuel was shaken at room temperature with a phosphate buffer solution in a graduated cylinder. The cleanliness of the glass cylinder as well as the change in volume of the aqueous layer and the appearance of the interface between layers were taken as the water reaction of the fuel. The fuel additivated with the fuel additive composition of Example 2 was tested and yields a separation rating of (1) (which is the complete absence of all emulsions and/or precipitates within either the water layer the treated fuel layer), and has minimal lacing at the interface between the fuel and water layers. As such, the fuel additive composition of Example 2, which includes a polyisobutenylsuccinimide, a polyisobutene amine, a polyether carrier oil, and a demulsifier package, was resistant to emulsification upon exposure to water.

[0154] Referring now to Table 4, the miscibility of the fuel additivated with the fuel additive composition of Example 2 with water was also tested over a repetitive timing cycle in a multi-contact test. In this test, each individual cycle is referred to as a contact. Specifically, 200 ml of fuel additivated with the fuel additive composition of Example 2 was mixed with 20 ml of water in a glass container and shaken for 5 minutes at the highest setting on a mechanical reciprocating shaker. The sample is then held, with no agitation, for 24 hours and observations regarding the fuel layer, the water layer, and any interface therebetween are made. The fuel is then decanted from the glass container, and 200 ml of fresh fuel additivated with the fuel additive composition of Example 2 are added to the glass container and the cycle was repeated 10 times, with the results set forth in Table 4. The contact number is the number of times the additivated fuel and the water have come into contact, thus there are 10 contacts per test, with each contact 24 hours apart.

[0155] Emulsion observations regarding the mixture of the fuel additive composition of Example 2 and water were made as follows:

[0156] 0) Both the water layer and the fuel layer are clean with no lacing skin, or bubbles;

[0157] 1) Slight skin at the interface between the water and the fuel layer that does not break on tilting the bottle;

[0158] 2) Slight skin at the oil-water interface, heavier than 1) and usually accompanied by dirt and bubbles on the skin (no evidence of emulsion);

[0159] 3) Minimal amounts of emulsion at the bottom and in the center of the bottle. It is circular in shape and approximately ¼ to 1 inch in diameter;

[0160] 4) Emulsion at the interface between the water and the fuel layer (approximately the same amount of emulsion on the bottom of the bottle as 3);

[0161] 5) Emulsion at bottom on the bottle expands upward and the thickness of the emulsion at the interface slightly thicker than 4).

[0162] 6) Emulsion amounts increase with an emulsion film forming on sides of bottle surrounding the water layer;

[0163] 7) Emulsion on bottom of water layer is almost solid and the water layer is barely visible;

[0164] 8) Emulsion with bubbles and the water layer is non longer visible;

[0165] 9) Emulsion with fewer greater than 75% of the emulsion is solid;

[0166] 10) Emulsion is almost completely solid, with only a few air bubbles visible; and

[0167] 11) Emulsion is completely solid.

[0168] Further, observations regarding the water layer and the fuel layer were made with “C” for clear and “H” for hazy.

TABLE 4

Contact Number	The Water Layer	The Fuel Layer	Interface
1	C	C	0
2	C	C	0
3	C	C	0
4	C	C	1
5	C	C	2
6	C	C	2
7	C	C	2
8	C	C	1
9	C	C	1
10	C	C	2
7 Days Later	C	C	2

[0169] Referring now to Table 4, the fuel additive composition of Example 2, which includes the polyisobutenylsuccinimide, the polyisobutene amine, the polyether carrier oil, and the demulsifier package, was resistant to emulsification upon exposure to multi-contact exposure to water.

[0170] Referring now to Table 5, the storage stability of the fuel additive composition of Example 2 was also tested at 23° C. and -15° C. To test storage stability, 100 ml the fuel additive composition of Example 2 was added to a centrifuge container which has a conical bottom end. The centrifuge container is typically clear, and has amount marks on the side thereof. The conical portion of the centrifuge container is about the size of a sharpened pencil tip. The samples were held for 4 weeks, with weekly observations made regarding the amount of phase separation and sediment formed. After testing a digital photo of the conical tip of the centrifuge container was taken.

TABLE 5

Week	23° C.		-15° C.	
	Phase Separation	Sediment	Phase Separation	Sediment
1	None	None	None	None
2	None	None	None	None
3	None	None	None	None
4	None	None	None	None

[0171] Referring now to Table 5, the fuel additive composition of Example 2, which includes a polyisobutenylsuccinimide, a polyisobutene amine, a polyether carrier oil, and a demulsifier package, remained clear and in a single phase even after 4 weeks of storage at 23° C. and -15° C. Further, little (less than 0.05 ml per 100 ml of composition) or no sediment forms on the bottom of the clear centrifuge container.

[0172] It is to be understood that the appended claims are not limited to express and particular compounds, compositions, or methods described in the detailed description, which may vary between particular embodiments which fall within the scope of the appended claims. With respect to any Markush groups relied upon herein for describing particular features or aspects of various embodiments, it is to be appreciated that different, special, and/or unexpected results may be obtained from each member of the respective Markush group independent from all other Markush members. Each member of a Markush group may be relied upon individually and or in combination and provides adequate support for specific embodiments within the scope of the appended claims.

[0173] It is also to be understood that any ranges and subranges relied upon in describing various embodiments of the present disclosure independently and collectively fall within the scope of the appended claims, and are understood to describe and contemplate all ranges including whole and/or fractional values therein, even if such values are not expressly written herein. One of skill in the art readily recognizes that the enumerated ranges and subranges sufficiently describe and enable various embodiments of the present disclosure, and such ranges and subranges may be further delineated into relevant halves, thirds, quarters, fifths, and so on. As just one example, a range “of from 0.1 to 0.9” may be further delineated into a lower third, i.e., from 0.1 to 0.3, a middle third, i.e., from 0.4 to 0.6, and an upper third, i.e., from 0.7 to 0.9, which individually and collectively are within the scope of the appended claims, and may be relied upon individually and/or collectively and provide adequate support for specific embodiments within the scope of the appended claims. In addition, with respect to the language which defines or modifies a range, such as “at least,” “greater than,” “less than,” “no greater than,” and the like, it is to be understood that such language includes subranges and/or an upper or lower limit. As another example, a range of “at least 10” inherently includes a subrange of from at least 10 to 35, a subrange of from at least 10 to 25, a subrange of from 25 to 35, and so on, and each subrange may be relied upon individually and/or collectively and provides adequate support for specific embodiments within the scope of the appended claims. Finally, an individual number within a disclosed range may be relied upon and provides adequate support for specific embodiments within the scope of the appended claims. For example, a range “of from 1 to 9” includes various individual

integers, such as 3, as well as individual numbers including a decimal point (or fraction), such as 4.1, which may be relied upon and provide adequate support for specific embodiments within the scope of the appended claims.

[0174] In addition, it is contemplated that the weight percents or other numerical values or ranges of values described above may vary and may be further defined as any value or range of values, both whole and fractional, within those ranges and values described above and/or may vary from the values and/or range of values above by $\pm 5\%$, $\pm 10\%$, $\pm 15\%$, $\pm 20\%$, $\pm 25\%$, $\pm 30\%$, etc, so long as the variations remain within the scope of the disclosure. As one example, any of the numerical values or ranges described herein may be further defined as “about” and, as such, may vary in accordance with this paragraph. As used in the preceding sentence the word about means reasonably close to.

[0175] The disclosure has been described in an illustrative manner, and it is to be understood that the terminology which has been used is intended to be in the nature of words of description rather than of limitation. Many modifications and variations of the present disclosure are possible in light of the above teachings, and the disclosure may be practiced otherwise than as specifically described.

What is claimed is:

1. A fuel additive composition comprising:
 - (A) a polyalkenylsuccinimide comprising the reaction product of;
 - (1) a hydrocarbyl dicarboxylic acid producing reaction intermediate comprising the reaction product of;
 - (a) a polyolefin comprising C_2 to C_{18} olefin units and having a number average molecular weight (M_n) of about 500 to 5,000 g/mol, and
 - (b) a C_4 to C_{10} monounsaturated acid reactant, wherein said hydrocarbyl dicarboxylic acid producing reaction intermediate includes from 0.5 to 10 dicarboxylic acid producing moieties per molecule of said polyolefin; and
 - (2) a nucleophilic reactant selected from the group of amines, alcohols, amino alcohols, and combinations thereof;
 - (B) a mono or polyfunctional polyisobutene amine; and
 - (C) a carrier oil selected from the group of mineral oils, polyethers, polyetheramines, esters, and combinations thereof.
2. A fuel additive composition as set forth in claim 1 further comprising (D) a demulsifier package.
3. A fuel additive composition as set forth in claim 2 wherein said demulsifier package (D) comprises a demulsifier selected from a salt of a fatty acid, an alkyl amino carboxylic acid, an organo sulfur compound, a polyetherol, and combinations thereof.
4. A fuel additive composition as set forth in claim 3 wherein said polyetherol is selected from alkoxylated alkyl phenol resins, alkoxylated alkyl phenol formaldehyde resins, alkoxylated epoxy resins, alkoxylated polyethyleneamines, amine alkoxylates, ethoxylated polyetherols, propoxylated polyetherols, ethoxylated-propoxylated polyetherols, and combinations thereof.
5. A fuel additive composition as set forth in claim 4 wherein said polyetherol is a block copolymer.
6. A fuel additive composition as set forth in claim 4 wherein said polyetherol is a random copolymer.

7. A fuel additive composition as set forth in claim 2 wherein said demulsifier package (D) is substantially free of sulfur.

8. A fuel additive composition as set forth in claim 2 wherein said organo sulfur compound comprises a sulfonic acid.

9. A fuel additive composition as set forth in claim 1 wherein said polyolefin (a) is a first reactive polyisobutene having a content of terminal double bonds of greater than 50 mol %.

10. A fuel additive composition as set forth in claim 1 wherein said C_4 to C_{10} monounsaturated acid reactant (b) is selected from the group of maleic acid, maleic anhydride, functional derivatives thereof, and combinations thereof.

11. A fuel additive composition as set forth in claim 1 wherein said hydrocarbyl dicarboxylic acid producing reaction intermediate (1) is a polyalkenylsuccinic anhydride.

12. A fuel additive composition as set forth in claim 1 wherein said hydrocarbyl dicarboxylic acid producing reaction intermediate (1) is a polyisobutenylsuccinic anhydride.

13. A fuel additive composition as set forth in claim 1 wherein said nucleophilic reactant (2) comprises tetraethyl-enepentamine.

14. A fuel additive composition as set forth in claim 1 wherein said nucleophilic reactant (2) is a C_2 to C_{40} polyalkylene polyamine which includes from 2 to 9 nitrogen atoms per molecule and wherein 0.1 to 3.0 mol of dicarboxylic acid moieties are reacted per equivalent of nucleophilic reactant to form said polyalkenylsuccinimide (A).

15. A fuel additive composition as set forth in claim 1 wherein said polyalkenylsuccinimide (A) is the reaction product of said reaction intermediate (1) which is further defined as a polyisobutylene of having a number average molecular weight (M_n) of about 500 to 5,000 molecular weight substituted with succinic anhydride moieties, and said nucleophilic reactant (2) which is further defined as a C_2 to C_{40} polyalkylene polyamine which includes from 3 to 9 nitrogen atoms per molecule.

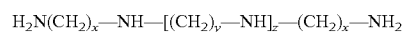
16. A fuel additive composition as set forth in claim 1 wherein said polyalkenylsuccinimide (A) comprises the reaction product of:

- (1) a polyisobutenylsuccinic anhydride; and
- (2) a first amine;

wherein said polyisobutenylsuccinic anhydride is first reacted with an alcohol, then reacted with said first amine to form said polyisobutenylsuccinimide, and wherein said alcohol, which is either unreacted or cleaved, is optionally removed.

17. A fuel additive composition as set forth in claim 16 wherein said alcohol is selected from the group consisting of monohydric alcohols of the formula R^1OH , where R^1 is straight-chain or branched, cyclic or branched cyclic alkyl of 1 to 16 carbon atoms, and combinations thereof.

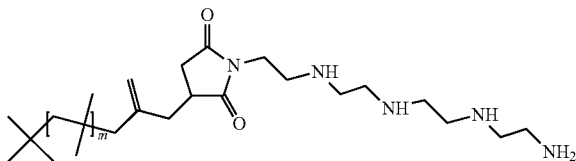
18. A fuel additive composition as set forth in claim 16 wherein said first amine has the following formula:



where x and y are each independently an integer from 1 to 5 and z is an integer from 0 to 8, or mixtures thereof.

19. A fuel additive composition as set forth in claim 1 wherein said polyalkenylsuccinimide (A) has the following general structure:

(A) a polyisobutenylsuccinimide having the following structure;



wherein m is an integer of from 2-80.

20. A fuel additive composition as set forth in claim 1 wherein said mono or polyfunctional polyisobutene amine (B) comprises a reaction product formed via hydroformylation of a second reactive polyisobutene having a content of terminal double bonds of greater than 50 mol % to form an oxo intermediate and subsequent reductive amination of said oxo intermediate.

21. A fuel additive composition as set forth in claim 1 wherein said mono or polyfunctional polyisobutene amine (B) comprises the reaction product of a second reactive polyisobutene having a content of terminal double bonds of greater than 50 mol % and a second amine having the following formula;

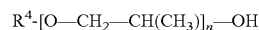


wherein R^2 and R^3 are each independently H, a C_1 - C_{18} -alkyl, C_2 - C_{18} -alkenyl, C_4 - C_{18} -cycloalkyl, C_1 - C_{18} -alkylaryl, hydroxy- C_1 - C_{18} -alkyl, poly(oxyalkyl), polyalkylene polyamine or a polyalkylene amine radical; or, together with the nitrogen atom to which they are bonded, form a heterocyclic ring.

22. A fuel additive composition as set forth in claim 20 wherein said second reactive polyisobutene has a dispersity of less than 6.

23. A fuel additive composition as set forth in claim 20 wherein said second reactive polyisobutene has a number average molecular weight (M_n) of from 500 to 5,000 g/mol.

24. A fuel additive composition as set forth in claim 1 wherein said carrier oil (C) comprises a propoxylate carrier oil having the following formula:



wherein n is an integer of from 8 to 35, and R^4 is straight-chain or branched C_8 - C_{18} -alkyl or C_8 - C_{18} -alkenyl.

25. A fuel additive composition as set forth in claim 1 wherein said carrier oil (C) comprises propoxylated isotridecanol.

26. A fuel additive composition as set forth in claim 2 comprising 1 to 75 parts by weight of said polyalkenylsuccinimide (A), 5 to 70 parts by weight of said polyisobutene amine (B), 2 to 94 parts by weight of said carrier oil (C), and less than 5 parts by weight of said demulsifier package (D), based on 100 parts by weight of said fuel additive composition.

27. An additivated fuel comprising 10 to 10,000 mg of said fuel additive composition set forth in claim 1 per 1 kg of fuel.

28. An additivated fuel as set forth in claim 27 in which less than 1.5 mg of sulfur per kg of additivated fuel is contributed by the fuel additive composition to the additivated fuel.

29. A method of reducing fuel consumption of an internal combustion engine comprising the step of adding the fuel additive composition of claim 1 to fuel.

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