

ANTIFOAM FUEL ADDITIVES

Field of the Invention

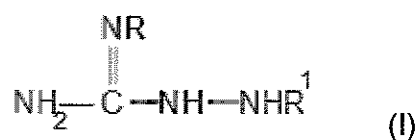
[0001] This disclosure relates generally to fuel additive concentrates. More specifically, the present disclosure is directed to fuel additive concentrates that are effective to enhance the antifoam performance of fuel, and methods of use thereof.

Background of the Invention

[0002] Automotive lubricants, including diesel fuels, are often used in environments in which the lubricant is subject to mechanical agitation, thereby resulting in foaming of the lubricant. Lubricant foaming can cause in insufficient lubrication and/or inefficient combustion, resulting in decreased engine life and/or increased fuel usage. Lubricant foaming can be exacerbated by the presence of other additives in the lubricant. Thus, antifoam agents are incorporated into automotive lubricants to reduce the tendency of the lubricant to foam during operation of the engine.

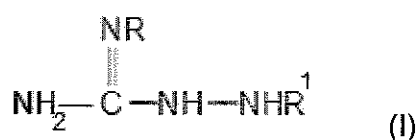
[0003] As automotive technology continues to develop, lubricant formulations will require increasing performance demands. Accordingly, it is desirable and valuable to develop new antifoam agents that can function independently of conventional antifoam agents and also work in conjunction with antifoam agents known in the art.

[0004] In accordance with the disclosure, there is provided a fuel additive composition comprising (a) an aminotriazole compound comprising the reaction product of (i) a hydrocarbyl carbonyl compound, and (ii) an amine compound or salt thereof of formula (I):



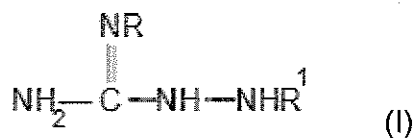
wherein R is selected from the group consisting of a hydrogen and a hydrocarbyl group containing from about 1 to about 15 carbon atoms, and R¹ is selected from the group consisting of hydrogen and a hydrocarbyl group containing from about 1 to about 20 carbon atoms; (b) a hydrocarbyl-substituted succinimide dispersant, wherein the ratio of (a) to (b) ranges from about 1:10 to about 10:1.

[0005] Another aspect of the disclosure provides a fuel composition comprising a major amount of fuel; and a minor amount of an additive composition comprising (a) an aminotriazole compound comprising the reaction product of (i) a hydrocarbyl carbonyl compound, and (ii) an amine compound or salt thereof of formula (I)



wherein R is selected from the group consisting of a hydrogen and a hydrocarbyl group containing from about 1 to about 15 carbon atoms, and R¹ is selected from the group consisting of hydrogen and a hydrocarbyl group containing from about 1 to about 20 carbon atoms; (b) a hydrocarbyl-substituted succinimide dispersant, wherein the ratio of (a) to (b) ranges from about 1:10 to about 10:1.

[0006] A further aspect of the disclosure provides a method of improving the antifoam performance of a fuel comprising: combining a major amount of fuel, and a minor amount of an additive composition comprising (a) an aminotriazole compound comprising the reaction product of (i) a hydrocarbyl carbonyl compound, and (ii) an amine compound or salt thereof of formula (I)



wherein R is selected from the group consisting of a hydrogen and a hydrocarbyl group containing from about 1 to about 15 carbon atoms, and R¹ is selected from the group consisting of hydrogen and a hydrocarbyl group containing from about 1 to about 20 carbon atoms; (b) a hydrocarbyl-substituted succinimide dispersant, wherein the ratio of (a) to (b) ranges from about 1:10 to about 10:1.

[0007] Additional embodiments and advantages of the disclosure will be set forth in part in the detailed description which follows, and/or can be learned by practice of the disclosure. It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the disclosure, as claimed.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] Various features of the embodiments can be more fully appreciated, as the same become better understood with reference to the following detailed description of the embodiments when considered in connection with the accompanying figures, in which:

FIG. 1 illustrates test results of Fuels A and B; and

FIG. 2 illustrates the test results of Fuels C and D.

DETAILED DESCRIPTION OF DISCLOSURE

[0009] The present disclosure relates to a fuel additive concentrate comprising an aminotriazole compound comprising the reaction product of a hydrocarbyl-substituted dicarboxylic acid or anhydride and an amine compound or salt thereof.

[0010] As used herein, “middle distillate fuel” is understood to mean one or more fuels selected from the group consisting of diesel fuel, biodiesel, biodiesel-derived fuel, synthetic diesel, jet fuels, kerosene, diesel fuel treated with oxygenates for particulate control, mixtures thereof, and other products meeting the definitions of ASTM D975. As used herein, “biodiesel” is understood to mean diesel fuel comprising fuel derived from biological sources. In an aspect, the middle distillate fuel can contain up to 30%, for example from about 0.5% to about 30%, such as from about 10% to about 20%, fuel derived from biological sources.

[0011] The middle distillate fuel can be derived from biological sources such as oleaginous seeds, for example rapeseed, sunflower, soybean seeds, and the like. The seeds can be submitted to grinding and/or solvent extraction treatments (e.g., with n-hexane) in order to extract the oil, which comprises triglycerides of saturated and unsaturated (mono- and poly-unsaturated, in mixture with each other, in proportions depending on the selected oleaginous seed) C₁₆ -C₂₂ fatty acids. The oil can be submitted to a filtration and refining process, in order to remove any possible free fats and phospholipids present, and can be submitted to a transesterification reaction with methanol in order to prepare the methyl esters of the fatty acids (fatty acid methyl esters, also known as “FAME” and commonly referred to as biodiesel.)

[0012] As used herein, the term “hydrocarbyl group” or “hydrocarbyl” is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group having a carbon atom directly attached to the remainder of a molecule and having a predominantly hydrocarbon character. Examples of hydrocarbyl groups include:

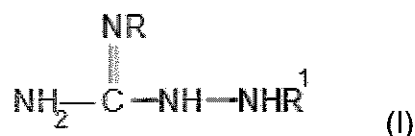
(1) hydrocarbon substituents, that is, aliphatic (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl, cycloalkenyl) substituents, and aromatic-, aliphatic-, and alicyclic-substituted aromatic substituents, as well as cyclic substituents wherein the ring is completed through another portion of the molecule (e.g., two substituents together form an alicyclic radical);

(2) substituted hydrocarbon substituents, that is, substituents containing non-hydrocarbon groups which, in the context of the description herein, do not alter the predominantly hydrocarbon substituent (e.g., halo (especially chloro and fluoro), hydroxy, alkoxy, mercapto, alkylmercapto, nitro, nitroso, and sulfoxy);

(3) hetero-substituents, that is, substituents which, while having a predominantly hydrocarbon character, in the context of this description, contain other than carbon in a ring or chain otherwise composed of carbon atoms. Hetero-atoms include sulfur, oxygen, nitrogen, and encompass substituents such as pyridyl, furyl, thienyl, and imidazolyl. In general, no more than two, or as a further example, no more than one, non-hydrocarbon substituent will be present for every ten carbon atoms in the hydrocarbyl group; in some embodiments, there will be no non-hydrocarbon substituent in the hydrocarbyl group.

[0013] As used herein, the term “major amount” is understood to mean an amount greater than or equal to 50 wt. %, for example from about 80 to about 98 wt.% relative to the total weight of the composition. Moreover, as used herein, the term “minor amount” is understood to mean an amount less than 50 wt. % relative to the total weight of the composition.

[0014] The compositions of the present disclosure can comprise a compound of formula (III) comprising the reaction product of an amine compound or salt thereof with a hydrocarbyl carbonyl compound. Suitable amine compounds for use herein can be amine compounds or salts thereof of formula (I):

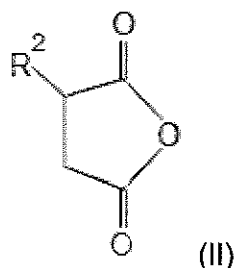


wherein R is selected from the group consisting of a hydrogen and a hydrocarbyl group containing from about 1 to about 15 carbon atoms, and R¹ is selected from the group consisting of hydrogen and a hydrocarbyl group containing from about 1 to about 20 carbon atoms. Such amine compounds can be chosen from guanidines and aminoguanidines or salts thereof, wherein R and R¹ are as defined above. Accordingly, the amine compound can be chosen from the inorganic salts of aminoguanidines and guanidines, such as the halide, carbonate, bicarbonate, nitrate, phosphate, and orthophosphate salts of aminoguanidines and guanidines. As used herein, the term “guanidines” is understood to refer to guanidine and guanidine derivatives, such as aminoguanidine. In an embodiment, the amine compound for the preparation of the additive can be aminoguanidine bicarbonate. Aminoguanidine bicarbonates are readily obtainable from commercial sources, or can be prepared in a well-known manner.

[0015] Suitable hydrocarbyl carbonyl compounds for use herein can be any suitable compound having a hydrocarbyl moiety and a carbonyl moiety, and that is capable of bonding with the amine compound to form the additives of the disclosure. Non-limiting examples of suitable hydrocarbyl carbonyl compounds include, but are not limited to, hydrocarbyl substituted dicarboxylic acids or anhydrides, such as hydrocarbyl-

substituted succinic anhydrides, hydrocarbyl-substituted succinic acids, and esters of hydrocarbyl-substituted succinic acids.

[0016] In some aspects, the hydrocarbyl carbonyl compound can be a hydrocarbyl-substituted succinic anhydride of formula (II):



[0017] wherein R^2 is a hydrocarbyl group having a number average molecular weight ranging from about 100 to about 5,000, such as from about 200 to about 3,000, as measured by gel permeation chromatograph (GPC). Unless indicated otherwise, molecular weights in the present disclosure are number average molecular weights.

[0018] In some aspects, the R^2 group of the hydrocarbyl carbonyl compound can comprise one or more polymer units chosen from linear or branched alkenyl units. For example, the alkenyl units can comprise from about 2 to about 10 carbon atoms. In embodiments, the R^2 group can comprise one or more linear or branched polymer units chosen from ethylene radicals, propylene radicals, butylene radicals, pentene radicals, hexene radicals, octene radicals, and decene radicals. In some aspects, the R^2 group can be in the form of, for example, a homopolymer, copolymer, or terpolymer. In an embodiment, the R^2 group can be isobutylene. Accordingly, in an embodiment, the R^2 group can be a homopolymer of polyisobutylene comprising from about 10 to about 60 isobutylene groups, such as from about 20 to about 30 isobutylene groups. The

compounds used to form the R^2 hydrocarbyl groups can be formed by any suitable methods, such as by conventional catalytic oligomerization of alkenes. A non-limiting example of R^2 can be a polyalkenyl radical, such as a polyisobutylene radical, having a number average molecular weight of from about 100 to about 5,000, such as from about 200 to about 3,000, as measured by GPC.

[0019] In some aspects, the R^2 group of the hydrocarbyl carbonyl compound can be formed from highly reactive polyisobutylenes (HR-PIB) having relatively high terminal vinylidene content. As used herein, "terminal vinylidene content" is understood to mean terminal olefinic double bond content. In an embodiment, the R^2 group can be formed from HR-PIB having at least about 60%, such as about 70% to about 90% and above, terminal vinylidene content. There is a general trend in the industry to convert to HR-PIB, and well known HR-PIBs are disclosed, for example, in U.S. Pat. No. 4,152,499, the disclosure of which is herein incorporated by reference in its entirety.

[0020] The hydrocarbyl carbonyl compounds can be made using any suitable method. Methods for forming hydrocarbyl carbonyl compounds are well known in the art. One example of a known method for forming a hydrocarbyl carbonyl compound comprises blending a polyolefin and an anhydride, such as maleic anhydride. The polyolefin and anhydride reactants can be heated to temperatures of, for example, about 150° C to about 250° C, optionally, with the use of a catalyst, such as chlorine or peroxide. Another exemplary method of making the hydrocarbyl carbonyl compounds is described in U.S. Pat. No. 4,234,435, which is incorporated herein by reference in its entirety.

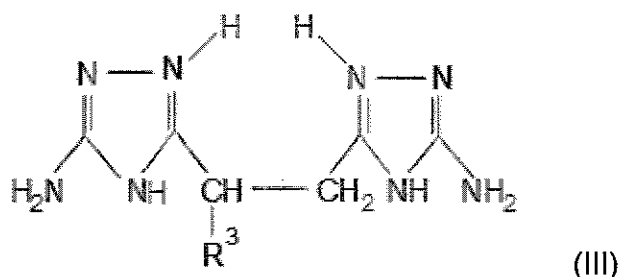
[0021] In some aspects, approximately one mole of maleic anhydride can be reacted per mole of polyolefin, such that the resulting hydrocarbyl-substituted succinic anhydride has about 0.8 to about 1 succinic anhydride group per hydrocarbyl group. In other aspects, the weight ratio of succinic anhydride groups to hydrocarbyl group can range from about 0.5 to about 3.5, such as from about 1 to about 1.1.

[0022] Examples of hydrocarbyl carbonyl compounds useful herein include, but are not limited to, such compounds as dodecenylsuccinic anhydrides, C₁₆₋₁₈ alkenyl succinic anhydride, and polyisobutenyl succinic anhydride (PIBSA). In some embodiments, the PIBSA can have a polyisobutylene substituent with a terminal vinylidene content ranging from about 4% to at least about 60%, such as about 70% to about 90% and above. In some embodiments, the ratio of the number of carbonyl groups to the number of hydrocarbyl moieties in the hydrocarbyl carbonyl compound can range from about 1:1 to about 6:1.

[0023] The hydrocarbyl carbonyl and amine compounds described above can be mixed together under any suitable conditions to provide the desired reaction products of the present disclosure. In an aspect, the reactant compounds can be mixed together in a mole ratio of hydrocarbyl carbonyl compound to amine compound ranging from about 1:1 to about 1:2.5. For example, the mole ratio of the reactants can range from about 1:1 to about 1:2.2. Suitable reaction temperatures can range from about 155° C to about 200° C at atmospheric pressure. For example, reaction temperatures can range from about 160° C to about 190° C. Any suitable reaction pressures can be used, such as subatmospheric pressures or superatmospheric pressures. However, the range of temperatures can be different from those listed where the reaction is carried out at other

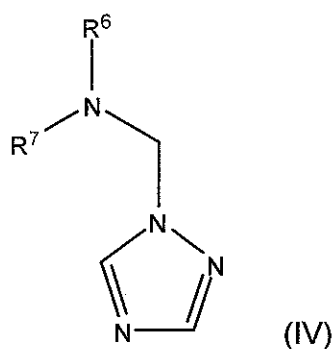
than atmospheric pressure. The reaction can be carried out for a period of time within the range of about 1 hour to about 8 hours, preferably, within the range of about 2 hours to about 6 hours.

[0024] Without desiring to be bound by theoretical considerations, it is believed that the reaction product of the amine and hydrocarbyl carbonyl compound is an aminotriazole compound, such as a bis-aminotriazole compound of formula (III):



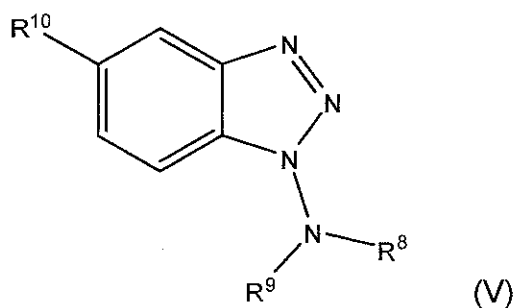
including tautomers and enantiomers thereof, wherein R^3 has a number average molecular weight ranging from about 100 to about 5000, and comprises from about 40 to about 80 carbon atoms. In an embodiment, R^3 is a polyisobutenyl substituent, for example a polyisobutenyl substituent formed from HR-PIB having at least about 60%, such as about 70% to about 90% and above, terminal vinylidene content. The reaction product can contain at least one aminotriazole group. The five-membered ring of the triazole is considered to be aromatic. The aminotriazoles can be fairly stable to oxidizing agents and can be extremely resistant to hydrolysis. It is believed, although it is not certain, that the reaction product is polyalkenyl bis-3-amino-1,2,4-triazole. Such a product contains a relatively high nitrogen content, within the range of about 1.8 wt % to about 2.9 wt % nitrogen.

[0025] In aspects of the present disclosure, the disclosed compositions can comprise 1,2,4 triazoles other than the triazoles described above. For example, the compositions can include triazoles of formula (IV):



wherein R⁶ and R⁷ are independently chosen from hydrogen and hydrocarbyl groups, with the proviso that at least one of R⁶ and R⁷ is not hydrogen. Examples of hydrocarbyl groups include, but are not limited to, C₂ to C₅₀ linear, branched or cyclic alkyl groups; C₂ to C₅₀ linear, branched or cyclic alkenyl groups; and substituted or unsubstituted aryl groups, such as phenyl groups, tolyl groups and xylyl groups. A commercially available example of such triazoles includes Irgamet® 30 (available from Ciba of Tarrytown, NY.)

[0026] The disclosed compositions can also include triazoles of formula (V):



wherein R^8 , R^9 , and R^{10} are independently chosen from hydrogen and hydrocarbyl groups, with the proviso that at least one of R^8 and R^9 is not hydrogen. Examples of hydrocarbyl groups include, but are not limited to, C_2 to C_{50} linear, branched or cyclic alkyl groups; C_2 to C_{50} linear, branched or cyclic alkenyl groups; and substituted or unsubstituted aryl groups, such as phenyl groups, tolyl groups and xylyl groups. R^8 and R^9 can comprise functional groups, such as halogen, carboxyl, hydroxyl, amino, nitro, sulfonate groups, and the like. Commercially available examples of such triazoles include Irgamet® 39 and Irgamet® 42 (available from Ciba of Tarrytown, NY).

[0027] The presently disclosed compositions can also comprise additional antifoam agents in addition to the aminotriazole compounds described above, including silicone-based antifoam agents, such as polydimethyl siloxane, polyethyl siloxane, polydiethyl siloxane, polyacrylates and polymethacrylates, trimethyl-trifluoro-propylmethyl siloxane, mixtures thereof, and the like. Non-limiting examples of such antifoam agents are disclosed in, for example, U.S. Pat. Nos. 3,166,508 and 5,492,638, the disclosures of which are incorporated herein by reference in their entirety. Commercially available antifoam agents include, for example, Y14182 (available from Chemtura Corp. of Middlebury, CT.)

[0028] The presently disclosed aminotriazole compounds can be used alone or in combination with supplemental antifoam agents. The aminotriazole compounds can be used in an amount ranging from about 0.1 wt.% to about 50 wt.%, such as from about 2.5 wt.% to about 10 wt.%, for example from about 5 wt.% to about 10 wt.%, relative to the total weight of the additive concentrate. The silicone-based antifoam agents can

used in the range of about 0.1 wt.% to about 5 wt.%, such as about 0.5 wt.% to about 3.5 wt.%, relative to the total weight of the additive concentrate.

[0029] In some aspects of the present disclosure, the disclosed fuel compositions can comprise a dispersant, such as an amine-containing dispersant. Suitable amine-containing dispersants can comprise hydrocarbyl-substituted succinimide dispersants. Suitable hydrocarbyl-substituted succinimides are well known in the art and are described, for example, in U.S. Pat. No. 4,482,356, the disclosure of which is incorporated herein by reference in its entirety.

[0030] As used herein the term "succinimide" is meant to encompass the completed reaction product from reaction between an amine and a hydrocarbyl-substituted succinic acid or anhydride (or like succinic acylating agent), and is intended to encompass compounds wherein the product may have amide, and/or salt linkages in addition to the imide linkage of the type that results from the reaction of or contact with an amine and an anhydride moiety.

[0031] Suitable hydrocarbyl-substituted succinic anhydrides can be formed by first reacting an olefinically unsaturated hydrocarbon of a desired molecular weight with maleic anhydride. Reaction temperatures of about 100°C to about 250°C can be used. With higher boiling olefinically-unsaturated hydrocarbons, good results are obtained at about 200°C to about 250°C. This reaction can be promoted by the addition of chlorine.

[0032] Typical olefins include, but are not limited to, cracked wax olefins, linear alpha olefins, branched chain alpha olefins, polymers and copolymers of lower olefins. The olefins can be chosen from ethylene, propylene, butylene, such as isobutylene, 1-octene, 1-hexene, 1-decene and the like. Useful polymers and/or copolymers include,

but are not limited to, polypropylene, polybutenes, polyisobutene, ethylene-propylene copolymers, ethylene-isobutylene copolymers, propylene-isobutylene copolymers, ethylene-1-decene copolymers and the like.

[0033] In an aspect, the hydrocarbyl substituents of the hydrocarbyl-substituted succinic anhydrides can be derived from butene polymers, for example polymers of isobutylene. Suitable polyisobutenes for use herein include those formed from HR-PIB having having at least about 60%, such as about 70% to about 90% and above, terminal vinylidene content. Suitable polyisobutenes can include those prepared using BF_3 catalysts. The average number molecular weight of the hydrocarbyl substituent can vary over a wide range, for example from about 100 to about 5000, such as from about 500 to about 5000, as determined by GPC.

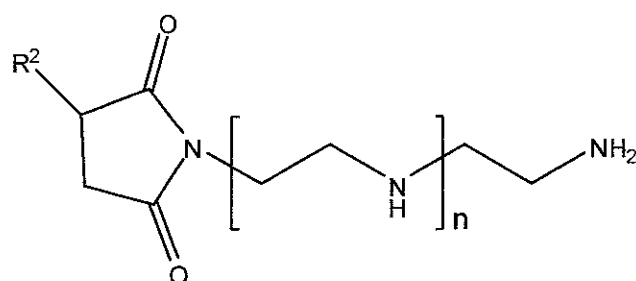
[0034] Carboxylic reactants other than maleic anhydride can be employed such as maleic acid, fumaric acid, malic acid, tartaric acid, itaconic acid, itaconic anhydride, citraconic acid, citraconic anhydride, mesaconic acid, ethylmaleic anhydride, dimethylmaleic anhydride, ethylmaleic acid, dimethylmaleic acid, hexylmaleic acid, and the like, including the corresponding acid halides and lower aliphatic esters.

[0035] The mole ratio of maleic anhydride to olefin can vary widely. It can vary from about 5:1 to about 1:5, for example from about 3:1 to about 1:3, and as a further example, the maleic anhydride can be used in stoichiometric excess to force the reaction to completion. The unreacted maleic anhydride can be removed by vacuum distillation.

[0036] Any of numerous polyamines can be utilized in preparing the hydrocarbyl-substituted succinimide dispersant. Non-limiting exemplary polyamines can include

aminoguanidine bicarbonate (AGBC), diethylene triamine (DETA), triethylene tetramine (TETA), tetraethylene pentamine (TEPA), pentaethylene hexamine (PEHA) and heavy polyamines. A heavy polyamine can comprise a mixture of polyalkylenepolyamines comprising small amounts of lower polyamine oligomers such as TEPA and PEHA, but primarily oligomers with 7 or more nitrogens, 2 or more primary amines per molecule, and more extensive branching than conventional polyamine mixtures. Additional non-limiting polyamines which can be utilized in preparing the hydrocarbyl-substituted succinimide dispersant are disclosed in U.S. Pat. No. 6,548,458, the disclosure of which is incorporated herein by reference in its entirety. In an embodiment, the polyamine can comprise tetraethylene pentamine (TEPA).

[0037] In an embodiment, the dispersant can include compounds of formula (IV):



wherein *n* represents 0 or an integer of from 1 to 5, and R² is a hydrocarbyl substituent as defined above. In an embodiment, *n* is 3 and R² is a polyisobutenyl substituent, such as that derived from polyisobutylenes having at least about 60%, such as about 70% to about 90% and above, terminal vinylidene content. Compounds of formula (IV) can be the reaction product of a hydrocarbyl-substituted succinic anhydride, such as a polyisobutenyl succinic anhydride (PIBSA), and a polyamine, for example tetraethylene pentamine (TEPA).

[0038] The presently disclosed dispersants can be used in the range of about 0.01 wt.% to about 99.99 wt.%, such as from about 5 wt.% to about 25 wt.%, relative to the total weight of the additive concentrate. In an aspect, the disclosed aminotriazole compound and dispersant can be present in a fuel composition at a ratio ranging from about 1:10 to about 10:1, such as from about 1:2 to about 10:1, for example 1:8.

[0039] In other aspects of the present disclosure, the disclosed compositions can comprise a fuel soluble carrier. Such carriers can be of various types, such as liquids or solids, e.g., waxes. Examples of liquid carriers include, but are not limited to, mineral oil and oxygenates, such as liquid polyalkoxylated ethers (also known as polyalkylene glycols or polyalkylene ethers), liquid polyalkoxylated phenols, liquid polyalkoxylated esters, liquid polyalkoxylated amines, and mixtures thereof. Examples of the oxygenate carriers can be found in U.S. Pat. No. 5,752,989, the description of which carriers is herein incorporated by reference in its entirety. Additional examples of oxygenate carriers include alkyl-substituted aryl polyalkoxylates described in U.S. Patent Publication No. 2003/0131527, published July 17, 2003 to Colucci et. al., the description of which is herein incorporated by reference in its entirety.

[0040] In other aspects, compositions of the present application may not contain a carrier. For example, some compositions of the present application may not contain mineral oil or oxygenates, such as those oxygenates described above.

[0041] One or more additional optional additives can be present in the compositions disclosed herein. For example, the compositions can comprise supplementary antifoam agents, dispersants, detergents, antioxidants, thermal stabilizers, carrier fluids, metal

deactivators, dyes, markers, corrosion inhibitors, biocides, antistatic additives, drag reducing agents, friction modifiers, demulsifiers, emulsifiers, dehazers, anti-icing additives, antiknock additives, surfactants, cetane improvers, corrosion inhibitors, cold flow improvers, pour point depressants, solvents, demulsifiers, lubricity additives, extreme pressure agents, viscosity index improvers, seal swell agents, amine stabilizers, combustion improvers, dispersants, conductivity improvers, metal deactivators, marker dyes, organic nitrate ignition accelerators, manganese tricarbonyl compounds, and mixtures thereof. In some aspects, the compositions described herein can contain about 10 wt.% or less, or in other aspects, about 5 wt.% or less, based on the total weight of the additive concentrate or fuel composition, of one or more of the above additives. Similarly, the fuel compositions can contain suitable amounts of fuel blending components such as methanol, ethanol, dialkyl ethers, and the like.

[0042] When formulating the presently disclosed compositions, the disclosed additive composition can be employed in amounts sufficient to reduce foaming in a fuel, such as a middle distillate fuel, for example a diesel fuel. In an aspect, the disclosed fuel compositions can contain a major amount of a fuel and a minor amount of the above-described fuel additive composition sufficient to control or reduce the formation of foam in fuels, for example from about 0.005 wt.% to about 0.300 wt.%, relative to the total weight of the composition. In another aspect, the fuels of present disclosure can comprise, on an active ingredient basis, an aminotriazole in an amount ranging from about 1 ppm to about 5000 ppm, such as from about 20 ppm to about 5000 ppm, for example from about 1000 ppm to about 5000 ppm. In another aspect, the fuels of the present disclosure can comprise, on an active ingredient basis, a silicone-based

antifoam agent in an amount ranging from about 1 ppm to about 50 ppm, such as from about 4 ppm to about 25 ppm.

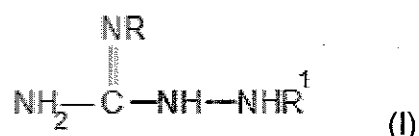
[0043] In another aspect, the presently disclosed fuel compositions can comprise, on an active ingredient basis, a dispersant in an amount ranging from about 20 ppm to about 300 ppm, such as from about 40 ppm to about 300 ppm, for example from about 100 ppm to about 300 ppm. In aspects where a carrier is employed, the fuel compositions can contain, on an active ingredients basis, an amount of the carrier ranging from about 1 mg to about 100 mg of carrier per kg of fuel, such as about 5 mg to about 50 mg of carrier per kg of fuel. The active ingredient basis excludes the weight of (i) unreacted components associated with and remaining in the antifoam agent as produced and used, and (ii) solvent(s), if any, used in the manufacture of the antifoam agent either during or after its formation but before addition of a carrier, if a carrier is employed.

[0044] The additives of the present disclosure and optional additives used in formulating the disclosed compositions can be blended into a base fuel individually or in various sub-combinations. In some embodiments, the additive components of the present disclosure can be blended into a fuel concurrently using an additive concentrate, as this takes advantage of the mutual compatibility and convenience afforded by the combination of ingredients when in the form of an additive concentrate. Also, use of a concentrate can reduce blending time and lessen the possibility of blending errors.

[0045] The fuel compositions of the present disclosure can be applicable to the operation of both stationary diesel engines (e.g., engines used in electrical power generation installations, in pumping stations, etc.) and ambulatory diesel engines (e.g., engines used as prime movers in automobiles, trucks, road-grading equipment, military vehicles, etc.).

[0046] In an aspect, there is provided a method of improving the antifoam performance of a fuel comprising: providing a major amount of fuel, and a minor amount of an additive composition comprising:

(a) an aminotriazole compound comprising the reaction product of (i) a hydrocarbyl-substituted dicarboxylic acid or anhydride, and (ii) an amine compound or salt thereof of formula (I)



wherein R is selected from the group consisting of a hydrogen and a hydrocarbyl group containing from about 1 to about 15 carbon atoms, and R¹ is selected from the group consisting of hydrogen and a hydrocarbyl group containing from about 1 to about 20 carbon atoms;

(b) a hydrocarbyl-substituted succinimide dispersant;

wherein the molar ratio of (a) to (b) ranges from about 1:10 to about 10:1.

EXAMPLES

[0047] The following examples are illustrative of exemplary embodiments of the disclosure. In these examples as well as elsewhere in this application, all parts and

percentages are by weight unless otherwise indicated. It is intended that these examples are being presented for the purpose of illustration only and are not intended to limit the scope of the invention disclosed herein.

EXAMPLE 1

[0048] A 950 number average molecular weight polybutenyl succinic anhydride was heated to 95° C. An oil slurry of aminoguanidine bicarbonate (AGBC) was added over a 45 minute period. The mixture was heated under vacuum to 160° C and held at that temperature for about 6 hours, removing water and carbon dioxide. The resulting mixture was filtered. It is believed, without being limited by theory, that the resultant mixture comprises an aminotriazole as described herein.

[0049] In the following examples, various base diesel fuels were each combined with various additives as described in Table 1, including the aminotriazole mixture described above, to produce fuel formulations that were evaluated for foam decay as described below.

Table 1

Additive (mg/kg)	Fuel A	Fuel B	Fuel C	Fuel D
Dispersant ¹	42.10	42.10	42.10	42.10
Aminotriazole Antifoam Agent	0.00	5.00	0.00	5.00
Solvent A ²	20.00	20.00	75.50	75.50
Solvent B ³	132.00	132.00	103.90	103.90
Siloxane Antifoam Agent	8.00	8.00	8.00	8.00
Demulsifier A	3.00	3.00	3.00	3.00
Demulsifier B	3.00	3.00	3.00	3.00

¹ Reaction product of PIBSA with triethylenepentamine (TEPA) at a 1:1 mole ratio.

² 2-Ethyl hexanol solvent

³ Aromatic 150 solvent

[0050] Fuels A through D were tested using the BNPe antifoam test apparatus, a widely accepted method for determining the foam characteristics of diesel fuel. Essentially, a 100mL sample of diesel fuel was injected at a constant pressure (400 mb) from a fixed height (245 mm) into a 250 mL test jar. The collapse time of the foam produced were measured and recorded. The collapse time was calculated as the total time elapsed between when the sample finished injecting into the test jar and when the visible surface of the fuel appeared.

[0051] As seen in Figure 1, Fuel B (comprising the aminotriazole mixture) demonstrated reduced foam decay times across Days 1, 8, and 15, as compared to Fuel A. For example, Fuel B demonstrated a foam decay time that was a full second faster than Fuel A on Day 1 (Fuel A = 2.43 seconds; Fuel B = 1.43 seconds). Furthermore, Fuel B demonstrated a foam decay time that was more than two seconds faster than Fuel A on Day 8 (Fuel A = 8.17 seconds; Fuel B = 5.47 seconds) and exhibited a similar time difference on Day 15 (Fuel A = 9.1 seconds; Fuel B = 7.07).

[0052] Moreover, as seen in Figure 2, Fuel D (comprising the aminotriazole mixture) demonstrated reduced foam decay times across Days 1, 8, and 15, as compared to Fuel C. For example, Fuel C demonstrated a foam decay time of 1.47 seconds, whereas Fuel D demonstrated a foam decay time of 1.43 seconds. Furthermore, Fuel D demonstrated a foam decay time that was more than a second faster than Fuel C on Day 8 (Fuel C = 6.03 seconds; Fuel D = 4.7 seconds) and exhibited a similar time difference on Day 15 (Fuel C = 7.4 seconds; Fuel D = 6.03). Thus, as shown by the foregoing examples, fuel compositions comprising the disclosed aminotriazole

compounds are effective antifoam agents. Accordingly, it is believed that the antifoam agents as described herein can be effective for improving the antifoam performance of fuels.

[0053] It is noted that, as used in this specification and the appended claims, the singular forms “a,” “an,” and “the,” include plural referents unless expressly and unequivocally limited to one referent. Thus, for example, reference to “an antifoam agent” includes two or more different antifoam agents. As used herein, the term “include” and its grammatical variants are intended to be non-limiting, such that recitation of items in a list is not to the exclusion of other like items that can be substituted or added to the listed items

[0054] For the purposes of this specification and appended claims, unless otherwise indicated, all numbers expressing quantities, percentages or proportions, and other numerical values used in the specification and claims, are to be understood as being modified in all instances by the term “about.” Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that can vary depending upon the desired properties sought to be obtained by the present disclosure. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

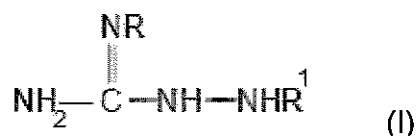
[0055] While particular embodiments have been described, alternatives, modifications, variations, improvements, and substantial equivalents that are or can be

presently unforeseen can arise to applicants or others skilled in the art. Accordingly, the appended claims as filed and as they can be amended are intended to embrace all such alternatives, modifications variations, improvements, and substantial equivalents.

WHAT IS CLAIMED IS:

1. A fuel additive concentrate comprising:

(a) an aminotriazole compound comprising the reaction product of (i) a hydrocarbyl carbonyl compound, and (ii) an amine compound or salt thereof of formula (I)



wherein R is selected from the group consisting of a hydrogen and a hydrocarbyl group containing from about 1 to about 15 carbon atoms, and R¹ is selected from the group consisting of hydrogen and a hydrocarbyl group containing from about 1 to about 20 carbon atoms; and

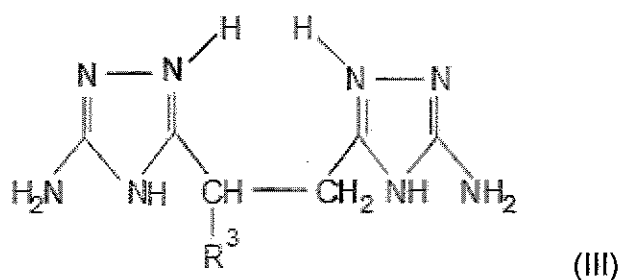
(b) a hydrocarbyl-substituted succinimide dispersant,

wherein the ratio of (a) to (b) ranges from about 1:10 to about 10:1.

2. The additive concentrate of claim 1, wherein (a)(i) is chosen from hydrocarbyl-substituted succinic anhydrides, hydrocarbyl-substituted succinic acids, and esters of hydrocarbyl-substituted succinic acids.

3. The additive concentrate of claim 2, wherein the hydrocarbyl substituent of (b) comprises a hydrocarbyl group having a number average molecular weight ranging from about 100 to about 5,000.

4. The additive concentrate of claim 3, wherein the hydrocarbyl substituent comprises a polyisobutylene group derived from high reactivity polyisobutenes having at least 60% or more terminal olefinic double bonds.
5. The additive concentrate of claim 1, wherein (a)(ii) comprises a salt of aminoguanidine.
6. The additive concentrate of claim 1, wherein (a)(ii) comprises an salt of guanidine.
7. The additive concentrate of claim 1, wherein (a)(ii) comprises aminoguanidine bicarbonate.
8. The additive concentrate of claim 1, wherein (a) comprises a bis-aminotriazole compound of formula (III)



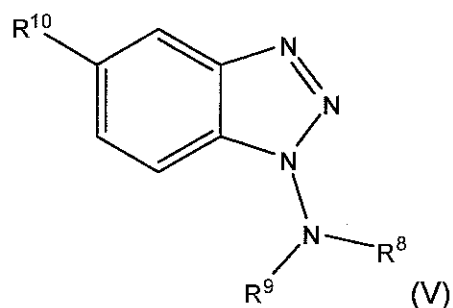
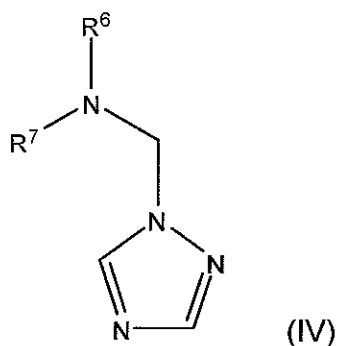
and tautomers and enantiomers thereof, wherein R^3 is a hydrocarbyl group having a number average molecular weight ranging from about 100 to about 5000.

9. The additive concentrate of claim 1, wherein (a) is present in an amount ranging from about 0.1 wt.% to about 50 wt.%; and (b) is present in an amount ranging from about 0.1 wt.% to about 99.99 wt.%, relative to the total weight of the concentrate.

10. The additive concentrate of claim 1, further comprising a silicone-based antifoam agent.

11. The additive concentrate of claim 10, wherein the silicone-based antifoam agent is present in an amount ranging from about 0.1 wt.% to about 5 wt.%, relative to the total weight of the concentrate.

12. The additive concentrate of claim 1, further comprising at least one triazole chosen from triazoles of formulae (IV) and (V):



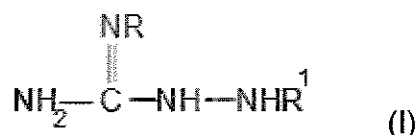
wherein R^6 , R^7 , R^8 , R^9 , and R^{10} are independently chosen from hydrogen and hydrocarbyl groups, with the proviso that at least one of R^6 and R^7 and at least one of R^8 and R^9 is not hydrogen.

13. A fuel composition comprising:

a major amount of a fuel; and

a minor amount of an additive composition comprising:

(a) an aminotriazole compound comprising the reaction product of (i) a hydrocarbyl carbonyl compound, and (ii) an amine compound or salt thereof of formula (I)



wherein R is selected from the group consisting of a hydrogen and a hydrocarbyl group containing from about 1 to about 15 carbon atoms, and R¹ is selected from the group consisting of hydrogen and a hydrocarbyl group containing from about 1 to about 20 carbon atoms; and

(b) a hydrocarbyl-substituted succinimide dispersant,

wherein the ratio of (a) to (b) ranges from about 1:10 to about 10:1.

14. The fuel composition of claim 13, wherein (a)(i) is chosen from hydrocarbyl-substituted succinic anhydrides, hydrocarbyl-substituted succinic acids, and esters of hydrocarbyl-substituted succinic acids.

15. The fuel composition of claim 13, wherein the hydrocarbyl substituent of (b) is a polyisobutylene group.

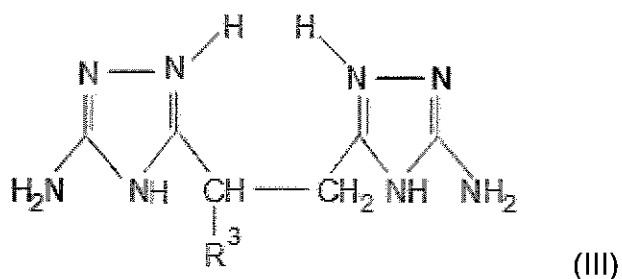
16. The fuel composition of claim 15, wherein the polyisobutylene group is derived from high reactivity polyisobutenes having at least 60% or more terminal olefinic double bonds.

17. The fuel composition of claim 13, wherein (a)(ii) comprises a salt of aminoguanidine.

18. The fuel composition of claim 13, wherein (a)(ii) comprises an inorganic salt of guanidine.

19. The fuel composition of claim 13, wherein (a)(ii) comprises aminoguanidine bicarbonate.

20. The fuel composition of claim 13, wherein (a) comprises a bis-aminotriazole compound of formula (III)



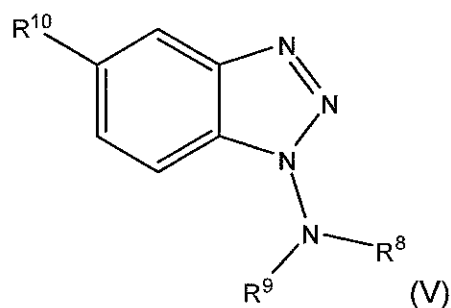
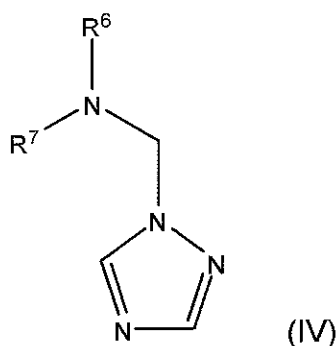
and tautomers and enantiomers thereof, wherein R^3 is a hydrocarbyl group having a number average molecular weight ranging from about 100 to about 5000.

21. The fuel composition of claim 13, wherein the additive composition is present in an amount ranging from about 0.005 wt.% to about 0.3000 wt.%, relative to the total weight of the fuel composition.

22. The fuel composition of claim 13, further comprising at least one additive selected from the group consisting of supplementary antifoam agents, dispersants, detergents, antioxidants, thermal stabilizers, carrier fluids, metal deactivators, dyes, markers, corrosion inhibitors, biocides, antistatic additives, drag reducing agents, friction modifiers, demulsifiers, emulsifiers, dehazers, anti-icing additives, antiknock additives, surfactants, cetane improvers, corrosion inhibitors, cold flow improvers, pour point depressants, solvents, demulsifiers, lubricity additives, extreme pressure agents, viscosity index improvers, seal swell agents, amine stabilizers, combustion improvers, dispersants, conductivity improvers, metal deactivators, marker dyes, organic nitrate ignition accelerators, manganese tricarbonyl compounds, and mixtures thereof.

23. The fuel composition of claim 13, further comprising a silicone-based antifoam agent.

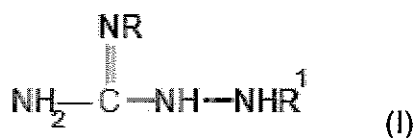
24. The fuel composition of claim 13, further comprising at least one triazole chosen from triazoles of formulae (IV) and (V):



wherein R^6 , R^7 , R^8 , R^9 , and R^{10} are independently chosen from hydrogen and hydrocarbyl groups, with the proviso that at least one of R^6 and R^7 and at least one of R^8 and R^9 is not hydrogen.

25. A method of improving the antifoam performance of a fuel comprising:
combining a major amount of fuel, and a minor amount of an additive composition comprising:

(a) an aminotriazole compound comprising the reaction product of (i) a hydrocarbyl carbonyl compound, and (ii) an amine compound or salt thereof of formula (I)



wherein R is selected from the group consisting of a hydrogen and a hydrocarbyl group containing from about 1 to about 15 carbon atoms, and R^1 is selected from the group consisting of hydrogen and a hydrocarbyl group containing from about 1 to about 20 carbon atoms;

(b) a hydrocarbyl-substituted succinimide dispersant,
wherein the ratio of (a) to (b) ranges from about 1:10 to about 10:1.