

POLYACRYLAMIDE ANTIFOAM COMPONENTS FOR USE IN DIESEL FUELS

BACKGROUND

5 **[0001]** The disclosed technology relates to compounds that are useful as antifoam components in diesel fuels. In particular, diesel fuel compositions and concentrates comprising said antifoam components and the use of same are disclosed.

[0002] Diesel fuel has a tendency to foam and is particularly problematic at point of sale applications when diesel fuel is pumped into the tank of a vehicle ("fill-ups").
10 As the diesel fuel is pumped into the tank, a large amount of foam is quickly generated thereby greatly reducing the amount of diesel that can be pumped into a tank at each fill-up.

[0003] Reducing the amount of foam produced during fill-ups would greatly increase the volume capacity of diesel tanks, but there are no viable antifoam options
15 for the North American market. Currently, only nitrogen, oxygen, carbon and/or hydrogen ("NOCH") based chemistries are allowed in North American diesel applications. This precludes known silicone antifoams and fluorinated (poly)acrylate antifoams as viable options in North America. Thus, there is a need for non-silicone, fluorine-free antifoam for diesel fuel.

20 SUMMARY OF THE INVENTION

[0004] Compositions comprising acrylamide polymers prepared by polymerizing certain (meth)acrylamide monomers have been shown to be surprisingly effective antifoams in diesel. The acrylamide polymers may be prepared by polymerizing a (meth)acrylamide monomer to yield a homopolymer. Alternatively, the acrylamide
25 polymers may be prepared by polymerizing a (meth)acrylamide monomer and a (meth)acrylate monomer to yield a heteropolymer. Suitable (meth)acrylamide monomers include (meth)acrylamide monomers comprising mono- or di-C₁ to C₂₇ alkyl-substituted (meth)acrylamide. In some embodiments, the (meth)acrylamide monomer may comprise a mono- or di-C₁ to C₂₇ alkyl-substituted (meth)acrylamide. Suitable (meth)acrylamide
30 monomers comprise, N,N-diethylacrylamide ("NNDEAD"), N-(tertbutyl)acrylamide ("NTBAD"), or combinations thereof. In some embodiments, the acrylamide polymer may comprise a heteropolymer prepared from a (meth)acrylate monomer comprising

[0006] In some embodiments compositions are disclosed comprising an acrylamide polymer as described above and at least one acrylate polymer prepared by polymerizing one or more (meth)acrylate monomers comprising a C1 to C30 alkyl-substituted (meth)acrylate. In some embodiments the acrylate polymer may be at least one of a copolymer, block polymer, random polymer, terpolymer, or combinations thereof. In some embodiments, the composition may comprise (i) from 1 wt% to 99 wt% of the acrylamide polymer; and (ii) from 99 wt% to 1 wt% of the acrylate polymer.

[illegible]

wherein R¹ is H or CH₃; R² is a C₁ to C₁₀ linear or branched hydrocarbonyl group; R³ is a C₁ to C₄ linear or branched hydrocarbonyl group; R⁴ is H, OH, or CH₃; n₁ is an integer ranging from 120 to 3000; X is O or N; R₅ is only present if X is N and can be H, a C₁ to C₁₀ linear or branched hydrocarbonyl group, or when taken together with R₂, may form a saturated or unsaturated ring containing 5 to 6 carbon atoms; and n₂ is an integer ranging from 0 to 3.

[0008] Methods of reducing the amount of foam produced while filling the diesel tank of a vehicle are also disclosed. The method may comprise adding at least one acrylamide polymer described above to a diesel fuel.

DETAILED DESCRIPTION OF THE INVENTION

5 [0009] Various preferred features and embodiments will be described below by way of non-limiting illustration.

[0010] The disclosed technology provides a composition including an antifoam component which includes an acrylamide polymer. Without limiting this disclosure to the theory of operation disclosed herein, it is believed that antifoam components
10 break foam bubbles by adsorbing on the surface of the bubbles and lowering their surface tension. It is further believed the effectiveness of antifoam components in a given fluid is a function of two factors relative to the bulk fluid. The first factor is the component's solubility in the bulk fluid. Generally, antifoams that have poor solubility (insoluble or almost insoluble) in a fluid will have improved performance
15 than easily soluble antifoams. The second factor is the component's surface tension. Generally, antifoam components having a lower surface tension are more effective as antifoam components than components having a higher surface tension.

[0011] Because diesel fuel is a fairly good solvent, there are few antifoam components having suitable solubility and surface tension properties for use in diesel
20 fuels. It was found, however, that the acrylamide polymers disclosed herein are surprisingly effective at reducing foam in a diesel fuel.

[0012] As used herein, the term "acrylamide polymers" are polymers derived from monomers comprising acrylamide or methacrylamide groups. The terms "(meth)acrylamide", "(meth)acrylate" and related terms include both acrylamide or
25 methacrylamide, or acrylate and methacrylate groups, i.e. the methyl group is optional. For example, the term (meth)acrylamide monomer includes monomers of both acrylamide or methacrylamide. Accordingly, in some embodiments, a (meth)acrylamide may comprise at least one acrylamide, methacrylamide, or combinations thereof.

30 [0013] When referring to a specified monomer(s) that is incorporated or used to prepare an acrylamide polymer disclosed herein, the ordinarily skilled person will

recognize that the monomer(s) will be incorporated as at least one unit into the acrylamide polymer.

[0014] Compositions comprising acrylamide polymers prepared by polymerizing certain (meth)acrylamide monomers have been shown to be surprisingly effective antifoams in diesel. The acrylamide polymers may be prepared by polymerizing a (meth)acrylamide monomer to yield a homopolymer. Alternatively, the acrylamide polymers may be prepared by polymerizing a (meth)acrylamide monomer and a (meth)acrylate monomer to yield a heteropolymer.

[0015] Suitable (meth)acrylamide monomers include (meth)acrylamide monomers comprising mono- or di-C₁ to C₂₇ alkyl-substituted (meth)acrylamide. As used herein, C_x to C_y, when used to describe the alkyl-substituted (meth)acrylamide, refers to the number of carbon atoms in the alkyl group connected to the nitrogen on the (meth)acrylamide moiety and does not include the number of carbon atoms in the (meth)acrylamide moiety itself. The alkyl group can be linear, branched, cyclic, or cyclic with hetero atoms or with an aromatic substituted group.

[0016] In some embodiments, the (meth)acrylamide monomer may comprise a mono- or di-C₁ to C₂₇ alkyl-substituted (meth)acrylamide. In other embodiments, the (meth)acrylamide monomer may comprise a mono- or di-C₁ to C₁₂ or C₁, C₂, C₃, C₄, C₅, C₆, C₇, C₈, C₉, C₁₀, C₁₁, or C₁₂ alkyl-substituted (meth)acrylamide. Suitable (meth)acrylamide monomers comprise, N,N-diethylacrylamide ("NNDEAD"), N-(tertbutyl)acrylamide ("NTBAD"), or combinations thereof. In some embodiments, the acrylamide polymer may comprise a heteropolymer prepared from a (meth)acrylate monomer comprising tert-butyl acrylate ("TBAT"). The acrylamide polymer may have a weight average molecular weight ("M_w") ranging from 10,000 or 15,000 to 300,000 Daltons ("Da") or 30,000 to 200,000 Da.

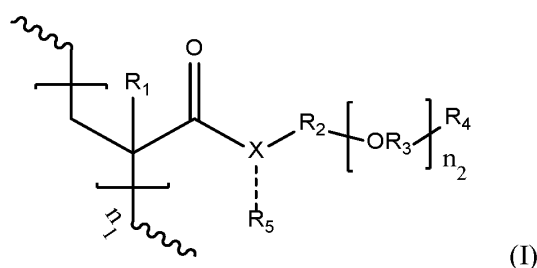
[0017] The acrylamide polymers described above may be added to a diesel fuel to reduce the amount of foam produced in the diesel fuel. The acrylamide polymer may be present in the diesel fuel in an amount from 0.1 ppm to 3000 ppm by weight, or 1 ppm to 100 ppm, based on a total weight of the diesel fuel composition. Accordingly, methods of reducing foam in a diesel fuel are also disclosed. The use of at least one acrylamide polymer as described above to reduce a foam in a diesel fuel is also disclosed.

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[0018] In some embodiments compositions are disclosed comprising an acrylamide polymer as described above and at least one acrylate polymer prepared by polymerizing one or more (meth)acrylate monomers comprising a C₁ to C₃₀ alkyl-substituted (meth)acrylate. In some embodiments, the (meth)acrylate monomer may
 5 comprise C₂ to C₂₇ alkyl esters of (meth)acrylic acid. In other embodiments, the (meth)acrylate monomer may comprise C₂ to C₁₂, or C₂, C₃, C₄, C₅, C₆, C₇, C₈, C₉, C₁₀, C₁₁, or C₁₂ alkyl esters of (meth)acrylic acid. Exemplary (meth)acrylate monomers include, but are not limited to, monomers comprising tertiary butyl (meth)acrylate or trimethylhexyl (meth)acrylate, 3,3-dimethylbutyl(meth)acrylate,
 10 neopentyl(meth)acrylate, or combinations thereof. In yet other embodiments, the acrylate polymer may be a homopolymer.

[0019] In some embodiments the acrylate polymer may be at least one of a copolymer, block polymer, random polymer, terpolymer, or combinations thereof. In some embodiments, the composition may comprise (i) from 1 wt% to 99 wt% of the
 15 acrylamide polymer; and (ii) from 99 wt% to 1 wt% of the acrylate polymer. In yet other embodiments, the composition may comprise (i) from 5 wt% to 95 wt% of the acrylamide polymer; and (ii) from 95 wt% to 5 wt% of the acrylate polymer. In yet another embodiment, the composition may comprise 1 wt% of the acrylamide polymer and 99 wt% of the acrylate polymer.

20 [0020] In some embodiments, the acrylamide polymer disclosed herein may have the structure of formula (I):



wherein R¹ is H or CH₃; R² is a C₁ to C₁₀ linear or branched hydrocarbyl group; R³ is a C₁ to C₄ linear or branched hydrocarbyl group; R⁴ is H, OH, or CH₃; n₁ is an integer ranging from 120 to 3000; X is O or N; R₅ is only present if X is N and can be H, a C₁
 25 to C₁₀ linear or branched hydrocarbyl group, or when taken together with R₂, may form a saturated or unsaturated ring containing 5 to 6 carbon atoms; and n₂ is an integer

ranging from 0 to 3. As used herein, the term "hydrocarbyl substituent" or "hydrocarbyl group" 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 the molecule and having predominantly hydrocarbon character. Examples of hydrocarbyl groups include:

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 a ring);

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

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

[0021] Accordingly, in one embodiment, there are no halo substituents in the hydrocarbyl group. In some embodiments, X is N. In some embodiments, at least two polymer moieties are present and, for at least one polymer moiety X is N, and for at least one polymer moiety X is O. In some embodiments R^2 and/or R^3 may be branched. In yet other embodiments, R^2 may be linear and R^3 may be branched.

[0022] In some embodiments, the acrylamide polymer may comprise at least one heteropolymer prepared by polymerizing a (meth)acrylamide monomer and a (meth)acrylate monomer. In other embodiments, the acrylamide polymer may comprise a heteropolymer prepared from a (meth)acrylate monomer comprising tert-butyl acrylate ("TBAT").

[0023] In any of the homopolymer or heteropolymer embodiments, the (meth)acrylamide monomer may comprise N,N-diethylacrylamide ("NNDEAD"), N-(tertbutyl)acrylamide ("NTBAD"), or combinations thereof.

[0024] The acrylamide polymer may have a weight average molecular weight ("M_w") of from 10,000 or 15,000 to 300,000 Da. In some embodiments, the acrylamide polymer may have a M_w of from 30,000 to 200,000 Da.

[0025] As used herein, the weight average molecular weight (M_w) is measured using gel permeation chromatography ("GPC") (Waters Alliance e2695) based on polystyrene standards. The instrument is equipped with a refractive index detector and Waters EmpowerTM data acquisition and analysis software. The columns are polystyrene/divinylbenzene (PLgel, (3 "Mixed-C" and one 100 Angstrom, 5 micron particle size), available from Agilent Technologies). For the mobile phase, individual samples are dissolved in tetrahydrofuran and filtered with PTFE filters before they are injected into the GPC port.

Waters Alliance e2695 Operating Conditions:

Column Temperature: 40° C

Autosampler Control: Run time: 45 minutes

Injection volume: 300 microliter

Flow rate: 1.0 ml/minute

Differential Refractometer (RI) (2414): Sensitivity: 16; Scale factor: 20

[0026] Persons ordinarily skilled in the art will understand that the number average molecular weight ("M_n") may be measured using a similar technique to the one described above.

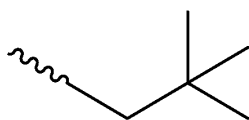
[0027] The acrylamide polymers described herein may be added to a diesel fuel in an amount from 0.1 ppm to 3000 ppm by weight, or 1 ppm to 100 ppm, or 75 to 1500 ppm, or even 500 to 3000 ppm by weight, based on a total weight of the fuel composition.

[0028] Methods of reducing foam in a diesel fuel are also disclosed. The methods may comprise adding the acrylamide polymers described above to a diesel fuel. Methods of reducing the amount of foam produced while filling the diesel tank of a vehicle are also disclosed. The methods may comprise adding the acrylamide polymers described above to a diesel fuel. The acrylamide polymers may be added to

the diesel fuel at the refinery, at storage tanks or fuel pumping stations, or even as the fuel is pumped into a vehicle. The use of an acrylamide polymer as described above to reduce foam in a diesel fuel is also disclosed.

[0029] The acrylamide polymer antifoam components disclosed herein can be prepared by methods generally known in the art. The polymerization may be effected in mass, emulsion or solution in the presence of a free-radical liberating agent as catalyst and in the presence or absence of known polymerization regulators. In one embodiment, the antifoam can be polymerized in the presence of a solvent. The solvent may be aliphatic (such as heptanes) or aromatic (such as xylene or toluene). In another embodiment, the antifoam can be polymerized in a hydrocarbon oil. In yet other embodiments, the antifoam may be polymerized in light aromatic petroleum naphtha, heavy aromatic naphtha, or combinations thereof.

[0030] The surface tension of the acrylamide polymer varies with the number of carbon atoms in the (meth)acrylamide monomer or (meth)acrylate monomer used to make the acrylamide polymer. In some embodiments, the monomer may comprise C₇, C₈, C₉, C₁₀, C₁₁, or C₁₂ alkyl acrylamides and, optionally C₇, C₈, C₉, C₁₀, C₁₁, or C₁₂ alkyl esters of (meth)acrylic acid ("surface tension monomers"). In some embodiments, the surface tension monomer may comprise C₉ acrylamide and/or C₉ alkyl esters of (meth)acrylic acid. It was further found that the surface tension monomers having branched alkyl groups tended to result in poly(acrylate) polymers with lower surface tension properties than monomers having the same number of carbon atoms in a linear configuration. Accordingly, in some embodiments, R² and/or R³ may be branched. In other embodiments, R² may be linear and R³ may be branched. The (meth)acrylamide or (meth)acrylate monomers having the lowest surface tension for a given carbon number tend to include a neopentyl group having the structure of formula (II):



(II).

[0031] Accordingly, in some embodiments (meth)acrylate monomers having a terminal neopentyl group are disclosed. Exemplary monomers include, but are not limited to, monomers comprising 2,2-dimethylheptane, 2,2,4-trimethylhexane, 2,2,4,4-

tetramethylpentane, 2,2,5-trimethylhexane, and combinations thereof as terminal neopentyl groups. In yet another embodiment, the surface tension monomer may comprise C₉ acrylamide and/or C₉ alkyl esters of (meth)acrylic acid having a terminal neopentyl group.

5 Fuel and Fuel Compositions

[0032] The fuel compositions described herein can comprise a fuel which is liquid at room temperature and is useful in fueling an engine. The fuel is normally a liquid at ambient conditions e.g., room temperature (20 to 30°C). The fuel can be a hydrocarbon fuel, a nonhydrocarbon fuel, or a mixture thereof. The hydrocarbon fuel
10 can be a diesel fuel as defined by EN590 or ASTM specification D975. The hydrocarbon fuel can be a hydrocarbon prepared by a gas to liquid process to include, for example, hydrocarbons prepared by a process such as the Fischer-Tropsch process. Accordingly, in some embodiments, the fuel may be a gas to liquid (“GTL”) diesel, biomass to liquid (“BTL”) fuel, or combinations thereof.

15 [0033] The nonhydrocarbon fuel can include transesterified oils and/or fats from plants and animals such as rapeseed methyl ester and soybean methyl ester, commonly called biodiesel. Mixtures of hydrocarbon and nonhydrocarbon fuels can include, for example, diesel fuel and ethanol, and diesel fuel and a transesterified plant oil such as rapeseed methyl ester. In an embodiment of the invention the liquid
20 fuel is an emulsion of water in a hydrocarbon fuel, a nonhydrocarbon fuel, or a mixture thereof.

[0034] In some embodiments, the fuel may comprise a hydro-treated vegetable oil (“HVO”), commonly called a renewable diesel. In other embodiments, the fuel may comprise mixtures of diesel and HVO. In yet other embodiments the fuel can
25 comprise blends of biodiesel and diesel, blends of HVO and diesel, or blends of HVO and biodiesel.

[0035] In several embodiments, the fuel can have a sulfur content on a weight basis that is 5000 ppm or less, 1000 ppm or less, 300 ppm or less, 200 ppm or less, 30 ppm or less, or 10 ppm or less. In another embodiment the fuel can have a sulfur
30 content on a weight basis of 1 to 100 ppm.

[0036] The fuel is present in a fuel composition in a major amount that is generally greater than 50 percent by weight, and in other embodiments is present at greater than

90 percent by weight, greater than 95 percent by weight, greater than 99.5 percent by weight, or greater than 99.8 percent by weight.

[0037] In some embodiments, the fuel composition may comprise at least one combustion improver. Combustion improvers include for example octane and cetane
5 improvers. Suitable cetane number improvers are, for example, aliphatic nitrates such as 2-ethylhexyl nitrate and cyclohexyl nitrate and peroxides such as di-tert-butyl peroxide.

[0038] In yet another embodiment, the fuel composition comprises antifoam components of the disclosed technology as described above and at least one
10 demulsifier. Suitable demulsifiers can include, but are not limited to arylsulfonates and polyalkoxylated alcohol, such as, for example, polyethylene and polypropylene oxide copolymers and the like. The demulsifiers can also comprise nitrogen containing compounds such as oxazoline and imidazoline compounds and fatty amines, as well as Mannich compounds. Mannich compounds are the reaction
15 products of alkylphenols and aldehydes (especially formaldehyde) and amines (especially amine condensates and polyalkylenepolyamines). The materials described in the following U.S. Patents are illustrative: U.S. Pat. Nos. 3,036,003; 3,236,770; 3,414,347; 3,448,047; 3,461,172; 3,539,633; 3,586,629; 3,591,598; 3,634,515; 3,725,480; 3,726,882; and 3,980,569 herein incorporated by reference. Other suitable
20 demulsifiers are, for example, the alkali metal or alkaline earth metal salts of alkyl-substituted phenol- and naphthalenesulfonates and the alkali metal or alkaline earth metal salts of fatty acids, and also neutral compounds such as alcohol alkoxylates, e.g. alcohol ethoxylates, phenol alkoxylates, e.g. tert-butylphenol ethoxylate or tert-pentylphenol ethoxylate, fatty acids, alkylphenols, condensation products of ethylene
25 oxide (EO) and propylene oxide (PO), for example including in the form of EO/PO block copolymers, polyethyleneimines or else polysiloxanes. Any of the commercially available demulsifiers may be employed, suitably in an amount sufficient to provide a treat level of from 5 to 50 ppm in the fuel. In one embodiment the fuel composition of the invention does not comprise a demulsifier. The
30 demulsifiers may be used alone or in combination. Some demulsifiers are commercially available, for example from Nalco or Baker Hughes. Typical treat rates

of the demulsifiers to a fuel may range from 0 to 50 ppm by total weight of the fuel, or 5 to 50 ppm, or 5 to 25 ppm, or 5 to 20 ppm.

[0039] The disclosed technology may also be used with demulsifiers comprising a hydrocarbyl-substituted dicarboxylic acid in the form of the free acid, or in the form of the anhydride which may be an intramolecular anhydride, such as succinic, glutaric, or phthalic anhydride, or an intermolecular anhydride linking two dicarboxylic acid molecules together. The hydrocarbyl substituent may have from 12 to 2000 carbon atoms and may include polyisobutenyl substituents having a number average molecular weight of 300 to 2800. Exemplary hydrocarbyl-substituted dicarboxylic acids include, but are not limited to, hydrocarbyl-substituted acids derived from malonic, succinic, glutaric, adipic, pimelic, suberic, azelaic, sebacic, undecanedioic, dodecanedioic, phthalic, isophthalic, terphthalic, ortho, meta, or paraphenylene diacetic, maleic, fumaric, or glutaconic acids.

[0040] In another embodiment, the fuel compositions further comprise at least one detergent/dispersant. Customary detergent/dispersant additives are amphiphilic substances which possess at least one hydrophobic hydrocarbon radical with a number average molecular weight of 100 to 10000 and at least one polar moiety selected from (i) Mono- or polyamino groups having up to 6 nitrogen atoms, at least one nitrogen atom having basic properties; (ii) Hydroxyl groups in combination with mono or polyamino groups, at least one nitrogen atoms having basic properties; (iii) Carboxyl groups or their alkali metal or alkaline earth metal salts; (iv) Sulfonic acid groups or their alkali metal or alkaline earth metal salts; (v) Polyoxy-C₂ to C₄ alkylene moieties terminated by hydroxyl groups, mono- or polyamino groups, at least one nitrogen atom having basic properties, or by carbamate groups; (vi) Carboxylic ester groups; (vii) Moieties derived from succinic anhydride and having hydroxyl and/or amino and/or amido and/or imido groups; and/or (viii) Moieties obtained by Mannich reaction of substituted phenols with aldehydes and mono-or polyamines.

[0041] The hydrophobic hydrocarbon radical in the above detergent/dispersant additives which ensures the adequate solubility in the fuel, has a number average molecular weight (M_n) of 85 to 20,000, or 100 to 10,000, or 300 to 5000. In yet another embodiment, the detergent/dispersant additives have a M_n of 300 to 3000, of

500 to 2500, of 700 to 2500, or 800 to 1500. Typical hydrophobic hydrocarbon radicals, may be polypropenyl, polybutenyl and polyisobutenyl radicals, with a number average molecular weight M_n , of 300 to 5000, of 300 to 3000, of 500 to 2500, or 700 to 2500. In one embodiment the detergent/dispersant additives have a M_n of
5 800 to 1500.

[0042] The additional performance additives may comprise a high TBN nitrogen containing detergent/dispersant, such as a succinimide, that is the condensation product of a hydrocarbyl-substituted succinic anhydride with a poly(alkyleneamine). Succinimide detergents/dispersants are more fully described in U.S. patents
10 4,234,435 and 3,172,892. Another class of ashless dispersant is high molecular weight esters, prepared by reaction of a hydrocarbyl acylating agent and a polyhydric aliphatic alcohol such as glycerol, pentaerythritol, or sorbitol. Such materials are described in more detail in U.S. Patent 3,381,022.

[0043] Nitrogen-containing detergents may be the reaction products of a
15 carboxylic acid-derived acylating agent and an amine. The acylating agent can vary from formic acid and its acylating derivatives to acylating agents having high molecular weight aliphatic substituents of up to 5,000, 10,000 or 20,000 carbon atoms. The amino compounds can vary from ammonia itself to amines typically having aliphatic substituents of up to 30 carbon atoms, and up to 11 nitrogen atoms.
20 Acylated amino compounds suitable for use in the present invention may be those formed by the reaction of an acylating agent having a hydrocarbyl substituent of at least 8 carbon atoms and a compound comprising at least one primary or secondary amine group. The acylating agent may be a mono- or polycarboxylic acid (or reactive equivalent thereof) for example a substituted succinic, phthalic or propionic acid and
25 the amino compound may be a polyamine or a mixture of polyamines, for example a mixture of ethylene polyamines. Alternatively, the amine may be a hydroxyalkyl-substituted polyamine. The hydrocarbyl substituent in such acylating agents may comprise at least 10 carbon atoms. In one embodiment, the hydrocarbyl substituent may comprise at least 12, for example 30 or 50 carbon atoms. In yet another
30 embodiment, it may comprise up to 200 carbon atoms. The hydrocarbyl substituent of the acylating agent may have a number average molecular weight (M_n) of 170 to 2800, for example from 250 to 1500. In other embodiments, the substituent's M_n may

range from 500 to 1500, or alternatively from 500 to 1100. In yet another embodiment, the substituent's M_n may range from 700 to 1300. In another embodiment, the hydrocarbyl substituent may have a number average molecular weight of 700 to 1000, or 700 to 850, or, for example, 750.

5 **[0044]** Another class of ashless dispersant is Mannich bases. These are materials which are formed by the condensation of a higher molecular weight, alkyl substituted phenol, an alkylene polyamine, and an aldehyde such as formaldehyde and are described in more detail in U.S. Patent 3,634,515.

10 **[0045]** A useful nitrogen containing dispersant includes the product of a Mannich reaction between (a) an aldehyde, (b) a polyamine, and (c) an optionally substituted phenol. The phenol may be substituted such that the Mannich product has a molecular weight of less than 7500. Optionally, the molecular weight may be less than 2000, less than 1500, less than 1300, or for example, less than 1200, less than 1100, less than 1000. In some embodiments, the Mannich product has a molecular weight of
15 less than 900, less than 850, or less than 800, less than 500, or less than 400. The substituted phenol may be substituted with up to 4 groups on the aromatic ring. For example, it may be a tri or di-substituted phenol. In some embodiments, the phenol may be a mono-substituted phenol. The substitution may be at the ortho, and/or meta, and/or para position(s). To form the Mannich product, the molar ratio of the aldehyde to
20 amine is from 4:1 to 1:1 or, from 2:1 to 1:1. The molar ratio of the aldehyde to phenol may be at least 0.75:1; preferably from 0.75 to 1 to 4:1, preferably 1:1 to 4:1 more preferably from 1:1 to 2:1. To form the preferred Mannich product, the molar ratio of the phenol to amine is preferably at least 1.5:1, more preferably at least 1.6:1, more preferably at least 1.7:1, for example at least 1.8:1, preferably at least 1.9:1. The
25 molar ratio of phenol to amine may be up to 5:1; for example it may be up to 4:1, or up to 3.5:1. Suitably it is up to 3.25:1, up to 3:1, up to 2.5:1, up to 2.3:1 or up to 2.1:1.

30 **[0046]** Other dispersants include polymeric dispersant additives, which are generally hydrocarbon-based polymers which contain polar functionality to impart dispersancy characteristics to the polymer. An amine is typically employed in preparing the high TBN nitrogen-containing dispersant. One or more poly(alkyleneamine)s may be used, and these may comprise one or more poly(ethyleneamine)s having 3 to 5 ethylene units and 4 to 6 nitrogen units. Such

materials include triethylenetetramine (TETA), tetraethylenepentamine (TEPA), and pentaethylenehexamine (PEHA). Such materials are typically commercially available as mixtures of various isomers containing a range number of ethylene units and nitrogen atoms, as well as a variety of isomeric structures, including various cyclic structures. The poly(alkyleneamine) may likewise comprise relatively higher molecular weight amines known in the industry as ethylene amine still bottoms.

[0047] In an embodiment, the fuel composition can additionally comprise quaternary ammonium salts. The quaternary ammonium salts can comprise (a) a compound comprising (i) at least one tertiary amino group as described above, and (ii) a hydrocarbyl-substituent having a number average molecular weight of 100 to 5000, or 250 to 4000, or 100 to 4000 or 100 to 2500 or 3000; and (b) a quaternizing agent suitable for converting the tertiary amino group of (a)(i) to a quaternary nitrogen, as described above. The other quaternary ammonium salts are more thoroughly described in U.S. Patent Nos. 7,951,211, issued May 31, 2011, and 8,083,814, issued December 27, 2011, and U.S. Publication Nos. 2013/0118062, published May 16, 2013, 2012/0010112, published January 12, 2012, 2013/0133243, published May 30, 2013, 2008/0113890, published May 15, 2008, and 2011/0219674, published September 15, 2011, US 2012/0149617 published May 14, 2012, US 2013/0225463 published August 29, 2013, US 2011/0258917 published October 27, 2011, US 2011/0315107 published December 29, 2011, US 2013/0074794 published March 28, 2013, US 2012/0255512 published October 11, 2012, US 2013/0333649 published December 19, 2013, US 2013/0118062 published May 16, 2013, and international publications WO Publication Nos. 2011/141731, published November 17, 2011, 2011/095819, published August 11, 2011, and 2013/017886, published February 7, 2013, WO 2013/070503 published May 16, 2013, WO 2011/110860 published September 15, 2011, WO 2013/017889 published February 7, 2013, WO 2013/017884 published February 7, 2013.

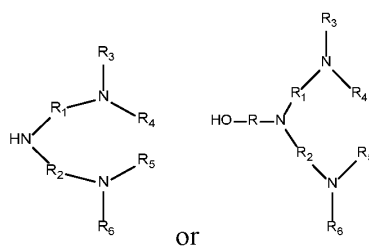
[0048] The quaternary ammoniums salts can be prepared from hydrocarbyl substituted acylating agents, such as, for example, polyisobutyl succinic acids or anhydrides, having a hydrocarbyl substituent with a number average molecular weight of greater than 1200 M_n , polyisobutyl succinic acids or anhydrides, having a hydrocarbyl substituent with a number average molecular weight of 300 to 750, or

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polyisobutyl succinic acids or anhydrides, having a hydrocarbyl substituent with a number average molecular weight of 1000 M_n .

[0049] In an embodiment, the additional salts may be an imide prepared from the reaction of a nitrogen containing compound and a hydrocarbyl substituted acylating agent having a hydrocarbyl substituent with a number average molecular weight of 1300 to 3000. In an embodiment, the quaternary ammonium salts prepared from the reaction of nitrogen containing compound and a hydrocarbyl substituted acylating agent having a hydrocarbyl substituent with a number average molecular weight of greater than 1200 M_n or, having a hydrocarbyl substituent with a number average molecular weight of 300 to 750 is an amide or ester.

[0050] In an embodiment, the nitrogen containing compound of the additional quaternary ammonium salts is an imidazole or nitrogen containing compound of either of formulas:



wherein R may be a C_1 to C_6 alkylene group; each of R_1 and R_2 , individually, may be a C_1 to C_6 hydrocarbylene group; and each of R_3 , R_4 , R_5 , and R_6 , individually, may be a hydrogen or a C_1 to C_6 hydrocarbyl group.

[0051] In other embodiments, the quaternizing agent used to prepare the additional quaternary ammonium salts can be a dialkyl sulfate, an alkyl halide, a hydrocarbyl substituted carbonate, a hydrocarbyl epoxide, a carboxylate, alkyl esters, or mixtures thereof. In some cases, the quaternizing agent can be a hydrocarbyl epoxide. In some cases, the quaternizing agent can be a hydrocarbyl epoxide in combination with an acid. In some cases, the quaternizing agent can be a salicylate, oxalate or terephthalate. In an embodiment, the hydrocarbyl epoxide is an alcohol functionalized epoxides or C_4 to C_{14} epoxides.

[0052] In some embodiments, the quaternizing agent is multi-functional resulting in the additional quaternary ammonium salts being a coupled quaternary ammoniums salts.

5 [0053] Typical treat rates of additional detergents/dispersants to a fuel of the invention is 0 to 500 ppm, or 0 to 250 ppm, or 0 to 100 ppm, or 5 to 250 ppm, or 5 to 100 ppm, or 10 to 100 ppm.

[0054] In a yet another embodiment, a fuel composition comprises further comprises a cold flow improver. The cold flow improver is typically selected from (1) copolymers of a C₂- to C₄₀-olefin with at least one further ethylenically
10 unsaturated monomer; (2) comb polymers; (3) polyoxyalkylenes; (4) polar nitrogen compounds; and (5) poly(meth)acrylic esters made from linear alcohols having 10 to 22 carbon atoms. It is possible to use either mixtures of different representatives from one of the particular classes (1) to (5) or mixtures of representatives from different classes (1) to (5).

15 [0055] Suitable C₂- to C₄₀-olefin monomers for the copolymers of class (1) are, for example, those having 2 to 20 and especially 2 to 10 carbon atoms, and 1 to 3 and preferably 1 or 2 carbon-carbon double bonds, especially having one carbon-carbon double bond. In the latter case, the carbon-carbon double bond may be arranged either terminally (α -olefins) or internally. However, preference is given to α -olefins, more
20 preferably α -olefins having 2 to 6 carbon atoms, for example propene, 1-butene, 1-pentene, 1-hexene and in particular ethylene. The at least one further ethylenically unsaturated monomer of class (1) is preferably selected from alkenyl carboxylates; for example, C₂- to C₁₄-alkenyl esters, for example the vinyl and propenyl esters, of carboxylic acids having 2 to 21 carbon atoms, whose hydrocarbon radical may be
25 linear or branched among these, preference is given to the vinyl esters, examples of suitable alkenyl carboxylates are vinyl acetate, vinyl propionate, vinyl butyrate, vinyl 2-ethylhexanoate, vinyl neopentanoate, vinyl hexanoate, vinyl neononanoate, vinyl neodecanoate and the corresponding propenyl esters, (meth)acrylic esters; for example, esters of (meth)acrylic acid with C₁- to C₂₀-alkanols, especially C₁- to C₁₀-
30 alkanols, in particular with methanol, ethanol, propanol, isopropanol, n-butanol, sec-butanol, isobutanol, tert-butanol, pentanol, hexanol, heptanol, octanol, 2-ethylhexanol, nonanol and decanol, and structural isomers thereof and further olefins;

preferably higher in molecular weight than the abovementioned C₂- to C₄₀-olefin base monomer for example, the olefin base monomer used is ethylene or propene, suitable further olefins are in particular C₁₀- to C₄₀- α -olefins.

5 [0056] Suitable copolymers of class (1) are also those which comprise two or more different alkenyl carboxylates in copolymerized form, which differ in the alkenyl function and/or in the carboxylic acid group. Likewise, suitable are copolymers which, as well as the alkenyl carboxylate(s), comprise at least one olefin and/or at least one (meth)acrylic ester in copolymerized form.

10 [0057] Terpolymers of a C₂- to C₄₀- α -olefin, a C₁- to C₂₀-alkyl ester of an ethylenically unsaturated monocarboxylic acid having 3 to 15 carbon atoms and a C₂- to C₁₄-alkenyl ester of a saturated monocarboxylic acid having 2 to 21 carbon atoms are also suitable as copolymers of class (K1). Terpolymers of this kind are described in WO 2005/054314. A typical terpolymer of this kind is formed from ethylene, 2-ethylhexyl acrylate and vinyl acetate.

15 [0058] The at least one or the further ethylenically unsaturated monomer(s) are copolymerized in the copolymers of class (1) in an amount of preferably 1 to 50% by weight, especially 10 to 45% by weight and in particular 20 to 40% by weight, based on the overall copolymer. The main proportion in terms of weight of the monomer units in the copolymers of class (1) therefore originates generally from the C₂ to C₄₀ base olefins. The copolymers of class (1) may have a number average molecular weight M_n of 1000 to 20,000, or 1000 to 10,000 or 1000 to 8000.

20 [0059] Typical comb polymers of component (2) are, for example, obtainable by the copolymerization of maleic anhydride or fumaric acid with another ethylenically unsaturated monomer, for example with an α -olefin or an unsaturated ester, such as vinyl acetate, and subsequent esterification of the anhydride or acid function with an alcohol having at least 10 carbon atoms. Further suitable comb polymers are copolymers of α -olefins and esterified comonomers, for example esterified copolymers of styrene and maleic anhydride or esterified copolymers of styrene and fumaric acid. Suitable comb polymers may also be polyfumarates or polymaleates.

25

30 Homo- and copolymers of vinyl ethers are also suitable comb polymers. Comb polymers suitable as components of class (2) are, for example, also those described in WO 2004/035715 and in "Comb-Like Polymers. Structure and Properties", N. A.

Platé and V. P. Shibaev, J. Poly. Sci. Macromolecular Revs. 8, pages 117 to 253 (1974). Mixtures of comb polymers are also suitable.

[0060] Polyoxyalkylenes suitable as components of class (3) are, for example, polyoxyalkylene esters, polyoxyalkylene ethers, mixed polyoxyalkylene ester/ethers and mixtures thereof. These polyoxyalkylene compounds preferably comprise at least one linear alkyl group, preferably at least two linear alkyl groups, each having 10 to 30 carbon atoms and a polyoxyalkylene group having a number average molecular weight of up to 5000. Such polyoxyalkylene compounds are described, for example, in EP-A 061 895 and also in U.S. Pat. No. 4,491,455. Particular polyoxyalkylene compounds are based on polyethylene glycols and polypropylene glycols having a number average molecular weight of 100 to 5000. Additionally, suitable are polyoxyalkylene mono- and diesters of fatty acids having 10 to 30 carbon atoms, such as stearic acid or behenic acid.

[0061] Polar nitrogen compounds suitable as components of class (4) may be either ionic or nonionic and may have at least one substituent, or at least two substituents, in the form of a tertiary nitrogen atom of the general formula $>NR^7$ in which R^7 is a C_8 - to C_{40} -hydrocarbon radical. The nitrogen substituents may also be quaternized i.e. be in cationic form. An example of such nitrogen compounds is that of ammonium salts and/or amides which are obtainable by the reaction of at least one amine substituted by at least one hydrocarbon radical with a carboxylic acid having 1 to 4 carboxyl groups or with a suitable derivative thereof. The amines may comprise at least one linear C_8 - to C_{40} -alkyl radical. Primary amines suitable for preparing the polar nitrogen compounds mentioned are, for example, octylamine, nonylamine, decylamine, undecylamine, dodecylamine, tetradecylamine and the higher linear homologs. Secondary amines suitable for this purpose are, for example, dioctadecylamine and methylbehenylamine. Also suitable for this purpose are amine mixtures, in particular amine mixtures obtainable on the industrial scale, such as fatty amines or hydrogenated tallow amines, as described, for example, in Ullmann's Encyclopedia of Industrial Chemistry, 6th Edition, "Amines, aliphatic" chapter. Acids suitable for the reaction are, for example, cyclohexane-1,2-dicarboxylic acid, cyclohexene-1,2-dicarboxylic acid, cyclopentane-1,2-dicarboxylic acid, naphthalene

dicarboxylic acid, phthalic acid, isophthalic acid, terephthalic acid, and succinic acids substituted by long-chain hydrocarbon radicals.

[0062] Poly(meth)acrylic esters suitable as cold flow improvers of class (5) are either homo- or copolymers of acrylic and methacrylic esters. Preference is given to copolymers of at least two different (meth)acrylic esters which differ with regard to the esterified alcohol. The copolymer optionally comprises another different olefinically unsaturated monomer in copolymerized form. The weight-average molecular weight of the polymer is preferably 50,000 to 500,000. The polymer may be a copolymer of methacrylic acid and methacrylic esters of saturated C₁₄ and C₁₅ alcohols, the acid groups having been neutralized with hydrogenated tallow amine. Suitable poly(meth)acrylic esters are described, for example, in WO 00/44857.

[0063] The cold flow improver or the mixture of different cold flow improvers is added to the middle distillate fuel or diesel fuel in a total amount of preferably 0 to 5000 ppm by weight, or 10 to 5000 ppm by weight, or 20 to 2000 ppm by weight, or 50 to 1000 ppm by weight, or 100 to 700 ppm by weight, for example of 200 to 500 ppm by weight.

[0064] Additional antifoams and/or foam inhibitors may be used in addition to the acrylamide polymer antifoam components disclosed herein. These additional foam inhibitors include polysiloxanes, copolymers of ethyl acrylate and 2-ethylhexylacrylate and optionally vinyl acetate; demulsifiers including fluorinated polysiloxanes, trialkyl phosphates, polyethylene glycols, polyethylene oxides, polypropylene oxides and (ethylene oxide-propylene oxide) polymers. The disclosed technology may also be used with a silicone-containing antifoam agent in combination with a C₅ – C₁₇ alcohol. In yet other embodiments, the additional antifoams may include organic silicones such as polydimethyl siloxane, polyethylsiloxane, polydiethylsiloxane, polyacrylates and polymethacrylates, trimethyl-trifluoro-propylmethyl siloxane and the like.

[0065] The compositions disclosed herein may also comprise lubricity improvers or friction modifiers typically based on fatty acids or fatty acid esters. Typical examples are tall oil fatty acid, as described, for example, in WO 98/004656, and glyceryl monooleate. The reaction products, described in U.S. Pat. No. 6,743,266 B2, of natural or synthetic oils, for example triglycerides, and alkanolamines are also

suitable as such lubricity improvers. Additional examples include commercial tall oil fatty acids containing polycyclic hydrocarbons and/or rosin acids.

[0066] The compositions disclosed herein may also comprise additives to reduce the amount of metal solubilized in the fuel (reduces “metal pick-up”). These additives may be a hydrocarbon substituted with at least two carboxy functionalities in the form of acids or at least one carboxy functionality in the form an anhydride. Suitable metal pick-up additives include di-acid polymers derived from fatty acids and/or polyolefins, including polyalkenes. Exemplary polyolefins include C₁₀ to C₂₀ polyolefins, C₁₂ to C₁₈ polyolefins, and/or C₁₆ to C₁₈ polyolefins. The polyalkene may be characterized by a M_n (number average molecular weight) of at least about 300. In some embodiments, the metal-pick-up additive comprises more hydrocarbyl substituted succinic anhydride groups. In some embodiments the hydrocarbyl substituted acylating agent comprises one or more hydrolyzed hydrocarbyl substituted succinic anhydride groups (i.e., hydrocarbyl substituted succinic acid). In some embodiments the hydrocarbyl substituents are derived from homopolymers and/or copolymers containing 2 to 10 carbon atoms. In some embodiments the hydrocarbyl substituents above are derived from polyisobutylene. In one embodiment, the metal pick-up additive comprises hydrolyzed polyisobutylene succinic anhydride (PIBSA) or polyisobutylene succinic acid.

[0067] The fuel compositions disclosed herein may also comprise one or more antistatic agents, also commonly referred to as static dissipators or conductivity improvers. Suitable antistatic agents include, but are not limited to, alkyl benzene sulfonic acid.

Additive Packages

[0068] The acrylamide polymer antifoam components disclosed herein may be provided with one or more additives described above in an additive package composition. The additive package composition may comprise one or more additives in a concentrated solution suitable for adding to a diesel fuel. Exemplary additive package compositions are included in Table 1. The amounts shown are in weight percents, based on a total weight of the additive package.

Table 1

	Additive Package A	Additive Package B	Additive Package C	Additive Package D	Additive Package E	Additive Package F
Quaternary ammonium salts	5 to 20	10 to 30	10 to 30	10 to 30	10 to 30	30 to 45
Hydrolyzed PIBSA	10 to 20	5 to 15	5 to 15	5 to 15	5 to 15	10 to 20
Commercial demulsifier	1 to 2	2 to 6	2 to 6	2 to 6	2 to 4	1 to 2
Acrylamide polymer antifoam component	0.1 to 1.5	0.5 to 2	1 to 3	2 to 3	0.5 to 1	0.01 to 0.5
Aromatic 150 solvent	50 to 70	60 to 80	60 to 80	60 to 80	55 to 70	30 to 40
Ethyl hexyl alcohol	5 to 20	0	0	0	5 to 10	10 to 20

Industrial Application

5 **[0069]** In one embodiment, the invention is useful in a liquid fuel in an internal combustion engine. The internal combustion engine may be a diesel engine. Exemplary internal combustion engines include, but are not limited to, compression ignition engines; 4-stroke cycles; liquid fuel supplied via direct injection, indirect injection, common rail and unit injector systems; light (e.g. passenger car) and heavy

10 duty (e.g. commercial truck) engines; and engines fueled with hydrocarbon and non-hydrocarbon fuels and mixtures thereof. The engines may be part of integrated emissions systems incorporating such elements as; EGR systems; aftertreatment including three-way catalyst, oxidation catalyst, NO_x absorbers and catalysts, catalyzed and non-catalyzed particulate traps optionally employing fuel-borne

15 catalyst; variable valve timing; and injection timing and rate shaping.

[0070] In one embodiment, the technology may be used with diesel engines having direct fuel injection systems wherein the fuel is injected directly into the engine's combustion chamber. The ignition pressures may be greater than 1000 bar and, in one embodiment, the ignition pressure may be greater than 1350 bar.

20 Accordingly, in another embodiment, the direct fuel injection system maybe a high-pressure direct fuel injection system having ignition pressures greater than 1350 bar. Exemplary types of high-pressure direct fuel injection systems include, but are not limited to, unit direct injection (or "pump and nozzle") systems, and common rail systems. In unit direct injection systems, the high-pressure fuel pump, fuel metering

system and fuel injector are combined into one apparatus. Common rail systems have a series of injectors connected to the same pressure accumulator, or rail. The rail in turn, is connected to a high-pressure fuel pump. In yet another embodiment, the unit direct injection or common rail systems may further comprise an optional turbocharged or supercharged direct injection system.

[0071] Methods reducing the amount of foam produced while filling the diesel tank of a vehicle are also disclosed. The method may comprise adding an acrylamide polymer made from a (meth)acrylamide monomer to a diesel fuel. The acrylamide polymer may be as described above.

[0072] It is known that some of the materials described above may interact in the final formulation, so that the components of the final formulation may be different from those that are initially added. For instance, metal ions (of, e.g., a detergent) can migrate to other acidic or anionic sites of other molecules. The products formed thereby, including the products formed upon employing the composition of the present invention in its intended use, may not be susceptible of easy description. Nevertheless, all such modifications and reaction products are included within the scope of the present invention; the present invention encompasses the composition prepared by admixing the components described above.

[0073] The following examples provide illustrations of the disclosed technology. These examples are non-exhaustive and are not intended to limit the scope of the disclosed technology.

EXAMPLES

Preparation of Inventive Composition 1 (TMHAT:NTBAD heteropolymer, 85:15 by Wt) – In toluene process:

[0074] Inventive Composition 1 is prepared by charging 3,5,5-trimethylhexyl acrylate (TMHAT) (85.0 g), N-(tert-butyl)acrylamide (NTBAD) (15.0 g) and toluene (100.0 g) into a 500 ml round bottom flask equipped with a mechanical stirrer, Claisen adapter with water-cooled condenser and nitrogen inlet (set at 0.2 standard cubic feet per hours (scfh), a thermocouple and stopper (“reaction vessel”). This mixture is heated to 70°C and is held at that temperature until the complete solubilization of NTBAD. Tert-butyl peroxy-2-ethylhexanoate (TBPE) (0.11 g) is added. Then the mixture is heated to 90 °C and maintained at 90 °C for 180 min.

Then the temperature is adjusted to 100 °C, and TBPE (0.03 g) is added to the reaction vessel and held for 60 min. Similarly, three more TBPE aliquots (0.03 g ea.) are charged and allowed to react 60 min at each addition. Once sufficient monomer consumption is observed, the reaction contents are cooled, and 50 g of the toluene diluted mixture is transferred to a 25 ml single neck round-bottom flask. Toluene is removed under reduced pressure to yield a colorless polymer having a M_w of 152311 Daltons.

Preparation of Inventive Composition 2 (NNDEAD homopolymer) – In toluene process:

10 [0075] Inventive composition 2 is prepared by reacting N,N-diethylacrylamide (NNDEAD) in the presence of tert-butyl peroxy-2-ethylhexanoate (TBPE). NNDEAD (75.0 g), TBPE (0.08 g) and toluene (75.0 g) are thoroughly mixed in a glass bottle. A 250 ml round bottom flask equipped with a mechanical stirrer, Claisen adapter with water-cooled condenser and nitrogen inlet (set at 0.2 standard cubic feet per hours (scfh), thermocouple and stopper is charged with 50.0 g of the above reaction mixture. This mixture is heated to 110°C. The remaining 100.0 g of the reaction mixture is added over 30 minutes via peristaltic pump and maintained at 110°C for the duration of the addition. After the addition, the reaction temperature is maintained at 110 °C for another 60 min. Next, with the reaction temperature at 100 °C, TBPE (0.02 g) is added to the reaction vessel and allowed to react for 60 min. Similarly, three more TBPE (0.02 g) aliquots are charged and allowed to react for 60 min after each addition. Once sufficient monomer consumption is observed, the reaction contents are cooled to obtain a colorless liquid polymer solution in toluene and 50 g of this solution is transferred to a 25ml single neck round-bottom flask. Toluene is removed under reduced pressure to yield a polymer having a M_w of 74063 Daltons.

Preparation of Inventive Composition 3 (NTBAD homopolymer) – In toluene process:

30 [0076] Inventive Composition 3 is prepared by charging N-(tert-butyl)acrylamide (NTBAD) (15.0 g), tert-butyl peroxy-2-ethylhexanoate (TBPE) (0.016 g) and toluene (100.0 g) into a 250 ml round bottom flask equipped with a mechanical stirrer, Claisen adapter with water-cooled condenser and nitrogen inlet (set at 0.2 standard

cubic feet per hours (scfh)), a thermocouple and stopper ("reaction vessel"). This mixture is heated to 70 °C and is held at that temperature until the complete solubilization of NTBAD. Then the mixture is heated to 110 °C and maintained at 110 °C for 60 min. TBPE (0.02g) is added to the reaction vessel and held for 60 min.

5 Similarly, three more TBPE (0.02g) aliquots are charged and allowed to react 60 min at each addition. Once sufficient monomer consumption is observed, the reaction contents are cooled, and 50 g of the toluene diluted mixture is transferred to a 25 ml single neck round-bottom flask. Toluene is removed under reduced pressure to yield a colorless polymer having a M_w of 61020 Da.

10 **Preparation of Inventive Composition 4 (TBAT:NTBAD, 99:1 by Wt) – In toluene process:**

[0077] Inventive composition 4 is prepared by reacting tert-Butyl acrylate (TBAT), N-(tert-butyl)acylamide (NTBAD), and tert-butyl peroxy-2-ethylhexanoate (TBPE) in toluene. TBAT, (198.0g), NTBAD (2.0g), tert-butyl peroxy-2-

15 ethylhexanoate (TBPE) (0.22g) and toluene (200.0 g) are thoroughly mixed in a glass bottle. A 1L round bottom flask equipped with a mechanical stirrer, Claisen adapter with water-cooled condenser and nitrogen inlet (set at 0.2 standard cubic feet per hours (scfh)), thermocouple and stopper is charged with 133.33 g of the above reaction mixture. This mixture is heated to 110°C. The remaining 266.67 g of the

20 reaction mixture is added over 90 minutes via peristaltic pump and maintained at 110°C for the duration of the addition. After the addition, the reaction temperature is maintained at 110 °C for additional 60 min. Next, with the reaction temperature at 110 °C, TBPE (0.06g) is added to the reaction vessel and allowed to react for 60 min. Similarly, three more TBPE (0.06g) aliquots are charged and allowed to react for 60

25 min after each addition. Once sufficient monomer consumption is observed, the reaction contents are cooled to obtain a colorless liquid polymer solution in toluene, 50 g of this solution is transferred to a 25ml single neck round-bottom flask. Toluene is removed under reduced pressure to yield a colorless polymer having a M_w of 103457 Daltons.

Preparation of Inventive Composition 5 (TBAT:NNDEAD, 99:01 by Wt) –**In toluene process:**

[0078] Inventive composition 5 is prepared by reacting *Tert*-Butyl acrylate (TBAT), N,N-diethylacrylamide (NNDEAD), and tert-butyl peroxy-2-ethylhexanoate (TBPE) in toluene. TBAT, (198.0g), NNDEAD (2.0g), tert-butyl peroxy-2-ethylhexanoate (TBPE) (0.22g) and toluene (200.0 g) are thoroughly mixed in a glass bottle. A 1L round bottom flask equipped with a mechanical stirrer, Claisen adapter with water-cooled condenser and nitrogen inlet (set at 0.2 standard cubic feet per hours (scfh)), thermocouple and stopper is charged with 133.33 g of the above reaction mixture. This mixture is heated to 110°C. The remaining 266.67 g of the reaction mixture is added over 90 minutes via peristaltic pump and maintained at 110°C for the duration of the addition. After the addition, the reaction temperature is maintained at 110 °C for additional 60 min. Next, with the reaction temperature at 110 °C, TBPE (0.06 g) is added to the reaction vessel and allowed to react for 60 min. Similarly, three more TBPE (0.06 g) aliquots are charged and allowed to react for 60 min after each addition. Once sufficient monomer consumption is observed, the reaction contents are cooled to obtain a colorless liquid polymer solution in toluene, 50 g of this solution is transferred to a 25ml single neck round-bottom flask. Toluene is removed under reduced pressure to yield a colorless polymer having a M_w of 72862 Daltons.

[0079] The effectiveness of the acrylamide polymers disclosed herein at reducing foam in diesel fuels is tested by observing the amount of foam generated and the time it takes for the foam to collapse. Diesel fuel samples additized with 1600 ppm of the acrylamide polymer were prepared.

[0080] For the test, 100 ml of the additized diesel is transferred to a graduated cylinder using a pressurized injector nozzle placed 245 mm above the graduated cylinder. As the additized diesel is transferred to the cylinder, the volume of foam generated is monitored and immediately after the transfer is complete, the maximum volume of the foam is recorded in milliliters (“Max Foam”). The foam volume immediately after the transfer is complete is also recorded in milliliters (“Settle Foam”). The surface of the additized diesel is then visually monitored. A stop watch

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is used to measure the time it takes the foam to visually disappear from the surface of the additized diesel and the time is recorded in seconds ("Collapse Time").

[0081] The test is repeated 5 times and the average Max Foam, Settle Foam, and Collapse Time is calculated. The average foam test results of various acrylamide polymers at different treat rates in a diesel fuel are shown in Table 2 below.

Table 2

Example	Inventive Composition / Monomer Units	Weight Ratio	Polymer Mw (Da)	Max Foam (ml)	Settle Foam (ml)	Collapse Time (s)
Control	N/A			106	96	32.0
Ex A	1 / TMHAT:NTBAD	85:15	152,311	105	97	28.0
Ex B	2 / NNDEAD	100	74,063	102	90	24.3
Ex C	3 / NTBAD	100	61,020	106	92	12.5
Ex D	4 / TBAT:NTBAD	99:1	103,457	95	82	7.4
Ex E	5 / TBAT:NNDEAD	99:1	72,862	98	86	8.3

[0082] The results show that the acrylamide polymers are effective at reducing foam in diesel fuels.

[0083] Additional suitable test methods for measuring the effectiveness of the acrylamide polymers disclosed herein at reducing foam in diesel fuels include the "Determination of the foaming tendency of diesel fuels" NF M 07-075, published and distributed by l'Association Française de Normalisation (AFNOR – www.afnor.org).

[0084] Each of the documents referred to above is incorporated herein by reference, including any prior applications, whether or not specifically listed above, from which priority is claimed. The mention of any document is not an admission that such document qualifies as prior art or constitutes the general knowledge of the skilled person in any jurisdiction. Except in the Examples, or where otherwise explicitly indicated, all numerical quantities in this description specifying amounts of materials, reaction conditions, molecular weights, number of carbon atoms, and the like, are to be understood as modified by the word "about." It is to be understood that the upper and lower amount, range, and ratio limits set forth herein may be independently combined. Similarly, the ranges and amounts for each element of the invention can be used together with ranges or amounts for any of the other elements.

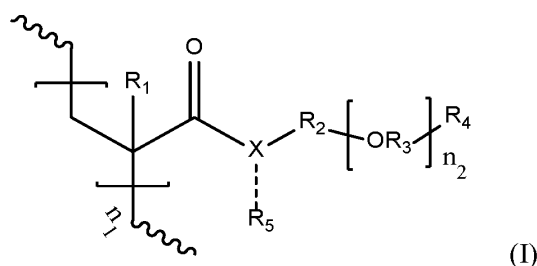
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As used herein, the term “comprising” is intended also to encompass as alternative embodiments “consisting essentially of” and “consisting of.” “Consisting essentially of” permits the inclusion of substances that do not materially affect the basic and novel characteristics of the composition under consideration.

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1. A composition comprising a diesel fuel and at least one acrylamide polymer prepared by polymerizing:
 - (a) a (meth)acrylamide monomer to yield a homopolymer; or
 - (b) a (meth)acrylamide monomer comprising (meth)acrylamide and a (meth)acrylate monomer to yield a heteropolymer.
2. The composition of claim 1, wherein the at least one acrylamide polymer is a homopolymer.
3. The composition of claim 1 or 2, wherein the (meth)acrylamide monomer comprises a mono- or di-C₁ to C₂₇ alkyl-substituted (meth)acrylamide.
4. The composition of any claim 1 to 3, wherein the (meth)acrylamide monomer comprises a mono- or di-C₁ to C₁₂ alkyl-substituted (meth)acrylamide.
5. The composition of any claim 1 to 4, wherein the (meth)acrylate monomer comprises a C₁ to C₃₀ alkyl-substituted (meth)acrylate.
6. The composition of any claim 1 to 5, wherein the at least one acrylamide polymer is a heteropolymer.
7. The composition of any claim 1 to 6, wherein the acrylamide polymer comprises a heteropolymer prepared from a (meth)acrylate monomer comprising tert-butyl acrylate ("TBAT").
8. The composition of any claim 1 to 7, wherein the (meth)acrylamide monomer comprises N,N-diethylacrylamide ("NNDEAD"), N-(tertbutyl)acrylamide ("NTBAD"), or combinations thereof.
9. The composition of any claim 1 to 8, wherein the at least one polymer has a weight average molecular weight ("M_w") of from 10,000 to 350,000 Da.
10. The composition of any claim 1 to 9, wherein the at least one polymer has a M_w of from 30,000 to 200,000 Da.
11. The composition of any claim 1 to 10, wherein the at least one polymer has a concentration of 0.1 ppm to 3000 ppm by weight, based on a total weight of the composition.

12. The composition of any claim 1 to 11, wherein the at least one polymer has a concentration of 1 ppm to 100 ppm by weight, based on a total weight of the composition.
13. The composition of any claim 1 to 12, wherein the foam in the composition is reduced as compared to a diesel fuel without the at least one polymer.
14. A composition comprising at least one acrylamide polymer prepared by polymerizing:
- a (meth)acrylamide monomer to yield a homopolymer; or
 - a (meth)acrylamide monomer and a (meth)acrylate monomer to yield a heteropolymer.
15. The composition of claim 14, further comprising at least one acrylate polymer prepared by polymerizing one or more (meth)acrylate monomers comprising a C₁ to C₃₀ alkyl-substituted (meth)acrylate.
16. The composition of claim 15, wherein the acrylate polymer is at least one of a copolymer, block polymer, random polymer, terpolymer, or combinations thereof.
17. The composition of claim 15 or 16, comprising:
- from 1 wt% to 99 wt% (or 5 wt% to 95 wt%) of the acrylamide polymer; and
 - from 99 wt% to 1 wt% (or 95 wt% to 5 wt%) of the acrylate polymer.
18. The composition of any claim 1 to 17, wherein the at least one acrylamide polymer has units with the structure of formula (I):



wherein R¹ is H or CH₃; R² is a C₁ to C₁₀ linear or branched hydrocarbonyl group; R³ is a C₁ to C₄ linear or branched hydrocarbonyl group; R⁴ is H, OH, or CH₃; n₁ is an integer ranging from 120 to 3000; X is O or N; R₅ is only present if X is N and can be H, a C₁ to C₁₀ linear or branched hydrocarbonyl group, or when taken together with R₂, may form

a saturated or unsaturated ring containing 5 to 6 carbon atoms; and n_2 is an integer ranging from 0 to 3.

19. The composition of claim 18, wherein the acrylamide polymer is a homopolymer and X is N.

20. The composition of claim 18 or 19, wherein the acrylamide polymer is a heteropolymer having at least two polymer moieties and wherein for at least one polymer moiety X is N and for at least one polymer moiety X is O.

21. The composition of any claim 18 to 20, wherein R^2 and/or R^3 is branched.

22. The composition of any claim 18 to 21, wherein R^2 is linear and R^3 is branched.

23. The composition of any claim 14 to 22, wherein the (meth)acrylamide monomer comprises a mono- or di- C_1 to C_{27} alkyl-substituted (meth)acrylamide.

24. The composition of any claim 14 to 23, wherein the (meth)acrylamide monomer comprises a mono- or di- C_1 to C_{12} alkyl-substituted (meth)acrylamide.

25. The composition of any claim 14 to 24, wherein the acrylamide polymer comprises at least one heteropolymer prepared by polymerizing a (meth)acrylamide monomer and a (meth)acrylate monomer.

26. The composition of any claim 14 to 25, wherein the acrylamide polymer comprises a heteropolymer prepared from a (meth)acrylate monomer comprising tert-butyl acrylate ("TBAT").
27. The composition of any claim 14 to 26, wherein the (meth)acrylamide monomer comprises N,N-diethylacrylamide ("NNDEAD"), N-(tertbutyl)acrylamide ("NTBAD"), or combinations thereof.

27. The composition of any claim 14 to 26, wherein the at least one polymer has a weight average molecular weight (" M_w ") of from 10,000 to 350,000 Da.

28. The composition of any claim 14 to 27, wherein the at least one polymer has a M_w of from 30,000 to 200,000 Da

29. The composition of any claim 14 to 28, further comprising a diesel fuel and wherein the at least one polymer is present in the diesel fuel in an amount from 0.1 ppm to 3000 ppm by weight, based on a total weight of the diesel fuel and composition.

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30. The composition of claim 29, wherein the at least one polymer is present in the diesel fuel in an amount from 1 ppm to 100 ppm by weight, based on a total weight of the of the diesel fuel and composition.
31. A method of reducing foam in a diesel fuel, said method comprising adding the composition of any claim 14 to 28 to a diesel fuel.
32. A method of reducing the amount of foam produced while filling the diesel tank of a vehicle, said method comprising adding the composition of any claim 14 to 28, to a diesel fuel.
33. The use of a composition as in any claim 14 to 28 to reduce foam in a diesel fuel.