

SYNERGISTIC POLYACRYLATE ANTIFOAM SYSTEMS FOR USE IN INDUSTRIAL GEAR LUBRICANTS

FIELD OF THE INVENTION

5 **[0001]** The field of the invention relates to synergistic polyacrylate antifoam systems for use in industrial gear lubricants.

BACKGROUND OF THE INVENTION

10 **[0002]** Foam in industrial gear oils can cause problems in the gearbox, including, excessive wear, heat, and oxidation. Foam can contribute to wear because air can displace the lubricant between the gears and other metal components in the gearbox causing metal to metal contact to occur. The air in the foam can also cause an insulating barrier preventing efficient heat dissipation throughout the gearbox. Excessive heat can cause various components in the industrial gear lubricant to decompose and thereby reduce its effectiveness. Entrapped air can also cause excessive oxidation of the lubricant and lubricant components which also reduces their effectiveness.

15 **[0003]** It is known to introduce silicon or polyacrylate-based antifoams into industrial gear lubricants to alleviate foam tendencies of the lubricant. It is also common to filter industrial lubricants in gearbox systems to reduce system contaminants to prolong gear life as well as the lubricant life. Generally, polyacrylate antifoams are used in mineral oil-based industrial gear oils. Industrial gear lubricants containing polyacrylate antifoams, however, can suffer loss of defoam retention properties with prolonged filtration at elevated temperatures.

20 **[0004]** Therefore, there is a need for antifoam components that retain their defoaming properties when at elevated temperatures and/or after filtering.

SUMMARY OF THE INVENTION

25 **[0005]** The disclosed technology is a synergistic polyacrylate antifoam system that maintains defoaming properties at elevated temperatures, after filtering, and/or high turbulent flow conditions. Accordingly, an antifoam polymer composition is disclosed. The composition comprises at least two polymers, wherein: a first polymer is prepared by polymerizing a first monomer composition comprising (i) at least one alkyl (meth)acrylate ester monomer and (ii) 2 to 20 mole percent of at least one vinyl acetate monomer, based on the total moles of the first monomer composition; and a second polymer is prepared by polymerizing a second monomer composition comprising (i) at least one alkyl (meth)acrylate ester monomer.

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[0006] The first polymer of the antifoam polymer composition may be insoluble in mineral oil, or substantially insoluble in mineral oil. In some embodiments, the first monomer composition may comprise: 20 to 48 mole percent of a C₁ to C₄ alkyl (meth)acrylate ester monomer; 50 to 78 mole percent of a C₈ to C₁₆ alkyl (meth)acrylate ester monomer; and 2 to 20 mole percent of a vinyl acetate monomer, wherein the mole percent is based on the total moles of the first monomer composition. In some embodiments, the first monomer composition may comprise 5 to 15 mole percent (or 8 to 12 mole percent) of the vinyl acetate monomer. In some embodiments, the first polymer may have a number average molecular weight M_n of 8,000 to 15,000 Daltons.

[0007] In some embodiments, the second monomer composition may comprise: 5 to 35 mole percent of C₁ to C₄ alkyl (meth)acrylate ester monomer; and 65 to 95 mole percent of C₈ to C₁₆ alkyl (meth)acrylate ester monomer, wherein the mole percent is based on the total moles of the second monomer composition. In some embodiments, second polymer may be prepared by polymerizing (i) at least one alkyl (meth)acrylate ester monomer and (ii) less than 1 mole percent (for example 0 to less than 1 mole percent) of at least one vinyl acetate monomer, based on the total moles of the second monomer composition. In some embodiments, the second polymer may have a number average molecular weight M_n of 15,000 to 25,000 Daltons. In some embodiments, the second polymer may be more soluble in mineral oil than the first polymer.

[0008] In some embodiments, the first monomer composition and/or second monomer composition may comprise 20 to 40 mole percent of a C₁ to C₃ alkyl (meth)acrylate ester monomer or a C₁ to C₂ alkyl (meth)acrylate ester monomer, for example, ethyl acrylate or ethyl methacrylate. In the same or different embodiments, the C₈ to C₁₆ alkyl group of the (meth)acrylate ester monomer in the first monomer composition and/or the second monomer composition may comprise a branched or linear aliphatic group. In some embodiments, the C₈ to C₁₆ alkyl group of the (meth)acrylate ester monomer in the first monomer composition and/or the second monomer composition may be 2-ethylhexyl acrylate or 2-ethylhexyl methacrylate.

[0009] In some embodiments, the first polymer may be prepared from a first monomer composition comprising 30 to 40 mole percent (or 35.6 mol%) ethyl acrylate, 60 to 70 mole percent (or 66.1 mol%) 2-ethylhexyl acrylate, and 8 to 12 mole percent (or 10.2 mol%) vinyl acetate. In the same or different embodiments, the second polymer may be prepared from a second monomer composition comprising 20 to 30 mole percent (or 28 mol%) ethyl acrylate and 70 to 80 mole percent (or 72 mol%) 2-ethylhexyl acrylate. In

yet other embodiments, the weight ratio of the first polymer to the second polymer ranges from 4:1 to 1:1 or 3:1 to 1:1.

5 [0010] In some embodiments, an industrial gear additive package is disclosed. The industrial gear additive package may comprise the antifoam polymer composition as described above; and at least one sulfurized olefin compound. In some embodiments, the at least one sulfurized olefin may be present at 0.01 to 3.0 wt% (or 1.2 wt%), based on a total weight of the industrial gear additive package. In some embodiments, the at least one sulfurized olefin comprises sulfurized isobutylene and/or di-isobutylene.

10 [0011] In the same or different embodiments, the industrial gear additive package may further comprise at least one phosphorus-containing anti-wear agent that is a phosphite, phosphonate, amine salted phosphate, phosphine, or any combination thereof, for example oleyl phosphite or a salt of 2-ethylhexylamine and isooctyl phosphoric acid. In the same or different embodiments, the industrial gear additive package may further comprise at least one organic friction modifier, for example imidazoline, oleylamine, and/or oleylamide.

[0012] In some embodiments, an industrial gear lubricant is disclosed. The industrial gear lubricant may comprise, (a) a mineral base oil in an amount of at least 50 weight percent of the industrial gear lubricant; (b) the antifoam polymer composition as described above; and/or (c) the industrial gear additive package as described above.

20 [0013] In the same or different embodiments, the industrial gear lubricant may contain less than 0.2 weight percent sulfated ash. In some embodiments, the industrial gear lubricant contains less than 0.01 weight percent of a zinc dialkyl dithiophosphate compound.

25 [0014] In some embodiments, the industrial gear lubricant comprises the mineral base oil in an amount of at least 60 weight percent, or at least 75 weight percent, or at least 90 weight percent, based on a total weight of the industrial gear lubricant. Suitable mineral oils are not overly limited and may include at least one API Group I, Group II, and Group III oil, or any combination thereof. In some embodiments the industrial gear additive package is present in the industrial gear lubricant at 0.5 to 3 wt% (or 1 to 2.5 wt%, or 1.5 to 2.5 wt%), based on a total weight of the industrial gear lubricant.

DETAILED DESCRIPTION OF THE INVENTION

30 [0015] Various preferred features and embodiments will be described below by way of non-limiting illustration.

[0016] An antifoam polymer composition is disclosed. The composition comprises at least two polymers, wherein: a first polymer is prepared by polymerizing a first monomer composition comprising (i) at least one alkyl (meth)acrylate ester monomer and (ii) 2 to 20 mole percent of at least one vinyl acetate monomer, based on the total moles of the first monomer composition; and a second polymer is prepared by polymerizing a second monomer composition comprising (i) at least one alkyl (meth)acrylate ester monomer.

[0017] As used herein, the term “(meth)acrylate” and related terms include both acrylate and methacrylate groups, i.e. the methyl group is optional. For example, the term (meth)acrylate ester monomer includes acrylate ester monomers and methacrylate ester monomers. Accordingly, in some embodiments, the at least one alkyl (meth)acrylate ester monomer may comprise at least one acrylate ester monomer, methacrylate ester monomer, or combinations thereof.

[0018] Prior to the present invention, polyacrylate antifoams were known for use in industrial lubricant applications. It was found, however, that these polyacrylate antifoams lost their effectiveness in gearbox systems with filtration and/or elevated operating temperatures. It was surprisingly found, however, that using a combination of at least two polyacrylate antifoams in a lubricant, wherein one antifoam is less soluble in the lubricant than the other, resulted in lubricants that do not lose their effectiveness in reducing foam, even with filtration and/or elevated operating temperatures.

[0019] Without limiting the disclosed technology to one theory of operation, the present inventor(s) hypothesized that some types of polyacrylate antifoams form droplets that are prone to shearing as they pass through the filter, resulting in smaller droplets of antifoam present throughout the lubricant. These smaller droplets may be less effective at reducing foam. The more insoluble antifoam may be interacting in the lubricant in some way that allows for the smaller more soluble antifoam droplets to agglomerate into larger droplets, thereby maintaining the more soluble antifoam's effectiveness. Accordingly, the antifoam polymer composition may comprise at least two polymers, wherein one polymer is more insoluble in the lubricant than the other polymer. Accordingly, in some embodiments the first polymer may be less soluble in mineral oil than the second polymer. Similarly, the second polymer may be more soluble in mineral oil than the first polymer. The first polymer of the antifoam polymer composition may be insoluble in mineral oil, or substantially insoluble in mineral oil. In the same or other embodiments, the second polymer may be more soluble in mineral oil than the first polymer, or substantially more soluble in mineral oil than the first polymer.

[0020] In some embodiments, the first monomer composition may comprise: 20 to 48 mole percent of a C₁ to C₄ alkyl (meth)acrylate ester monomer; 50 to 78 mole percent of a C₈ to C₁₆ alkyl (meth)acrylate ester monomer; and 2 to 20 mole percent of a vinyl acetate monomer, wherein the mole percent is based on the total moles of the first monomer composition. In some embodiments, the first monomer composition may comprise 5 to 15 mole percent (or 8 to 12 mole percent) of the vinyl acetate monomer.

[0021] In some embodiments, the first polymer may have a number average molecular weight M_n of 8,000 to 15,000 Daltons. As used herein, the number average molecular weight (“ M_n ”) 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

[0022] Persons ordinarily skilled in the art will understand that the weight average molecular weight (M_w) may be measured using a similar technique to the one described above.

[0023] In some embodiments, the second monomer composition may comprise: 5 to 35 mole percent of C₁ to C₄ alkyl (meth)acrylate ester monomer; and 65 to 95 mole percent of C₈ to C₁₆ alkyl (meth)acrylate ester monomer, wherein the mole percent is based on the total moles of the second monomer composition. In some embodiments, second polymer may be prepared by polymerizing (i) at least one alkyl (meth)acrylate ester monomer and (ii) less than 1 mole percent (for example 0 to less than 1 mole percent) of at least one vinyl acetate monomer, based on the total moles of the second monomer composition. In some embodiments, the second polymer may have a number average molecular weight M_n of 15,000 to 25,000 Daltons.

[0024] The second polymer will generally be more soluble in mineral oil and/or in the finished lubricant composition than the first polymer. The solubility properties of the second monomer may be qualified using Hansen Solubility Parameters (“HSP”), which include δD for dispersion (van der Waals), δP for Polarity (related to dipole moment) and δH for hydrogen bonding. These are used to determine the Hansen Solubility Sphere, R, which is the radius of the solubility sphere. Generally, good solvents for a particular material will lie within the sphere and bad solvents will lie outside the sphere. More information about HSP may be found at <https://www.hansen-solubility.com>.

[0025] The second polymer may have a double sphere behavior. The sphere in the more polar and hydrogen part of the HSP space is reflective of the head moiety of the polymer and the non-polar sphere corresponds to the tail moiety of the polymer. Accordingly, the second polymer may have the Hansen Solubility parameters (in MPa) as shown in the table below.

	δD	δP	δH	R
2 nd polymer; sphere 1	14.8	9.93	14.18	4.9
2 nd polymer; sphere 2	16.9	3.95	3.54	7

[0026] In some embodiments, the first monomer composition and/or second monomer composition may comprise 20 to 40 mole percent of a C₁ to C₃ alkyl (meth)acrylate ester monomer or a C₁ to C₂ alkyl (meth)acrylate ester monomer, for example, ethyl acrylate or ethyl methacrylate. In some embodiments, the first polymer will be insoluble, or substantially insoluble in mineral oil, thus, mineral oil will be outside the Hansen Solubility Sphere(s), R, for the first polymer. In some embodiments, the first polymer may have 2 Hansen Solubility Spheres. In some embodiments, the first polymer and mineral oil will have a Distance (Ra) greater than the Distance (Ra) between the second polymer and mineral oil. In some embodiments, the first polymer and mineral oil will have a Distance (Ra) of greater than 8. In some embodiments, the second polymer may have 1 Hansen Solubility Sphere with the Hansen Solubility parameters (in MPa) as shown in the table below.

	δD	δP	δH	R
1 st polymer	16.4	5.2	8.2	8.3

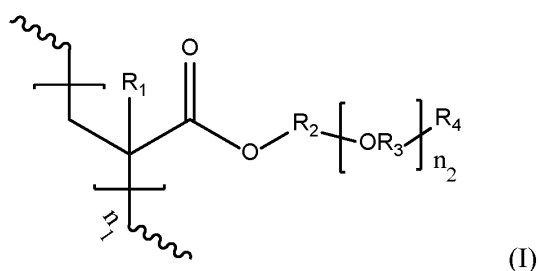
[0027] In the same or different embodiments, the C₈ to C₁₆ alkyl group of the (meth)acrylate ester monomer in the first monomer composition and/or the second monomer composition may comprise a branched or linear aliphatic group. In some

embodiments, the C₈ to C₁₆ alkyl group of the (meth)acrylate ester monomer in the first monomer composition and/or the second monomer composition may be 2-ethylhexyl acrylate or 2-ethylexy methacrylate.

[0028] The antifoam polymers disclosed herein are poly(acrylate) polymers that can be prepared by methods generally known in the art. The polymerization may be affected 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 monomers 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 monomers can be polymerized in a hydrocarbon oil. In yet other embodiments, the monomers may be polymerized in light aromatic petroleum naphtha, heavy aromatic naphtha, or combinations thereof. When referring to a specified monomer(s) that is included in or used to prepare the antifoam polymer(s) disclosed herein, the ordinarily skilled person will recognize that the monomer(s) will be incorporated as at least one unit into the resulting antifoam polymer.

[0029] As used herein, C_x to C_y, when used to describe the (meth)acrylate ester monomer, refers to the number of carbon atoms in the alkyl group connected to the oxygen on the (meth)acrylate moiety and does not include the number of carbon atoms in the (meth)acrylate moiety itself.

[0001] In some embodiments, the poly(acrylate) polymer may comprise units with the structure of formula (I):



wherein R¹ is H or CH₃; R² is a C₂ to C₁₀ linear, branched, or cyclic hydrocarbyl group; R³ is a C₂ to C₄ linear or branched hydrocarbyl group; R⁴ is H, OH, or CH₃; n₁ is an integer ranging from 75 to 3000; and n₂ is an integer ranging from 0 to 3. In some embodiments, R² and/or R³ is branched. In other embodiments, R² is linear and R³ is branched.

[0030] As used herein, the term “hydrocarbyl” refers to a group having a carbon atom directly attached to the remainder of the molecule, where the group includes at

least carbon and hydrogen atoms. If the hydrocarbyl group comprises more than one carbon atom, then those carbons need not necessarily be linked to each other. For example, at least two of the carbons may be linked via a suitable element or group. In various embodiments, the term “hydrocarbyl” refers to a group having a carbon atom directly attached to the remainder of the molecule, where the group consists of carbon, hydrogen, optionally one or more heteroatoms provided the heteroatoms do not alter the predominantly hydrocarbon nature of the substituent. The heteroatom may link at least two of the carbons in the hydrocarbyl group, and optionally no more than two non-hydrocarbon substituents. Suitable heteroatoms will be apparent to those skilled in the art and include, for instance, sulphur, nitrogen, oxygen, phosphorus and silicon. Where the hydrocarbyl contains heteroatoms, optionally, no more than two heteroatoms will be present for every ten carbon atoms in the hydrocarbyl group. Suitable non-hydrocarbon substituents will also be apparent to those skilled in the art and include, for instance, halo, hydroxy, alkoxy, mercapto, alkylmercapto, nitro, nitroso, and sulphony.

[0031] Examples of hydrocarbyls within the context of the present technology therefore include:

- (i) hydrocarbon groups selected from aliphatic (e.g. alkyl or alkenyl), alicyclic (e.g. cycloalkyl, cycloalkenyl, cycloalkadienyl), and aromatic groups;
- (ii) substituted hydrocarbon groups, selected from hydrocarbon groups defined in (i) substituted with no more than two non-hydrocarbon substituents and/or one or more hydrocarbon substituents, the non-hydrocarbon substituents being selected from the group consisting of halo, hydroxy, alkoxy, mercapto, alkylmercapto, nitro, nitroso, and sulphony;
- (iii) hetero-containing hydrocarbon groups, selected from hydrocarbon groups defined in (i) containing one or more heteroatom in the ring or chain, provided that the group has no more than two heteroatoms present for every ten carbon atoms in the group, the heteroatoms being selected from sulphur, nitrogen, oxygen, phosphorus and silicon. The hetero-containing hydrocarbon groups may be substituted with no more than two non-hydrocarbon substituents and/or one or more hydrocarbon substituents.

[0032] In some embodiments, the term “hydrocarbyl” refers to a group having a carbon atom directly attached to the remainder of the molecule, where the group consists of carbon and hydrogen atoms.

[0033] In some embodiments, the first polymer may be prepared from a first monomer composition comprising 30 to 40 mole percent (or 35.6 mol%) ethyl acrylate, 60 to 70 mole percent (or 66.1 mol%) 2-ethylhexyl acrylate, and 8 to 12 mole percent (or 10.2 mol%) vinyl acetate. In the same or different embodiments, the second polymer may be prepared from a second monomer composition comprising 20 to 30 mole percent (or 28 mol%) ethyl acrylate and 70 to 80 mole percent (or 72 mol%) 2-ethylhexyl acrylate. In some embodiments, the weight ratio of the first polymer to the second polymer may range from 4:1 to 1:1 or 3:1 to 1:1.

[0034] In some embodiments, an industrial gear additive package is disclosed. The industrial gear additive package may comprise the antifoam polymer composition as described above; and at least one sulfurized olefin compound. The sulfurized olefin may function as an extreme pressure agent.

Sulfurized Olefins

[0035] Sulfurized olefins are well known commercial materials, and those which are substantially nitrogen-free, that is, not containing nitrogen functionality, are readily available. The olefinic compounds which may be sulfurized are diverse in nature. They contain at least one olefinic double bond, which is defined as a non-aromatic double bond; that is, one connecting two aliphatic carbon atoms. In its broadest sense, the olefin may be defined by the formula $R^1R^2C=CR^3R^4$, wherein each of R^1 , R^2 , R^3 and R^4 is hydrogen or an organic group. In general, the R groups in the above formula which are not hydrogen may be satisfied by such groups as $-C(R^5)_3$, $-COOR^5$, $-COOM$, $-X$, $-YR^5$ or $-Ar$, wherein each R^5 is independently hydrogen, alkyl, alkenyl, aryl, substituted alkyl, substituted alkenyl or substituted aryl, with the proviso that any two R^5 groups can be alkylene or substituted alkylene whereby a ring of up to 12 carbon atoms is formed; M is one equivalent of a metal cation (preferably Group I or II, e.g., sodium, potassium, barium, calcium); X is halogen (e.g., chloro, bromo, or iodo); Y is oxygen or divalent sulfur; Ar is an aryl or substituted aryl group of up to 12 carbon atoms. Any two of R^1 , R^2 , R^3 and R^4 may also together form an alkylene or substituted alkylene group; i.e., the olefinic compound may be alicyclic.

[0036] One type of sulfurized olefin is prepared in accordance with the detailed teachings of U.S. Pat. No. 4,957,651. Described therein is a cosulfurized mixture of 2 or more reactants selected from the group consisting of (1) at least one fatty acid ester of a polyhydric alcohol, (2) at least one fatty acid, (3) at least one olefin, and (4) at least one fatty acid ester of a monohydric alcohol. Reactant (3), the olefin component, comprises

at least one olefin. This olefin is preferably an aliphatic olefin, which usually will contain 4 to 40 carbon atoms, preferably from 8 to 36 or 12 to 18 carbon atoms. Terminal olefins, or alpha-olefins, are preferred, especially those having from 12 to 20 carbon atoms. Mixtures of these olefins are commercially available, and such mixtures are contemplated for use in this invention.

[0037] The sulfurized olefin can be prepared by reacting a single reactant or a mixture of appropriate reactants with a source of sulfur. The sulfurization reaction generally is affected at an elevated temperature, e.g., 50-350 °C or 100-200 °C, with efficient agitation and often in an inert atmosphere such as nitrogen, optionally in the presence of an inert solvent. The sulfurizing agents useful in the process of the present invention include elemental sulfur, which is preferred, hydrogen sulfide, sulfur halide, sodium sulfide and a mixture of hydrogen sulfide and sulfur or sulfur dioxide. Usually, the amount of sulfur or sulfurizing agent employed calculated based on the total olefinic unsaturation of the mixture. Typically, often 0.5 to 3 moles of sulfur are employed per mole of olefinic bonds.

[0038] The olefinic compound is usually one in which each R group, above, which is not hydrogen is independently alkyl, alkenyl or aryl group. Monoolefinic and diolefinic compounds, particularly the former, are preferred, and especially terminal monoolefinic hydrocarbons; that is, those compounds in which R³ and R⁴ are hydrogen and R¹ and R² are alkyl or aryl, especially alkyl (that is, the olefin is aliphatic) having 1 to 30, or 1 to 16, or 1 to 8, or 1 to 4 carbon atoms. Olefinic compounds having 3 to 30 or 3 to 16 (often fewer than 9) carbon atoms can be used.

[0039] Isobutene, propylene and their dimers, trimers and tetramers, and mixtures thereof are useful as olefinic compounds for sulfurization, as are terpene compounds, that is, various isomeric terpene hydrocarbons having the empirical formula C₁₀H₁₆, as well as various synthetic and naturally occurring oxygen-containing derivatives thereof.

[0040] In one embodiment, the sulfurized organic composition is a sulfur-containing material which comprises the reaction product of a sulfur source and at least one Diels-Alder adduct, in a molar ratio of at least 0.75:1. Generally, the molar ratio of sulfur source to Diels-Alder adduct is 0.75 to 4.0, or 1 to 2.0, or 1 to 1.8. The Diels-Alder adducts can be prepared from dienophiles having at least one carboxylic ester group represented by —C(O)O—R₀ where R₀ is the residue of a saturated aliphatic alcohol of up to 40 carbon atoms, the aliphatic alcohol from which —R₀ is derived being a mono or polyhydric alcohol such as alkylene glycols, alkanols, aminoalkanols, alkoxy-substituted

alkanols, ethanol, ethoxy ethanol, propanol, butanol, beta-diethylamino-ethanol, dodecyl alcohol, diethylene glycol, tripropylene glycol, tetrabutylene glycol, hexanol, octanol, and isooctyl alcohol. Generally, not more than two —C(O)—O—R_0 groups will be present, preferably only one —C(O)—O—R_0 group. Such materials can also be described as cyclohexene compounds bearing ester substituents. A preferred sulfurized olefin is sulfurized 4-carbobutoxy cyclohexene. This and other sulfurized olefins can be further treated with other materials such as an aryl phosphate, e.g., triphenyl phosphite.

[0041] Other sulfurized olefins include sulfurized vegetable oils and sulfurized lard oil (that is, sulfurized oils of animal sources generally).

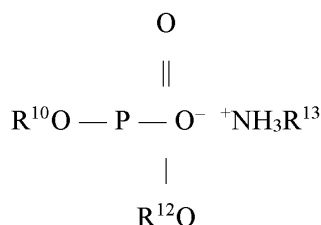
[0042] In some embodiments, suitable sulfur-containing compounds include sulfurized olefins and polysulfides. The sulfurized olefin or polysulfides may be derived from isobutylene, butylene, propylene, ethylene, or some combination thereof. In some examples the sulfur-containing compound is a sulfurized olefin derived from any of the natural oils or synthetic oils described above, or even some combination thereof. For example, the sulfurized olefin may be derived from vegetable oil. The sulfurized olefin may be present in the lubricant composition from 0 wt % to 5.0 wt % or from 0.01 wt % to 4.0 wt % or from 0.1 wt % to 3.0 wt %. In some embodiments, the at least one sulfurized olefin may be present at 0.01 to 3.0 wt % (or 1.2 wt %), based on a total weight of the industrial gear additive package. In some embodiments, the at least one sulfurized olefin comprises sulfurized isobutylene sulfurized isobutylene and/or di-isobutylene.

Phosphorus-containing anti-wear agents

[0043] In the same or different embodiments, the industrial gear additive package may further comprise at least one phosphorus-containing anti-wear agent. Suitable phosphorus-containing anti-wear agents are not overly limited and can include at least one phosphorus acid, phosphorus acid salt, phosphorus acid ester or derivative thereof including sulfur-containing analogs. The phosphorus acids, salts, esters or derivatives thereof include phosphoric acid, phosphorous acid, phosphorus acid esters or salts thereof, phosphites, phosphorus-containing amides, phosphorus-containing carboxylic acids or esters, phosphorus-containing ethers, and mixtures thereof.

[0044] In one embodiment, the phosphorus acid, ester or derivative can be an organic or inorganic phosphorus acid, phosphorus acid ester, phosphorus acid salt, or derivative thereof. The phosphorus acids include the phosphoric, phosphonic, phosphinic, and thiophosphoric acids including dithiophosphoric acid as well as the

monothiophosphoric, thiophosphinic and thiophosphonic acids. One group of phosphorus compounds are alkylphosphoric acid mono alkyl primary amine salts as represented by the formula



where R^{10} , R^{12} , R^{13} are alkyl or hydrocarbyl groups or one of R^{12} and R^{13} can be H. The materials can be a 1:1 mixture of dialkyl and monoalkyl phosphoric acid esters. Compounds of this type are described in U.S. Patent 5,354,484.

[0045] Other phosphorus-containing materials that may be present include dialkylphosphites (sometimes referred to as dialkyl hydrogen phosphonates) such as dibutyl phosphite. Yet other phosphorus materials include phosphorylated hydroxy-substituted triesters of phosphorothioic acids and amine salts thereof, as well as sulfur-free hydroxy-substituted di-esters of phosphoric acid, sulfur-free phosphorylated hydroxy-substituted di- or tri-esters of phosphoric acid, and amine salts thereof. These materials are further described in U.S. patent application US 2008-0182770.

[0046] The compositions disclosed herein will generally be free or substantially free of phosphorus-containing anti-wear agents that are coordination compounds having a metal ion. Such materials include zinc dialkyldithiophosphates or simply zinc dithiophosphates. They are well known and readily available to those skilled in the art of lubricant formulation. While these materials may be used, in some embodiments, the industrial gear additive package and/or the industrial gear lubricant is free or substantially free of zinc dialkyl dithiophosphate compounds. Accordingly, in some embodiments, the industrial gear additive package or industrial gear lubricant may contain less than 0.01 weight percent of a zinc dialkyl dithiophosphate compound.

[0047] In one embodiment, the lubricating composition may comprise a phosphorus-containing anti-wear agent that is a phosphite, phosphonate, amine salted phosphate, phosphine, or any combination thereof, for example oleyl phosphite and/or a salt of 2-ethylhexylamine and isooctyl phosphoric acid. In some embodiments, the lubricating composition may comprise a phosphorus-containing anti-wear agent that is dialkyl

hydrogen phosphite. The amount of phosphorus-containing anti-wear agents in an industrial gear additive package, if present, may range from 5 to 60 wt%, or 5 to 25 wt%, or 15 to 30 wt%, based on a total weight of the additive package. The amount of phosphorus-containing anti-wear agents in a completely formulated lubricant, if present, will typically be 0.01 to 6 percent by weight, 0.01 to 5 percent by weight, or 0.03 to 2 percent by weight, 0.1 to 0.6 by weight, or even 0.05 to 0.5 percent by weight.

Friction Modifiers

[0048] Another component that may be used in the composition used in the present technology is a friction modifier. Friction modifiers are well known to those skilled in the art. A list of friction modifiers that may be used is included in U.S. Patents 4,792,410, 5,395,539, 5,484,543 and 6,660,695. U.S. Patent 5,110,488 discloses metal salts of fatty acids and especially zinc salts, useful as friction modifiers. A list of friction modifiers that may be used may include: fatty phosphites; borated alkoxylated fatty amines; fatty acid amides; metal salts of fatty acids; fatty epoxides; sulfurized olefins; borated fatty epoxides; fatty imidazolines; fatty amines; condensation products of carboxylic acids and polyalkylene-polyamines; glycerol esters; metal salts of alkyl salicylates; borated glycerol esters; amine salts of alkylphosphoric acids; alkoxylated fatty amines; ethoxylated alcohols; oxazolines; imidazolines; hydroxyalkyl amides; polyhydroxy tertiary amines; and mixtures of two or more thereof.

[0049] As used herein, the term "condensation product" is intended to encompass esters, amides, imides and other such materials that may be prepared by a condensation reaction of an acid or a reactive equivalent of an acid (e.g., an acid halide, anhydride, or ester) with an alcohol or amine, irrespective of whether a condensation reaction is actually performed to lead directly to the product. Thus, for example, a particular ester may be prepared by a transesterification reaction rather than directly by a condensation reaction. The resulting product is still considered a condensation product.

[0050] Representatives of each of these types of friction modifiers are known and are commercially available. For instance, fatty phosphites may be generally of the formula $(RO)_2PHO$ or $(RO)(HO)PHO$ where R may be an alkyl or alkenyl group of sufficient length to impart oil solubility. Suitable phosphites are available commercially and may be synthesized as described in U.S. Patent 4,752,416.

[0051] Borated fatty epoxides that may be used are disclosed in Canadian Patent No. 1,188,704. These oil-soluble boron-containing compositions may be prepared by reacting a boron source such as boric acid or boron trioxide with a fatty epoxide which may

contain at least 8 carbon atoms. Non-borated fatty epoxides may also be useful as friction modifiers.

[0052] Borated amines that may be used are disclosed in U.S. Patent 4,622,158. Borated amine friction modifiers (including borated alkoxyated fatty amines) may be prepared by the reaction of a boron compounds, as described above, with the corresponding amines, including simple fatty amines and hydroxy containing tertiary amines. The amines useful for preparing the borated amines may include commercial alkoxyated fatty amines known by the trademark "ETHOMEEN" and available from Akzo Nobel, such as bis[2-hydroxyethyl]-cocoamine, polyoxyethylene[10]cocoamine, bis[2-hydroxyethyl]soyamine, bis[2-hydroxyethyl]-tallowamine, polyoxyethylene-[5]tallowamine, bis[2-hydroxyethyl]oleylamine, bis[2-hydroxyethyl]octadecylamine, and polyoxyethylene[15]octadecylamine. Such amines are described in U.S. Patent 4,741,848.

[0053] Alkoxyated fatty amines and fatty amines themselves (such as oleylamine) may be useful as friction modifiers. These amines are commercially available.

[0054] Both borated and unborated fatty acid esters of glycerol may be used as friction modifiers. Borated fatty acid esters of glycerol may be prepared by borating a fatty acid ester of glycerol with a boron source such as boric acid. Fatty acid esters of glycerol themselves may be prepared by a variety of methods well known in the art. Many of these esters, such as glycerol monooleate and glycerol tallowate, are manufactured on a commercial scale. Commercial glycerol monooleates may contain a mixture of 45% to 55% by weight monoester and 55% to 45% by weight diester.

[0055] Fatty acids may be used in preparing the above glycerol esters; they may also be used in preparing their metal salts, amides, and imidazolines, any of which may also be used as friction modifiers. The fatty acids may contain 6 to 24 carbon atoms, or 8 to 18 carbon atoms. A useful acid may be oleic acid.

[0056] The amides of fatty acids may be those prepared by condensation with ammonia or with primary or secondary amines such as diethylamine and diethanolamine. Fatty imidazolines may include the cyclic condensation product of an acid with a diamine or polyamine such as a polyethylenepolyamine. In one embodiment, the friction modifier may be the condensation product of a C₈ to C₂₄ fatty acid with a polyalkylene polyamine, for example, the product of isostearic acid with tetraethylenepentamine. The condensation products of carboxylic acids and polyalkyleneamines may be imidazolines or amides.

[0057] The fatty acid may also be present as its metal salt, e.g., a zinc salt. These zinc salts may be acidic, neutral, or basic (overbased). These salts may be prepared from the reaction of a zinc containing reagent with a carboxylic acid or salt thereof. A useful method of preparation of these salts is to react zinc oxide with a carboxylic acid. Useful carboxylic acids are those described hereinabove. Suitable carboxylic acids include those of the formula RCOOH where R is an aliphatic or alicyclic hydrocarbon radical. Among these are those wherein R is a fatty group, e.g., stearyl, oleyl, linoleyl, or palmityl. Also suitable are the zinc salts wherein zinc is present in a stoichiometric excess over the amount needed to prepare a neutral salt. Salts wherein the zinc is present from 1.1 to 1.8 times the stoichiometric amount, e.g., 1.3 to 1.6 times the stoichiometric amount of zinc, may be used. These zinc carboxylates are known in the art and are described in U.S. Pat. 3,367,869. Metal salts may also include calcium salts. Examples may include overbased calcium salts.

[0058] Metal salts of alkyl salicylates include calcium and other salts of long chain (e.g. C₁₂ to C₁₆) alkyl-substituted salicylic acids.

[0059] Amine salts of alkylphosphoric acids include salts of oleyl and other long chain esters of phosphoric acid, with amines such as tertiary-aliphatic primary amines, sold under the tradename Primene™.

[0060] Eighty-five percent phosphoric acid is a suitable material for addition to the fully-formulated compositions to increase frictional properties and can be included at a level of 0.01-0.3 weight percent based on the weight of the composition, such as 0.03 to 0.2 or to 0.1 percent.

[0061] The amount of friction modifier in an additive package, if it is present, may be 0.01 to 10 or 5 percent by weight of the lubricating composition, 0.1 to 2.5 percent by weight of the lubricating composition, such as 0.1 to 2.0, 0.2 to 1.75, 0.3 to 1.5 or 0.4 to 1 percent. When present in the finished lubricant, however, the amount of friction modifier may be present 0.5 to 1 percent or less than 0.2 percent or less than 0.1 percent by weight, for example, 0.01 to 0.1 percent. In some embodiments, the friction modifier may be present at 500 to 1500ppm (on a weight basis) of the finished lubricant. In some embodiments at least two friction modifiers may be present, wherein each one may be individually present at the concentrations listed above.

[0062] Accordingly, in the same or different embodiments, the industrial gear additive package may further comprise at least one organic friction modifier, for example imidazoline, oleylamine, and/or oleylamide.

Industrial Gear Lubricant

[0063] In some embodiments, an industrial gear lubricant is disclosed. The industrial gear lubricant may comprise, (a) a mineral base oil in an amount of at least 50 weight percent of the industrial gear lubricant; (b) the antifoam polymer composition as described above; and/or (c) the industrial gear additive package as described above.

[0064] Suitable mineral base oils may be defined as specified in the American Petroleum Institute (API) Base Oil Interchangeability Guidelines. The five base oil groups are as follows: Group I (sulfur content >0.03 wt %, and/or <90 wt % saturates, viscosity index 80 to less than 120); Group II (sulfur content <0.03 wt %, and >90 wt % saturates, viscosity index 80 to less than 120); and Group III (sulfur content <0.03 wt %, and >90 wt % saturates, viscosity index >120).

[0065] In some embodiments, a thickener may be used to increase the viscosity of the lubricant. Suitable thickeners include olefin copolymers, for example Lucant™ HC-2000L, HC-1100, HC-1000 and HC-600 from Mitsui.

[0066] The amount of mineral oil present is typically the balance remaining after subtracting from 100 wt% the sum of the amount of the compound of the invention and the other performance additives. In a fully formulated industrial gear lubricant, typically the oil of lubricating viscosity, including any diluent oil present in the composition, will be present in an amount of from 70 to 95 wt%, or from 80 or 85 to 93 wt%.

[0067] If the lubricating composition of the invention is in the form of a concentrate (which may then be combined with additional oil to form, in whole or in part, a finished lubricant), typically the mineral oil, including any diluent oil present in the composition, will be present in an amount of from 0.1 wt % to 40 wt % or 0.2 wt % to 35 wt % or 0.4 wt % to 30 wt % or 0.6 wt % to 25 wt % or 0.1 wt % to 15 wt % or 0.3 wt % to 6 wt %.

[0068] In other embodiments the overall industrial additive package may be present from 1 to 20, or from 1 to 10 wt % of the overall lubricant composition. However, it is noted that some additives, including viscosity modifying polymers, which may alternatively be considered as part of the base fluid, may be present in higher amounts including up to 30 wt %, 40 wt %, or even 50 wt % when considered separate from the base fluid. The additives may be used alone or as mixtures thereof. In some embodiments, the industrial gear additive package is present at 0.5 to 3 wt% (or 1 to 2.5 wt%, or 1.5 to 2.5 wt%), based on a total weight of the industrial gear lubricant.

[0069] In some embodiments, the compositions of the invention are lubricating compositions, wherein the antifoam polymer composition in an amount of at least 50 ppm, or at least 100 ppm, or from 50 ppm to 1500 ppm, or from about 50 to about 1000, or from 50 ppm to 800 ppm or 600 ppm of the overall composition on an oil free basis. In some embodiments, the first polymer may be present in the finished lubricant at 200 ppm to 600 ppm and the second polymer may be present at 200 to 400 ppm on a weight basis.

[0070] The balance of these lubricating compositions may be one or more additional additives as described below and a major amount of oil of lubricating viscosity (mineral oil) including any diluent oil or similar material carried into the composition from one or more of the components described herein. By major amount is meant greater than 50 wt % based on the composition.

[0071] In some embodiments, the industrial gear lubricant comprises the mineral base oil in an amount of at least 60 weight percent, or at least 75 weight percent, or at least 90 weight percent, based on a total weight of the industrial gear lubricant. Suitable mineral oils are not overly limited and may include at least one API Group I, Group II, and Group III oil, or any combination thereof. In some embodiments, the industrial gear additive package or industrial gear lubricant may contain less than 0.2 weight percent sulfated ash.

20 Additional Additives

[0072] In some embodiments, the industrial gear lubricant may comprise additives in addition to the ones described above. These additional additives may include dispersants, corrosion inhibitors, metal passivators, and demulsifiers. The additives may each be present in the range from 50 ppm, 75 ppm, 100 ppm or even 150 ppm up to 5 wt%, 4 wt%, 3 wt%, 2 wt% or even 1.5 wt%, or from 75 ppm to 0.5 wt%, from 100 ppm to 0.4 wt%, or from 150 ppm to 0.3 wt%, where the wt% values are with regards to the overall lubricant composition.

[0073] In some embodiments, the industrial lubricant may comprise one or more corrosion inhibitors, metal passivators, or metal deactivators. Metal deactivators are used to neutralize the catalytic effect of metal for promoting oxidation in the industrial gear lubricant. Suitable metal deactivators include but are not limited to triazoles, tolyltriazoles, a thiadiazole, or combinations thereof, as well as derivatives thereof. Examples include derivatives of benzotriazoles, benzimidazole, 2-alkyldithiobenzimidazoles, 2-alkyldithiobenzothiazoles, 2-(N,N'-dialkyldithio-carbamoyl)benzothiazoles, 2,5-

bis(alkyl-dithio)-1,3,4-thiadiazoles, 2,5-bis(N,N'-dialkyldithiocarbamoyl)-1,3,4-thiadiazoles, 2-alkyldithio-5-mercapto thiadiazoles or mixtures thereof. These additives may be used from 0.01 to 0.25 wt% in the overall composition. In some embodiments the metal deactivator is a hydrocarbyl substituted benzotriazole compound. The benzotriazole compounds with hydrocarbyl substitutions include at least one of the following ring positions 1- or 2- or 4- or 5- or 6- or 7- benzotriazoles. The hydrocarbyl groups contain about 1 to about 30, preferably about 1 to about 15, more preferably about 1 to about 7 carbon atoms, and most preferably the metal deactivator is 5-methylbenzotriazole used alone or mixtures thereof. The metal deactivators may be present in the range from 0.001 to 0.5, from 0.01 to 0.04 or from 0.015 to 0.03 wt% of the industrial gear lubricant. Metal deactivators may also be present in the composition from 0.002 or 0.004 to 0.02 wt%. The metal deactivator may be used alone or mixtures thereof.

[0074] The lubricant may also include nitrogen-containing dispersants, for example a hydrocarbyl substituted nitrogen-containing additive. Suitable hydrocarbyl substituted nitrogen-containing additives include ashless dispersants and polymeric dispersants. Ashless dispersants are so-named because, as supplied, they do not contain metal and thus do not normally contribute to sulfated ash when added to a lubricant. However, they may, of course, interact with ambient metals once they are added to a lubricant which includes metal-containing species. Ashless dispersants are characterized by a polar group attached to a relatively high molecular weight hydrocarbon chain. Examples of such materials include succinimide dispersants, Mannich dispersants, and borated derivatives thereof.

[0075] The lubricant may also include demulsifier. The demulsifier may include derivatives of propylene oxide, ethylene oxide, polyoxyalkylene alcohols, alkyl amines, amino alcohols, diamines or polyamines reacted sequentially with ethylene oxide or substituted ethylene oxides or mixtures thereof. Examples of a demulsifier include polyethylene glycols, polyethylene oxides, polypropylene oxides, (ethylene oxide-propylene oxide) polymers and mixtures thereof. The demulsifier may be a polyethers. The demulsifier may be present in the composition from 0.002 wt% to 0.2 wt%.

[0076] The amount of each chemical component described is presented exclusive of any solvent or diluent oil, which may be customarily present in the commercial material, that is, on an active chemical basis, unless otherwise indicated. However, unless otherwise indicated, each chemical or composition referred to herein should be interpreted as being a commercial grade material which may contain the isomers, by-products, derivatives,

and other such materials which are normally understood to be present in the commercial grade.

[0077] 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.

[0078] The invention herein is useful for reducing foam in industrial gear lubricants, which may be better understood with reference to the following examples.

EXAMPLES

[0079] Industrial Gear Additive Packages were prepared as shown in Table 1 below.

Table 1 – Industrial Gear Additive Packages

Functional Type	Chemistry Type	ADD1 (wt%)	ADD2 (wt%)	ADD3 (wt%)
Dispersant	Polyisobutenyl succinimide ¹	2.1	2.1	6.2
Extreme Pressure Agent	Sulfurized isobutylene	62.8	64.5	67.4
Antiwear	Oleyl phosphite	26.1	26.9	16.8
	Amine phosphate ²	2.4	2.4	2.5
Friction Modifier	Imidazoline	2.6	-	-
	Oleylamine	-	-	2.8
Other additives ³		4.0	4.1	4.3

1. Polyisobutenyl succinimide dispersant (includes 40 wt% oil; PIB 1000 M_n; TBN, 70 mg KOH/g)
2. Salt of 2-ethylhexylamine and iso-octylphosphoric acid
3. Other additives include corrosion inhibitors, metal passivators, and demulsifiers

[0080] The additive packages were then blended with a mineral oil and the disclosed antifoam polymer composition to make a finished industrial gear lubricant. The finished industrial gear lubricants were divided into two portions to test their antifoam performance.

[0081] One portion was filtered and tested for foaming tendency after filtration. The filtration test was completed using a modified FFT 7300 Siemens Filtration Test that was found to more accurately simulate filtration conditions observed in industrial gearboxes in the field.

For the modified Siemens Filtration Test, the filtration test rig comprised a heated tank equipped with a temperature sensor. The tank was fluidly connected to a circulating pump and a filter housing equipped with a filter having a pore size of 10 microns. The heated tank was then filled with the lubricant to be tested to at least 50% capacity (1.5 liters). The lubricant was then heated in the tank to 80 °C. The lubricant was maintained at 80°C and circulated (at about 1 L/min) through the filtration test rig using the circulation pump for 125 hours so that the lubricant passed through the 10-micron filter at least 5,000 times. A sample of the filtered lubricant was then obtained.

[0082] After filtration, the lubricants' defoam properties were tested by running Sequence II of the ASTM D892 Standard Test Method for Foaming Characteristics of Lubricating Oils. For the Sequence II test, a portion of the test fluid (180 mL) is transferred to a transparent 1000 mL graduated cylinder and heated to 93.5 °C. When the fluid has reached thermal equilibrium, air is blown through the sample at a rate of 94 mL/min for 5 minutes. After 5 minutes, the air source is turned off and the volume of foam (mL) is recorded immediately. The sample is then allowed to settle for 10 minutes, and the volume of foam (mL) is recorded again.

[0083] The other portion of the industrial gear lubricants was subjected to oxidation using the ASTM D2893 -Standard Test Methods of Oxidation Characteristics of Extreme Pressure Lubrication Oils, followed by D892 Seq II testing. For the D2893 oxidation, a 300 mL test sample was stirred at 121 °C for 312 hours while sparging the test sample with air. After oxidation, the lubricants' defoam properties were tested by running Sequence II of the ASTM D892 Standard Test Method for Foaming Characteristics of Lubricating Oils as described above.

[0084] The finished industrial gear lubricant compositions with additive packages ADD 1 and ADD 2 (including the concentration of phosphorus and sulfur calculated on a theoretical basis) and their Sequence II foam results are shown in Table 2 below.

Table 2 – Lubricating Compositions

	EX1	EX2	EX3	EX4	EX5	EX6
ISO Grade	150	150	150	150	150	150
Group I Base Oil	Balance to 100%					
ADD1	1.91	-	1.91	1.91	1.91	1.91
ADD2	-	1.86	-	-	-	-
First polymer ¹	0	0	0	0	0.04	0.04
Second polymer ²	0.020	0.020	0.06	0.12	0	0.02
Phosphorus (ppm)	330		300	310	305	310

Sulfur (ppm)	13175				12520	12520
D892 Seq II (mL) ³ Filt	700; 610	300; 0	480; 390	710; 670	500; 400	0; 0
D892 Seq II (mL) ³ Ox	350; 0	0; 0	0; 0	0; 0	10; 0	0; 0

1. Polymer of ethylacrylate (35.6 mol%), 2-ethylhexylacrylate (66.1 mol %), and vinyl acetate (10.2 mol %), includes 50 wt % oil
2. Polymer of ethylacrylate (28 mol%) and 2-ethylhexylacrylate (72 mol%), includes 69 wt% oil
- 5 3. The data includes the volume of foam (mL) that was recorded immediately after the air source was turned off and after settling for 10 minutes in "immediate;settled" format.

[0085] The finished industrial gear lubricant compositions with additive package ADD 3 (including the concentration of phosphorus and sulfur calculated on a theoretical basis) and their Sequence II foam results are shown in Table 3 below.

Table 3

	EX7	EX8	EX9	EX10
ISO Grade	150	150	150	150
Group I Base Oil	Balance to 100%		-	-
Group II Base Oil	-	-	Balance to 100%	
ADD3	1.78	1.78	1.78	1.78
First Polymer ¹	0	0.04	0	0.04
Second Polymer ²	0.02	0.02	0.02	0.02
Phosphorus (ppm)	210	200	200	200
Sulfur (ppm)	12640	12300	7200	7010
D892 Seq II (mL) Filtration ³	390;0	10;0	100;0	10;0
D892 Seq II (mL) Oxidation ³	330;0	0;0	0;0	0;0

1. Polymer of ethylacrylate (35.6 mol%), 2-ethylhexylacrylate (66.1 mol %), and vinyl acetate (10.2 mol %), includes 50 wt % oil
2. Polymer of ethylacrylate (28 mol%) and 2-ethylhexylacrylate (72 mol%), includes 69 wt% oil
- 15 3. The data includes the volume of foam (mL) that was recorded immediately after the air source was turned off and after settling for 10 minutes in "immediate;settled" format.

20 [0086] As can be seen in Tables 2 and 3 above, the combination of the more oil soluble antifoam with the oil insoluble antifoam has a synergistic effect in significantly reducing foam in the finished industrial gear lubricants. This synergistic effect can be observed at a combined treat rate of both antifoams of 0.06 wt% as shown in EX6, EX8, and EX10. The reduction in foam is significantly reduced, even when compared to industrial gear lubricants having the

same or greater treat rate with just the more oil soluble antifoam, in particular EX3 and EX4, or with just using the oil insoluble antifoam alone, as shown in EX5.

5 [0087] 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
10 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.

[0088] As used herein, the transitional term "comprising," which is synonymous with "including," "containing," or "characterized by," is inclusive or open-ended and does not exclude additional, un-recited elements or method steps. However, in each recitation of "comprising" herein, it is intended that the term also encompass, as alternative embodiments, the phrases "consisting essentially of" and "consisting of," where "consisting of" excludes any element or step not specified and "consisting essentially of" permits the inclusion of additional un-recited elements or steps that do not materially affect the basic and novel characteristics of the composition or method under consideration.
20

[0089] While certain representative embodiments and details have been shown for the purpose of illustrating the subject invention, it will be apparent to those skilled in this art that various changes and modifications can be made therein without departing from the scope of the subject invention. In this regard, the scope of the invention is to be limited only by the
25 following claims.

What is claimed is:

1. An antifoam polymer composition comprising at least two polymers, a first polymer and a second polymer, wherein:
 - a. the first polymer is prepared by polymerizing a first monomer composition comprising (i) at least one alkyl (meth)acrylate ester monomer and (ii) 2 to 20 mole percent of at least one vinyl acetate monomer, based on the total moles of the first monomer composition; and
 - b. the second polymer is prepared by polymerizing a second monomer composition comprising (i) at least one alkyl (meth)acrylate ester monomer.
2. The antifoam polymer composition of claim 1, wherein the first polymer is insoluble or substantially insoluble in mineral oil (or less soluble in mineral oil than the second polymer).
3. The antifoam polymer composition of claim 1 or 2, wherein the second polymer is more soluble in mineral oil than the first polymer.
4. The antifoam polymer composition as in any one of the above claims, wherein the first monomer composition comprises:
 - a. 20 to 48 mole percent of a C₁ to C₄ alkyl (meth)acrylate ester monomer;
 - b. 50 to 78 mole percent of a C₈ to C₁₆ alkyl (meth)acrylate ester monomer; and
 - c. 2 to 20 mole percent of a vinyl acetate monomer,wherein the mole percent is based on the total moles of the first monomer composition.
5. The antifoam polymer composition as in any one of the above claims, wherein the first monomer composition comprises 5 to 15 mole percent (or 8 to 12 mole percent) of the vinyl acetate monomer.
6. The antifoam polymer composition as in any one of the above claims, wherein the second monomer composition comprises:
 - a. 5 to 35 mole percent of C₁ to C₄ alkyl (meth)acrylate ester monomer; and
 - b. 65 to 95 mole percent of C₈ to C₁₆ alkyl (meth)acrylate ester monomer,wherein the mole percent is based on the total moles of the second monomer composition.
7. The antifoam polymer composition as in any one of the above claims, wherein the second polymer is prepared by polymerizing (i) at least one alkyl (meth)acrylate

ester monomer and (ii) less than 1 mole percent (for example 0 to less than 1 mole percent) of at least one vinyl acetate monomer, based on the total moles of the second monomer composition.

8. The antifoam polymer composition as in any one of the above claims, wherein the first monomer composition and/or second monomer composition comprises 20 to 40 mole percent of a C₁ to C₃ alkyl (meth)acrylate ester monomer or a C₁ to C₂ alkyl (meth)acrylate ester monomer, for example, ethyl acrylate or ethyl methacrylate.
9. The antifoam polymer composition as in any one of the above claims, wherein the C₈ to C₁₆ alkyl group of the (meth)acrylate ester monomer in the first monomer composition and/or the second monomer composition comprises a branched or linear aliphatic group.
10. The antifoam polymer composition as in any one of the above claims, wherein the C₈ to C₁₆ alkyl group of the (meth)acrylate ester monomer in the first monomer composition and/or the second monomer composition is 2-ethylhexyl acrylate or 2-ethylexy methacrylate.
11. The antifoam polymer composition as in any one of the above claims, wherein the first polymer is prepared from a first monomer composition comprising 30 to 40 mole percent (or 35.6 mol%) ethyl acrylate, 60 to 70 mole percent (or 66.1 mol%) 2-ethylhexyl acrylate, and 8 to 12 mole percent (or 10.2 mol%) vinyl acetate.
12. The antifoam polymer composition as in any one of the above claims, wherein the second polymer is prepared from a second monomer composition comprising 20 to 30 mole percent (or 28 mol%) ethyl acrylate and 70 to 80 mole percent (or 72 mol%) 2-ethylhexyl acrylate.
13. The antifoam polymer composition as in any one of the above claims, wherein the first polymer has a number average molecular weight M_n of 8,000 to 15,000 Daltons.
14. The antifoam polymer composition as in any one of the above claims, wherein the second polymer has a number average molecular weight M_n of 15,000 to 25,000 Daltons.
15. The antifoam polymer composition as in any one of the above claims, wherein the weight ratio of the first polymer to the second polymer ranges from 4:1 to 1:1 or 3:1 to 1:1.
16. An industrial gear additive package comprising:

- a. the antifoam polymer composition as in any one of claims 1 to 15; and
 - b. at least one sulfurized olefin compound.
17. The industrial gear additive package of claim 16, wherein the at least one sulfurized olefin is present at 0.01 to 3.0 wt% (or 1.2 wt%), based on a total weight of the industrial gear additive package.
 18. The industrial gear additive package of claim 16 or 17, wherein the at least one sulfurized olefin is at least one of a sulfurized isobutylene and/or di-isobutylene.
 19. The industrial gear additive package as in any one of claims 16 to 18, further comprising at least one phosphorus-containing anti-wear agent that is a phosphite, phosphonate, amine salted phosphate, phosphine, or any combination thereof, for example oleyl phosphite or a salt of 2-ethylhexylamine and isooctyl phosphoric acid.
 20. The industrial gear additive package as in any one of claims 16 to 19, further comprising at least one organic friction modifier, for example imidazoline, oleylamine, and/or oleylamide.
 21. An industrial gear lubricant comprising, (a) a mineral base oil in an amount of at least 50 weight percent of the industrial gear lubricant; (b) the antifoam polymer composition as in any one of claims 1 to 15; and/or (c) the industrial gear additive package as in any one of claims 16 to 20.
 22. The industrial gear lubricant of claim 21, wherein the industrial gear lubricant contains less than 0.2 weight percent sulfated ash.
 23. The industrial gear lubricant of claim 21 or 22, wherein the industrial gear lubricant contains less than 0.01 weight percent of a zinc dialkyl dithiophosphate compound.
 24. The industrial gear lubricant as in any one of claims 21 to 23, wherein the mineral base oil is present in an amount of at least 60 weight percent, or at least 75 weight percent, or at least 90 weight percent, based on a total weight of the industrial gear lubricant.
 25. The industrial gear lubricant as in any one of claims 21 to 24, wherein the mineral base oil comprises at least one API Group I, Group II, and Group III oils or any combination thereof.
 26. The industrial gear lubricant as in any one of claims 21 to 25, comprising the industrial gear additive package as in any one of claims 16 to 20, and wherein the

industrial gear additive package is present at 0.5 to 3 wt% (or 1 to 2.5 wt%, or 1.5 to 2.5 wt%), based on a total weight of the industrial gear lubricant.