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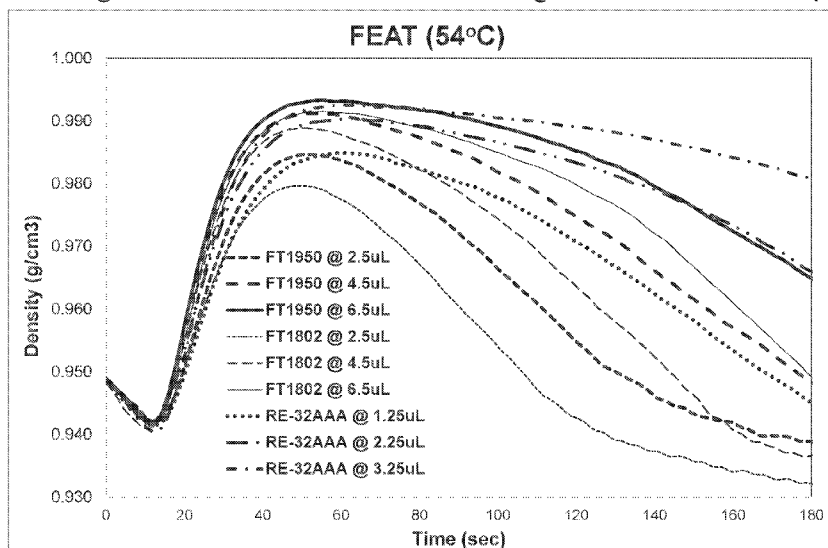


FIG. 1

(57) **Abstract:** This invention generally relates to high concentration water based defoaming compositions and methods of use thereof, as well as a method for preparing a high concentration water based defoaming composition. In particular, the disclosure provides defoaming compositions that are especially suitable in pulp and paper industry, as well as in any other processing industry when foaming is unwanted. The inventive high concentration water based defoaming compositions provide enhanced defoaming performance and display high stability.



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- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
- *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

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HIGH CONCENTRATION WATER BASED DEFOAMER

RELATED APPLICATIONS

[0001] The present application claims benefit of priority to US Provisional Application No.: 63/510,429, filed on June 27, 2023, and to Finnish Application Number 20236131 filed on October 12, 2023, the contents of both of which are incorporated by reference in their entireties.

FIELD OF THE INVENTION

[0002] The present invention relates to high concentration water based defoaming compositions and their use, as well as a method for preparing a high concentration water based defoaming composition. In particular, the disclosure provides defoaming compositions that are bio-based and especially suitable in pulp and paper industry, as well as in any other processing industry when foaming is unwanted.

BACKGROUND OF THE INVENTION

[0003] Defoamers are widely used in many industries including but not limited to pulp, paper, petroleum, textile and mining industries, water treatment, paints and coatings, food and beverage processing, and agriculture. For example, in pulp and paper mills, presence of entrained air can disturb sheet formation and drainage. Addition of a defoamer to a papermaking furnish or white water can alleviate these problems by significantly reducing or eliminating foam.

[0004] Defoamers have primarily two functions, these functions being defoaming and anti-foaming. Knockdown and persistence of defoamers provide important information about the performance of defoamers. Formation of foam in a solution decreases the density of the solution. Addition of a defoamer breaks the foam and the density of the solution increases again. The rate of the increase of the density due to the addition of a defoamer indicates how fast the defoamer acts, which is called the knockdown phase. The quicker the knockdown, the more efficient is the defoamer; however, the defoaming effect is temporary and with time, the defoamer begins to lose its efficacy and the density starts dropping again as the foam starts to regenerate. The longevity or persistence of a defoamer indicates how long the defoamer works. The longer the longevity or persistence of a defoamer, the more efficient is the defoamer. An ideal defoamer would have fast knockdown and long longevity or will persist over long time i.e., foam would disappear quickly upon addition of the defoamer and it would take long time for the foam to regenerate.

[0005] Defoamers are generally composed of a defoaming agent, such as, but not limited to ethylene bis(stearamides) (EBS) and/or hydrophobic silica, a carrier fluid, and other miscellaneous additives. Currently in the pulp and paper industry, silicone-based defoamers are preferred over other defoamers due to lower dosage requirement and cost-effective performance. However, these defoamers may be less compliant with environmental regulations or with Food and Drug Administration regulations and may not be suitable in food and beverage applications.

[0006] Furthermore, silicone based defoamers inherently present challenges and issues. These challenges are, in part, characterized by environmental and regulatory, carry over/deposit and cost

efficiency issues and are further related to complex manufacturing processes. However, in order to increase the longevity of silicone defoamers one would need to use larger amounts of these defoamers in the process. This would in turn result in additional inherent problems due to presence of higher amounts of hydrophobic components, such as silicone compounds, in the process. Hydrophobic components exhibit a tendency to stick on the fiber, and excess amount of hydrophobic components would necessitate additional washing steps later in the process. Therefore, the amount of hydrophobic components in the end fiber needs to be limited and excess amount of silicone defoamers cannot be a reliable solution to limited longevity of the defoamers.

[0007] Various industries have long sought for a substitution for silicone-based defoamers, in part, as a potential goal to overcome the challenges experienced thus far with silicone-based defoamers. Water-based defoamers are an alternative, however, they are limited in applicability. Water-based defoamers generally comprise a long chain fatty alcohol and a hydrocarbon oil or wax or both. These defoamers are formulated as an oil-in-water emulsion by means of an emulsification process. Existing water based defoamers, however, still present challenges including significant loss of defoaming efficiency and effectiveness at temperatures of 40 °C or higher, non-compliance with environmental or other regulations, or lack of storage stability, or combinations thereof.

[0008] Furthermore, for environmental and cost saving reasons, there is currently an unmet need in the market for highly concentrated, stable, and highly effective defoamers that are substantially bio-based. Transport, storage, and use of such defoamers provides economic, environmental, and regulatory advantages.

[0009] The present invention addresses these challenges and needs by providing novel and efficient defoamer compositions that are environmentally friendly, cost effective, simple to make and are stable, but at the same time are characterized by displaying longer longevity along with displaying a fast knockdown phase even at high temperatures. The inventive defoamers are highly effective, highly concentrated. It is an object of the invention to provide highly concentrated defoamers having higher total solids than commercially available competitors. It is a further objective of the present invention to provide defoamer compositions comprising over 50 wt % bio-based content based on total weight of solids.

SUMMARY OF THE INVENTION

[0010] This invention relates to high concentration water based defoaming compositions and their use, as well as a method for preparing a high concentration water based defoaming composition. In particular, the disclosure provides defoaming compositions that are especially suitable in pulp and paper industry, as well as in any other processing industry when foaming is unwanted. The inventive high concentration water based defoaming compositions provide enhanced defoaming performance and display high stability.

[0011] In one aspect, the present invention provides a defoamer composition comprising:

[0012] (a) an aqueous phase;

[0013] (b) an oil phase emulsified in the aqueous phase, the oil phase comprising: (i) at least one microcrystalline wax having a congealing point of at least about 70 °C; and (ii) at least one long chain

fatty alcohol having a carbon chain length of C₂₂ or more and a melting point of at least about 60 °C; and

[0014] (c) a combination of surfactants comprising at least one first anionic surfactant and at least one second anionic surfactant.

[0015] In some exemplary embodiments the defoamer composition further comprises:

[0016] (a) at least one emulsifier;

[0017] (b) at least one thickener;

[0018] (c) at least one preservative optionally comprising sodium nitrite, sodium metabisulfate, or a combination thereof;

[0019] (d) at least one biocide, or

[0020] (e) any combination of (a)-(d).

[0021] In some exemplary embodiments the defoamer composition further comprises a pH of greater than 7.0, 7.5-9, 7.5-8.5, or 7.5-8.

[0022] In some exemplary embodiments of the defoamer composition:

[0023] (a) said aqueous phase comprises 50%-65%, 52-60%, or 54-58% by weight, based on the weight of the defoamer composition;

[0024] (b) said at least one microcrystalline wax: (i) has a congealing point ranging from 70-80 °C, 71-79 °C, 72-78 °C, or 72-77 °C; and (ii) is present in said defoamer composition at an amount ranging from 5-25%, 10-20%, 12-18%, or 14-16% by weight, based on the weight of the defoamer composition;

[0025] (c) said at least one long chain fatty alcohol: (i) comprises at least 70% by weight of a carbon chain length ranging from C₂₂ to C₂₈, C₂₂ to C₂₆, or C₂₂ to C₂₄; (ii) has a melting point ranging from 60-70 °C, 62-68 °C, or 64-66 °C, or 62-65 °C; and (ii) is present in said defoamer composition at an amount ranging from 10-30%, 12-28%, 15-25%, or 20-22% by weight, based on the weight of the defoamer composition.

[0026] In some exemplary embodiments of the defoamer composition:

[0027] (a) said at least one emulsifier comprises one or more nonionic surfactants, including but not limited to, ethoxylated alcohols, including but not limited to, ethoxylated fatty alcohols comprising 1-4 ethyleneoxy groups, secondary alcohol ethoxylates, ethoxylated sorbitan esters, sorbitan esters, sorbitan monostearate, sorbitan esters of oleic acid, glycerol esters, including but not limited to, glycerol monostearate (GMS), and any combination thereof;

[0028] (b) said at least one first anionic surfactant comprises one or more alkyl ether sulfates, including but not limited to, ethoxylated and sulphated isotridecyl alcohols and 2-tridecoxyethyl sulfate; special soaps, including but not limited to, dodecyl poly(oxyethylene) ether sulfates; anionic long chain fatty acids; their corresponding alkali metal and alkaline earth metal salts; and any combination thereof;

[0029] (c) said at least one second anionic surfactant comprises one or more fatty alcohol ether sulfates, including but not limited to lauryl ether sulfate, and their alkali metal and alkaline earth metal salts, optionally combined with poly(ethylene oxide);

[0030] (d) said at least one thickener comprises one or more rheology modifiers, including but not limited to, alkali swellable emulsions, hydroxypropyl methylcellulose (HPMC), one or more bio-based hydrocolloids, one or more bio-based gums, including but not limited to, pre-hydrated cellulose gums, xanthan gums, or a mixture thereof; or

[0031] (e) any combination of (a)-(d).

[0032] In some exemplary embodiments said defoamer composition comprises one, two, three, four, or all of the following:

[0033] (a) said at least one emulsifier at an amount ranging from 0.5-10%, 1-5%, or 2-4% by weight, based on the weight of the defoamer composition;

[0034] (b) said at least one anionic surfactant at an amount ranging from 0.5-10%, 2-8%, or 3-5% by weight, based on the weight of the defoamer composition;

[0035] (c) said at least one thickener at an amount ranging from 0.1-1%, 0.1-0.5%, or 0.1-0.3% by weight, based on the weight of the defoamer composition;

[0036] (d) said at least one biocide at an amount ranging from 0.1-1%, 0.1-0.5%, or 0.1-0.3% by weight, based on the weight of the defoamer composition; and

[0037] (e) said at least one preservative at an amount ranging from 0.1-2%, 0.1-1%, or 0.2-0.6%, by weight, based on the weight of the defoamer composition.

[0038] In some exemplary embodiments the defoamer composition:

[0039] (a) comprises an emulsion prepared by phase inversion emulsification (PIE);

[0040] (b) does not contain oil, silicone fluid, silica, or ethylene bis(stearamide) (EBS);

[0041] (c) comprises a total solids content ranging from 30-50 %, 35-45 %, or 40-45 % by weight, based on the weight of the defoamer composition;

[0042] (d) comprises a bio-based solids content ranging from 50-70 %, 50-60 %, or 55-60 % by weight, based on the weight of said total solids content;

[0043] (e) exhibits a viscosity ranging from about 400 cp, 300-450 cP, 350-450, or 390-410 cP, determined using a Brookfield viscometer RVT115-Model RVT with a No 3 spindle at 50 rpm and room temperature; or

[0044] (f) any combination of (a)-(e).

[0045] In some exemplary embodiments the defoamer composition:

[0046] (a) performs as a defoamer at a defoaming temperature of at least 40 °C, 40-75 °C, 40-65 °C, or 40-55 °C 40-65 °C, or 40-55 °C; and/or

[0047] (b) exhibits a viscosity of <1200 cP when stored for up to 14 days at a temperature of about 40 °C; a viscosity of <450 cP when stored for up to 14 days at a temperature of about 23 °C, and/or a viscosity <450 cP when stored for up to 14 days at a temperature of about 5 °C.

[0048] In another aspect, the present invention provides a method for preparing a defoamer by phase inversion emulsion (PIE), the method comprising:

[0049] (a) heating in a first reactor a mixture of (i) at least one microcrystalline wax; (ii) at least one long chain fatty alcohol, and (iii) at least one emulsifier to a first temperature sufficient to liquify all solids, thereby forming an oil phase,

[0050] wherein said at least one microcrystalline wax has a congealing point of at least about 70 °C and said at least one long chain fatty alcohol has a carbon chain length of C22 or more and a melting point of at least about 60 °C;

[0051] (b) separately heating water to said first temperature, thereby forming an aqueous phase;

[0052] (c) slowly adding a portion of said aqueous phase into said oil phase while stirring at said first temperature, wherein said portion comprises 1-10%, 2-8% or 3-6% by weight of said aqueous phase;

[0053] (d) adding a remainder of said aqueous phase into said oil phase while stirring at said first temperature;

[0054] (e) adding at least one first anionic surfactant while stirring at said first temperature;

[0055] (f) homogenizing to form an oil in water (O/W) emulsion comprising said oil phase emulsified into said aqueous phase;

[0056] (g) adding to said O/W emulsion at least one thickener;

[0057] (h) cooling said O/W emulsion to a final temperature of 15-25 °C; and

[0058] (i) adding at least one second anionic surfactant and mixing to form said defoamer;

[0059] wherein steps (a)-(g) are performed successively.

[0060] In some exemplary embodiments of the method

[0061] (a) said first temperature ranges from 80-98 °C, 80-95 °C, or 85-95 °C;

[0062] (b) said (i) at least one microcrystalline wax; (ii) at least one long chain fatty alcohol, and (iii) at least one emulsifier are added (i)-(iii) successively;

[0063] (c) after step (c), stirring for 10-60 min, 10-40 min, or 10-30 min;

[0064] (d) after step (d), stirring for 30-90 min, 30-80 min, or 30-60 min; and

[0065] (e) homogenization step (f) is performed at 6000-9000 rpm, 6200-6800 rpm, or 6500-8500 rpm.

[0066] In some exemplary embodiments the method further comprises:

[0067] (a) after cooling, adding to said emulsion at least one preservative optionally comprising sodium nitrite, sodium metabisulfate, or a combination thereof, (ii) at least one biocide, or (iii) any combination of (i)-(ii); and

[0068] (b) adjusting the pH of said aqueous phase, said emulsion, and/or said defoamer to >7.0, 7.5-9, 7.5-8.5, or 7.5-8.

[0069] In some exemplary embodiments of the method:

[0070] (a) said aqueous phase comprises 50%-65%, 52-60%, or 54-58% by weight of said defoamer;

[0071] (b) said aqueous phase and said oil phase are present in a ratio of aqueous phase to oil phase ranging from 1:1 to 1.6:1, 1.1:1 to 1.5:1, 1.2:1 to 1.5:1; or 1.3:1 to 1.5:1;

[0072] (c) said at least one microcrystalline wax: (i) has a congealing point ranging from 70-80 °C, 71-79 °C, 72-78 °C, or 72-77 °C; and (ii) is present in said defoamer composition at an amount ranging from 5-25%, 10-20%, 12-18%, or 14-16% by weight, based on the weight of the defoamer composition;

[0073] (d) said at least one long chain fatty alcohol: (i) comprises at least 70% by weight of a carbon chain length ranging from C₂₂ to C₂₈, C₂₂ to C₂₆, or C₂₂ to C₂₄; (ii) has a melting point ranging from 60-70 °C, 61-69 °C, 61-68 °C, or 62-68 °C; and (ii) is present in said defoamer composition at an amount ranging from 10-30%, 12-28%, 15-25%, or 20-22% by weight, based on the weight of the defoamer composition;

[0074] (e) said at least one emulsifier comprises one or more nonionic surfactants, including but not limited to, ethoxylated alcohols, including but not limited to, ethoxylated fatty alcohols comprising 1-4 ethyleneoxy groups, secondary alcohol ethoxylates, ethoxylated sorbitan esters, sorbitan esters, sorbitan monostearate, sorbitan esters of oleic acid, glycerol esters, including but not limited to, glycerol monostearate (GMS), and any combination thereof;

[0075] (f) said at least one first anionic surfactant comprises one or more alkyl ether sulfates, including but not limited to, ethoxylated and sulphated isotridecyl alcohols and 2-tridecoxyethyl sulfate; special soaps, including but not limited to, dodecyl poly(oxyethylene) ether sulfates; anionic long chain fatty acids; their corresponding alkali metal and alkaline earth metal salts; and any combination thereof;

[0076] (g) said at least one second anionic surfactant comprises one or more fatty alcohol ether sulfates, including but not limited to lauryl ether sulfate, and their alkali metal and alkaline earth metal salts, optionally combined with poly(ethylene oxide);

[0077] (h) said at least one thickener comprises one or more rheology modifiers, including but not limited to, alkali swellable emulsions, hydroxypropyl methylcellulose (HPMC), one or more bio-based hydrocolloids, one or more bio-based gums, including but not limited to, pre-hydrated cellulose gums, xanthan gums, or a mixture thereof; or

[0078] (i) any combination of (a)-(h).

[0079] In some exemplary embodiments of the method:

[0080] (a) said at least one emulsifier is comprised in an amount ranging from 0.5-10%, 1-5%, or 2-4% by weight, based on the weight of the defoamer composition;

[0081] (b) said at least one anionic surfactant is comprised in an amount ranging from 0.5-10%, 2-8%, or 3-5% by weight, based on the weight of the defoamer composition;

[0082] (c) said at least one thickener is comprised in an amount ranging from 0.1-1%, 0.1-0.5%, or 0.1-0.3% by weight, based on the weight of the defoamer composition;

[0083] (d) said at least one biocide is comprised in an amount ranging from 0.1-1%, 0.1-0.5%, or 0.1-0.3% by weight, based on the weight of the defoamer composition;

[0084] (e) said at least one preservative is comprised in an amount ranging from 0.1-2%, 0.1-1%, or 0.2-0.6%, by weight, based on the weight of the defoamer composition; or

[0085] (f) any combination of (a)-(e).

[0086] In some exemplary embodiments of the method said defoamer:

[0087] (a) comprises a total solids content ranging from 30-50 %, 35-45 %, or 40-45 % by weight, based on the weight of the defoamer composition;

[0088] (b) comprises a bio-based solids content ranging from 50-70 %, 50-60 %, or 55-60 % by weight, based on the weight of said total solids content;

[0089] (c) exhibits a viscosity ranging from about 400 cP, 300-450 cP, 350-450, or 390-410 cP, determined using a Brookfield viscometer RVT115-Model RVT with a No 3 spindle at 50 rpm and room temperature;

[0090] (d) exhibits a viscosity <1200 cP when stored for up to 14 days at a temperature of about 40 °C; a viscosity of <450 cP when stored for up to 14 days at a temperature of about 23 °C, and/or a viscosity <450 cP when stored for up to 14 days at a temperature of about 5 °C;

[0091] (e) performs as a defoamer at a defoaming temperature of at least 40 °C, 40-65 °C, or 40-55 °C; or

[0092] (f) any combination of (a)-(e).

[0093] In another aspect, the present invention provides a method of defoaming in an industrial process stream comprising the step of adding to the industrial process stream a defoamer composition according to the foregoing optionally obtainable by a method according to the foregoing, wherein:

[0094] (a) said defoamer composition is added to said industrial process stream in an amount effective to defoam or prevent foaming in the industrial process stream;

[0095] (b) said defoamer composition is added to said industrial process stream at a temperature of at least 40 °C, 40-75 °C, 40-65 °C, or 40-55 °C; and

[0096] (c) said industrial process stream comprises any process stream related to industries, including but not limited to, the pulp and paper industry, the oil and gas industry, water treatment, paints and coatings, food and beverage processing, the mining industry, textiles, or agriculture;

[0097] wherein said method of defoaming results in an enhanced defoaming performance compared to the same method of defoaming performed using a comparative defoamer composition which is the same as said defoamer composition with the exception that said comparative defoamer composition comprises:

[0098] (i) a microcrystalline wax having a higher congealing point;

[0099] (ii) a lower % by weight of said microcrystalline wax;

[0100] (iii) a lower % by weight of said long chain fatty alcohol; and/or

[0101] (iv) a lower % by weight total solids,

[0102] and further wherein said enhanced defoaming performance is determined by Foam and Entrained Air Testing (FEAT).

BRIEF DESCRIPTION OF THE DRAWINGS

[0103] The invention will be described in more detail with reference to appended drawings, described in detail below.

[0104] **FIG 1** provides an exemplary line graph of defoamer performance in a Foam and Entrained Air Test (FEAT) according to **Example 2**.

[0105] **FIG 2** provides an exemplary bar graph of defoamer performance determined by Area Under Curve (AUC) from FEAT line graphs over 30 sec and 3 min after defoamer injection according to **Example 2**.

[0106] **FIG 3** provides an exemplary line graph showing dose dependence of defoamer performance determined by Area Under Curve (AUC) from FEAT line graphs over 3 min after defoamer injection according to **Example 2**.

[0107] **FIG 4** provides an exemplary line graph of defoamer performance in a Foam and Entrained Air Test (FEAT) according to **Example 3**.

[0108] **FIG 5** provides an exemplary bar graph of defoamer performance determined by Area Under Curve (AUC) from FEAT line graphs over 30 sec and 3 min after defoamer injection according to **Example 3**.

[0109] **FIG 6** provides an exemplary line graph showing dose dependence of defoamer performance determined by Area Under Curve (AUC) from FEAT line graphs over 3 min after defoamer injection according to **Example 3**.

[0110] **FIG 7** provides an exemplary graph of viscosity over time while storing a high solids defoamer at 5 °C, ~23 °C, and 40 °C as an indicator of stability according to **Example 4**.

DETAILED DESCRIPTION OF THE INVENTION

[0111] Before describing the invention, the following definitions are provided. Unless stated otherwise all terms are to be construed as they would be by a person skilled in the art.

DEFINITIONS

[0112] All technical and scientific terms used herein have the same meaning as commonly understood to one of ordinary skill in the art to which this invention belongs unless clearly indicated otherwise.

[0113] As used herein the singular forms “a”, “an”, and “the” include plural referents unless the context clearly dictates otherwise. The singular forms “a,” “an,” and “the” may mean “one” but also

include plural referents such as “one or more” and “at least one” unless the context clearly dictates otherwise.

[0114] As used herein, the term “or” in the claims is used to mean “and/or” unless explicitly indicated to refer to alternatives only or the alternatives are mutually exclusive, although the disclosure supports a definition that refers to only alternatives and “and/or.”

[0115] As used herein, the term “about” means plus or minus 10% of the numerical value of the number with which it is being used.

[0116] As used herein the term “or combinations thereof” as used herein refers to all permutations and combinations of the listed items preceding the term unless stated otherwise.

[0117] Industrial Process Streams

[0118] As used herein, the term “paper” includes products comprising a cellulosic or lignocellulosic sheet material including paper sheet, paperboard, and the like.

[0119] As used herein, the terms “papermaking process” and “papermaking application” generally refers to any process in which any form of paper and/or paperboard product may be produced. For example, such processes include making paper products from pulp, such as methods comprising forming an aqueous cellulosic papermaking furnish, draining the furnish to form a sheet, and drying the sheet. The steps of forming the papermaking furnish, draining and drying may be carried out in any conventional manner generally known in the art.

[0120] As used herein, the term “white water” generally refers to process water within a paper machine system, especially referring to water that is drained from paper as the sheet is being formed.

[0121] As used herein, the term “process stream” or “industrial process stream” generally refers to any aqueous fluids, solutions, slurries, or dispersions produced during any type of industrial process, for example, processes relating to pulp and paper industry, oil or gas extraction or recovery including recovery, extraction, refining, or waste treatment, waste treatment, water treatment, paints and coatings, food and beverage processing, mining industries, textiles, agriculture, or any portion thereof. An exemplary embodiment of a process stream includes a white water from production of a paper or board product.

[0122] As used herein, the term “aqueous solution” or “solution” refers to a mixture of water and a water-soluble solute or solutes which are completely dissolved with little to no residual undissolved polymer gel. The solution may be homogenous.

[0123] As used herein, the term “aqueous suspension”, “aqueous slurry”, or “slurry” generally refer to a heterogeneous mixture of a fluid that contains insoluble or sparingly soluble solid particles sufficiently large for sedimentation. Suspensions and slurries of the present invention may also comprise some amount of solid particles, often termed colloidal particles, which do not completely settle or take a long time to settle completely.

[0124] As used herein, the term “foam” refers to entrained air, trapped undissolved gas bubbles, or air pockets in a liquid or solid composition.

[0125] Defoaming Composition, Preparation and Use Thereof

[0126] As used herein, the term “defoamer” or “defoaming agent” refers to a chemical additive that “breaks” (i.e., reduces or eliminates) foam in an industrial process stream. As used herein, the term “antifoamer” or “antifoaming agent” refers to a chemical additive that prevents the formation of foam in an industrial process stream. The terms defoamer and antifoamer are often used interchangeably. Strictly speaking, “defoamers” eliminate existing foam and “antifoamers” prevent the formation of further foam. Formation of foam in a solution decreases the density of the solution. Addition of a defoamer breaks the existing foam, allowing the density of the solution to increase again. The rate of the increase of the density due to the addition of a defoamer indicates how fast the defoamer acts, which is called the knockdown phase. The quicker the knockdown, the more efficient is the defoamer. Chemical defoamers function by disrupting and breaking surfactant-stabilized bubble walls to release trapped air from a foam. Commonly used defoaming/antifoaming agents include insoluble oils, polydimethylsiloxanes and other silicones, certain alcohols, stearates and glycols. These additive are used to prevent formation of foam or to break a foam already formed. Exemplary high concentration water based defoamers of the present invention exhibit defoaming and antifoaming properties simultaneously.

[0127] As used herein, the phase “defoamer performance” or “efficacy” refers to the relative defoaming response (i.e., % foam elimination) of a defoamer at a given dosage. Relative defoamer performance may be determined by testing several defoamers at a given by dosage in the same foamed process stream under the same conditions. Formation of foam in a solution decreases the density of the solution. Addition of a defoamer breaks the existing foam, allowing the density of the solution to increase again. Defoamer performance may be determined by measuring the density of a foamed solution after defoaming agent is introduced. For aqueous solutions having a density of 1.0 g/mL in the absence of foam, the closer the density after defoamer addition is to 1.0 g/mL, the better the defoamer performance. The Foam and Entrained Air Tester (FEAT) is a testing apparatus used to determine the efficacy of defoaming agents in a laboratory setting. The apparatus measures the change in the density as a function of time of the filtrate as the defoaming agent is introduced. The measure of the change in density of a filtrate is a direct measurement of the change in entrained air. In pulp and paper mills, presence of entrained air can disturb sheet formation and drainage.

[0128] As used herein, the term “emulsion” refers to multiphasic fluid systems in which liquid droplets are dispersed in another immiscible liquid. An emulsion is a mixture of two or more liquids that are normally immiscible (unmixable or unblendable) exhibiting liquid-liquid phase separation. Emulsions comprise two phases, “dispersed/internal phase” and “continuous/external phase”, which are liquids. In an emulsion, one liquid (the dispersed phase) is suspended or dispersed throughout the other liquid (the continuous phase) in separate droplets. Typical main components of an emulsion are the two liquid phases, typically oil and water, and an emulsifier, which stabilizes the interface between the two liquid phases. Emulsifiers can be a variety of molecules, such as polymers, amphiphilic surfactants, and proteins, and they can also be colloidal particles.

[0129] When naming emulsion type (e.g., “O/W and W/O emulsions), the first letter refers to the discontinuous phase and the second letter is the dispersed phase. In the absence of an O/W or W/O qualifier, the term “emulsion” generally refers to an O/W emulsion.

[0130] Exemplary immiscible liquid phases include oil and water, water and silicone, or water and organic liquids. Exemplary immiscible phases of the present invention comprise an “aqueous phase” comprising water and an “oil phase” comprising at least one microcrystalline wax having a congealing point of at least about 70 °C; and (ii) at least one long chain fatty alcohol having a carbon chain length of C22 or more and a melting point of at least about 60 °C. Surfactants, emulsifiers, and thickeners may be added to slow the process of separation of the immiscible phases and to adjust the rheology of the emulsion. Additional water soluble or organic soluble additives, such as rosin size, fortified rosin, biocides, and chemical preservatives may also be added as needed to adjust the properties of the emulsion.

[0131] As used herein, the terms “O/W emulsion”, “oil in water emulsion”, or “oil phase in water emulsion”, refer to an emulsion wherein the discontinuous phase (i.e., droplets) comprises an “oil phase” and the continuous phase comprises an “aqueous phase” (e.g., water). As used herein, the “oil phase” comprises all organic soluble components of a mixture.

[0132] As used herein, the term “W/O emulsion” or “water in oil emulsion”, or “invert emulsion”, refer to an emulsion wherein the discontinuous phase (i.e., droplets) comprises an “aqueous phase” (e.g., water) and the continuous phase comprises an “oil phase”.

[0133] As used herein, the term “phase inversion emulsification” or “PIE” refers to the process of interconversion between two types of simple emulsions: water-in-oil (W/O) and oil-in-water (O/W) emulsions. Phase inversion can be induced by shifting the emulsifier affinity from one phase to the other, which is called “transitional” phase inversion. It can also be triggered by a change in the water-to-oil ratio of the emulsion, which leads to a process known as “catastrophic” phase inversion. The critical volume ratio that induces phase inversion is called the emulsion inversion point, which depends upon the system formulation as well as the conditions of emulsification, such as the stirring intensity, the location of the impeller, and the rate of addition of the dispersed phase.

[0134] Exemplary PIE methods of the present invention comprise formation of a W/O emulsion followed by addition of water to increase the water-to-oil ratio of the emulsion, followed by catastrophic inversion to an O/W emulsion by the following:

[0135] (a) heating in a first reactor a mixture of (i) at least one microcrystalline wax; (ii) at least one long chain fatty alcohol, and (iii) at least one emulsifier to a first temperature sufficient to liquify all solids, thereby forming an oil phase, wherein said at least one microcrystalline wax has a congealing point of at least about 70 °C and said at least one long chain fatty alcohol has a carbon chain length of C22 or more and a melting point of at least about 60 °C;

[0136] (b) separately heating water to said first temperature, thereby forming an aqueous phase;

[0137] (c) slowly adding a portion of said aqueous phase into said oil phase while stirring at said first temperature, wherein said portion comprises 1-10%, 2-8% or 3-6% by weight of said aqueous phase;

[0138] (d) adding a remainder of said aqueous phase into said oil phase while stirring at said first temperature;

[0139] (e) adding at least one first anionic surfactant while stirring at said first temperature;

[0140] (f) homogenizing to form an oil in water (O/W) emulsion comprising said oil phase emulsified into said aqueous phase; and

[0141] (g) adding at least one second anionic surfactant and mixing to form said defoamer;

[0142] wherein steps (a)-(g) are performed successively.

[0143] As used herein, the term “bio-based” refers to any material that is (i) directly extracted from the biomass (natural materials) such as polysaccharides, proteins, and lipids, (ii) that is synthesized from the bio-derived materials, (iii) that is a biodegradable material, or (iv) that originates from sustainable and/or renewable resources. Such materials include monomers, polymers, lipids, or oils that are directly produced and extracted from microorganisms and then subjected to further processing techniques, such as hydrogenation, hydrolysis, esterification, fermentation, or enzymatic reactions.

[0144] Exemplary bio based materials of the present invention include long chain fatty alcohols, emulsifiers (e.g., glyceryl monostearate), thickeners (e.g., Ticaloid 5415 Gum), and preservatives (e.g., sodium nitrite, NaNO_2).

[0145] As used herein the term “substantially bio-based defoamer” means that the “defoamer composition” defined as above is substantially or predominantly comprised of “bio-based” materials, e.g., the composition comprises at least 50, 60, 70, 80, 90, or 95% or more weight percent of bio-based materials as a percent of total solids.

[0146] As used herein, the terms, “total solids” refer the total amount by weight of solids contained in water based defoamer compositions.

[0147] As used herein, the term “microcrystalline wax” refers to a type of hydrocarbon wax produced by de-oiling petrolatum, as part of the petroleum refining process, contains a relatively higher percentage of isoparaffinic (branched) hydrocarbons and naphthenic hydrocarbons compared to paraffin wax, and is characterized by the fineness of its crystals. Microcrystalline waxes generally consist of hydrocarbon waxes that predominantly comprise saturated acyclic and cyclic hydrocarbons or contains such structures as a major portion of the molecules therein. Naphthenic hydrocarbons are a type of organic compound of carbon and hydrogen that contains one or more saturated cyclic (ring) structures, or contains such structures as a major portion of the molecule. Other Naphthenic compounds are sometimes called naphthenes, cycloparaffins, or hydrogenated benzenes.

[0148] Exemplary microcrystalline wax of the present invention: (i) has a congealing point ranging from 70-80 °C, 71-79 °C, 72-78 °C, or 72-77 °C; and (ii) is present in said defoamer composition at an amount ranging from 5-25%, 10-20%, 12-18%, or 14-16% by weight, based on the weight of the defoamer composition

[0149] As used herein, the term “long chain fatty alcohol” or “high molecular weight fatty alcohol” refers to fatty alcohols (or long-chain alcohols) which are usually high-molecular-weight, having as many as 22–30 carbons, derived from natural fats and oils. The precise chain length varies with the source and are typically straight-chain primary alcohols, but may also be branched. Some commercially important fatty alcohols are lauryl, stearyl, and oleyl alcohols. They are colorless oily liquids (for smaller carbon numbers) or waxy solids, although impure samples may appear yellow.

Fatty alcohols usually have an even number of carbon atoms and a single alcohol group (–OH) attached to the terminal carbon. Some are unsaturated and some are branched. They are widely used in industry. As with fatty acids, they are often referred to generically by the number of carbon atoms in the molecule, such as "a C22 alcohol", that is an alcohol having 22 carbons, for example 1-docosanol or behenyl alcohol. Long chain fatty alcohols may be a single molecule or a mixture of fatty alcohols with various chain lengths. They may be linear or branched, saturated or unsaturated, or a combination thereof and may also contain mixtures of alcohols with ethers, carboxylic acids, and esters as minor components.

[0150] As used herein, the term "rheology modifier" refers to any substance that can alter the rheological properties (e.g., resistance to deformation and flow) of a material. They are added to formulations to increase or decrease viscosity and to control a finished the properties and characteristics of a liquid composition in a desired manner.

[0151] As used herein, the term "thickener" refers to a rheology modifier which increases viscosity of a liquid, solution, suspension, or emulsion

[0152] As used herein, "surfactant" refers to a chemical which tends to act as emulsifiers by reducing the surface tension or interfacial tension between two liquids. Surfactants tend to be amphiphilic and comprise a hydrophilic water-soluble head and a hydrophobic organic-soluble tail. In oil water mixtures, surfactants migrate to the interface between oil and water wherein organic-soluble tail tails project into the organic oil phase, while the water-soluble ends remain in contact with the water phase, thereby stabilizing emulsions. When there are a sufficient amount of surfactant molecules present in a solution they combine together to form structures called micelles. "Nonionic surfactants" have a neutral hydrophilic end. "Anionic surfactants" bear a negative charge at the hydrophilic end.

[0153] As used herein, "emulsifier" refers to a subset of surfactants, which stabilize emulsions by reducing the oil-water interface tension. Emulsifiers that are more soluble in water (and, conversely, less soluble in oil) will generally form oil-in-water emulsions, while emulsifiers that are more soluble in oil will form water-in-oil emulsions. Exemplary emulsifiers include, but are not limited to, sorbitan esters, in particular sorbitan monoesters with C12-C18-groups such as sorbitan monolaurate, sorbitan monopalmitate, sorbitan monostearate, sorbitan monooleate, sorbitan esters with more than one ester group such as sorbitan tristearate, sorbitan trioleate, ethoxylated fatty alcohols with 1 to 4 ethyleneoxy groups, e.g. polyoxyethylene (4) dodecylether ether, polyoxyethylene (2) hexadecyl ether, or polyoxyethylene (2) oleyl ether. Other exemplary non-limiting surfactants include the sorbitan esters, phthalic esters, fatty acid glycerides, glycerine esters, as well as the ethoxylated versions of the above. Examples of such compounds include sorbitan monooleate, the reaction product of oleic acid with isopropanolamide, hexadecyl sodium phthalate, decyl sodium phthalate, sorbitan stearate, ricinoleic acid, hydrogenated ricinoleic acid, glyceride monoester of lauric acid, glyceride monoester of stearic acid, glycerol diester of oleic acid, glycerol triester of 12-hydroxystearic acid, glycerol triester of ricinoleic acid, and the ethoxylated versions thereof containing 1 to 10 moles of ethylene oxide per mole of the basic emulsifier. Examples of emulsifying surfactants also include modified polyester surfactants, anhydride substituted ethylene copolymers, N,N-dialkanol substituted fatty amides, and tallow amine ethoxylates.

[0154] Exemplary emulsifiers of the present invention may comprise, one or more “nonionic surfactants”, anionic surfactants, or a combination thereof. Exemplary “nonionic surfactants may include, among others, ethoxylated alcohols, including but not limited to, TERGITOL™ 15-S-40, ethoxylated sorbitan esters, sorbitan esters, glycerol esters, including but not limited to, glycerol monostearate (GMS), and any combination thereof, and

[0155] In exemplary embodiments “anionic surfactants” may comprise alkyl ether sulfates, including but not limited to, ethoxylated and sulphated isotridecyl alcohols and 2-tridecoxyethyl sulfate; special soaps, including but not limited to, dodecyl poly(oxyethylene) ether sulfates; anionic long chain fatty acids; their corresponding alkali metal and alkaline earth metal salts; fatty alcohol ether sulfates, including but not limited to lauryl ether sulfate, and their alkali metal and alkaline earth metal salts, optionally combined with poly(ethylene oxide); or any combination thereof.

[0156] As used herein, the term “biocide” refers to an antimicrobial agent or chemical substance that can deter, render harmless, or exert a controlling effect on any harmful organism. Examples of non-oxidizing biocides useful in the compositions of the present invention, particularly for use in the pulp and paper making processes, include, for instance, 2-bromo-2-nitropropane-1,3-diol, 5-chloro-2-methyl-4-iso- thiazolin-3-one, DBNPA, n-octyl-isothiazolin-3-one, MBT, quaternary ammonium compounds, THPS and glutaraldehyde. In an embodiment, the biocide is selected from the group consisting of glutaraldehyde, 2,2-dibromo-3-nitrilo-propionamide (DBNPA), 2-bromo-2-nitropropane-1,3-diol (Bronopol), 5-chloro-2-methy 1-4-isothiazolin-3-one (CMIT), n-alkyl dimethyl benzyl ammonium chloride, dide-cyl dimethyl ammonium chloride (DDAC), alkenyl dim-ethylethyl ammonium chloride, tetrakis hydroxymethyl phosphonium sulfate (THPS). The biocide is usually present in the emulsion, if at all, in an amount of from about 0.05% to about 1.0%, by weight of the emulsion, or about 0.1% to about 0.5%, by weight of the emulsion.

[0157] As used herein, the term “preservative” refers to inorganic compounds, including but not limited to sodium nitrite, sodium metabisulfate, or a combination thereof ,which act as an antimicrobial agent.

[0158] Units

[0159] As used herein, the term “ppm” refers to parts per million on the basis of milligrams of solute per liter of aqueous solution or slurry (e.g., mg/L).

[0160] As used herein, the phrases “% by weight” or “% by wt.” denotes pounds of dry mass of additive per dry mass of solids in the formulation, solution, or slurry, multiplied by 100%.

DESCRIPTION OF THE INVENTION

[0161] Defoamers are chemical additives widely used in pulping and paper industry. In addition to the pulp and paper industry, defoamers are also use in the Oil and Gas industry, water treatment, paints and coatings, food and beverage processing, the mining industry, textiles, agriculture.

[0162] Typical water based defoamers are generally composed of a high molecular weight fatty alcohol as the main active ingredient, a hydrocarbon oil (mineral oil/ white oil), and/or different waxes. These defoamers are formulated as oil-in-water (O/W) emulsions by means of an emulsification process. The existing water based defoamers present challenges relating to (a)

antifoaming /defoaming efficiency, particularly at high temperatures; (b) concentration; (c) cost efficiency; (d) environmental and regulatory issues; and (d) shelf-life.

[0163] The present invention has been made in view of the above circumstances. Defoamers of the present invention have two functions – both defoaming and antifoaming. These high concentration water based defoamer (> 40% total solids) display excellent antifoaming/defoaming performance (over double the performance of comparative defoamers) at high temperatures (>50 °C). The defoamer is prepared by using a high molecular weight fatty alcohol, a Microcrystalline Wax, and emulsifiers, by a phase inversion emulsification (PIE) method.

[0164] The present defoamers are formulated without any oil, EBS, silicone fluid and silica, which are undesirable and may be less compliant with environmental regulations or with Food and Drug Administration regulations and may not be suitable in food and beverage applications.

[0165] Defoaming Compositions

[0166] Generally, defoaming compositions according to embodiments of the present invention comprise an aqueous phase and an oil phase emulsified in the aqueous phase and comprise (a) an aqueous phase comprising at least water; (b) an oil phase emulsified in the aqueous phase, the oil phase comprising: (i) at least one microcrystalline wax having a congealing point of at least about 70 °C; and (ii) at least one long chain fatty alcohol having a carbon chain length of C₂₂ or more and a melting point of at least about 60 °C; and (c) a combination of surfactants comprising at least one first anionic surfactant and at least one second anionic surfactant.

[0167] Embodiments of the present defoamer composition may also comprise (a) at least one emulsifier; (b) at least one thickener; (c) at least one preservative comprising sodium nitrite, sodium metabisulfate, or a combination thereof; (d) at least one biocide, or (e) any combination of (a)-(e). The defoamer preferably has a pH of greater than 7.0, 7.5-9, 7.5-8.5, or 7.5-8.

[0168] The aqueous phase and oil phase may be present in a ratio of about 1:1. In some embodiments said aqueous phase comprises 50%-65%, 52-60%, or 54-58% by weight, based on the weight of the defoamer composition.

[0169] Suitable microcrystalline waxes: (i) have a congealing point ranging from 70-80 °C, 71-79 °C, 72-78 °C, or 72-77 °C; and (ii) are present in said defoamer composition at an amount ranging from 5-25%, 10-20%, 12-18%, or 14-16% by weight, based on the weight of the defoamer composition.

[0170] Suitable long chain fatty alcohols according to embodiments of this invention include C₂₂ to C₂₈, or even longer monohydric to trihydric alcohols. These alcohols include natural and synthesized fatty alcohols. Said fatty alcohols may be selected from the group consisting of C₂₂ alcohol, C₂₄ alcohol, C₂₆ alcohol, C₂₈ alcohol, C₃₀ alcohol, C₃₂ alcohol, and C₃₄ alcohol, which have a single carbon atom number respectively. Alternatively, the fatty alcohols may be selected from mixed fatty alcohols that have different numbers of carbon atoms having a carbon chain length of at least C₂₂. If synthetic alcohols are to be used, the fatty alcohols can be obtained from alkyl aluminum oxide through a Ziegler process, and also can be obtained by carbonyl synthesis. Usually, fatty alcohols obtained through such a process are mixed and saturated straight chain alcohols.

[0171] In certain embodiments the long chain fatty alcohols: (i) comprise at least 70% by weight of a carbon chain length ranging from C₂₂ to C₂₈, C₂₂ to C₂₆, or C₂₂ to C₂₄; (ii) have a melting point ranging

from 60-70 °C, 62-68 °C, or 64-66 °C, or 62-65°C; and (ii) are present in said defoamer composition at an amount ranging from 10-30%, 12-28%, 15-25%, or 20-22% by weight, based on the weight of the defoamer composition.

[0172] Suitable emulsifiers comprise nonionic surfactants, including but not limited to, ethoxylated alcohols, including but not limited to, ethoxylated fatty alcohols comprising 1-4 ethyleneoxy groups, secondary alcohol ethoxylates, ethoxylated sorbitan esters, sorbitan esters, sorbitan monostearate, sorbitan esters of oleic acid, glycerol esters, including but not limited to, glycerol monostearate (GMS), and any combination thereof.

[0173] Suitable first anionic surfactants comprise alkyl ether sulfates, including but not limited to, ethoxylated and sulphated isotridecyl alcohols and 2-tridecoxyethyl sulfate; special soaps, including but not limited to, dodecyl poly(oxyethylene) ether sulfates; anionic long chain fatty acids; their corresponding alkali metal and alkaline earth metal salts; and any combination thereof.

[0174] Suitable second anionic surfactants comprise fatty alcohol ether sulfates, including but not limited to lauryl ether sulfate, and their alkali metal and alkaline earth metal salts, optionally combined with poly(ethylene oxide).

[0175] Suitable thickeners comprise rheology modifiers known in the art, including but not limited to, alkali swellable emulsions, hydroxypropyl methylcellulose (HPMC), one or more bio-based hydrocolloids, one or more bio-based gums, including but not limited to, pre-hydrated cellulose gums, xanthan gums, or a mixture thereof.

[0176] In some embodiments the defoamer composition comprises one, two, three, four, or preferably all of the following: (a) said at least one emulsifier at an amount ranging from 0.5-10%, 1-5%, or 2-4% by weight, based on the weight of the defoamer composition; (b) said at least one anionic surfactant at an amount ranging from 0.5-10%, 2-8%, or 3-5% by weight, based on the weight of the defoamer composition; (c) said at least one thickener at an amount ranging from 0.1-1%, 0.1-0.5%, or 0.1-0.3% by weight, based on the weight of the defoamer composition; (d) said at least one biocide at an amount ranging from 0.1-1%, 0.1-0.5%, or 0.1-0.3% by weight, based on the weight of the defoamer composition; and (e) said at least one preservative at an amount ranging from 0.1-2%, 0.1-1%, or 0.2-0.6%, by weight, based on the weight of the defoamer composition.

[0177] Preferred embodiments of the defoamer composition comprise an emulsion prepared by phase inversion emulsification (PIE); do not contain oil, silicone fluid, silica, or ethylene bis(stearamide) (EBS); comprise a total solids content ranging from comprises a total solids content ranging from 30-50 %, 35-45 %, or 40-45 % by weight, based on the weight of the defoamer composition; and exhibit a viscosity ranging from about 400 cp, 300-450 cP, 350-450, or 390-410 cP, determined using a Brookfield viscometer RVT115-Model RVT with a No 3 spindle at 50 rpm and room temperature.

[0178] The defoamer compositions according to embodiments of this invention may further have bio-based content of at least 50%, at least 60%, 50-70 %, 50-60 %, or 55-60 % by weight, based on the weight of said total solids content. Bio-based content means the amount of bio-based carbon in the material or product as a % of weight (mass) of the total organic carbon in the material or product determined by testing representative samples using American Society for Testing and Materials

specification D6866. Bio-based carbon means new carbon such as carbon directly from plants as opposed to fossil fuel based organic carbon. Total organic carbon includes both new carbon and fossil fuel based carbon.

[0179] In preferred embodiments the defoamer composition: (a) performs as a defoamer at a defoaming temperature of at least 40 °C, 40-75 °C, 40-65 °C, or 40-55 °C 40-65 °C, or 40-55 °C; and/or (b) exhibits a viscosity of <1200 cP when stored for up to 14 days at a temperature of about 40 °C; a viscosity of <450 cP when stored for up to 14 days at a temperature of about 23 °C, and/or a viscosity <450 cP when stored for up to 14 days at a temperature of about 5 °C.

[0180] Method for Making Defoaming Compositions

[0181] Generally, defoaming compositions according to embodiments of the present invention may be made by a phase inversion emulsion (PIE) method comprising the steps of:

[0182] Step (a) heating in a first reactor a mixture of (i) at least one microcrystalline wax; (ii) at least one long chain fatty alcohol, and (iii) at least one emulsifier to a first temperature sufficient to liquify all solids, thereby forming an oil phase. Components (i)-(ii) may be added in any order. Preferable order of addition is in the order of increasing melting point (e.g., (i), (ii), then (iii)). In preferred embodiments, said at least one microcrystalline wax has a congealing point of at least about 70 °C and said at least one long chain fatty alcohol has a carbon chain length of C22 or more and a melting point of at least about 60 °C;

[0183] Step (b) in a separate reactor, heating water to said first temperature, thereby forming an aqueous phase;

[0184] Step (c) slowly adding a portion of said aqueous phase into said oil phase while stirring at said first temperature, wherein said portion comprises 1-10%, 2-8% or 3-6% by weight of said aqueous phase;

[0185] Step (d) adding a remainder of said aqueous phase into said oil phase while stirring at said first temperature;

[0186] Step (e) adding at least one first anionic surfactant while stirring at said first temperature;

[0187] Step (f) homogenizing to form an oil in water (O/W) emulsion comprising said oil phase emulsified into said aqueous phase;

[0188] Step (g) adding to said O/W emulsion at least one thickener;

[0189] Step (h) cooling said O/W emulsion to a final temperature of 15-25 °C; and

[0190] Step (i) adding at least one second anionic surfactant and mixing to form said defoamer.

[0191] Steps (a)-(i) are preferably performed successively, although the order of addition may vary based on the particular needs of the practitioner.

[0192] In some exemplary embodiments of the method (a) said first temperature ranges from 80-98 °C, 80-95 °C, or 85-95 °C; (b) said (i) at least one microcrystalline wax; (ii) at least one long chain fatty alcohol, and (iii) at least one emulsifier are added (i)-(iii) successively; (c) after step (c), stirring for 10-60 min, 10-40 min, or 10-30 min; (d) after step (d), stirring for 30-90 min, 30-80 min, or 30-60

min; and (e) during step (f), homogenization is performed at 6000-9000 rpm, 6200-6800 rpm, or 6500-8500 rpm.

[0193] In some exemplary embodiments the method further comprises: (a) after cooling, adding to said emulsion at least one preservative comprising sodium nitrite, sodium metabisulfate, or a combination thereof, (ii) at least one biocide, or any combination of (i)-(ii); and (b) adjusting the pH of said aqueous phase, said emulsion, and/or said defoamer to >7.0, 7.5-9, 7.5-8.5, or 7.5-8.

[0194] In some exemplary embodiments of the method: (a) said aqueous phase comprises 50%-65%, 52-60%, or 54-58% by weight of said defoamer; (b) said aqueous phase and said oil phase are present in a ratio of aqueous phase to oil phase ranging from 1:1 to 1.6:1, 1.1:1 to 1.5:1, 1.2:1 to 1.5:1; or 1.3:1 to 1.5:1; (c) said at least one microcrystalline wax: (i) has a congealing point ranging from 70-80 °C, 71-79 °C, 72-78 °C, or 72-77 °C; and (ii) is present in said defoamer composition at an amount ranging from 5-25%, 10-20%, 12-18%, or 14-16% by weight, based on the weight of the defoamer composition; (d) said at least one long chain fatty alcohol: (i) comprises at least 70% by weight of a carbon chain length ranging from C₂₂ to C₂₈, C₂₂ to C₂₆, or C₂₂ to C₂₄; (ii) has a melting point ranging from 60-70 °C, 61-69 °C, 61-68 °C, or 62-68 °C; and (iii) is present in said defoamer composition at an amount ranging from 10-30%, 12-28%, 15-25%, or 20-22% by weight, based on the weight of the defoamer composition; (e) said at least one emulsifier comprises nonionic surfactants, including but not limited to, ethoxylated alcohols, including but not limited to, ethoxylated fatty alcohols comprising 1-4 ethyleneoxy groups, secondary alcohol ethoxylates, ethoxylated sorbitan esters, sorbitan esters, sorbitan monostearate, sorbitan esters of oleic acid, glycerol esters, including but not limited to, glycerol monostearate (GMS), and any combination thereof; (f) said at least one first anionic surfactant comprises alkyl ether sulfates, including but not limited to, ethoxylated and sulphated isotridecyl alcohols and 2-tridecoxyethyl sulfate; special soaps, including but not limited to, dodecyl poly(oxyethylene) ether sulfates; anionic long chain fatty acids; their corresponding alkali metal and alkaline earth metal salts; and any combination thereof; (g) said at least one second anionic surfactant comprises fatty alcohol ether sulfates, including but not limited to lauryl ether sulfate, and their alkali metal and alkaline earth metal salts, optionally combined with poly(ethylene oxide); (h) said at least one thickener comprises rheology modifiers, including but not limited to, alkali swellable emulsions, hydroxypropyl methylcellulose (HPMC), one or more bio-based hydrocolloids, one or more bio-based gums, including but not limited to, pre-hydrated cellulose gums, xanthan gums, or a mixture thereof; or (i) any combination of (a)-(h).

[0195] In some exemplary embodiments of the method said defoamer comprises: (a) said at least one emulsifier at an amount ranging from 0.5-10%, 1-5%, or 2-4% by weight, based on the weight of the defoamer composition; (b) said at least one anionic surfactant at an amount ranging from 0.5-10%, 2-8%, or 3-5% by weight, based on the weight of the defoamer composition; (c) said at least one thickener at an amount ranging from 0.1-1%, 0.1-0.5%, or 0.1-0.3% by weight, based on the weight of the defoamer composition; (d) said at least one biocide at an amount ranging from 0.1-1%, 0.1-0.5%, or 0.1-0.3% by weight, based on the weight of the defoamer composition; (e) said at least one preservative at an amount ranging from 0.1-2%, 0.1-1%, or 0.2-0.6%, by weight, based on the weight of the defoamer composition; or (f) any combination of (a)-(e).

[0196] In some exemplary embodiments of the method said defoamer: (a) comprises a total solids content ranging from 30-50 %, 35-45 %, or 40-45 % by weight, based on the weight of the defoamer composition; (b) comprises a bio-based solids content ranging from 50-70 %, 50-60 %, or 55-60 % by weight, based on the weight of said total solids content; (c) exhibits a viscosity ranging from about 400 cP, 300-450 cP, 350-450, or 390-410 cP, determined using a Brookfield viscometer RVT115-Model RVT with a No 3 spindle at 50 rpm and room temperature; (d) exhibits a viscosity <1200 cP when stored for up to 14 days at a temperature of about 40 °C; a viscosity of <450 cP when stored for up to 14 days at a temperature of about 23 °C, and/or a viscosity <450 cP when stored for up to 14 days at a temperature of about 5 °C; (e) performs as a defoamer at a defoaming temperature of at least 40 °C, 40-65 °C, or 40-55 °C; or (f) any combination of (a)-(f).

[0197] Method for Defoaming An Industrial Process Stream

[0198] Generally, defoaming compositions according to embodiments of the present invention may be used for defoaming in an industrial process stream in a method comprising the step of adding to the industrial process stream a defoamer composition in an amount effective to defoam or prevent foaming in the industrial process stream.

[0199] Defoaming methods according to embodiments of the present invention can be practiced in any industrial process in which foaming is a concern, including process streams commonly encountered when processing or manufacturing wood pulp, paper, textiles, cement or paint, in addition to processes for treating industrial wastewater, food processing, and oil drilling. The methods can be used in practically any industrial water system where foaming is a problem, but are particularly well-adapted to recirculating water systems as found in papermaking systems, cooling water systems (including cooling towers, open and closed loop cooling units), industrial raw water systems, drinking water distribution systems, sanitizing drinking water system, oil production or recovery systems (oil field water system, drilling fluids), fuel storage system, metal working systems, heat exchangers, reactors, equipment used for storing and handling liquids, boilers and related steam generating units, radiators, flash evaporating units, refrigeration units, reverse osmosis equipment, gas scrubbing units, blast furnaces, sugar evaporating units, steam power plants, geothermal units, nuclear cooling units, water treatment units, pool recirculating units, mining circuits, closed loop heating units, machining fluids used in operations such as for example drilling, boring, milling, reaming, drawing, broaching, turning, cutting, sewing, grinding, thread cutting, shaping, spinning and rolling, hydraulic fluids, cooling fluids, and the like. In some embodiments, the industrial process stream is an industrial process stream in a cement-making process or a paint making process.

[0200] In one embodiment the defoamer compositions and/or emulsions disclosed herein are added or dosed to a pulp and/or paper processing system. The composition can be generally utilized throughout the system to minimize and to prevent foam. In certain examples, the composition is added in a short loop of the system. Other examples of suitable addition points are large storage towers for process water (circulating water towers, filtrate water towers), clear or cloudy filtrate storage tanks, pulpers or process streams upstream/downstream of the pulpers, broke system or process streams upstream/downstream of vessels therein, wire pit process streams upstream/downstream of the pit, paper machine blend chest process streams

upstream/downstream of the chest, fresh water tank, warm water tank and shower water tank. Suitable addition points for a pulp mill system include the digester, the brown stock stream, washers (such as the brown stock washer), the black liquor stream in a Kraft process, or the red or brown liquor in a sulfite process. The composition can be dosed continuously or periodically as a batch process. The composition can be fed for about 3 to about 45 minutes each about 6 to about 24 times a day, or for example for about 10 to about 30 minutes for about 12 to about 24 times a day.

[0201] Paper-Making Processes

[0202] In the paper industry, the Kraft process is a frequently used alkaline pulping process. Spent chemicals in the process can be recycled and reused thus decreasing processing costs. A large disadvantage of this process is the occurrence of foam during the pulp screening and washing procedures.

[0203] The Kraft process (as taught in U.S. Pat. No. 3,215,635 to Liebling, for instance) first cooks the wood chips in digesters and then draws off the spent chemicals for reuse. The resulting pulp fibers are then washed free of a large amount of residual chemicals in brown stock washers. These washers are a series of vats usually three or four in number that alternatively dilute the pulp with water and thicken it by picking it up on large rotary screens. From the brown stock washers, the pulp travels to the screen room where it is again diluted with water and put through vibrating screens that accept the now completely delignified fibers and reject the clumps of unpulped fibers, knots, and other foreign material. Foam problems can be severe in the screen room because the diluted pulp is subjected to violent agitation by the screens. The water removed from the pulp after the screening operations is referred to as the dilute black liquor and, for the sake of economy, is normally used as the dilution water for the third and fourth stage of the brown stock washers. The dilute black liquor is a foaming material, containing, for example, from about 0.001 % to about 0.1 % by weight of solids and having a pH of about 12. The foaming of the dilute black liquor increases along with the resin content of the wood used in this process.

[0204] Defoamers can be used in alkaline pulp mills during the screening operations so that a more efficient screening is accomplished and to prevent the pulp thickeners, used after the screening operations from becoming clogged with entrapped air. When water-dispersible defoamers are used during the screening operation, the control of foam and entrained air in the screening operation contributes to the washing efficiency of the pulp during the alkaline pulping process. This occurs because the screening efficiency of the pulp is increased, allowing ease of flow of the pulp throughout the thickeners and subsequent washers.

[0205] De-inking detergents used to de-ink paper in paper recycling operations can also cause significant defoaming problems. Detailed descriptions of such processes are found in standard textbooks, such as A. M. Schwartz and J. W. Perry, SURFACE ACTIVE AGENTS, Vol. I (1949); and SURFACE ACTIVE AGENTS AND DETERGENTS, Vol. II (1958), Interscience Publishers, New York, the descriptions of which are incorporated herein by reference.

[0206] The de-inking agents, in amounts ranging from about 0.3 to about 3 percent based on the weight of the paper, are used in solution in substantially aqueous media. The temperature of the de-inking solution can vary anywhere from room temperature, including about 40° F. to about 70° F. (about 4° C. to about 20° C.), up to about 200° F. (about 95° C.). The processes are generally

performed at an alkaline pH (i.e., from about 7.0 and about 11.5). In general, the percent of cellulosic by weight of the aqueous de-inking solution should be below 10 percent and preferably below 6.0 percent, or between about 4.0 and 6.0 percent.

[0207] Following deinking treatment, the defibered material is dropped to a chest or other reservoir, after which it is diluted with water to a solids content of between about 0.5 and about 1.5 percent (including about 1.0 percent), based upon the solution weight. Following dilution, the pulp is separated from the solution and washed and thickened by well-known methods. Optionally, the pulp is then acidified to a pH of between about 4 and about 6.5 (including about 4.5 to about 5.5), thickened and then formed into a web. The recovered stock can be blended with fresh virgin sulfate or sulfite stock, or with additional recovered stock to make cellulosic articles, such as newspaper and so forth. The defoamer can be added during any of the foregoing stages to control or prevent foam formation.

[0208] When used in cement making, defoamer embodiments the present invention may be added to the water or the cement powder before the water and powder are mixed, or they can be added to the wet cement after the water and powder have been mixed.

[0209] Defoamer embodiments the present invention may also be added at any point during a textile making or textile dyeing process.

[0210] In a preferred embodiments the present invention provides a method of defoaming in an industrial process stream comprising the step of adding to the industrial process stream a defoamer composition according to the foregoing obtainable by a method according to the foregoing, wherein:

[0211] (a) said defoamer composition is added to said industrial process stream in an amount effective to defoam or prevent foaming in the industrial process stream;

[0212] (b) said defoamer composition is added to said industrial process stream at a temperature of at least 40 °C, 40-75 °C, 40-65 °C, or 40-55 °C; and

[0213] (c) said industrial process stream comprises any process stream related to industries, including but not limited to, the pulp and paper industry, the oil and gas industry, water treatment, paints and coatings, food and beverage processing, the mining industry, textiles, or agriculture;

[0214] wherein said method of defoaming results in an enhanced defoaming performance compared to the same method of defoaming performed using a comparative defoamer composition which is the same as said defoamer composition with the exception that said comparative defoamer composition comprises: (i) a microcrystalline wax having a higher congealing point; (ii) a lower % by weight of said microcrystalline wax; (iii) a lower % by weight of said long chain fatty alcohol; and/or (iv) a lower % by weight total solids, and further wherein said enhanced defoaming performance is determined by Foam and Entrained Air Testing (FEAT).

[0215] The methods and compositions illustratively disclosed herein suitably may be practiced in the absence of any element which is not specifically disclosed herein and/or any element specifically disclosed herein. Exemplary embodiments of the invention and its advantages are further disclosed in the following examples.

EXAMPLES

[0216] The examples provided herein are for illustrative purposes so that the invention may be more fully understood. These examples should not be construed as limiting the invention in any way.

Example 1: Preparation of a high concentration water based defoamer

[0217] **Preparation of a high concentration water based defoamer by phase inversion emulsion (PIE)**

[0218] (A) Microcrystalline Wax, High molecular weight Long Chain Fatty Alcohol, and two Emulsifiers were added to a reactor, and then heated to 80-95 °C with stirring for 10-30 minutes to form a liquid mixture.

[0219] (B) Water was added to a second reactor and heated to 80-95 °C.

[0220] (C) A portion of the hot water (3-6 % by wt.) from (B) was added to reactor (A) with stirring for 10-30 minutes, and then the reminder of hot water was added while stirring at 80-95 °C. The resulting emulsion was mixed for 0.5-1.0 h.

[0221] (D) Anionic Surfactant 1 was added to the emulsion while stirring at 80-95 °C for 3-8 minutes.

[0222] (E) The emulsion solution from (D) was immediately homogenized at 6500-8500 rpm for 90 to 150 seconds.

[0223] (F) A thickener was added into the homogenized emulsion (E) while stirring 3-5 minutes.

[0224] (G) The homogenized emulsion from (F) was quickly cooled in an ice water bath to room temperature while stirring for 5-10 minutes and then sodium nitrite, Anionic Surfactant 2, and a biocide was added, sequentially while stirring over 0.5-1 h to form the high concentration water based defoamer emulsion as a phase inverted oil in water (O/W) emulsion. Defoamer specifications are shown in **Table 1**.

[0225] Notably, the inventive defoamer RE-32AAA composition contains approximately 1.5-2× higher total solids than a commercially available competitor defoamer composition. RE-32AAA satisfies an objective of the present invention by comprising nearly over 50 % (e.g., nearly 60 %) bio-based content.

[0226] **Table 1:** High concentration water based defoamer (RE-32AAA)

Component	Defoamer RE-32AAA (% by wt)
Microcrystalline Wax (Pomona Microwax 162M)	14.95
Long Chain Fatty Alcohol (1-docosanol, behenyl alcohol, C22, Vegarol 2270)	21.14
Emulsifier 1 (TERGITOL™ 15-S-40, 70%)	1.17
Emulsifier 2 (glyceryl monostearate)	1.83
Hot water	56.26
Anionic Surfactant 1 (SERMUL EA 266)	2.66
Thickener (Ticaloid 5415 Gum)	0.22
Preservative (sodium nitrite, NaNO ₂)	0.37

Anionic Surfactant 2 (sodium lauryl ether sulfate + 30 EO, Certipol™ FES 77)	1.20
Biocide (AMA-420)	0.20
Total	100.0
Viscosity (cP)	390
Total Solids (%)	40.46
Bio content in Total Solids (%)	58.24

Example 2: FEAT evaluation of a high concentration water based defoamer in Foaming Media A

[0227] Defoamer compositions of the present invention were evaluated against comparative compositions using the Foam and Entrained Air Test (FEAT).

[0228] Foam and Entrained Air Testing (FEAT) protocol

[0229] Foam elimination and suppression performance was evaluated using a Foam and Entrained Air Testing (FEAT) protocol. FEAT employs a testing apparatus used to determine the efficacy of defoaming agents in a laboratory setting. FEAT utilizes an air injection system that induces foam and measures entrained air to evaluate defoamer performance. The apparatus measures the change in the density as a function of time of the filtrate as the defoaming agent is introduced. The measure of the change in density of a filtrate is a direct measurement of the change in entrained air. Defoamer dosage is selected to adequately show the performance differences in the various products at industrially relevant concentrations.

[0230] The experimental set up contains a water bath, temperature control, a foam column, a micropump, a density meter, a computer, and acquisition software. Testing of the samples utilizes a recirculatory foam column attached to a pump. The hose leading from the pump is connected to a density meter, which is connected back to the top of the foam column. The foaming medium is added to the test unit and pumped through the unit to fill the lines. As the foaming medium is circulated, the density of the medium drops due to formation of foams. Once the pump is turned on and the density drops due to air entrainment, a defoamer composition is added. The test is run for a predetermined time and adequate number of data points are collected by the data acquisition software. A line graph is generated to show the change in density of the liquor of the time period. The area under the curve for each test is then calculated. Those samples having the highest area under the curve measurements are those samples that performed the best.

[0231] FEAT evaluation of defoamer performance in Foaming Media A

[0232] High concentration water based defoamer composition of the present invention (RE-32AAA), prepared according to **Example 1**, was evaluated for foam elimination and suppression performance against comparative defoamer compositions FennoTech 1950 (FT1950) and FennoTech 1802 (FT1802) using FEAT. The comparative defoamer compositions were sourced from Kemira Oyj, based in Helsinki, Finland and include FT1950 (commercially available water based defoamer) and FT1802 (commercially available defoamer product). FT1950 has lower Total Solids (<25 wt%) and contains undesirable materials including mineral oil.

[0233] FEAT method was used to evaluate RE-32AAA (Dosage: 1.25 μ L, 2.25 μ L, and 3.25 μ L) against FT1950 and FT1802 (Dosage: 2.5 μ L, 4.5 μ L, and 6.5, μ L) in Foaming Media A: White Water (WW). Testing was performed at 54 °C and 50% Power.

[0234] FEAT line graph results of density over time are shown in **FIG 1**.

[0235] Results indicate that, in a first Foaming Media A, the inventive defoamer composition RE-32AAA (green lines) shows improved efficacy (i.e., higher density over the entire 180 sec time frame) over the comparative defoamers FT1950 and FT1802 at 54 °C.

[0236] Defoaming performance was also determined by Area Under Curve (AUC) from the FEAT line graphs over 30 sec and 3 min after defoamer injection. AUC results are shown as a bar graph in **FIG 2** and as a line graph in **FIG 3**.

[0237] AUC results indicate, over 30 sec and 3 min after defoamer injection, that the inventive defoamer composition RE-32AAA (injected at lower dosages) significantly outperforms the comparative defoamers FT1950 and FT1802 (injected at higher dosages). The difference in defoaming performance is most readily observable in the dose response curves in **FIG 3**, wherein RE-32AAA is significantly left shifted and up shifter, showing higher efficacy at lower dosages.

[0238] These results provide initial proof of concept that the inventive defoamer composition, which contains high total solids and high bio-based content, outperforms comparative defoamers at an operational temperature of 54 °C.

[0239] Without being bound to theory, it can be rationalized that the inventive high solids defoamer composition surprisingly outperforms the comparative defoamers due to the high concentration and lower congealing point of the microcrystalline wax in the formulation. The inventive defoamer contains a lower congealing point microcrystalline wax, the molecular structure of which is highly branched. This branching provides improved stability and defoaming properties, particularly defoaming performance, compared to typical wax and oil structures, which are less branched. The highly branched microcrystalline wax provides a synergistic enhancement, when formulated with a high molecular weight fatty alcohol.

Example 3: FEAT evaluation of a high concentration water based defoamer in Foaming Media B

[0240] High concentration water based defoamer composition of the present invention (RE-32AAA), prepared according to **Example 1**, was evaluated using FEAT against comparative defoamer compositions (FT1950 and FT1802) in the same process according to **Example 2**, in a different foaming media at different dosages.

[0241] FEAT method was used to evaluate RE-32AAA (Dosage: 1.5 μ L, 2.0 μ L, and 2.5 μ L) against FT1950 and FT1802 (Dosage: 1.5 μ L, 2.0 μ L, and 6.5, μ L) in Foaming Media B: White Water (WW). Testing was performed at 54 °C and 50% Power.

[0242] FEAT line graph results of density over time are shown in **FIG 4**.

[0243] Results indicate that in a second Foaming Media B, the inventive defoamer composition RE-32AAA (green lines) shows improved efficacy (i.e., higher density over the entire 180 sec time frame) over the comparative defoamers FT1950 and FT1802 at 54 °C.

[0244] AUC results are shown as a bar graph in **FIG 5** and as a dose-response line graph in **FIG 6**.

[0245] AUC results indicate, over 30 sec and 3 min after defoamer injection, that the inventive defoamer composition RE-32AAA significantly outperforms the comparative defoamers FT1950 and FT1802. The difference in defoaming performance is most readily observable in the dose response curves in **FIG 6**, wherein RE-32AAA provided significantly higher efficacy at all dosages, with the greatest improvement at 1.5 μ L dosage.

[0246] These results provide further proof of concept that the inventive defoamer composition, which contains high total solids and high bio-based content, outperforms comparative defoamers at an operational temperature of 54 °C in a second white water sample.

Example 4: Stability testing of high concentration water based defoamer

[0247] Stability of a high concentration water based defoamer composition of the present invention (RE-32AAA) prepared according to **Example 1** was analyzed by the following method. The defoamer sample was divided into three parts, and each part was placed in at 5 °C, ambient temperature (~23 °C), and 40 °C for 14 days. Samples were taken for analysis at days 7 and 14. Samples were allowed to reach ambient temperature, and their viscosity was determined using RVT115-Model RVT equipment.

[0248] A graph of viscosity over time is shown in **FIG 7**. Maintenance of stable viscosity at ~400 cP over time is considered an indicator of good stability.

[0249] Results indicate that the inventive defoamer composition displayed excellent stability at 5 °C and ~23 °C. Adequate stability was observed at 40 °C.

CLAIMS

What is claimed is:

1. A defoamer composition comprising:
 - (a) an aqueous phase;
 - (b) an oil phase emulsified in the aqueous phase, the oil phase comprising:
 - (i) at least one microcrystalline wax having a congealing point of at least about 70 °C; and
 - (ii) at least one long chain fatty alcohol having a carbon chain length of C₂₂ or more and a melting point of at least about 60 °C; and
 - (c) a combination of surfactants comprising at least one first anionic surfactant and at least one second anionic surfactant.
2. The defoamer composition of **claim 1**, further comprising:
 - (a) at least one emulsifier;
 - (b) at least one thickener;
 - (c) at least one preservative optionally comprising sodium nitrite, sodium metabisulfate, or a combination thereof;
 - (d) at least one biocide, or
 - (e) any combination of (a)-(d).
3. The defoamer composition of **claim 1 or 2**, further comprising a pH of greater than 7.0, 7.5-9, 7.5-8.5, or 7.5-8.
4. The defoamer composition of **claim 1, 2 or 3**, wherein:
 - (a) said aqueous phase comprises 50%-65%, 52-60%, or 54-58% by weight, based on the weight of the defoamer composition;
 - (b) said at least one microcrystalline wax:
 - (i) has a congealing point ranging from 70-80 °C, 71-79 °C, 72-78 °C, or 72-77 °C; and
 - (ii) is present in said defoamer composition at an amount ranging from 5-25%, 10-20%, 12-18%, or 14-16% by weight, based on the weight of the defoamer composition; and
 - (c) said at least one long chain fatty alcohol:
 - (i) comprises at least 70% by weight of a carbon chain length ranging from C₂₂ to C₂₈, C₂₂ to C₂₆, or C₂₂ to C₂₄;
 - (ii) has a melting point ranging from 60-70 °C, 62-68 °C, or 64-66 °C, or 62-65°C; and
 - (iii) is present in said defoamer composition at an amount ranging from 10-30%, 12-28%, 15-25%, or 20-22% by weight, based on the weight of the defoamer composition.
5. The defoamer composition of **claim 2, 3 or 4**, wherein
 - (a) said at least one emulsifier comprises nonionic surfactants, including but not limited to,

ethoxylated alcohols, including but not limited to, ethoxylated fatty alcohols comprising 1-4 ethyleneoxy groups, secondary alcohol ethoxylates, ethoxylated sorbitan esters, sorbitan esters, sorbitan monostearate, sorbitan esters of oleic acid, glycerol esters, including but not limited to, glycerol monostearate (GMS), and any combination thereof;

- (b) said at least one first anionic surfactant comprises alkyl ether sulfates, including but not limited to, ethoxylated and sulphated isotridecyl alcohols and 2-tridecoxyethyl sulfate; special soaps, including but not limited to, dodecyl poly(oxyethylene) ether sulfates; anionic long chain fatty acids; their corresponding alkali metal and alkaline earth metal salts; and any combination thereof;
 - (c) said at least one second anionic surfactant comprises fatty alcohol ether sulfates, including but not limited to lauryl ether sulfate, and their alkali metal and alkaline earth metal salts, optionally combined with poly(ethylene oxide);
 - (d) said at least one thickener comprises rheology modifiers, including but not limited to, alkali swellable emulsions, hydroxypropyl methylcellulose (HPMC), one or more bio-based hydrocolloids, one or more bio-based gums, including but not limited to, pre-hydrated cellulose gums, xanthan gums, or a mixture thereof; or
 - (e) any combination of (a)-(d).
6. The defoamer composition of **any one of the foregoing claims**, wherein said defoamer composition comprises one, two, three, four, or all of the following:
- (a) said at least one emulsifier at an amount ranging from 0.5-10%, 1-5%, or 2-4% by weight, based on the weight of the defoamer composition;
 - (b) said at least one anionic surfactant at an amount ranging from 0.5-10%, 2-8%, or 3-5% by weight, based on the weight of the defoamer composition;
 - (c) said at least one thickener at an amount ranging from 0.1-1%, 0.1-0.5%, or 0.1-0.3% by weight, based on the weight of the defoamer composition;
 - (d) said at least one biocide at an amount ranging from 0.1-1%, 0.1-0.5%, or 0.1-0.3% by weight, based on the weight of the defoamer composition; and
 - (e) said at least one preservative at an amount ranging from 0.1-2%, 0.1-1%, or 0.2-0.6%, by weight, based on the weight of the defoamer composition.
7. The defoamer composition of **any one of the foregoing claims**, wherein said defoamer composition:
- (a) comprises an emulsion prepared by phase inversion emulsification (PIE);
 - (b) does not contain oil, silicone fluid, silica, or ethylene bis(stearamide) (EBS);
 - (c) comprises a total solids content ranging from 30-50 %, 35-45 %, or 40-45 % by weight, based on the weight of the defoamer composition;
 - (d) comprises a bio-based solids content ranging from 50-70 %, 50-60 %, or 55-60 % by weight, based on the weight of said total solids content;
 - (e) exhibits a viscosity ranging from about 400 cp, 300-450 cP, 350-450, or 390-410 cP, determined using a Brookfield viscometer RVT115-Model RVT with a No 3 spindle at 50 rpm and room temperature; or

- (f) any combination of (a)-(e).
8. The defoamer composition of **any one of the foregoing claims**, wherein said defoamer composition:
- (a) performs as a defoamer at a defoaming temperature of at least 40 °C, 40-75 °C, 40-65 °C, or 40-55 °C 40-65 °C, or 40-55 °C; and/or
 - (b) exhibits a viscosity of <1200 cP when stored for up to 14 days at a temperature of about 40 °C; a viscosity of <450 cP when stored for up to 14 days at a temperature of about 23 °C, and/or a viscosity <450 cP when stored for up to 14 days at a temperature of about 5 °C.
9. A method for preparing a defoamer by phase inversion emulsion (PIE), the method comprising:
- (a) heating in a first reactor a mixture of
 - (i) at least one microcrystalline wax;
 - (ii) at least one long chain fatty alcohol, and
 - (iii) at least one emulsifier to a first temperature sufficient to liquify all solids, thereby forming an oil phase,wherein said at least one microcrystalline wax has a congealing point of at least about 70 °C and said at least one long chain fatty alcohol has a carbon chain length of C₂₂ or more and a melting point of at least about 60 °C;
 - (b) separately heating water to said first temperature, thereby forming an aqueous phase;
 - (c) slowly adding a portion of said aqueous phase into said oil phase while stirring at said first temperature, wherein said portion comprises 1-10%, 2-8% or 3-6% by weight of said aqueous phase;
 - (d) adding a remainder of said aqueous phase into said oil phase while stirring at said first temperature;
 - (e) adding at least one first anionic surfactant while stirring at said first temperature;
 - (f) homogenizing to form an oil in water (O/W) emulsion comprising said oil phase emulsified into said aqueous phase;
 - (g) adding to said O/W emulsion at least one thickener;
 - (h) cooling said O/W emulsion to a final temperature of 15-25 °C; and
 - (i) adding at least one second anionic surfactant and mixing to form said defoamer;
- wherein steps (a)-(i) are performed successively.
10. The method of **claim 9**, wherein:
- (a) said first temperature ranges from 80-98 °C, 80-95 °C, or 85-95 °C;
 - (b) said
 - (i) at least one microcrystalline wax;
 - (ii) at least one long chain fatty alcohol; and
 - (iii) at least one emulsifier;

- wherein (i), (ii) and (iii) are optionally added successively;
- (c) after step (c), stirring for 10-60 min, 10-40 min, or 10-30 min;
 - (d) after step (d), stirring for 30-90 min, 30-80 min, or 30-60 min; and
 - (e) during step (f), homogenization is performed at 6000-9000 rpm, 6200-6800 rpm, or 6500-8500 rpm.

11. The method of **claim 9 or 10**, further comprising:

- (a) after cooling, adding to said emulsion
 - (i) at least one preservative which optionally comprises sodium nitrite, sodium metabisulfate, or a combination thereof,
 - (ii) at least one biocide, or
 - (iii) any combination of (i)-(ii); and
- (b) adjusting the pH of said aqueous phase, said emulsion, and/or said defoamer to >7.0, 7.5-9, 7.5-8.5, or 7.5-8.

12. The method of any one of **claims 9-11**, wherein:

- (a) said aqueous phase comprises 50%-65%, 52-60%, or 54-58% by weight of said defoamer;
- (b) said aqueous phase and said oil phase are present in a ratio of aqueous phase to oil phase ranging from 1:1 to 1.6:1, 1.1:1 to 1.5:1, 1.2:1 to 1.5:1; or 1.3:1 to 1.5:1;
- (c) said at least one microcrystalline wax:
 - (i) has a congealing point ranging from 70-80 °C, 71-79 °C, 72-78 °C, or 72-77 °C; and
 - (ii) is present in said defoamer composition at an amount ranging from 5-25%, 10-20%, 12-18%, or 14-16% by weight, based on the weight of the defoamer composition;
- (d) said at least one long chain fatty alcohol:
 - (i) comprises at least 70% by weight of a carbon chain length ranging from C₂₂ to C₂₈, C₂₂ to C₂₆, or C₂₂ to C₂₄;
 - (ii) has a melting point ranging from 60-70 °C, 61-69 °C, 61-68 °C, or 62-68 °C; and
 - (iii) is present in said defoamer composition at an amount ranging from 10-30%, 12-28%, 15-25%, or 20-22% by weight, based on the weight of the defoamer composition;
- (e) said at least one emulsifier comprises nonionic surfactants, including but not limited to, ethoxylated alcohols, including but not limited to, ethoxylated fatty alcohols comprising 1-4 ethyleneoxy groups, secondary alcohol ethoxylates, ethoxylated sorbitan esters, sorbitan esters, sorbitan monostearate, sorbitan esters of oleic acid, glycerol esters, including but not limited to, glycerol monostearate (GMS), and any combination thereof;
- (f) said at least one first anionic surfactant comprises alkyl ether sulfates, including but not limited to, ethoxylated and sulphated isotridecyl alcohols and 2-tridecoxyethyl sulfate; special soaps, including but not limited to, dodecyl poly(oxyethylene) ether sulfates; anionic long chain fatty acids; their corresponding alkali metal and alkaline earth metal salts; and any combination thereof;
- (g) said at least one second anionic surfactant comprises one or more fatty alcohol ether

sulfates, including but not limited to lauryl ether sulfate, and their alkali metal and alkaline earth metal salts, optionally combined with poly(ethylene oxide);

- (h) said at least one thickener comprises one or more rheology modifiers, including but not limited to, alkali swellable emulsions, hydroxypropyl methylcellulose (HPMC), one or more bio-based hydrocolloids, one or more bio-based gums, including but not limited to, pre-hydrated cellulose gums, xanthan gums, or a mixture thereof; or
- (i) any combination of (a)-(h).

13. The method of preparing a defoamer according to any one of **claims 9-12**, wherein:

- (a) said at least one emulsifier is comprised in an amount ranging from 0.5-10%, 1-5%, or 2-4% by weight, based on the weight of the defoamer composition;
- (b) said at least one anionic surfactant is comprised in an amount ranging from 0.5-10%, 2-8%, or 3-5% by weight, based on the weight of the defoamer composition;
- (c) said at least one thickener is comprised in an amount ranging from 0.1-1%, 0.1-0.5%, or 0.1-0.3% by weight, based on the weight of the defoamer composition;
- (d) said at least one biocide is comprised in an amount ranging from 0.1-1%, 0.1-0.5%, or 0.1-0.3% by weight, based on the weight of the defoamer composition;
- (e) said at least one preservative is comprised in an amount ranging from 0.1-2%, 0.1-1%, or 0.2-0.6%, by weight, based on the weight of the defoamer composition; or
- (f) any combination of (a)-(e).

14. The method of preparing a defoamer according to any one of **claims 9-13**, wherein said defoamer:

- (a) comprises a total solids content ranging from 30-50 %, 35-45 %, or 40-45 % by weight, based on the weight of the defoamer composition;
- (b) comprises a bio-based solids content ranging from 50-70 %, 50-60 %, or 55-60 % by weight, based on the weight of said total solids content;
- (c) exhibits a viscosity ranging from about 400 cP, 300-450 cP, 350-450, or 390-410 cP, determined using a Brookfield viscometer RVT115-Model RVT with a No 3 spindle at 50 rpm and room temperature;
- (d) exhibits a viscosity <1200 cP when stored for up to 14 days at a temperature of about 40 °C; a viscosity of <450 cP when stored for up to 14 days at a temperature of about 23 °C, and/or a viscosity <450 cP when stored for up to 14 days at a temperature of about 5 °C;
- (e) performs as a defoamer at a defoaming temperature of at least 40 °C, 40-65 °C, or 40-55 °C; or
- (f) any combination of (a)-(e).

15. A method of defoaming in an industrial process stream comprising the step of adding to the industrial process stream a defoamer composition according to any one of **claims 1-8** optionally obtainable by a method according to **claims 9-14**, wherein:

- (a) said defoamer composition is added to said industrial process stream in an amount effective to defoam or prevent foaming in the industrial process stream;

- (b) said defoamer composition is added to said industrial process stream at a temperature of at least 40 °C, 40-75 °C, 40-65 °C, or 40-55 °C; and
- (c) said industrial process stream comprises any process stream related to industries, including but not limited to, the pulp and paper industry, the oil and gas industry, water treatment, paints and coatings, food and beverage processing, the mining industry, textiles, and agriculture;

wherein optionally said method of defoaming results in an enhanced defoaming performance compared to the same method of defoaming performed using a comparative defoamer composition which is the same as said defoamer composition with the exception that said comparative defoamer composition comprises:

- (i) a microcrystalline wax having a higher congealing point;
- (ii) a lower % by weight of said microcrystalline wax;
- (iii) a lower % by weight of said long chain fatty alcohol; and/or
- (iv) a lower % by weight total solids,

further wherein said enhanced defoaming performance is determined by Foam and Entrained Air Testing (FEAT).

Defoaming Performance Results On Foaming Media A White Water (WW)

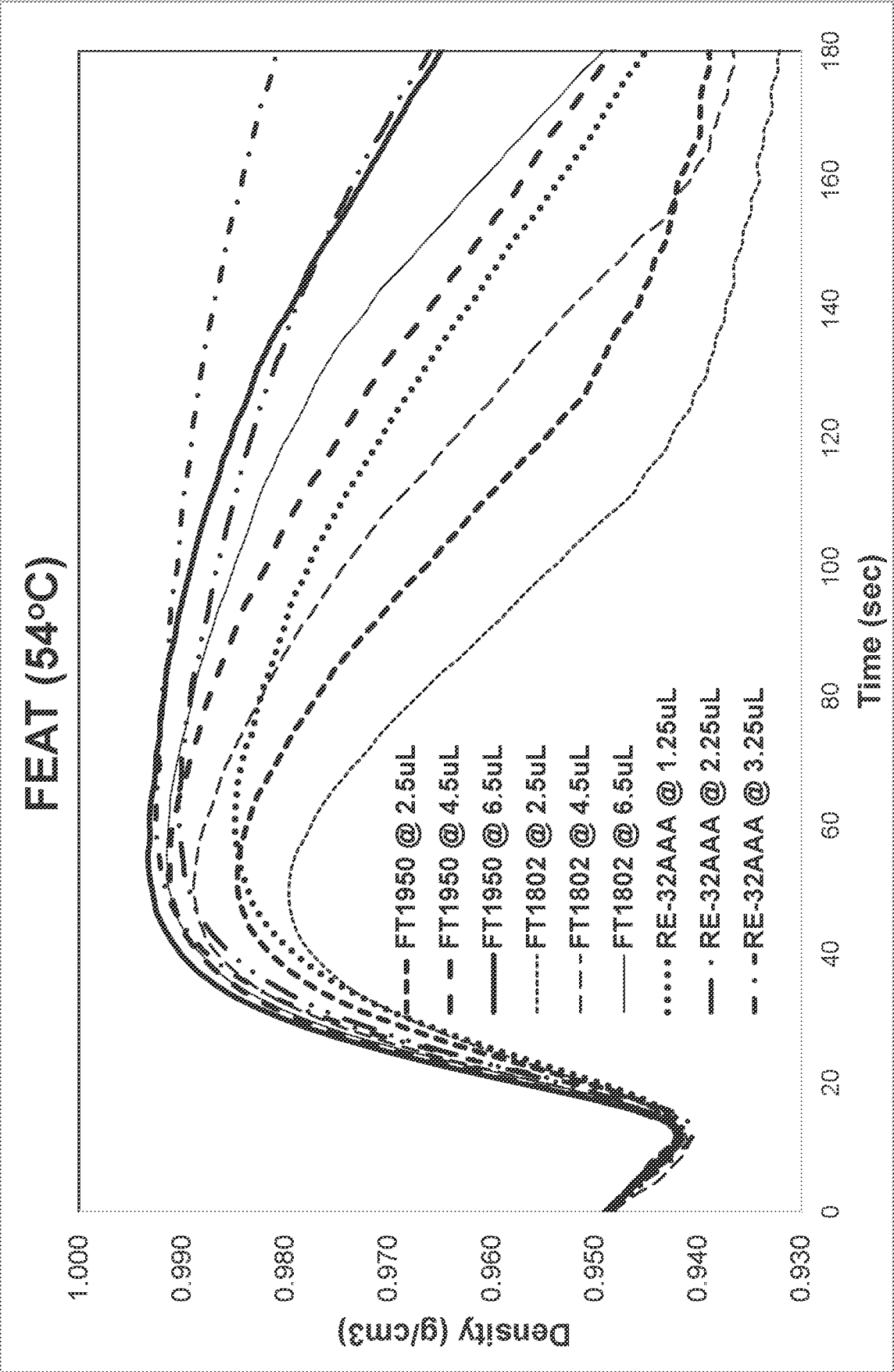


FIG. 1

Defoaming Performance Results On Foaming Media A White Water (WW)

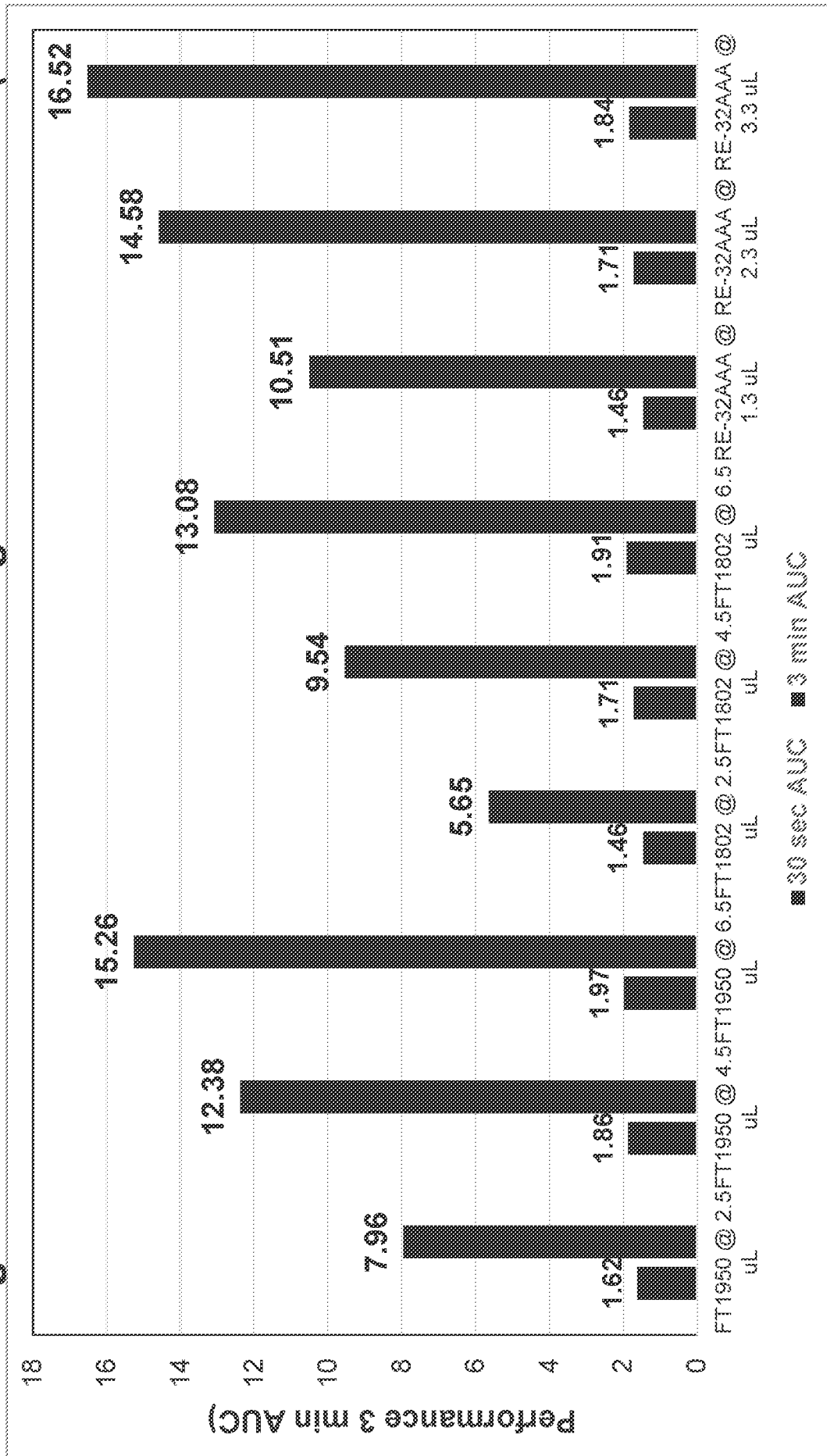


FIG. 2

Defoaming Performance Results On Foaming Media A White Water (WW)

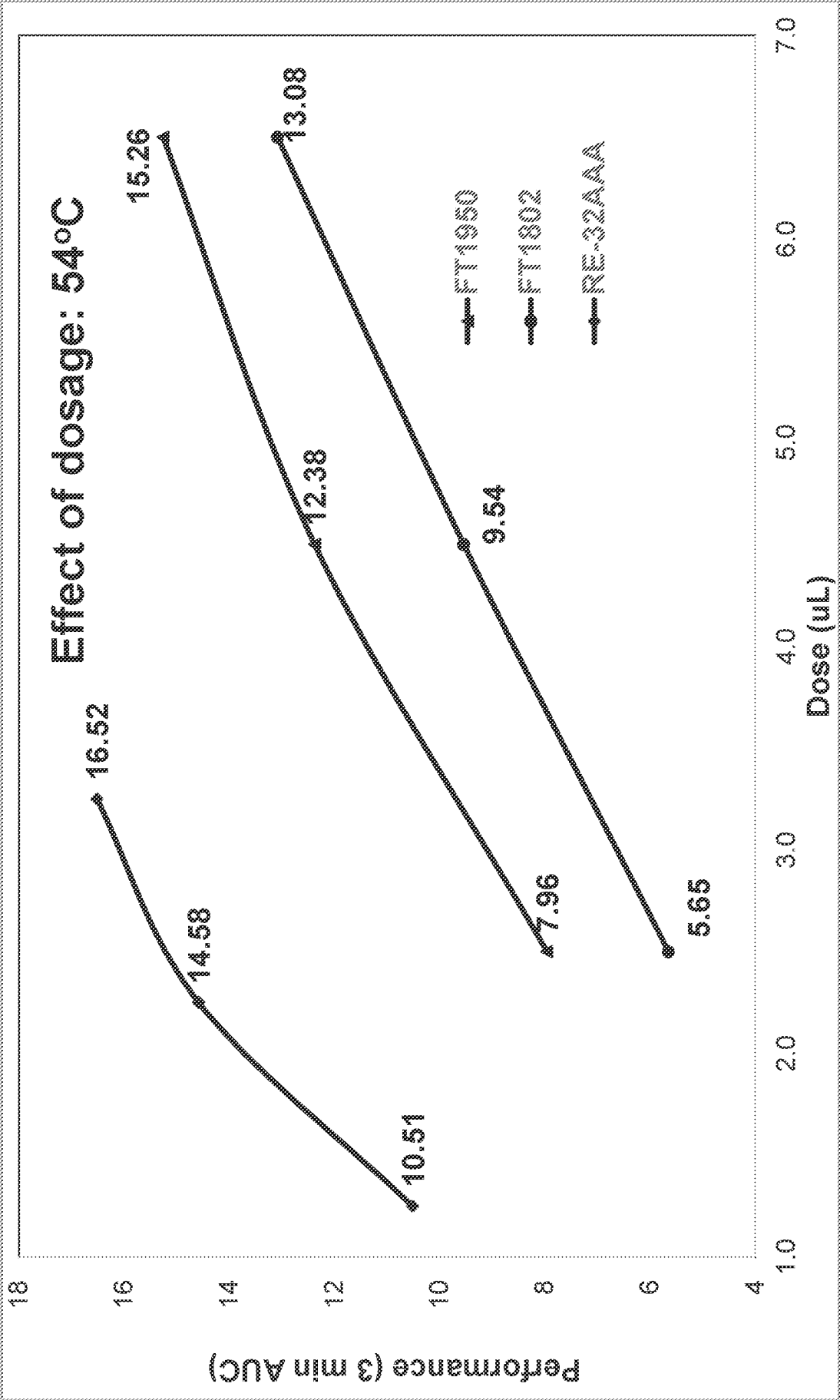


FIG. 3

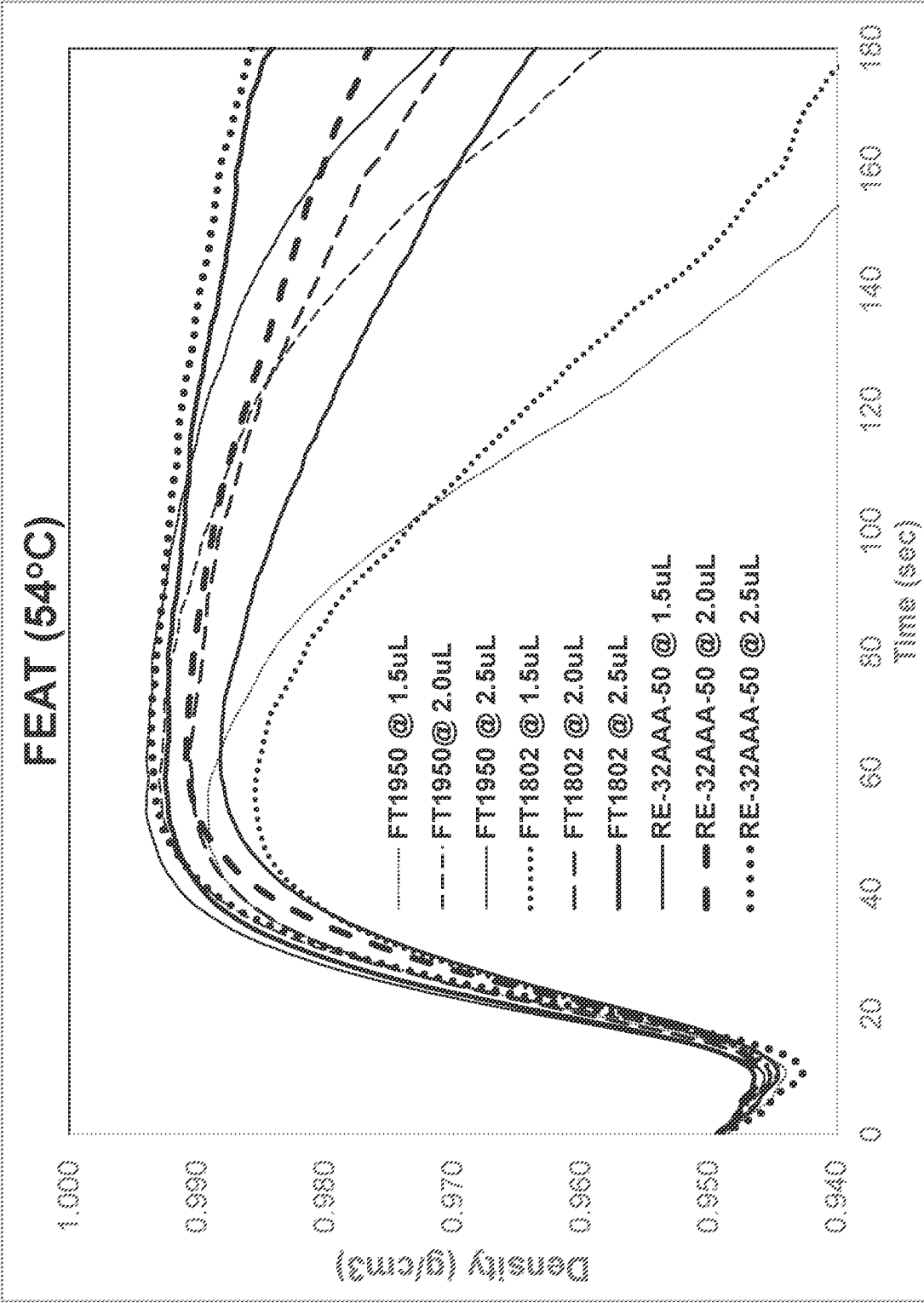


FIG. 4

Defoaming Performance Results On Foaming Media B White Water (WW)

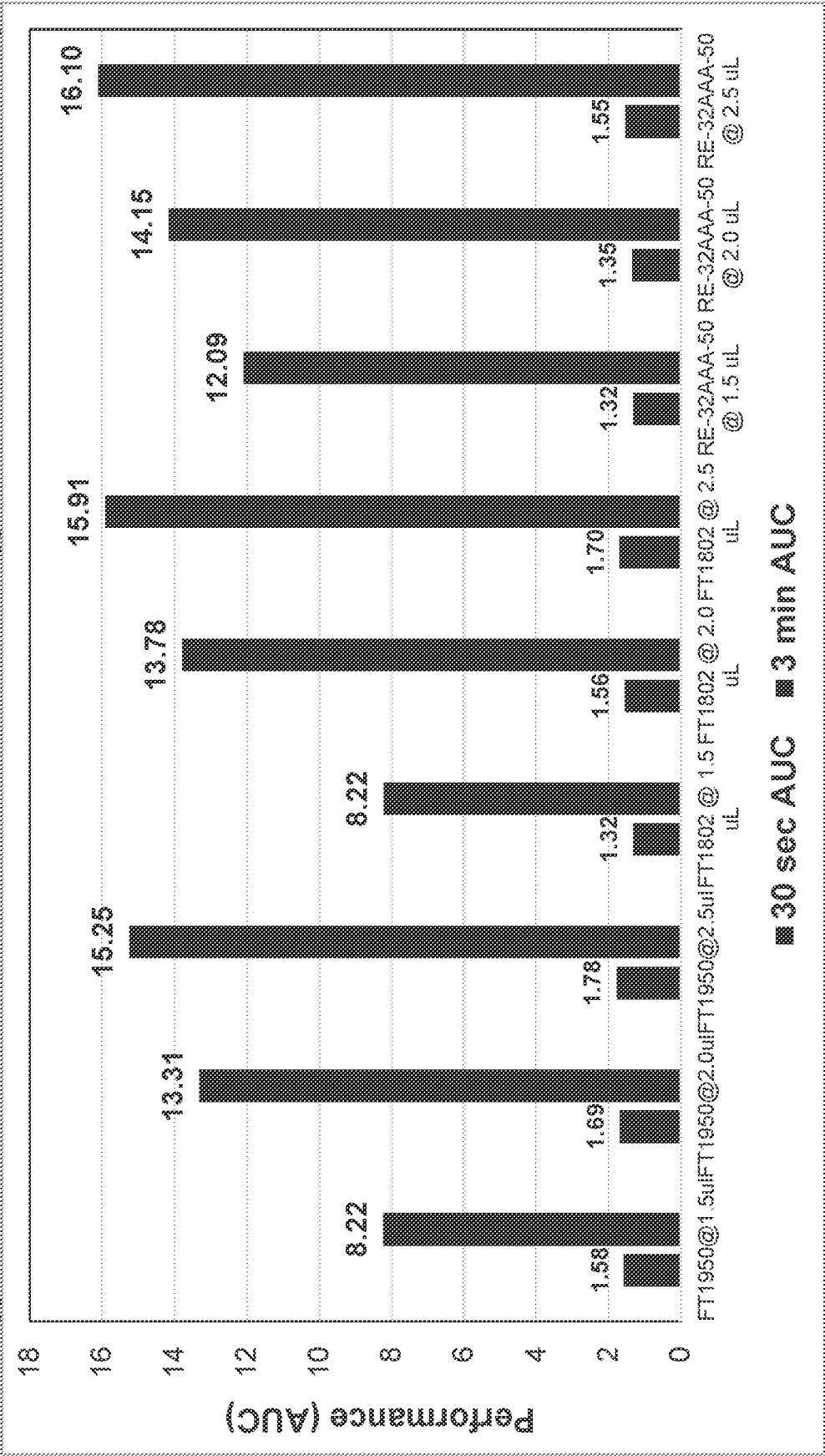


FIG. 5

Defoaming Performance Results On Foaming Media B White Water (WW)

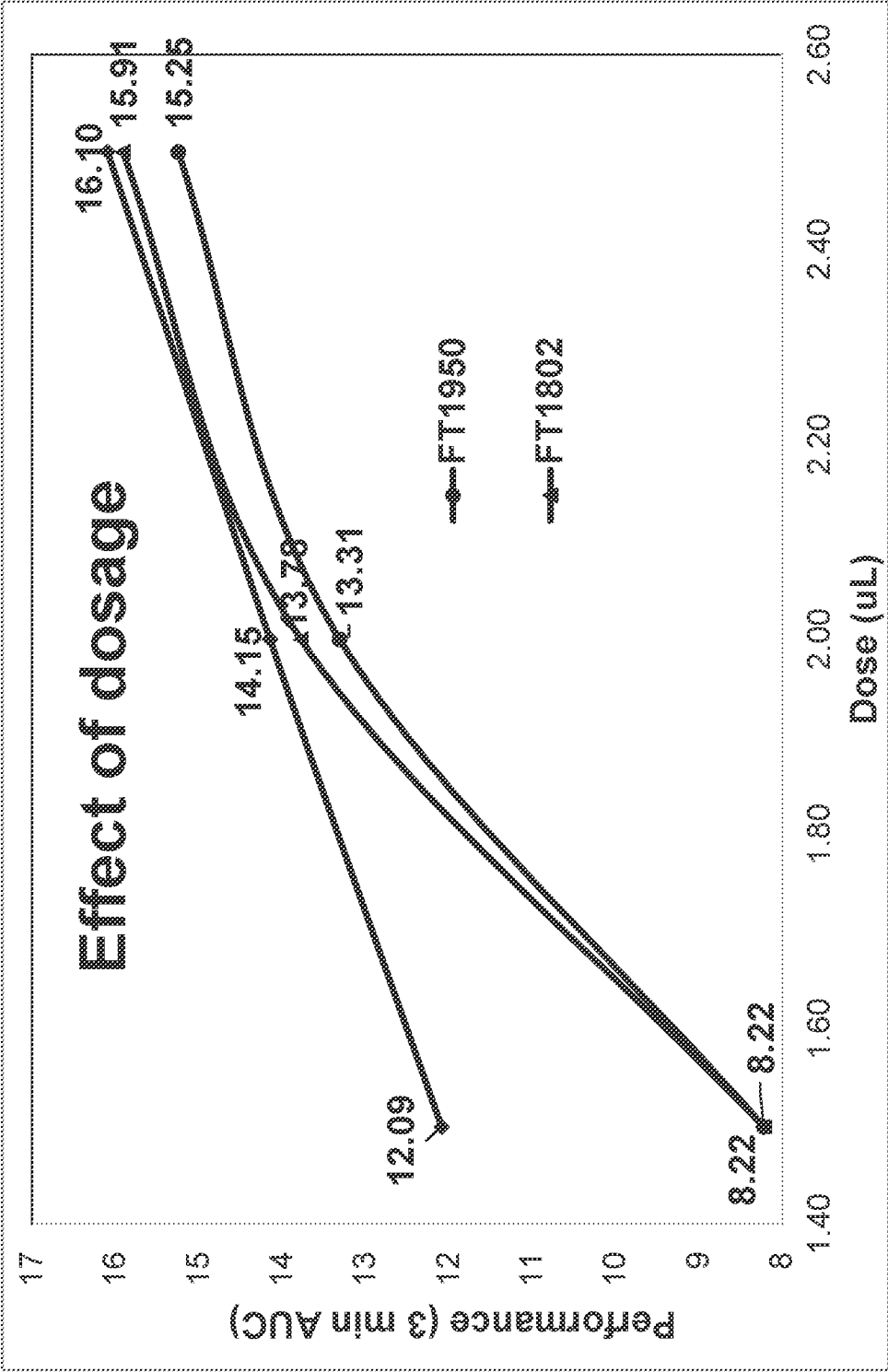


FIG. 6

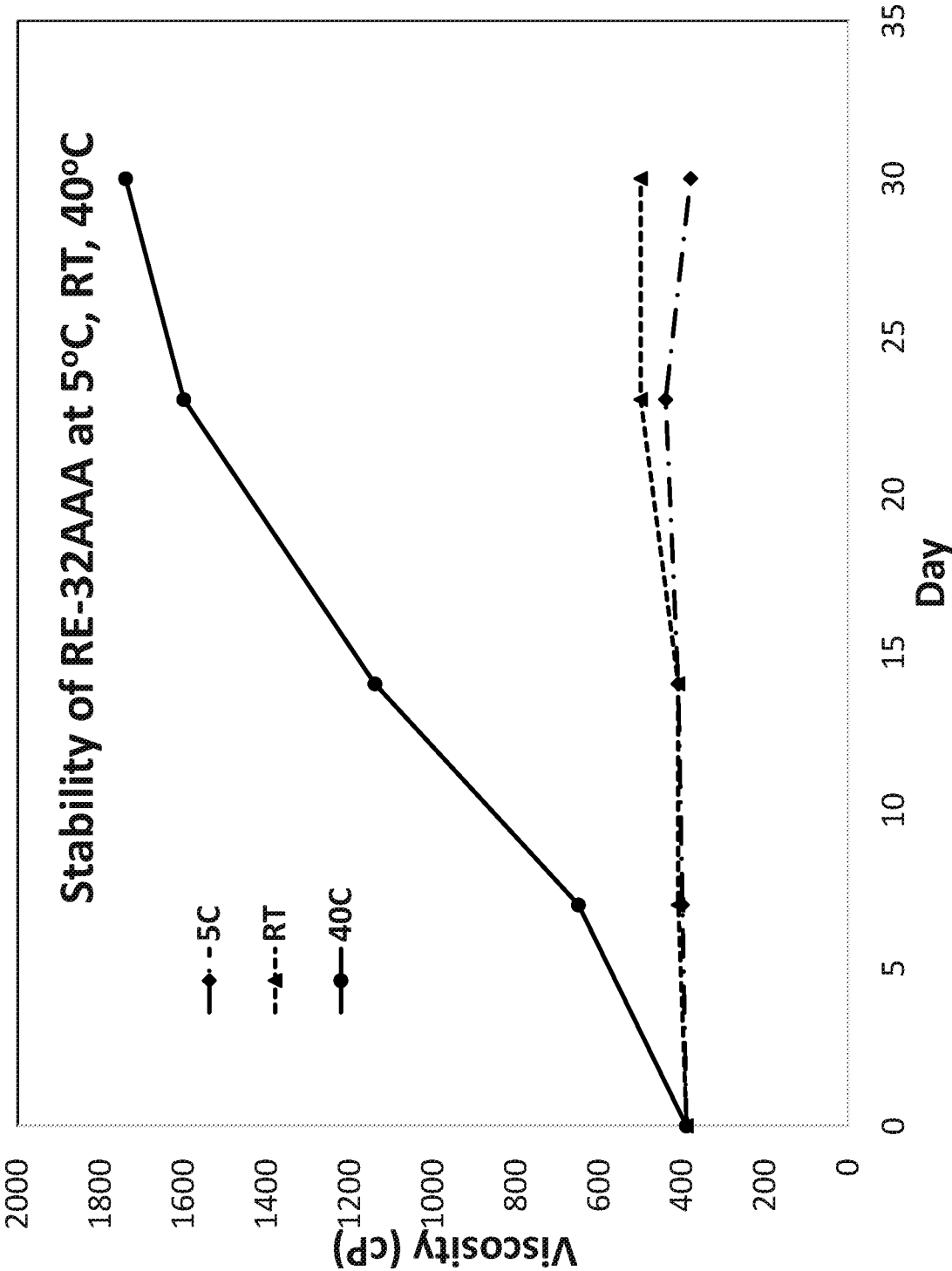


FIG. 7