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(19) **United States**(12) **Patent Application Publication****Vyakaranam et al.**(10) **Pub. No.: US 2025/0257274 A1**(43) **Pub. Date: Aug. 14, 2025**(54) **CORROSION-INHIBITING ADDITIVES AND METHODS OF MAKING AND USE THEREOF**(52) **U.S. Cl.**
CPC **C10G 75/02** (2013.01); **C10G 2300/80** (2013.01)(71) Applicant: **Ecolab USA Inc.**, St. Paul, MN (US)(72) Inventors: **Kameswara R. Vyakaranam**, Sugar Land, TX (US); **Meng Kong**, Shanghai (CN); **Ashish DHAWAN**, Aurora, IL (US)(21) Appl. No.: **18/289,057**(22) PCT Filed: **Nov. 3, 2022**(86) PCT No.: **PCT/CN2022/129434**

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(2) Date: **Oct. 31, 2023****Publication Classification**(51) **Int. Cl.**
C10G 75/02 (2006.01)(57) **ABSTRACT**

Additives, and methods of making and using the additives are described. The additives may be provided as concentrates for addition to one or more hydrocarbons in crude oil refining and processing facilities to inhibit corrosion of corrodible metal parts in contact with the process streams. The additives may be made by reacting glycerol-restricted vegetable oil fatty acid with amine, wherein the glycerol-restricted vegetable oil fatty acid may be a hydrolyzed vegetable oil that is at least partially purified with respect to glycerol. The additives may be further reacted to provide ammonium salts that may be added to aqueous compositions to provide corrosion protection of corrodible surfaces in contact with the aqueous compositions.

CORROSION-INHIBITING ADDITIVES AND METHODS OF MAKING AND USE THEREOF

TECHNICAL FIELD

[0001] The invention is directed to fatty amide additives and their combinations with fatty ester additives, ammonium salts of the fatty amide additives, and methods of making and using the additives. The additives are derived from glycerol-restricted vegetable oil fatty acids and amine compounds. The additives may be used as corrosion inhibitors, for example in the crude oil processing and refining industries, but may also find use as dispersants, lubricants, anti-foaming agents, foaming agents, and release agents.

BACKGROUND

[0002] In 1861, early petroleum refining converted crude oil into kerosene. Today, refinery processes typically include processing and/or treatment of crude oil to provide not only kerosene, but also a wide range of other products and product intermediates. While certain process steps such as distillation, cracking, and removal of impurities and byproducts are common, the technology adapted to the same processes can differ considerably across refineries. Petroleum refining may begin with the desalination of feedstock, followed by the distillation or fractionation of the hydrocarbon process stream into different hydrocarbon groups. By changing the size and structure of the hydrocarbon molecules by cracking, reforming, and other transformation processes, most distillation products are further converted into the desired, more usable products or product intermediates. To eliminate unnecessary constituents or enhance product quality, these converted products and/or intermediates may then be subjected to various treatment and separation processes, such as extraction, hydrotreatment, and sweetening. Integrated refineries not only provide multiple separation and/or treatment steps such as fractionation, refining, treatment, and blending operations, but such refineries may also include petrochemical processing.

[0003] The refinery industry relies heavily on certain important materials, including carbon and alloy steel, copper, aluminum, and nonferrous alloy, for the construction of petroleum refinery equipment such as pressure vessels, storage vessels, separation units, reaction vessels, pumps, sensors, valves, columns, boilers, heat exchangers, condensers, pipelines, and the like. Corrosion of these metallic components is, however, a major cause of inefficiency in the refining process as it leads to degradation, shortened service life, or even failure of equipment at great annual cost to the refining industry to handle maintenance, service, repair, replacement, and the like. Corrosion risk generally intensifies with the elevated temperatures used in refinery equipment.

[0004] Crude oil is a complex mixture of many different hydrocarbons and typically a relatively small portion of nonhydrocarbons. Besides hydrocarbons, crude oils may include not only other organic materials but also sulfur, chlorine, nitrogen, and oxygen-containing compounds as dissolved gases, liquids, and solid phases in the oil. Many of these nonhydrocarbon constituents may be in form of corrosive agents, or precursors of corrosive agents, that attack the refinery equipment.

[0005] Crude oils may be graded by two methods. A first is based on the proportions of organic compounds such as paraffinic compounds, naphthenic compounds, aromatic compounds, or mixtures thereof. A second method of classifying crude oils is by their American Petroleum Institute (API) gravity, which is generally inversely proportional to the density of crude oil. The greater the API gravity, the lighter the crude oil is. Low carbon, high hydrogen, and high API gravity crude oils are usually rich in paraffin and tend to produce higher proportions of petrol and light petroleum products. Lower carbon, low hydrogen, and low API gravity oils are generally relatively richer in aromatics.

[0006] Crude oils may contain entrained water and/or brine. Corrodents may reside in the hydrocarbons and/or the aqueous portions of the crude oil. Corrodents that may be contained in crude oil include hydrogen chloride, organic and inorganic chlorides, hydrogen sulfide, mercaptans and/or other organic sulfur compounds, carbon dioxide, dissolved oxygen, water, organic acids, and/or nitrogen compounds.

[0007] Crude oils containing large quantities of hydrogen sulfide (H_2S) are called “sour” crudes, and those with less H_2S are known as “sweet” crudes.

[0008] Naphthenic acid is an organic acid that is often present in crude oils and hydrocarbon streams in oil refining and processing. Naphthenic acid is corrosive towards carbon steel and stainless steel, especially at higher temperatures (e.g. at or above $260^\circ C$). Corrosion is greatly increased by the presence of naphthenic acid and/or sulfur compounds in the high-temperature areas of distillation systems. The presence of some organic acids such as formic, acetic, and propionic acids may induce corrosion even at lower temperatures (e.g. below $260^\circ C$).

[0009] In order to inhibit the expensive problem of corrosion in oil refining, corrosion inhibitors are widely used in the petroleum recovery and processing industries. Corrosion inhibitors and/or other types of additives may be incorporated into corresponding formulations (also “compositions”) that are diluted to some degree with solvent or used undiluted in neat form. These formulations, with or without solvent, may also include one or more other optional ingredients. Hence, the term “additive formulation” refers to a composition that comprises one or more additives, optionally a solvent, and optionally one or more other ingredients. Similarly, as used herein, a “corrosion inhibitor” is an additive that helps to protect against corrosion. As used herein, a “corrosion inhibitor formulation” is a composition that comprises one or more corrosion inhibitors, optionally a solvent, and optionally one or more other ingredients. Such additive and corrosion inhibitor formulations may be provided in a variety of forms such as a solid (e.g. powder, pellets, granules, blocks, or the like), liquid, dispersion, gel, putty, gas, and/or the like. The liquid, solution, dispersion, and gel embodiments of these formulations tend to be more prone to stability issues associated with phase separation.

[0010] Batches of manufactured additive formulations are typically stored for some period of time before use or further processing. It is desirable that during storage and/or transport additive formulations are stable, for example to undue phase separation into separate liquids, to precipitation of solids and/or gels, to settling, or to other undesired phase separation. Additive formulations exhibiting such changes may require special treatment to return the additive formulation to its original state. It may not even be possible to

return the additive formulation to its original state in a practical manner, and in its changed form the additive formulation may be unusable. For example, in additive formulations including precipitates, settled material may not be pumpable or pourable. In any case, undue phase separation of additive compositions during storage or transport is highly undesirable. In contrast, in some instances phase separation during actual use in a refinery may be acceptable or even desired in cases in which the additive can still provide the desired function, e.g., corrosion protection in the case of a corrosion inhibitor. In other instances, it may be desirable to protect against phase separation even during use in a refinery as well.

[0011] For addition to industrial process streams or batches, such as hydrocarbon-containing processing streams or batches in petroleum refining operations, additive formulations may be conveniently provided in a variety of forms such as in the form of a solution or dispersion in an organic solvent that is miscible in hydrocarbon petroleum streams such as crude oil and other hydrocarbon petroleum streams. Since such solutions or dispersions of the additives are typically shipped and stored, it can be economical if the solutions or dispersions are relatively concentrated with respect to the additives, thereby avoiding the extra expense that shipping and storing a commodity such as organic solvent entails. Such solutions or dispersions provide flexibility in that they can easily be further diluted at a more suitable time such as at or close to point-of-use if so desired, while they can be used without further dilution if higher concentrations are desired.

[0012] Like the additives themselves, such solutions and/or dispersions or more diluted formulations of additives are desirably sufficiently stable during storage, shipping, and use. Solutions, dispersions, and/or more diluted formulations of additives are routinely stored and/or transported in unheated winter environments, where they attain temperatures of, for example, 0° C. or below, -10° C. or below, -20° C. or below, -30° C., or even -40° C. or below. Accordingly, it would be an advantage if corrosion inhibitor formulations and other additive formulations could be found that do not unduly phase separate and/or settle in storage, handling, or use, and that when provided in solutions and/or dispersions in organic solvents do not unduly separate, even when stored, handled, transported, or otherwise used at low temperatures.

SUMMARY

[0013] We have discovered additive compositions with restricted glycerol content that are more stable to phase separation. For example, additive compositions that incorporate one or more additives derived from vegetable oil fatty acids such as soybean oil fatty acid are more stable to phase separation if the vegetable oil fatty acid content has a reduced glycerol content. In preferred mode of practice, additive compositions with improved stability incorporate one or more additives derived from glycerol-restricted soybean oil fatty acid. In other modes of practice, the formulations or one or more components thereof, may be processed to remove at least a portion of the glycerol content to thereby improve stability against phase separation.

[0014] We have also discovered that compositions of additives in organic solvent, when made from glycerol-restricted vegetable oil fatty acid, are more stable to precipitation (i.e. exhibit less or no precipitation) when stored

at temperatures such as 0° C. and -10° C. for three weeks than equivalent concentrates made from tall oil fatty acid.

[0015] In one aspect is provided an additive composition comprising a plurality of amides and/or ammonium salts thereof, wherein at least a portion of the plurality of amides comprises a reaction product derived from a first set of reactants comprising one or more glycerol-restricted vegetable oil fatty acids and polyamine, wherein the one or more glycerol-restricted vegetable oil fatty acids comprises 0 percent by weight to 0.1 percent by weight of glycerol with respect to the total weight of the one or more glycerol-restricted vegetable oil fatty acids, and wherein the polyamine comprises a polyamine having the formula $\text{NH}_2(\text{CH}_2\text{CH}_2\text{NH})_x\text{CH}_2\text{CH}_2\text{NH}_2$ wherein x is 0 to 100. For example, if the one or more glycerol-restricted vegetable oil fatty acids consists of 0.06 parts by weight of glycerol and 100 parts by weight of soybean oil fatty acid, then the total weight of the glycerol-restricted soybean oil fatty acid is 100.06 parts by weight, and the glycerol content is $0.06/100.06 \times 100\% = 0.06\%$. The plurality of amides and/or ammonium salts thereof function in some embodiments as a corrosion inhibitor additive in the additive compositions to help protect against corrosion.

[0016] In a further aspect, there is provided a combination additive composition comprising a plurality of amides and/or ammonium salts thereof, and further comprising a plurality of esters. At least a portion of the plurality of amides comprises a first reaction product derived from a first set of reactants comprising one or more glycerol-restricted vegetable oil fatty acids and polyamine, wherein the one or more glycerol-restricted vegetable oil fatty acids comprises 0 percent by weight to 0.1 percent by weight of glycerol with respect to the total weight of the one or more glycerol-restricted vegetable oil fatty acids, and wherein the polyamine comprises, consists of, or consists essentially of a polyamine that has the formula $\text{NH}_2(\text{CH}_2\text{CH}_2\text{NH})_x\text{CH}_2\text{CH}_2\text{NH}_2$ wherein x is 0 to 100. At least a portion of the plurality of esters comprises a second reaction product derived from a second set of reactants comprising second one or more glycerol-restricted vegetable oil fatty acids and one or more tertiary amines, each of the one or more tertiary amines having at least one hydroxyl group, wherein the second one or more glycerol-restricted vegetable oil fatty acids comprises 0 percent by weight to 0.1 percent by weight of glycerol with respect to the total weight of the second one or more glycerol-restricted vegetable oil fatty acids. Individually, each of the plurality of amides and the plurality of esters, and compositions containing the plurality of amides or compositions containing the plurality of esters, may be used in a variety of applications such as to inhibit corrosion. However, combinations of the plurality of amides and the plurality of esters, and compositions containing the combinations, are particularly effective in inhibition of corrosion.

[0017] In a further aspect is provided a composition comprising heavy aromatic naphtha and an additive comprising a plurality of amides and/or ammonium salts thereof, wherein at least a portion of the plurality of amides comprises a reaction product derived from a first set of reactants comprising one or more glycerol-restricted vegetable oil fatty acids and a polyamine, wherein the one or more glycerol-restricted vegetable oil fatty acids comprises 0 percent by weight to 0.1 percent by weight of glycerol with respect to the total weight of the one or more glycerol-restricted vegetable oil fatty acids, and wherein the

polyamine has the formula $\text{NH}_2 (\text{CH}_2\text{CH}_2\text{NH})_x \text{CH}_2\text{CH}_2\text{NH}_2$ wherein x is 0 to 100. The reaction product derived from the first set of reactants may be conveniently synthesized in heavy aromatic naphtha to provide the composition, and/or heavy aromatic naphtha may be added to the reaction product after the synthesis to form the composition. The composition comprising heavy aromatic naphtha is in a convenient form to add to one or more hydrocarbons to impart desirable properties thereto, such as corrosion inhibition, antifouling properties, and/or other desirable properties. Heavy aromatic naphtha is generally miscible with hydrocarbons and accordingly, on addition to one or more hydrocarbons, the composition may disperse in the one or more hydrocarbons, thereby imparting improved characteristics thereto.

[0018] In a further aspect is provided a composition comprising heavy aromatic naphtha, a plurality of amides and/or ammonium salts thereof, and further comprising a plurality of esters. At least a portion of the plurality of amides comprises a first reaction product derived from a first set of reactants comprising first one or more glycerol-restricted vegetable oil fatty acids and a polyamine, wherein the first one or more glycerol-restricted vegetable oil fatty acids comprises 0 percent by weight to 0.1 percent by weight of glycerol with respect to the total weight of the first one or more glycerol-restricted vegetable oil fatty acids, and wherein the polyamine comprises a polyamine that has the formula $\text{NH}_2 (\text{CH}_2\text{CH}_2\text{NH})_x \text{CH}_2\text{CH}_2\text{NH}_2$ wherein x is 0 to 100. At least a portion of the plurality of esters comprises a second reaction product derived from a second set of reactants comprising second one or more glycerol-restricted vegetable oil fatty acids and one or more tertiary amines, each of the one or more tertiary amines having at least one hydroxyl group, wherein the second one or more glycerol-restricted vegetable oil fatty acids comprises 0 percent by weight to 0.1 percent by weight glycerol with respect to the total weight of the second one or more glycerol-restricted vegetable oil fatty acids. Individually, each of the plurality of amides, the ammonium salts thereof, and the plurality of esters, and compositions containing them, may be used in a variety of applications such as to inhibit corrosion. However, combinations of the plurality of amides and the plurality of esters, and compositions containing the combinations, are particularly effective in inhibition of corrosion.

[0019] In a further aspect is provided a composition comprising more than 5 percent by weight of water with respect to the total weight of the composition and an additive comprising ammonium salts of a plurality of amides, wherein at least a portion of the plurality of amides comprises a reaction product derived from a set of reactants comprising one or more glycerol-restricted vegetable oil fatty acids and a polyamine, wherein the one or more glycerol-restricted vegetable oil fatty acids comprises 0 percent by weight to 0.1 percent by weight of glycerol with respect to the total weight of the one or more glycerol-restricted vegetable oil fatty acids, and wherein the polyamine has the formula $\text{NH}_2 (\text{CH}_2\text{CH}_2\text{NH})_x \text{CH}_2\text{CH}_2\text{NH}_2$ wherein x is 0 to 100. The ammonium salts may be more water-soluble and/or water-dispersible than the amides, and therefore the compositions are particularly useful for addition to aqueous materials to impart desirable properties thereto, for example to impart corrosion-inhibitory properties or dispersant properties in aqueous systems.

[0020] In a further aspect is provided a hydrocarbon composition comprising one or more hydrocarbons and at least one additive composition incorporated into the one or more hydrocarbons, wherein the at least one additive composition is selected from an amide composition, an ester composition, and a combination thereof. The amide composition comprises a plurality of amides, wherein at least a portion of the plurality of the amides comprises a first reaction product derived from a first set of reactants comprising first one or more glycerol-restricted vegetable oil fatty acids and a polyamine, wherein the first one or more glycerol-restricted vegetable oil fatty acids comprises 0 percent by weight to 0.1 percent by weight of glycerol with respect to the total weight of the first one or more glycerol-restricted vegetable oil fatty acids, and wherein the polyamine has the formula $\text{NH}_2 (\text{CH}_2\text{CH}_2\text{NH})_x \text{CH}_2\text{CH}_2\text{NH}_2$ wherein x is 0 to 100; and wherein the ester composition comprises a plurality of esters, wherein at least a portion of the plurality of the esters comprises a second reaction product derived from a second set of reactants comprising second one or more glycerol-restricted vegetable oil fatty acids and one or more tertiary amines, each of the one or more tertiary amines having at least one hydroxyl group, wherein the second one or more glycerol-restricted vegetable oil fatty acids comprises 0 percent by weight to 0.1 percent by weight glycerol with respect to the total weight of the second one or more glycerol-restricted vegetable oil fatty acids. Incorporation of the additive composition into the one or more hydrocarbons may impart corrosion-inhibiting properties to the combination of the one or more hydrocarbons and the additive composition, or may inhibit or otherwise ameliorate corrosion of metal components in contact with the one or more hydrocarbons from corrodents therein.

[0021] In a further aspect is provided a method of providing corrosion protection of a surface in contact with one or more hydrocarbons, the method comprising combining a corrosion inhibitor composition with the one or more hydrocarbons, wherein the corrosion inhibitor composition comprises a plurality of amides and/or ammonium salts thereof, wherein at least a portion of the plurality of amides comprises a reaction product derived from a first set of reactants comprising one or more glycerol-restricted vegetable oil fatty acids and a polyamine, wherein the one or more glycerol-restricted vegetable oil fatty acids comprises 0 percent by weight to 0.1 percent by weight of glycerol with respect to the total weight of the one or more glycerol-restricted vegetable oil fatty acids, and wherein the polyamine has the formula $\text{NH}_2 (\text{CH}_2\text{CH}_2\text{NH})_x \text{CH}_2\text{CH}_2\text{NH}_2$ wherein x is 0 to 100. The methods are, for example, useful in petroleum or other hydrocarbon industrial processing facilities, where addition of the corrosion inhibitor composition to the one or more hydrocarbons may inhibit the corrosion of metal parts in contact with the one or more hydrocarbons.

[0022] In a further aspect is provided a method of making an additive composition, the additive composition comprising a first reaction product. The method comprises combining one or more glycerol-restricted vegetable oil fatty acids with a polyamine to form a first reaction mixture, wherein the one or more glycerol-restricted vegetable oil fatty acids comprises 0% to 0.1% by weight glycerol with respect to the total weight of the one or more glycerol-restricted vegetable oil fatty acids; optionally adding a hydrocarbon solvent to

the first reaction mixture; heating the first reaction mixture at a reaction temperature and for a time period effective to form water and a first reaction product, the first reaction product comprising a plurality of amides. The additive composition is useful for addition, for example, to hydrocarbon process streams and batches in industrial processes to impart corrosion inhibiting properties thereto.

[0023] In a further aspect is provided a method of making a combination additive composition, the method comprising combining first one or more glycerol-restricted vegetable oil fatty acids with a polyamine to form a first reaction mixture, wherein the first one or more glycerol-restricted vegetable oil fatty acids comprises 0% to 0.1% by weight glycerol with respect to the total weight of the first one or more glycerol-restricted vegetable oil fatty acids; optionally adding a hydrocarbon solvent to the first reaction mixture; heating the first reaction mixture at a reaction temperature and for a time period effective to form water and a first reaction product, the first reaction product comprising a plurality of amides; combining second one or more glycerol-restricted vegetable oil fatty acids with one or more tertiary amines, each of the one or more tertiary amines comprising at least one hydroxyl group, to form a second reaction mixture; heating the second reaction mixture at a reaction temperature and for a time period effective to form a second product mixture comprising water and a second reaction product, wherein the second reaction product comprises a plurality of esters; and combining ingredients comprising the first reaction product and the second reaction product to form the combination additive composition. The combination of the first and second reaction products, and compositions comprising the combination, are useful as, for example, corrosion inhibitors for addition to hydrocarbon streams to impart corrosion-inhibiting properties thereto.

DETAILED DESCRIPTION

[0024] Although the present disclosure provides references to various embodiments, persons skilled in the art will recognize that changes may be made in form and detail without departing from the spirit and scope of the application. Various embodiments will be described in detail with reference to the figures. Reference to various embodiments does not limit the scope of the claims attached hereto. Additionally, any examples set forth in this application are illustrative and are not intended to be limiting and merely set forth some of the many possible embodiments for the appended claims.

Definitions

[0025] Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art. In case of conflict, the present document, including definitions, will control. Methods and materials are described below, although methods and materials similar or equivalent to those described herein can be used in practice or testing of the present application. All publications, patent applications, patents and other references mentioned herein are incorporated by reference in their respective entireties and for all purposes.

[0026] As used herein, the terms “comprise(s),” “include(s),” “having,” “has,” “can,” “contain(s),” and variants thereof are intended to be open-ended transitional phrases,

terms, or words that do not preclude the possibility of additional acts or structures. The singular forms “a,” “and” and “the” include plural references unless the context clearly dictates otherwise.

[0027] As used herein, the term “optional” or “optionally” means that the subsequently described material, condition, feature, event or circumstance may but need not occur, and that use thereof includes instances where the material, condition, feature, event or circumstance occurs and instances in which it does not.

[0028] As used herein, any recited ranges of values contemplate all values within the range and are to be construed as support for claims reciting any sub-ranges having endpoints which are real number values within the recited range. By way of example, a disclosure in this specification of a range of from 1 to 5 shall be considered to support claims to any of the following ranges: 1-5; 1-4; 1-3; 1-2; 2-5; 2-4; 2-3; 3-5; 3-4; and 4-5; and fractions thereof e.g. 1.5-3.5, 1.7-4.8, etc.

[0029] Herein, the combination of fatty acids that may be produced by hydrolysis of a single type of vegetable oil is referred to as “vegetable oil fatty acid”. Because a single type of vegetable oil comprises esters of a variety of fatty acids, hydrolysis of the vegetable oil produces a combination of fatty acids. For example, hydrolysis of soybean oil may produce “soybean oil fatty acid” in combination with byproduct glycerol. While used in the singular, soybean oil fatty acid comprises a combination of different fatty acid compounds, not a single fatty acid compound. Vegetable oils are natural products, and may vary in composition, for example with regard to the relative content of various fatty acid compounds in the form of esters. However, the types and ranges of each fatty acid compound in the vegetable oil fatty acid are generally characteristic of the type of vegetable oil from which the vegetable oil fatty acid may be derived. While “vegetable oil fatty acid” used in the singular refers to a combination of fatty acid compounds that may be produced by the hydrolysis of the namesake vegetable oil, “vegetable oil fatty acids” refers herein to a combination of fatty acids that may be produced by the hydrolysis of a combination of two or more types of vegetable oil.

[0030] As used herein, the term “glycerol-restricted” with respect to a material generally signifies that the material comprises no more than 0.1 percent by weight of glycerol with respect to the weight of that material (including glycerol if any). For example, “glycerol-restricted fatty amide” refers to a material comprising fatty amide(s), wherein the material comprises no more than 0.1 percent by weight of glycerol with respect to the weight of the glycerol-restricted fatty amide.

[0031] The term “glycerol-restricted vegetable oil fatty acid” refers to a mixture comprising no more than 0.1% by weight glycerol and no less than 99% by weight of fatty acids with respect to the mixture. Glycerol-restricted vegetable oil fatty acids may be made by various means. One commercially important means of making a glycerol-restricted vegetable oil fatty acid is by hydrolysis of the namesake vegetable oil and subsequent purification to remove glycerol, which is a byproduct of the hydrolysis. The types of fatty acid and their proportions in the glycerol-restricted vegetable oil fatty acid depend upon the composition of the vegetable oil hydrolyzed, especially the type of vegetable oil, that is the type of vegetable from which the vegetable oil was sourced. For example, while soybean oil

as a natural product may vary in composition with respect to fatty acid esters, it may do so within ranges that are characteristic of soybean oil. However, in principle the glycerol-restricted vegetable oil fatty acid could also be produced by combining the correct types of fatty acid in the correct proportions and for which the cumulative glycerol content, if any, is sufficiently low such that the resultant mixture is glycerol-restricted as defined in accordance with the present invention. In such a mode of practice, some degree of purification to reduce the glycerol content would not be needed, since the fatty acid materials are suitably glycerol-restricted at the outset. Solely for the purposes of illustration, a glycerol-restricted soybean oil fatty acid could in a particular example comprise 10% by weight palmitic acid, 4% by weight of stearic acid, 23% by weight oleic acid, 51% by weight of linoleic acid, and 9% by weight of alpha-linolenic acid with respect to the total weight of fatty acids. Such a glycerol-restricted soybean oil fatty acid could in principle be produced by combining 10 parts by weight palmitic acid, 4 parts by weight of stearic acid, 23 parts by weight of oleic acid, 51 parts by weight of linoleic acid, 9 parts by weight of alpha-linolenic acid, and any other components of the glycerol-restricted soybean oil fatty acid in which the glycerol is restricted as supplied or the mixture is purified to remove glycerol.

[0032] Herein, “hydrolyzed vegetable oil” and like terms including specific vegetable oil names refers to a composition that is produced by hydrolysis of the vegetable oil. For example, the composition comprising soybean oil fatty acid and glycerol that may be produced by the hydrolysis of soybean oil is termed herein “hydrolyzed soybean oil”.

[0033] As used herein, “polyamine”, “a polyamine”, and “the polyamine” are construed to refer to discrete compounds having a single molecular weight, such as tetraethylenepentamine

($\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$), as well as combinations of individual polyamine compounds. For example, a polyamine may have the formula $\text{NH}_2(\text{CH}_2\text{CH}_2\text{NH})_x\text{CH}_2\text{CH}_2\text{NH}_2$ wherein x is from 0 to 100. In this particular example, the number x is an integer if the polyamine is a discrete polyamine compound, but x may also be a fraction or mixed number if the polyamine is a mixture of discrete polyamine compounds having differing molecular weights. The term “polyamine” as used herein is not used to refer solely to a discrete polyamine compound, although it may do so, but also to mixtures and/or combinations of discrete polyamine compounds. A polyamine may include 2 or more, even 3 or more, even 4 or more, or even 5 or more amine moieties. The amine moieties may be primary, secondary, and/or tertiary.

[0034] As used herein, the term “concentrate” generally refers to a composition in which the concentration of additive(s) is higher than the concentration of such additives after the composition is diluted for an intended use. A concentrate may be a solid, liquid, dispersion, gel, or gas. A concentrate may or may not include solvent until further diluted. In representative modes of practice, a concentrate may include 0 to 80 parts, or even 0 to 50 parts, or even 0 to 25 parts, or even 0 to 10 parts of solvent per 100 parts by weight of additive(s) prior to dilution with a solvent. If desired, a concentrate can be diluted by adding some amount of additional solvent, which may be the same and/or different than the solvent in the concentrate. By way of example, dilution may occur by adding 1 to 1000, or even 10 to 500,

or even 10 to 100 parts by weight of additional solvent per 50 to 100 parts by weight of solvent in the concentrate.

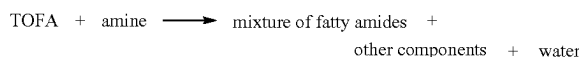
[0035] All reaction schemes herein are for the purpose of illustrating reactants and reaction products.

Discussion

[0036] Commercial practice has used fatty amides as corrosion inhibitors or as other types of additives, for example in oil refining. In conventional practice, fatty amides have been made by reacting tall oil or tall oil fatty acid with amines. Tall oil and tall oil fatty acid (TOFA) have been convenient sources of fatty acids. Tall oil is a byproduct of the Kraft process of wood pulp manufacture. Typically crude tall oil contains rosins, which contain resin acids (mainly abietic acid and its isomers); a mixture of fatty acids (mainly palmitic acid, oleic acid and linoleic acid); fatty alcohols; sterols; and other alkyl hydrocarbon derivatives. Tall oil fatty acid is a purified form of tall oil and contains a lower weight percentage of rosin (1-10 percent by weight) than tall oil. Tall oil fatty acid comprises fatty acids, predominantly oleic acid.

[0037] Tall oil fatty acid (TOFA) may be reacted with one or more amines to produce TOFA amide that is a reaction product comprising a mixture of fatty amides, as well as other components resulting from resin acids in the TOFA. The reaction can be summarized as follows:

Scheme 1



TOFA-derived fatty amides may find use as corrosion inhibiting additives, for example, in hydrocarbon streams of crude oil refining or other processing. Conveniently, additive compositions incorporating such additives into hydrocarbon streams may be provided as concentrates in an organic solvent. The concentrates, either as is or in a diluted form, are stored, shipped, and provided to oil processing plants for addition to hydrocarbon streams therein. However, concentrates or even diluted forms of such additives may be unstable when stored at lower temperatures, for example 0° C. or less, -10° C. or less, or -20° C. or less, over a period of days or weeks, exhibiting precipitates, other phase separation, or other instability so that the affected composition cannot be easily redissolved or redispersed. For example, a corrosion-inhibiting composition incorporating a reaction product of TOFA and 2-aminoethylethanolamine (AEEA) exhibited precipitation after only a few days at each of 0° C., -10° C., or -20° C. Long term storage, for example 64 days at -10° C. or -20° C., produced precipitates that could not be redissolved, even after warming to room temperature (15-25° C., or about 20° C.). Hence concentrates, or even diluted forms, of TOFA-derived corrosion inhibitors as conventionally used may be more unstable than desired at colder temperatures. Without being bound by theory, we speculate that this instability may be the result, direct or indirect, of rosin content in the TOFA.

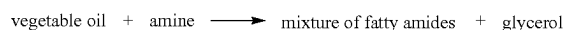
[0038] While the rosin acid content could be removed using a separation technique, a further drawback is much harder to overcome. It is becoming increasingly difficult to obtain tall oil or TOFA materials from commercial sources at prices that are economically practical. Accordingly, it has become increasingly desirable to find fatty amide materials that can be more easily sourced as an alternative to tall oil or TOFA materials.

[0039] Fatty amides may also be made by the reaction of vegetable oils with one or more amines. Vegetable oils comprise glycerides, predominantly triglycerides. Glycerides are the esters of glycerol (propan-1,2,3-triol) and fatty acids. Fatty amides derived from vegetable oils show great potential as alternative corrosion inhibitors to fatty amides derived from tall oil or TOFA. As one advantage, fatty amides derived from one or more vegetable oils can provide excellent corrosion protection and as a natural matter contain de minimis if any rosin acid content. Unfortunately, a technical challenge against use of such materials relates to stability. We have found that additives made from vegetable oils and incorporating glycerol tend to have poor stability in terms of undergoing phase separation.

[0040] Significantly, the practice of the present invention provides a technical solution that provides vegetable oil-derived fatty amides that are much more stable. As a consequence, the fatty amide materials of the present invention may be used as a substitute for all or a portion of the tall oil and TOFA materials that have been used previously.

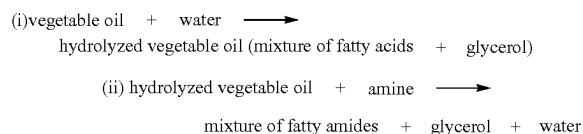
[0041] Because a vegetable oil comprises a mixture of glycerides, on reaction with even a single type of amine, a mixture of fatty amides results. The general reaction between a vegetable oil and an amine can be summarized as follows, wherein glycerol is a byproduct:

Scheme 2



[0042] Alternatively, one or more vegetable oils may be hydrolyzed to produce hydrolyzed vegetable oil, which includes a mixture of fatty acids with byproduct glycerol. The hydrolyzed vegetable oil (fatty acids and glycerol) may then be reacted with an amine to produce fatty amides in combination with the glycerol. The reactions may be summarized as follows:

Scheme 3



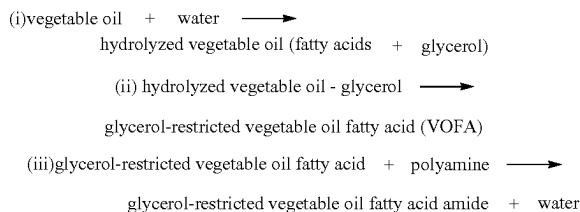
[0043] In Schemes 2 and 3 other components may be present. For example, the hydrolysis of a vegetable oil represented by Scheme 3, reaction (i) may be catalyzed by acid or base. It will be further understood that depending upon pH, the fatty acids may be present as salts thereof.

[0044] As can be seen from Schemes 2 and 3, production of fatty amide additives from vegetable oil provides a reaction product that includes glycerol. The reaction products of a vegetable oil and amine may be prone to phase separation. Without wishing to be bound by theory, we believe that the presence of byproduct glycerol in the intermediate and then the fatty amide products furnishes an additive composition that is more prone to phase separation, and hence less stable, as compared to similar additive composition that is at least partially purified with respect to glycerol. In other words, when using a fatty amide additive

derived from vegetable oil in an additive composition, stability is improved by using an additive composition with reduced glycerol content.

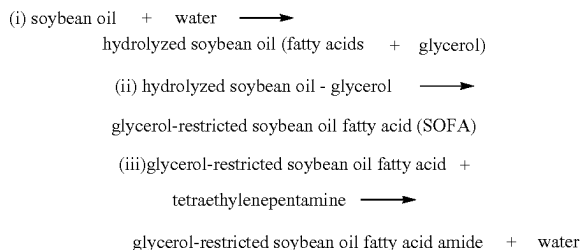
[0045] In accordance with the present invention, reduced-glycerol fatty amide additives may be made in accordance with a reaction as illustrated, for example, in Scheme 4a:

Scheme 4a



[0046] For example, as shown in Scheme 4b, glycerol-restricted fatty amide reaction products of tetraethylenepentamine ($\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$) (TEPA) with glycerol-restricted soybean oil fatty acid are much more stable and resistant to phase separation than fatty amides made by Schemes 2 and 3.

Scheme 4b



[0047] Glycerol-restricted soybean oil fatty acid (SOFA) is commercially available.

[0048] Glycerol-restricted vegetable oil fatty acids, including those derived from soybean oil, may be produced in accordance with Scheme 4a (i)-(ii) by the following procedure: To one or more vegetable oils such as soybean oil is added an alkali such as aqueous sodium hydroxide and/or aqueous potassium hydroxide to produce a mixture thereof. The mixture may be heated to a suitable temperature (such as in the range from 30° C. to 100° C., for example 30° C. to 100° C., or 40° C. to 90° C., or 50° C. to 100° C., or 60° C. to 100° C., or 50° C. to 90° C., or 50° C. to 80° C., or 50° C. to 70° C., or 55° C. to 65° C., or about 60° C.) for a suitable time (such as from one hour to 24 hours, for example 1 hour to 10 hours, or two hours to seven hours, or three hours to six hours, or three hours to five hours, or about four hours) effective for the saponification of the one or more vegetable oil to occur to the desired degree of completion. The saponification, the hydrolysis of the one or more vegetable oils, produces fatty acid salts and byproduct glycerol. To generate free fatty acids from the fatty acid salts, the pH of the mixture is reduced by adding a mineral acid such as sulfuric acid, hydrochloric acid, or a combination thereof. For example, the pH may be reduced to one to four, or one to three, or about two. An aqueous phase

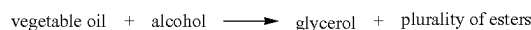
comprising water, a salt of the mineral acid, and glycerol separates from the organic phase into a distinct layer and the aqueous phase is separated from the organic phase. The organic phase may be dried. The organic phase may be further purified by separation into fractions, each fraction having a different range of acid numbers. For the present invention, the glycerol-restricted vegetable oil fatty acid may be derived from a fraction having an acid number of 170 to 230 mgKOH/g, or 180 to 220 mgKOH/g, or 190 to 210 mgKOH/g, or about 192 to 205 mgKOH/g. For example, the glycerol-restricted vegetable oil fatty acid may comprise, consist of, or consist essentially of glycerol-restricted soybean oil fatty acid having an acid number of about 192 to about 205 mgKOH/g.

[0049] Without wishing to be bound by theory, we believe that glycerol in hydrolyzed soybean oil and/or reaction products thereof destabilize the resultant additive compositions. Accordingly, at least partially removing the glycerol content from the ingredients or precursors thereof provides additive compositions with improved stability.

[0050] As further embodiments of the present invention, disclosed herein are combination additive compositions comprising mixtures of the glycerol-restricted fatty amide additives of Schemes 4a or 4b in combination with a plurality of fatty esters. For improved stability, it is preferred that the fatty esters are also glycerol restricted to the same reduced concentration range as are the glycerol-restricted fatty amides of Schemes 4a and 4b. The combination additive compositions of the present invention are useful in the oil processing and refining industries for similar applications as the amides, e.g., to protect against corrosion.

[0051] For example, fatty esters could be made by transesterification, as shown in scheme 5.

Scheme 5



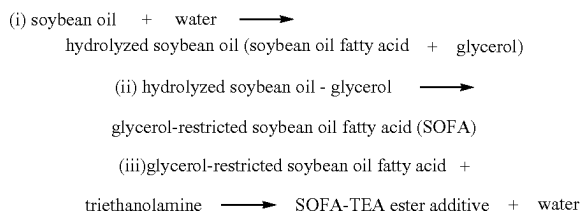
[0052] Scheme 5 shows that fatty esters generally may be made by reacting one or more vegetable oils in a transesterification reaction with one or more alcohols. A preferred vegetable oil is soybean oil.

[0053] Alcohols suitable in Scheme 5 may be primary, secondary, tertiary, or a mixture of these. A preferred alcohol comprises at least one nitrogen atom and a plurality of OH groups, or even 2 to 6, or even 2 to 4, or even 3 alcohols groups. A more preferred alcohol is triethanolamine (TEA), which includes three ethanol moieties (each including a primary OH group) coupled to a central N atom.

[0054] However, the reaction product of Scheme 5 again comprises glycerol. The practice of the present invention teaches that all or a portion of the glycerol is removed to improve stability of additive compositions that incorporate the fatty ester product. Consequently, in the practice of the present invention, the product mixture of Scheme 5 may be at least partially purified with respect to glycerol in order to provide glycerol-restricted fatty esters of the present invention.

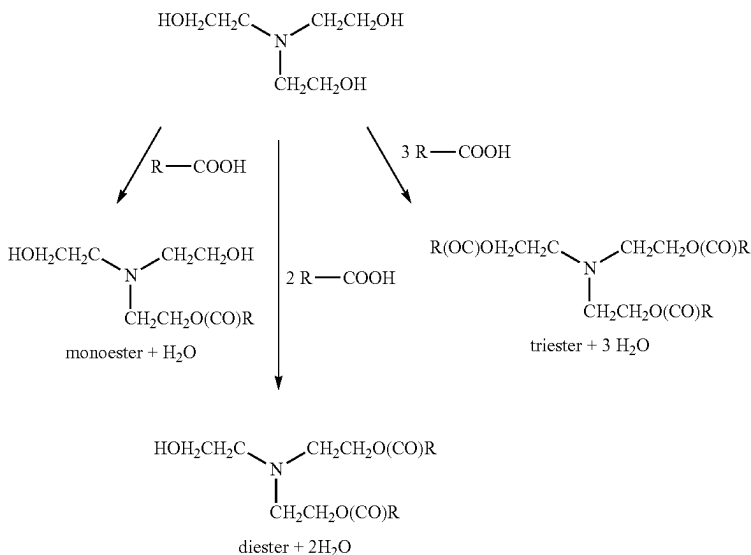
[0055] Alternatively, a preferred method of making the plurality of fatty esters is by the reaction of alcohol with one or more glycerol-restricted vegetable oil fatty acids, for example a hydrolyzed vegetable oil that has been purified with respect to glycerol, as exemplified in Scheme 6 in which the exemplified vegetable oil is soybean oil and the exemplified alcohol is triethanolamine:

Scheme 6



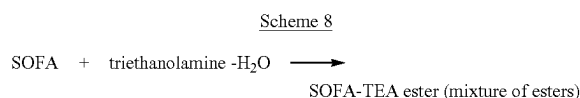
[0056] When practicing Scheme 6 (iii), the general reaction of a fatty acid (represented by RCOOH) with triethanolamine, which is a triol, to form fatty esters may be represented as follows in Scheme 7 (wherein each R independently represents a linear, branched, or cyclic hydrocarbyl group):

Scheme 7



[0057] As shown in Scheme 7, the reaction of even a single, particular fatty acid with a symmetrical triol such as triethanolamine may produce three different esters. Further, since a glycerol-restricted vegetable oil fatty acid such as glycerol-restricted soybean oil fatty acid comprises a mixture of fatty acids, reaction of the glycerol-restricted vegetable oil fatty acid with TEA is expected to produce a more complicated mixture of monoester, diester, and triester reaction products. Product mixtures also result using diols, tetrols, or other alcohols with a plurality of OH groups. Product mixtures may be more complex when the alcohol has at least one chiral carbon, as even more mono, di, tri, etc., ester products may result.

[0058] The esterification reaction between glycerol-restricted soybean oil fatty acid (SOFA, which comprises a mixture of fatty acids) and triethanolamine (TEA) may be represented as follows:



[0059] Methods of making additives disclosed herein may provide fatty amide and/or fatty ester reaction products that comprise little or no glycerol, no rosin acids and/or their derivatives, and little or no reaction products of glycerol and resin acids, for example no more than 0.1 weight percent (percent by weight) thereof with respect to the weight of the corresponding additive. The methods use glycerol-restricted vegetable oil fatty acids, which are reacted with amines to produce fatty amides that are restricted in their glycerol content. The use of glycerol-restricted vegetable oil fatty acids in the methods herein can produce additives that are restricted in glycerol content (for example 0.1 percent or less by weight of glycerol with respect to the total weight of fatty acid content).

[0060] The use of glycerol-restricted vegetable oil fatty acids as opposed to tall oil or tall oil fatty acid avoids rosin acid content such as rosin acid or its derivatives. Rosin acid content is a natural component of the tall oils and tall oil fatty acids. Being acidic, rosin acid may have a tendency to be a corrodent in refinery equipment. Hence, avoiding rosin acid is highly desirable. Advantageously, soybean oil and many other vegetable oils have little if any rosin acid content. Consequently, the fatty amides and fatty esters derived from soybean oil and other vegetable oils avoid the corrosion risk associated with rosin acids. Unfortunately, though, additives derived from vegetable oil are prone to phase separation, thereby reducing the appeal of using such additives. However, the present invention teaches how the stability of these materials can be improved, making their use practical and desirable. The significant result is that the present invention not only avoids rosin acid corrodents but allows more stable vegetable oil derived materials to be used for corrosion protection.

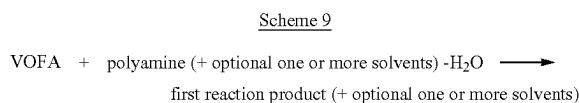
First Modes of the Invention

[0061] These modes illustrate glycerol-restricted fatty acid amides that can be derived from one or more vegetable oils and then used as an additive in additive compositions for a variety of purposes such as to protect against corrosion in an

oil refinery facility or in other environments in which corrosion protection is desired. Accordingly, in first modes of the invention there is provided a first additive composition. The first additive composition comprises, consists of, or consists essentially of a first reaction product. The first additive composition may comprise, consist of, or consist essentially of the first reaction product and one or more solvents. The first additive composition may comprise, consist of, or consist essentially of the first reaction product and one or more optional ingredients. The first additive composition may comprise, consist of, or consist essentially of the first reaction product, one or more solvents, and further optional ingredients. The further optional ingredients may be selected from a wide range of materials including but not limited to one or more of antipolymerants, antioxidants, amines, frothers, dispersants, and phenol-formaldehyde polymers.

[0062] The first reaction product comprises, consists of, or consists essentially of a plurality of amides.

[0063] The plurality of amides may be synthesized by reacting a first set of reactants to produce the first reaction product and water as shown in Scheme 9, wherein glycerol-restricted vegetable oil fatty acid is represented by VOFA, and wherein $-\text{H}_2\text{O}$ represents the removal of water, during and/or after the reaction:



[0064] As noted in Scheme 9, the reaction may be performed without added solvent or optionally in one or more solvents. If the reaction is performed in the one or more solvents, then the first additive composition comprises, consists of, or consists essentially of the first reaction product and the one or more solvents. Whether the reaction is performed in solvent or not, solvent, or further solvent may be added to the reaction product later to form a concentrate, as described in the third modes of the invention hereinbelow. The one or more solvents may be selected from hydrocarbons. The hydrocarbons may be selected from one or more of aromatic compounds, alkanes, any types of naphtha, and alkenes. Examples of suitable hydrocarbons include but are not limited to one or more of benzene, toluene, xylenes (o-xylene, m-xylene, p-xylene, and any combinations thereof) heavy aromatic naphtha (HAN), C5 to C17 alkanes, alkenes, and naphtha.

[0065] The first set of reactants comprises, consists of, or consists essentially of one or more glycerol-restricted vegetable oil fatty acids and a polyamine.

[0066] The first reaction product may comprise, consist of, or consist essentially of a plurality of amides, or the first reaction product may comprise, consist of, or consist essentially of the plurality of amides and one or more byproducts. The first reaction product with or without the optional solvent is preferably used without further purification to provide the first additive composition. The use of glycerol-restricted vegetable oil fatty acids in the present invention advantageously provides a first reaction product free of glycerol or containing less than 0.1 percent by weight

glycerol with respect to the weight of the first reaction product without further purification of the first reaction product.

[0067] As set forth in Scheme 4a (iii), the reaction of polyamine and glycerol-restricted vegetable oil fatty acid may produce a glycerol-restricted vegetable oil fatty acid amide and byproduct water. The glycerol-restricted vegetable oil fatty acid amide comprises, consists of, or consists essentially of a plurality of amides. The first reaction product may consist of or consist essentially of amides, or the first reaction product may comprise, consist of, or consist essentially of amides and byproduct and/or other materials. The first reaction product may comprise about 99 percent by weight to 100 percent by weight amides, or about 95 percent by weight to 100 percent by weight amides, or about 98 percent by weight to 100 percent by weight amides, or about 97 percent by weight to 100 percent by weight amides, or about 96 percent by weight to 100 percent by weight amides, or about 95 percent by weight to 99.5 percent by weight amides, or about 96 percent by weight to 99.5 percent by weight or about 97 to 99.5 percent by weight, or about 98 percent by weight to 99.5 percent by weight, or about 99 percent by weight to 99.5 percent by weight amides, or about 90 percent by weight to 100 percent by weight, or about 80 percent by weight to about 100 percent by weight, or about 90 percent by weight to about 99.5 percent by weight, or about 80 percent by weight to about 99.5 percent by weight amides with respect to the weight of the first reaction product.

[0068] Preferably water, a byproduct, is separated from the glycerol-restricted vegetable oil fatty acid amide. Conveniently, at least a portion or even most or all of the byproduct water may be removed during the reaction. Removal of the water during the reaction assists in moving the amide-forming reaction forward. Accordingly, the dried first reaction product may comprise, consist of, or consist essentially of the plurality of amides and any byproduct(s) (if any). In this context, “consist essentially” of allows for the presence of a small amount of water in the amide: even if dried or partially dried, the amides may include a small amount of residual water from the reaction and/or some water taken from the environment. The first reaction product may comprise about 0 percent by weight to 1 percent by weight water, or about 0 percent by weight to 5 percent by weight water, or about 0 percent by weight to 2 percent by weight water, or about 0 percent by weight to 3 percent by weight water, or about 0 percent by weight to 4 percent by weight water, or about 0.5 percent by weight to 5 percent by weight water, or about 0.5 percent by weight to 4 percent by weight or about 0.5 to 3 percent by weight, or about 0.5 percent by weight to 2 percent by weight, or about 0.5 percent by weight to 1 percent by weight water, or about 0 percent by weight to 10 percent by weight, or about 0 percent by weight to about 20 percent by weight, or about 0.5 percent by weight to about 10 percent by weight, or about 0.5 percent by weight to about 20 percent by weight water with respect to the weight of the plurality of amides.

[0069] Preferably, the first reaction product comprises mostly or exclusively amides and comprises no or a minimal amount of glycerol, no or a minimal amount of rosin acid, no or a minimal amount of imidazoline content, and no or a minimal amount of water. The first reaction product may comprise 0 percent by weight to 1 percent by weight or 0 percent by weight to 2 percent by weight, or 0 percent by

weight to 3 percent by weight, or 0 percent by weight to 4 percent by weight, or 0 percent by weight to 5 percent by weight or 0 percent by weight to 0.1 percent by weight, or 0 percent by weight to 0.01 percent by weight, or 0 percent by weight of a total of each of the following types of material with respect to the weight of the total fatty amide content in the first reaction product: rosin acid, salt of rosin acid, amide of rosin acid, ester of rosin acid, fatty acid ester, imidazoline, and C1-C10 monohydric alcohol.

[0070] The first reaction product may be used without further purification to provide the first additive, it may be further purified before use, or further materials such as additional fatty acid amides may be added to the first reaction product to provide the first additive, with the proviso that the further materials are free of rosin acid and derivatives thereof and comprise less than 0.1 percent by weight of glycerol with respect to the weight of the further materials.

[0071] The first set of reactants may comprise, consist of, or consist essentially of one or more glycerol-restricted vegetable oil fatty acids and a polyamine. Preferred polyamines comprise at least one primary amine moiety and at least one secondary polyamine moiety. Suitable polyamines may be linear, branched, or cyclic, and may be aliphatic or aromatic. Preferred polyamines have a linear carbon backbone and are aliphatic.

[0072] In preferred embodiments, a polyamine comprises a linear carbon backbone, comprises at least one primary terminal amine moiety and preferably terminal primary amine moieties at each end, and comprises one or more secondary and/or tertiary amine moieties pendant from the carbon backbone. In preferred embodiments, a polyamine may have the formula $\text{NH}_2(\text{CH}_2\text{CH}_2\text{NH})_x\text{CH}_2\text{CH}_2\text{NH}_2$ wherein x is from 0 to 100, or 0 to 90, or 0 to 80, or 0 to 70, or 0 to 60, or 0 to 50, or 0 to 40, or 0 to 30, or 0 to 20, or 0 to 10, or 0 to 5, or 0 to 4, or 0 to 3, or 0 to 2, or 0 to 1, or 1 to 5, or 2 to 4, or wherein x is 3. In any of the embodiments and modes herein, the polyamine may comprise, consist of, or consist essentially of tetraethylenepentamine (TEPA), $(\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2)$.

[0073] The one or more glycerol-restricted vegetable oil fatty acids used to make amides in Scheme 9 may be selected from one or more of glycerol-restricted avocado oil fatty acid, canola oil fatty acid, coconut oil fatty acid, corn oil fatty acid, cottonseed oil fatty acid, grape seed oil fatty acid, hazelnut oil fatty acid, hemp seed oil fatty acid, linseed oil fatty acid, olive oil fatty acid, palm oil fatty acid, palm kernel oil fatty acid, peanut seed oil fatty acid, rape seed oil fatty acid, rice bran oil fatty acid, safflower oil fatty acid, sesame oil fatty acid, soybean oil fatty acid, sunflower seed oil fatty acid, and walnut oil fatty acid. In some preferred embodiments and aspects disclosed herein, the one or more glycerol-restricted vegetable oil fatty acids may comprise, consist of, or consist essentially of glycerol-restricted soybean oil fatty acid.

[0074] The one or more glycerol-restricted vegetable oil fatty acids may comprise 0 percent by weight to 0.01 percent by weight, or 0 percent by weight to 0.02 percent by weight, or 0 percent by weight to 0.03 percent by weight, or 0 percent by weight to 0.05 percent by weight, or 0.05 percent by weight to 0.1 percent by weight, or about 0 percent by weight of glycerol with respect to the total weight of the one or more glycerol-restricted vegetable oil fatty acids.

[0075] The one or more glycerol-restricted vegetable oil fatty acids may comprise, consist of, or consist essentially of glycerol-restricted soybean oil fatty acid. The glycerol-restricted soybean oil fatty acid may be hydrolyzed soybean oil that has been purified with respect to glycerol. While the composition of soybean oil, as a natural product, may vary, the composition of soybean oil tends to fall into certain ranges. The glycerol-restricted soybean oil fatty acid may comprise, consist of, or consist essentially of about 2 percent by weight to 15 percent by weight alpha-linolenic acid, about 46 percent by weight to about 56 percent by weight linoleic acid, about 17 percent by weight to about 28 percent by weight oleic acid, about 1 percent by weight to about 10 percent by weight stearic acid, and about 5 percent by weight to about 15 percent by weight palmitic acid and/or respective salts thereof with respect to the weight of the glycerol-restricted soybean oil fatty acid. For clarity, the weight of the glycerol-restricted soybean oil fatty acid includes the glycerol content, if any.

[0076] In one exemplary embodiment, glycerol-restricted soybean oil fatty acid (89.6 parts per weight) is combined with tetraethylenepentamine (17.1 parts by weight) in a round-bottom flask equipped with temperature probe, stirrer, nitrogen inlet, and Dean-Stark apparatus. Heavy aromatic naphtha (HAN) (18.3 parts by weight) is added to the combination to form a mixture. Nitrogen purging is started, and the mixture is heated to about 170° C. for about 10 hours. An amount of HAN is added to the reaction mixture to compensate for the amount of HAN lost into the Dean-Stark trap. The contents of the flask are stirred for a further ten minutes and allowed to cool to room temperature to provide an additive composition. The additive composition comprises a plurality of amides and HAN. The additive may be used in a variety of applications including as a corrosion inhibitor.

[0077] The first additive as described in the first modes of the invention may be used as a highly effective corrosion inhibitor, dispersant, lubricant, antifoaming agent, foaming agent, and/or release agent in additive compositions. In preferred modes of practice, the first additive is used in corrosion inhibiting compositions. More preferably, such compositions are useful to protect against corrosion in oil refinery facilities. In such facilities, the compositions may be added to one or more process streams, whereby the presence of the additive in the streams helps to protect the equipment surface contacting the treated process streams from corrosion. Additionally, or an alternative, the compositions may be used to passivate equipment surfaces prior to contacted those surfaces with treated and/or untreated process streams.

[0078] Nevertheless, a combination additive comprising, consisting of, or consisting essentially of a combination of the first reaction product as described hereinabove with a second reaction product as described hereinbelow may be even more effective as corrosion inhibitor, dispersant, lubricant, antifoaming agent, foaming agent, and/or release agent. The second reaction product comprises one or more fatty acid esters, preferably glycerol-restricted fatty acid esters derived from one or more vegetable oil fatty acids as listed herein with respect to Scheme 9.

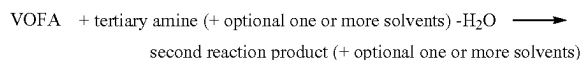
Second Modes of the Invention

[0079] This mode illustrates how the glycerol-restricted fatty acid amides described with respect to Scheme 9 can be used in combination with glycerol-restricted fatty acid esters

also derived from one or more vegetable oils. The combination is useful as an additive in additive compositions for a variety of purposes such as those listed with respect to Scheme 9, preferably to protect against corrosion in an oil refinery facility or in other environments in which corrosion protection is desired. Accordingly, in second modes of the invention there is provided a combination additive that comprises, consists of, or consists essentially of the first reaction product as described hereinabove and a second reaction product. The weight ratio of the first reaction product to the second reaction product respectively or alternatively the weight ratio of total fatty amide to total fatty ester in the combination additive may be selected from a wide range such as 50:1 to 1:50, or 4:1 to 1:5, or 3:1 to 1:4, or 2:1 to 1:4, or 1:1 to 1:4, or 1:2 to 1:4, or 1:3 to 1:4 or 4:1 to 1:6, or 4:1 to 1:7, or 1:1 to 1:7, or 2:1 to 1:6, or about 2:7. Whereas the first reaction product comprises a plurality of fatty acid amides, the second reaction product comprises a plurality of fatty acid esters.

[0080] The second reaction product may be made as shown in Scheme 10, wherein VOFA is glycerol-restricted vegetable oil fatty acid:

Scheme 10



[0081] The second reaction product comprises, consists of, or consists essentially of a plurality of esters. The second reaction product is derived from a second set of reactants comprising, consisting of, or consisting essentially of a second set of one or more glycerol-restricted vegetable oil fatty acids and a compound comprising at least one tertiary amine moiety and at least one hydroxyl group. The second set of one or more glycerol-restricted vegetable oil fatty acids may comprise, consist of, or consist essentially of one or more hydrolyzed vegetable oils that is/are purified with respect to glycerol.

[0082] As shown in Scheme 10, the reaction produces a second reaction product and byproduct water. Preferably, at least a portion or even most or all of the water that is a reaction byproduct is removed during the reaction.

[0083] Preferably water, a byproduct, is separated from the reaction mixture. Conveniently, at least a portion or even most or all of the byproduct water may be removed during the reaction. Removal of the water during the reaction assists in moving the ester-forming reaction forward. Accordingly, the dried second reaction product may comprise, consist of, or consist essentially of the plurality of esters and any byproduct(s) (if any). In this context, "consist essentially" of allows for the presence of a small amount of water in the esters: even if dried or partially dried, the esters may include a small amount of residual water from the reaction and/or some water taken from the environment. The second reaction product may comprise about 0 percent by weight to 1 percent by weight water, or about 0 percent by weight to 5 percent by weight water, or about 0 percent by weight to 2 percent by weight water, or about 0 percent by weight to 3 percent by weight water, or about 0 percent by weight to 4 percent by weight water, or about 0.5 percent by weight to 5 percent by weight water, or about 0.5 percent by weight to 4 percent by weight or about 0.5 to 3 percent by weight, or

about 0.5 percent by weight to 2 percent by weight, or about 0.5 percent by weight to 1 percent by weight water, or about 0 percent by weight to 10 percent by weight, or about 0 percent by weight to about 20 percent by weight, or about 0.5 percent by weight to about 10 percent by weight, or about 0.5 percent by weight to about 20 percent by weight water with respect to the weight of the plurality of esters.

[0084] The second reaction product may consist of or consist essentially of esters, or the second reaction product may comprise, consist of, or consist essentially of esters and byproduct and/or other materials. The second reaction product may comprise about 99 percent by weight to 100 percent by weight esters, or about 95 percent by weight to 100 percent by weight esters, or about 98 percent by weight to 100 percent by weight esters, or about 97 percent by weight to 100 percent by weight esters, or about 96 percent by weight to 100 percent by weight esters, or about 95 percent by weight to 99.5 percent by weight esters, or about 96 percent by weight to 99.5 percent by weight or about 97 to 99.5 percent by weight, or about 98 percent by weight to 99.5 percent by weight, or about 99 percent by weight to 99.5 percent by weight esters, or about 90 percent by weight to 100 percent by weight, or about 80 percent by weight to about 100 percent by weight, or about 90 percent by weight to about 99.5 percent by weight, or about 80 percent by weight to about 99.5 percent by weight esters with respect to the weight of the second reaction product.

[0085] The second reaction product may comprise 0 percent by weight to 1 percent by weight or 0 percent by weight to 2 percent by weight, or 0 percent by weight to 3 percent by weight, or 0 percent by weight to 4 percent by weight, or 0 percent by weight to 0.1 percent by weight, or 0 percent by weight to 0.01 percent by weight, or 0 percent by weight of a total of each of the following types of material individually and with respect to the weight of the second reaction product: rosin acid, salt of rosin acid, amide of rosin acid, ester of rosin acid, fatty acid ester, imidazoline, and C1-C10 monohydric alcohol.

[0086] The second set of reactants may comprise, consist of, or consist essentially of a second set of one or more glycerol-restricted vegetable oil fatty acids; and one or more compounds comprising one or more tertiary amine moieties and one or more hydroxyl groups (referred to herein as “tertiary amines” for convenience). The one or more tertiary amines may comprise, consist of, or consist essentially of one or more of a mono-, di-, and trialkanolamine. In some preferred embodiments and modes herein, the one or more tertiary amines may comprise, consist of, or consist essentially of triethanolamine (TEA) $((\text{HOCH}_2\text{CH}_2)_3\text{N})$.

[0087] The second set of the one or more glycerol-restricted vegetable oil fatty acids may be the same, partially the same, or different from those used to make the first reaction product as described with respect to Scheme 9, and may be selected from one or more of glycerol-restricted avocado oil fatty acid, canola oil fatty acid, coconut oil fatty acid, corn oil fatty acid, cottonseed oil fatty acid, grape seed oil fatty acid, hazelnut oil fatty acid, hemp seed oil fatty acid, linseed oil fatty acid, olive oil fatty acid, palm oil fatty acid, palm kernel oil fatty acid, peanut seed oil fatty acid, rape seed oil fatty acid, rice bran oil fatty acid, safflower oil fatty acid, sesame oil fatty acid, soybean oil fatty acid, sunflower seed oil fatty acid, and walnut oil fatty acid.

[0088] In some preferred embodiments and modes disclosed herein, the second set of one or more glycerol-

restricted vegetable oil fatty acids may comprise, consist of, or consist essentially of glycerol-restricted soybean oil fatty acid.

[0089] The second set of glycerol-restricted vegetable oil fatty acids may comprise 0 percent by weight to 0.01 percent by weight, or 0 percent by weight to 0.02 percent by weight, or 0 percent by weight to 0.03 percent by weight, or 0 percent by weight to 0.05 percent by weight, or 0.05 percent by weight to 0.1 percent by weight, or about 0 percent by weight of glycerol with respect to the weight of the second set of glycerol-restricted vegetable oil fatty acids (including the glycerol content, if any).

Third Modes of the Invention

[0090] In third modes of the invention, there is provided a concentrate comprising any of the additives of the first or second modes of the invention, and further comprising an organic solvent in which the plurality of amides, the ammonium salts thereof, and/or the plurality of esters are dissolved, dispersed, or otherwise in admixture with the organic solvent. The terminology “concentrate” is defined above in the detailed description, and that definition applies to the third modes of the Invention and to any modes in which one or more additives of the present invention are incorporated into a concentrate.

[0091] The organic solvent may be selected from a wide range of liquid carriers such as esters and/or hydrocarbons. The hydrocarbons may be selected from one or more of aromatic compounds, alkanes, any types of naphtha, and alkenes. Examples of suitable hydrocarbons include but are not limited to one or more of benzene, toluene, xylenes (o-xylene, m-xylene, p-xylene, and any combinations thereof) heavy aromatic naphtha (HAN), C5 to C17 alkanes, alkenes, and naphtha. Examples of esters include but are not limited to phthalate esters such as dimethyl phthalate, diethyl phthalate, dipropyl phthalates, dibutyl phthalates, and combinations thereof. The solvent may comprise, consist of, or consist essentially of dimethyl phthalate.

[0092] The ratio by weight of organic solvent to the first reaction product, the second reaction product or the combination of the first reaction product and the second reaction product may be 1:5 to 5:1, or 1:4 to 4:1, or 1:3 to 3:1, or 1:2 to 2:1, or about 1:1, or 1:3 to 1:5, or 1:2 to 1:6, or about 1:4.

[0093] The concentration by weight of the first reaction product, the second reaction product, or the combination of the first reaction product and the second reaction product in the concentrate may be 50 percent by weight to 99 percent by weight, or 50 percent by weight to 90 percent by weight, or 50 percent by weight to 80 percent by weight, or 60 percent by weight to 90 percent by weight, or 60 percent by weight to 80 percent by weight, or 70 percent by weight to 90 percent by weight, or 70 percent by weight to 99 percent by weight, or about 80 percent by weight with respect to the weight of the concentrate.

Fourth Modes of the Invention

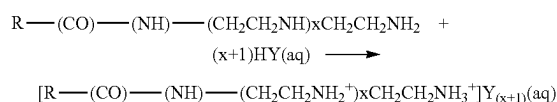
[0094] In fourth modes of the invention is provided an additive comprising, consisting of, or consisting essentially of one or more ammonium salts of any of the plurality of glycerol-restricted amides described hereinabove in the first modes of invention. The ammonium salts may be made by reacting ingredients comprising the plurality of amides with one or more of an inorganic acid, an organic acid, an alkyl

halide, and an aryl halide. The resultant ammonium salts may be incorporated into additive compositions, such as corrosion inhibitor compositions, optionally in combination with one or more glycerol-restricted amides, one or more glycerol-restricted esters described in the second modes, optionally solvent, optionally one or more additional optional ingredients, and combinations of these.

[0095] The inorganic acid may comprise, consist of, or consist essentially of hydrochloric acid. The organic acid may comprise, consist of, or consist essentially of one or more of acetic acid, acrylic acid, and methacrylic acid. The alkyl halide may comprise, consist of, or consist essentially of an alkyl chloride. The aryl halide may comprise, consist of, or consist essentially of an aryl chloride.

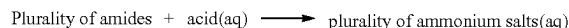
[0096] In an illustrative embodiment, the plurality of glycerol-restricted amides comprises amides, each amide having the structure $R-(CO)-(NH)-(CH_2CH_2NH)_xCH_2CH_2NH_2$, wherein R is a hydrocarbyl group and x is from 0 to 100. The amides are reacted with and dissolved in an acid, such as HY, H_2Y , H_3Y , and/or the like (for example acetic acid, hydrochloric acid, sulfuric acid, phosphoric acid, citric acid, oxalic acid, maleic acid, other carboxylic acids, and the like), wherein each Y independently is one or more anions such that the acid at least partially dissociates in water at 25° C. and 1 atmosphere of pressure to provide an aqueous composition having a pH under 7, even under 5, even under 4, or even under 3, and wherein the reaction in the case of an acid HY may be represented as follows in Scheme 11:

Scheme 11



[0097] In general, the reaction between acid and the plurality of amides may be summarized as:

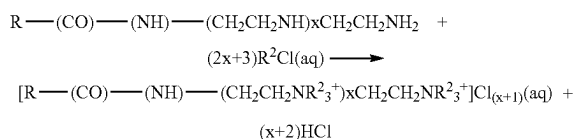
Scheme 12



[0098] Similarly, one or more of the amine groups of the plurality of amides may be converted to alkyl or aryl ammonium groups.

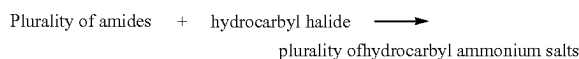
[0099] In a purely illustrative embodiment, the plurality of amides comprises amides having the structure $R^1-(CO)-(NH)-(CH_2CH_2NH)_xCH_2CH_2NH_2$, wherein R^1 is a hydrocarbyl group and x is from 0 to 100. The amides are reacted with an alkyl halide such as an alkyl halide having a formula R^2X , wherein one or more of the amine groups on the amides is converted to an ammonium salt, wherein R^2 is a hydrocarbyl group comprising 1 to 50 carbon atoms and X is a halide such as Cl and/or F. In a purely illustrative scheme, all or a portion of the amino-NH groups are converted to quaternary ammonium groups:

Scheme 13



[0100] In general, the reaction between a hydrocarbyl halide and the plurality of amides may be summarized as:

Scheme 14



[0101] While the additives comprising, consisting of, or consisting essentially of amides are especially useful, for example, as corrosion inhibiting additives to hydrocarbon process streams, the ammonium salts disclosed herein are especially useful as additives for aqueous process streams, for example as aqueous corrosion inhibitors.

[0102] Any of the additives and concentrates or other compositions of the first, second, third, or fourth modes of the invention may comprise one or more optional ingredients, such as one or more antipolymerants, antioxidants, and amines, or other optional ingredients as discussed with the other Schemes described herein.

Fifth Modes of the Invention

[0103] In fifth modes of the invention there is provided a method of making the first additive as described hereinabove with respect to Schemes 4a, 4b, and 9. The method comprises: (1) combining one or more glycerol-restricted vegetable oil fatty acids with polyamine to form a reaction mixture. The one or more glycerol-restricted vegetable oil fatty acids may comprise, consist of, or consist essentially of one or more hydrolyzed vegetable oils described above that are at least partially purified with respect to glycerol. Optionally, the method further includes (2) adding a hydrocarbon solvent, for example, heavy aromatic naphtha (HAN), to the reaction mixture as a liquid carrier. Preferably, the hydrocarbon solvent has a boiling point of at least 160° C. at one atmosphere pressure. However, the reaction may be conducted at a pressure exceeding one atmosphere to increase the boiling point of the hydrocarbon solvent and attain the desired reaction temperature.

[0104] The molar ratio of the one or more glycerol-restricted vegetable oil fatty acids to the polyamine in the reaction mixture after the combination may be 3:1 to 4:1, or 3.4:1 to 3.7:1, or about 3.5:1 to 3.6:1. While the glycerol-restricted vegetable oil fatty acid or fatty acids may be a complicated mixture of fatty acids, for calculating the aforementioned molar ratios, the acid number of the free fatty acid may be used to calculate a molecular weight for the free fatty acid. If the polyamine is a mixture of individual polyamine compounds having various molecular weights, for calculating the aforementioned molar ratios the number average molecular weight of the polyamines may be used. However, if the polyamine is a discrete compound, for example tetraethylenepentamine

($\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$), then the molecular weight of the discrete compound is used.

[0105] The method further comprises (3) heating the reaction mixture, optionally under an inert gas such as nitrogen, argon, or the like, at a suitable reaction temperature such as a temperature in the range from 150° C. to 200° C., or 160° C. to 190° C., or 160° C. to 175° C., or 165° C. to 170° C. for a time period in the range from 30 minutes to 20 hours, or one hour to 15 hours, or one hour to ten hours, or five hours to 15 hours, to form a first reaction product and byproduct water. Preferably, a reaction temperature of 200° C. is not exceeded to avoid formation of undue amounts of imidazoline as a by-product.

[0106] Preferably, the method further comprises (4) removing the byproduct water from the reaction mixture during the heating, for example by trapping the water during the heating in a Dean-Stark trap. Removing the water while heating the reactants assists in moving the reaction forward and producing the desired amides.

Sixth Modes of the Invention

[0107] In sixth modes of the invention, there is provided a method of making a combination additive as described hereinabove in the second modes of the invention. The method comprises: (1) combining one or more first glycerol-restricted vegetable oil fatty acids with polyamine to form a first reaction mixture, optionally but preferably under conditions such that the temperature of the reaction mixture does not exceed 100° C. The glycerol-restricted vegetable oil fatty acids may comprise, consist of, or consist essentially of one or more hydrolyzed vegetable oils that are at least partially purified with respect to glycerol. The one or more glycerol-restricted vegetable oil fatty acids may comprise, consist of, or consist essentially of glycerol-restricted soybean oil fatty acid. The polyamine may comprise, consist of, or consist essentially of tetraethylenepentamine ($\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$) (TEPA). Optionally, the method further includes (2) adding a hydrocarbon solvent, for example, heavy aromatic naphtha (HAN), to the reaction mixture. Preferably, the hydrocarbon solvent has a boiling point of at least 160° C. at one atmosphere pressure. However, the reaction may be conducted at a pressure exceeding one atmosphere to increase the boiling point of the hydrocarbon solvent and attain the desired reaction temperature.

[0108] The molar ratio of the total glycerol-restricted vegetable oil fatty acids to the total polyamines in the reaction mixture may be 3:1 to 4:1, or 3.4:1 to 3.7:1, or about 3.5:1 to 3.6:1. While the glycerol-restricted vegetable oil fatty acid or fatty acids may be a mixture of fatty acids, for calculating the aforementioned molar ratios the acid number of the free fatty acid may be used to calculate a molecular weight for the free fatty acid. If the polyamine is a mixture of individual polyamine compounds having various molecular weights, for calculating the aforementioned molar ratios the number average molecular weight of the polyamine may be used. However, if the polyamine is a discrete compound, for example tetraethylenepentamine ($\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$), then the molecular weight of the discrete compound is used.

[0109] The method further comprises (3) heating the reaction mixture, optionally under an inert gas such as nitrogen, argon, or the like, at a reaction temperature in the range from 150° C. to 200° C., or 160° C. to 190° C., or 160° C. to 175°

C., or 165° C. to 170° C. for a time period in the range from 30 minutes to 20 hours, or one hour to 15 hours, or one hour to ten hours, or five hours to 15 hours, to form first reaction products comprising water and a first additive. Preferably, a reaction temperature of 200° C. is not exceeded to avoid formation of undue amounts of imidazoline as a by-product.

[0110] Preferably, the method further comprises (4) removing water from the reaction mixture during the heating, for example by trapping the water during the heating in a Dean-Stark trap.

[0111] The method further comprises (5) combining second one or more glycerol-restricted vegetable oil fatty acids with one or more tertiary amines, each of the one or more tertiary amines comprising at least one hydroxyl group, to form a second reaction mixture; and (6) heating the second reaction mixture, optionally under an inert gas such as nitrogen, at a reaction temperature in the range from 150° C. to 300° C., or 160° C. to 275° C., or 170° C. to 250° C., or 180° C. to 230° C., or 190° C. to 220° C., or 200° C. to 220° C., or at about 210° C. for a time period in the range from 30 minutes to 10 hours, or one hour to 10 hours, or two hours to ten hours, or three hours to 10 hours, or three hours to seven hours, or three hours to six hours, or three hours to five hours, or about four hours to form a second reaction product and byproduct water.

[0112] The second one or more glycerol-restricted vegetable oil fatty acids may comprise, consist of, or consist essentially of hydrolyzed vegetable oils that are at least partially purified with respect to glycerol as described herein. The second one or more glycerol-restricted vegetable oil fatty acids may comprise, consist of, or consist essentially of glycerol-restricted soybean oil fatty acid. The one or more tertiary amines may comprise, consist of, or consist essentially of triethanolamine.

[0113] The molar ratio of the second one or more glycerol-restricted vegetable oil fatty acids to the one or more tertiary amines in the second reaction mixture may be selected from a wide range such as 1:1 to 2:1, or 1.5:1 to 1.7:1, or about 1.6:1. While the glycerol-restricted vegetable oil fatty acid or acids comprises a mixture of fatty acids, for calculating the aforementioned molar ratios, the acid number of the one or more glycerol-restricted vegetable oil fatty acids may be used to calculate a molecular weight.

[0114] Optionally, the method of making the combination additive further includes (7) adding a hydrocarbon solvent, for example, heavy aromatic naphtha (HAN), to the second reaction mixture, before, after, or during the heating thereof.

[0115] Preferably, the method further comprises (8) removing water from the second reaction mixture during the heating thereof, for example by trapping the water during the heating in a Dean-Stark trap.

[0116] The method of making the combination additive further comprises combining the first and second reaction products to form the combination additive. The weight ratio of the total amide to total ester content in the combination additive may be selected from a wide range such as 50:1 to 1:50, 4:1 to 1:5, or 3:1 to 1:4, or 2:1 to 1:4, or 1:1 to 1:4, or 1:2 to 1:4, or 1:3 to 1:4 or 4:1 to 1:6, or 4:1 to 1:7, or 1:1 to 1:7, or 2:1 to 1:6, or about 2:7 respectively.

[0117] Any of the first additives, second additives, and/or combination additives disclosed herein may be added to a hydrocarbon composition comprising one or more hydrocarbons to provide a treated hydrocarbon composition.

Seventh Modes of the Invention

[0118] Accordingly, in seventh modes of the invention, there is provided a method of inhibiting corrosion of a surface in contact with a hydrocarbon composition, the method comprising, consisting of, or consisting essentially of combining a hydrocarbon composition and any one or more of the first, second, and/or combination additive compositions disclosed herein.

[0119] The surface may comprise, consist of, or consist essentially of one or more of iron, copper, nickel, molybdenum, cobalt, carbon steel, chromium, stainless steel, and low-alloy steel.

[0120] The additives may be added to batches or process streams of a hydrocarbon composition in a wide range of amounts such as in the amount of 1-24 parts by weight of the one or more additives to one million parts by weight (ppm) of the hydrocarbon composition, or 2 to 9 ppm, or 0.1 to 1000 ppm, or 0.5 to 100 ppm, or 0.5 to 50 ppm, or 0.1 to 10000 ppm by weight of the one or more additives.

[0121] The hydrocarbon composition may be a process stream comprising, consisting of, or consisting essentially of one or more hydrocarbons; or a batch of hydrocarbon composition comprising, consisting of, or consisting essentially of one or more hydrocarbons. The hydrocarbon composition may comprise, consist of, or consist essentially of one or more of a crude oil, refined petroleum oil, cracked petroleum oil, a hydrotreatment process stream, liquid ethylene, liquid methane, and naphtha.

[0122] The additive compositions comprising a plurality of amides, the additive compositions comprising a plurality of esters, and the combination additive compositions described herein may be added to hydrocarbon compositions to provide protection against corrosion of surfaces, such as carbon steel surfaces, that come into contact with the hydrocarbon composition and/or hydrocarbon process stream. A common corrodent in hydrocarbon compositions derived from crude oil is naphthenic acid and/or its salts. Accordingly, in any of the embodiments described herein, the hydrocarbon composition or process stream may comprise naphthenic acid. The additives in the additive compositions provide corrosion protection but may also provide protection against deposits and/or precipitates by acting as a dispersant.

[0123] The hydrocarbon composition may comprise one or more corrodents selected from one or more of naphthenic acid and/or its salts, water, brine, organic chlorides, inorganic chlorides, hydrogen sulfide, organic sulfur compounds, carbon dioxide, dissolved oxygen gas, organic acids, sodium chloride, magnesium chloride, calcium chloride, and inorganic ammonium chloride (NH_4Cl). Organic sulfur compounds may include mercaptans such as one or more of methyl mercaptan, ethyl mercaptan and propyl mercaptan. The hydrocarbon composition comprising any one or more corrodents contacting metal parts and/or containments and may cause corrosion thereof. The addition of the additives disclosed herein inhibits such corrosion. Stated differently, when the disclosed additives are added to a hydrocarbon composition comprising one or more corrodents, corrosion of surfaces such as carbon steel surfaces in contact with the treated process stream appears to be retarded. Without being limited to theory, we speculate that the additives either temporarily or permanently modify metal surfaces that are in contact with the additives or have been contacted by the additives. Alternatively, the additives may somehow inhibit the effects of the corrodents within the

oil. Irrespective of the mechanism, the additives impart corrosion protection when added to hydrocarbon compositions that contact corrodible metal parts.

[0124] Any of the additives, reaction products, pluralities of amides, and pluralities of esters described herein may be used in compositions and methods in downstream oil processes in a manner described, for example, in U.S. Pat. No. 3,766,053, which is incorporated herein by reference in its entirety and for all purposes.

Eighth Modes of the Invention

[0125] Accordingly, in eighth modes of the invention is provided a treated hydrocarbon composition comprising, consisting of, or consisting essentially of any of the hydrocarbon compositions disclosed herein and any one or more of any of the additive compositions, reaction products, pluralities of amides, pluralities of esters, and combinations thereof described herein. Prior to addition of the additive(s), the hydrocarbon composition comprises, consists of, or consists essentially of one or more hydrocarbons.

[0126] The ratio of the weight of the additive compositions, reaction products, pluralities of amides, pluralities of esters, and combinations thereof to the weight of the treated hydrocarbon composition may be 1-24 parts per million (ppm) by weight, or 2 to 9 ppm, or 0.1 to 1000 ppm, or 0.5 to 100 ppm, or 0.5 to 50 ppm, or 0.1 to 10000 ppm by weight.

[0127] Any of the additive compositions, reaction products, pluralities of amides, pluralities of esters, and combinations thereof described herein may comprise 0 percent by weight to 5 percent by weight glycerol, or 0 percent by weight to 4 percent by weight, or 0 percent by weight to 3 percent by weight, or 0 percent by weight to 2 percent by weight, or 0 percent by weight to 1 percent by weight, or 0 percent by weight to 0.1 percent by weight, or 0 percent by weight to 0.01 percent by weight, or 0 percent by weight, or 0.0001 percent by weight to 0.1 percent by weight of glycerol with respect to the weight of the additive composition, reaction product, plurality of amides, plurality of esters, and combinations thereof respectively.

[0128] Any of the additive compositions, reaction products, pluralities of amides, pluralities of esters, and combinations thereof described herein may comprise 0 percent by weight to 4 percent by weight total rosin, total resin acid, total derivatives of resin acid, or any combination thereof, or 0 percent by weight to 3 percent by weight, or 0 percent by weight to 2 percent by weight, or 0 percent by weight to 1 percent by weight, or 0 percent by weight to 0.1 percent by weight, or 0 percent by weight to 0.01 percent by weight, or 0 percent by weight, or 0.0001 percent by weight to 0.1 percent by weight with respect to the weight of the additive composition, reaction product, plurality of amides, plurality of esters, and combinations thereof respectively.

EXAMPLES

[0129] The following examples are intended to illustrate different aspects and embodiments of the invention and are not to be considered limiting the scope of the invention. It will be recognized that various modifications and changes may be made without departing from the scope of the claims.

Example 1: Synthesis of SOFA-TEPA Amide from
Glycerol-Restricted Soybean Oil Fatty Acid
Obtained from Supplier a

[0130] To a 250 mL four-necked round-bottom flask equipped with a temperature probe, nitrogen inlet, Dean-Stark apparatus, condenser, and magnetic stirrer bar was added glycerol-restricted soybean oil fatty acid (89.6 g) obtained from a first supplier, Supplier A. Next, tetraethylenepentamine (17.1 g, 0.090 moles) was charged to the well-stirred reaction mixture. The temperature of the reaction mixture was observed to rise from 21° C. to about 44° C. Heavy aromatic naphtha (18.3 g) was then charged to the well-stirred reaction mixture. Nitrogen purging was started, and reaction was heated to about 170° C. and held for about 10 hours. The reaction was cooled to below 100° C., and an amount of heavy aromatic naphtha (HAN) equivalent in volume to that of the liquid collected in the Dean-Stark trap was added to the flask. The contents of the flask were stirred for a further ten minutes and allowed to cool to room temperature. The product remained a clear liquid and showed no signs of phase separation over time.

Example 2: Synthesis of SOFA-TEPA Amide from
Glycerol-Restricted Soybean Oil Fatty Acid
Obtained from Supplier B

[0131] To a 250 mL four-necked round-bottom flask equipped with a temperature probe, nitrogen inlet, Dean-Stark apparatus, condenser, and magnetic stirrer bar was added glycerol-restricted soybean oil fatty acid (72.73 g) obtained from a second supplier, Supplier B. Next, tetraethylenepentamine (13.68 g, 0.072 moles) was charged to the well-stirred reaction mixture. The temperature of the reaction mixture was observed to rise from 21° C. to about 61° C. Heavy aromatic naphtha (HAN) (13.59 g) was then charged to the well-stirred reaction mixture. Nitrogen purging was started, and the reaction was heated to about 170° C. and held for about 10 hours. The reaction was cooled to below 100° C., and an amount of heavy aromatic naphtha (HAN) equivalent in volume to that of the liquid collected in the Dean-Stark trap was added to the flask. The contents of the flask were stirred for a further ten minutes and allowed to cool to room temperature. The product remained a clear liquid and showed no signs of phase separation over time.

Example 3: Synthesis of SOFA-TEA Ester from
Glycerol-Restricted Soybean Oil Fatty Acid
Obtained from Supplier a

[0132] To a 250 mL four-necked round-bottom flask equipped with a temperature probe, nitrogen inlet, Dean-Stark apparatus, condenser, and magnetic stirrer bar was added glycerol-restricted soybean oil fatty acid (44.97 g) obtained from Supplier A. Next, triethanolamine (15.75 g, 0.10 moles) was charged to the well-stirred reaction mixture. The reaction was heated to about 210° C. and held at that temperature for about four hours. The reaction was cooled to below 100° C., and heavy aromatic naphtha (39.28 g) was added to flask. The contents of the flask were stirred for a further ten minutes and cooled to room temperature. The product remained a clear liquid and showed no signs of phase separation over time.

Example 4: Synthesis of SOFA-TEA Ester from
Glycerol-Restricted Soybean Oil Fatty Acid
Obtained from Supplier B

[0133] To a 250 mL four-necked round-bottom flask equipped with a temperature probe, nitrogen inlet, Dean-Stark apparatus, condenser, and magnetic stirrer bar was added glycerol-restricted soybean oil fatty acid (45.65 g) obtained from Supplier B. Next, triethanolamine (15.75 g, 0.10 moles) was charged to the well-stirred reaction mixture. The reaction was heated to about 210° C. and held at that temperature for about four hours. The reaction was cooled to less than 100° C., and heavy aromatic naphtha (38.60 g) was added to flask. The contents of the flask were stirred for a further ten minutes and cooled to room temperature. The product remained a clear liquid and showed no signs of phase separation over time.

Example 5: Additive from Soybean Oil

[0134] To a one-liter four-necked round-bottom flask equipped with a temperature probe, nitrogen inlet, Dean-Stark apparatus, condenser, and magnetic stirrer bar was added 343.5 g of soybean oil with a few drops (0.01 g) of antifoaming silicone. The flask and its contents were heated to 80° C. under a nitrogen purge and diethylene tetramine (129.99 g, 1.26 moles) was added slowly in order that the contents of the flask did not exceed 100° C. and to avoid foaming. After the addition was completed, the contents of the flask were heated at 165° C. for an hour to form the amide, and the reaction mixture was monitored for formation of the amide by removing small samples and checking them by infrared spectroscopy for the disappearance of the peak associated with ester carbonyl at 1742 cm⁻¹ and the appearance of the peak associated with amide carbonyl at 1645 cm⁻¹.

[0135] The contents of the reaction flask were then heated to 245° C. for three hours to cyclize amide to imidazoline. The reaction was monitored for formation of the imidazoline by removing small samples and checking them by infrared spectroscopy for the disappearance of the amide carbonyl peak at 1645 cm⁻¹ and the appearance of the imine peak at 1602 cm⁻¹.

[0136] The contents of the reaction vessel were cooled and transferred to a jar. Immediately after transfer, the contents of the jar were a clear liquid, but after three days the contents of the jar were turbid and had phase separated into layers.

Example 6: Additive from Glycerol-Restricted
Soybean Oil Fatty Acid

[0137] To a 250 mL four-necked round-bottom flask equipped with a temperature probe, nitrogen inlet, Dean-Stark apparatus, condenser, and magnetic stirrer bar was added glycerol-restricted soybean oil fatty acid (70.99 g). Next, 2-aminoethylethanolamine (29.00 g, 0.278 moles) was charged to the well-stirred reaction mixture. The temperature of the contents of the flask rose from room temperature to a temperature between about 50 and about 60° C. The viscous reaction mass was heated at about 180° C. for about eight hours. The reaction mixture was then heated to about 225° C. and held at that temperature for about five hours. About four to five mL of water was collected in the Dean-Stark trap. The contents of the flask were cooled to less than 100° C., and transferred to a jar.

[0138] A sample of the reaction product, SOFA-imidazoline, was stored at -10° C. and did not exhibit haze or a precipitate after 11 days and after three months.

[0139] A sample of the SOFA-imidazoline product (8 g) was blended with dimethyl phthalate (2 g) to form a concentrate. The concentrate was stored at -10° C., and showed no haze or precipitation after a week, after 44 days, or even after 95 days.

Example 7: Additive Concentrate from Tall Oil Fatty Acid

[0140] The procedure of Example 6 was repeated, but instead of glycerol-restricted soybean oil fatty acid, tall oil fatty acid was used.

[0141] A sample of the reaction product, TOFA imidazoline, was stored at -10° C. for 11 days and exhibited a precipitate.

[0142] A sample of the TOFA-imidazoline product (8 g) was blended with dimethyl phthalate (2 g) to form a concentrate. The concentrate was stored at -10° C. and exhibited precipitation after only a few days. After storage at -10° C. for 64 days, the precipitate could not be easily redissolved.

[0143] Comparison with Example 6 shows that the SOFA-imidazoline additive was more stable when stored at low temperatures than the corresponding TOFA-imidazoline additive, both in 100% form and when made up as a concentrate in organic solvent (dimethyl phthalate).

Example 9: Synthesis of TOFA-TEPA Amide from Tall Oil Fatty Acid

[0144] The synthetic procedure of Examples 1 and 2 was repeated, except that the glycerol-restricted soybean oil fatty acid was replaced with tall oil fatty acid.

Example 10: Synthesis of TOFA-TEA Ester from Tall Oil Fatty Acid

[0145] The synthetic procedure of Examples 3 and 4 was repeated, except that the glycerol-restricted soybean oil fatty acid was replaced with tall oil fatty acid.

Example 11: Combination Amide-Ester Corrosion Inhibitors (CAE)

[0146] TOFA-TEPA amide and TOFA-TEA ester made as in Example 9 and Example 10 respectively were mixed in a ratio of 1 part of TOFA-TEPA amide by weight to 3.5 parts of TOFA-TEA ester by weight to produce CAE2.

[0147] SOFA-TEPA amide and SOFA-TEPA ester made as in Examples 2 and 4 respectively were mixed in a ratio of 1 part of SOFA-TEPA amide by weight to 3.5 parts of SOFA-TEA ester by weight to produce CAE3.

[0148] SOFA-TEPA amide and SOFA-TEPA ester made as in Examples 2 and 4 respectively were mixed in a ratio of 1 part of SOFA-TEPA amide by weight to 3.5 parts of SOFA-TEA ester by weight to produce CAE4.

[0149] SOFA-TEPA amide and SOFA-TEPA ester made as in Examples 1 and 3 respectively were mixed in a ratio of 1 part of SOFA-TEPA amide by weight to 3.5 parts of SOFA-TEA ester by weight to produce CAE5.

Example 12: Corrosion Inhibitor Performance by Wheel Box Testing

[0150] Wheel box testing (NACE 1D182, "Wheel Test Method Used for Evaluation of Film-Persistent Corrosion Inhibitors for Oil Field Applications") was conducted to evaluate three different concentrations of each of CAE2 to CAE5 in hydrotreated light distillate as oil. A further sample of crude oil without any combination amide-ester corrosion inhibitor was also evaluated, labeled here CAE1, as shown in TABLE 1. A number of samples of each of CAE2 to CAE5 were evaluated.

[0151] The wheel box testing was conducted with brine (49.7 NH_4Cl grams per liter and 9.9 grams per liter of HCl in water), gases were H_2S saturated, coupons were $\frac{1}{4}$ " by $7\frac{3}{8}$ " 1018 mild steel with sandblast finish, rotation rate of the wheel was 26 revolutions per minute (RPM), test temperature 160° F. (71° C.), and the test length was 24 hours. The corrosion inhibition results are also displayed in TABLE 1.

TABLE 1

Corrosion inhibition samples				
Combination amide-ester corrosion inhibitor	Fatty acid source used to make amide and ester	Concentration of corrosion inhibitor/ppm by weight	Average % Protection	Standard deviation
CAE1	None	0	0	0
CAE2	TOFA	5	52.0	0.72
CAE3	Supplier B SOFA		52.1	0.93
CAE4	Supplier B SOFA		52.4	1.14
CAE5	Supplier A SOFA		53.2	0.75
CAE2	TOFA	10	78.8	0.60
CAE3	Supplier B SOFA		79.9	1.15
CAE4	Supplier B SOFA		79.0	0.56
CAE5	Supplier A SOFA		79.0	0.57
CAE2	TOFA	20	84.6	1.01
CAE3	Supplier B SOFA		83.5	0.67
CAE4	Supplier B SOFA		82.5	0.68
CAE5	Supplier A SOFA		85.6	0.84

[0152] Excellent corrosion protection results were obtained with corrosion inhibitors CAE2, CAE3, CAE4, and CAE5.

1. An additive composition comprising a plurality of amides and/or ammonium salts thereof, wherein at least a portion of the plurality of amides comprises a reaction product derived from a first set of reactants comprising first one or more glycerol-restricted vegetable oil fatty acids and a polyamine,

wherein the first one or more glycerol-restricted vegetable oil fatty acids comprise 0 percent by weight to 0.1 percent by weight of glycerol with respect to the weight of the first one or more glycerol-restricted vegetable oil fatty acids, and

wherein the polyamine has the formula $\text{NH}_2(\text{CH}_2\text{CH}_2\text{NH})_x\text{CH}_2\text{CH}_2\text{NH}_2$ wherein x is 0 to 100.

2. The additive composition of claim 1, wherein x is zero to ten.

3. The additive composition of claim 1, wherein the first one or more glycerol-restricted vegetable oil fatty acids comprise glycerol-restricted soybean oil fatty acid.

4. The additive composition of claim 1, wherein the additive composition further comprises a plurality of esters, wherein at least a portion of the plurality of esters comprises

a second reaction product derived from a second set of reactants comprising second one or more glycerol-restricted vegetable oil fatty acids and one or more tertiary amines, each of the one or more tertiary amines having at least one hydroxyl group,

wherein the second one or more glycerol-restricted vegetable oil fatty acids comprises 0 percent by weight to 0.1 percent by weight glycerol with respect to the weight of the second one or more glycerol-restricted vegetable oil fatty acids.

5. The additive composition of claim 4, wherein the one or more tertiary amines comprises triethanolamine.

6. The additive composition of claim 4, wherein the second one or more glycerol-restricted vegetable oil fatty acids comprise glycerol-restricted soybean oil fatty acid.

7. The additive composition of claim 1, wherein the one or more first glycerol-restricted vegetable oil fatty acids and the second one or more glycerol-restricted vegetable oil fatty acids consist of glycerol-restricted soybean oil fatty acid comprising 0 percent by weight to 0.1 percent by weight glycerol with respect to the additive composition.

8. The additive composition of claim 1, wherein the additive composition comprises 0 percent by weight to 0.1 percent by weight glycerol with respect to the additive composition.

9. The additive composition of claim 1, wherein the polyamine comprises tetraethylenepentamine ($\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$).

10. The additive composition of claim 1, wherein each of the first one or more and second one or more glycerol-restricted vegetable oil fatty acids independently comprises about 2 percent by weight to about 15 percent by weight alpha-linolenic acid, about 46 percent by weight to about 56 percent by weight linoleic acid, about 17 percent by weight to about 28 percent by weight oleic acid, about 1 percent by weight to about 10 percent by weight stearic acid, and about 5 percent by weight to about 15 percent by weight palmitic acid with respect to the first one or more glycerol-restricted vegetable oil fatty acids and the second one or more glycerol-restricted vegetable oil fatty acids respectively.

11. The additive composition of claim 1, wherein the additive composition comprises 0 percent by weight to 5 percent by weight of total imidazoline content, 0 percent by weight to 5 percent by weight of rosin acid, 0 percent by weight to 5 percent by weight of total derivative of rosin acid, 0 percent by weight to 5 percent by weight total C1-C10 monohydric alcohol, and 0 percent by weight to 5 percent by weight total fatty acid ester content with respect to the additive composition.

12. The additive composition of claim 1, wherein the additive composition comprises the plurality of amides and heavy aromatic naphtha.

13. The additive composition of claim 1, wherein

- (i) the additive composition comprises the ammonium salts of the plurality of amides; and
- (ii) the additive composition is aqueous.

14. The additive composition of claim 13, wherein the ammonium salts of the plurality of amides comprise at least a portion of a reaction product derived from reactants comprising:

- (a) the plurality of amides, and
- (b) one or more of an acid, an alkyl halide, and an aryl halide.

15. A hydrocarbon composition comprising:

- (a) one or more hydrocarbons; and
- (b) an additive composition comprising an ester composition,

wherein the ester composition comprises a plurality of esters, wherein at least a portion of the plurality of the esters comprises a reaction product derived reactants comprising one or more glycerol-restricted vegetable oil fatty acids and one or more tertiary amines, each of the one or more tertiary amines having at least one hydroxyl group,

wherein the one or more glycerol-restricted vegetable oil fatty acids comprises 0 percent by weight to 0.1 percent by weight glycerol with respect to the weight of the second one or more glycerol-restricted vegetable oil fatty acids.

16-31. (canceled)

32. A method of inhibiting the corrosion of a surface in contact with one or more hydrocarbons, the method comprising combining an inhibitor composition with the one or more hydrocarbons, wherein the inhibitor composition comprises the additive composition of claim 1.

33-39. (canceled)

40. A method of making an additive composition, the method comprising:

- (1) combining first one or more glycerol-restricted vegetable oil fatty acids with a polyamine to form a first reaction mixture, wherein the first one or more glycerol-restricted vegetable oil fatty acids comprise 0-0.1 percent by weight of glycerol with respect to the weight of the first one or more glycerol-restricted vegetable oil fatty acids;
- (2) optionally adding a hydrocarbon solvent to the first reaction mixture;
- (3) heating the first reaction mixture at a reaction temperature of between 150° C. and 200° C. for a time period between 30 minutes and 20 hours to form water and a first reaction product, the first reaction product comprising a plurality of amides.

41-47. (canceled)

48. The method of claim 40, further comprising:

- (4) combining second one or more glycerol-restricted vegetable oil fatty acids with one or more tertiary amines to form a second reaction mixture,

wherein the second one or more glycerol-restricted vegetable oil fatty acids comprises 0 percent to 0.1 weight percent of glycerol with respect to the weight of the second one or more glycerol-restricted vegetable oil fatty acids, and

wherein each of the one or more tertiary amines comprises at least one hydroxyl group; and

- (5) heating the second reaction mixture at a reaction temperature of between 150° C. and 300° C. for a time period between 30 minutes and 10 hours to form water and a second reaction product, the second reaction product comprising a plurality of esters; and
- (6) combining ingredients comprising the first reaction product and the second reaction product to form the additive composition.

49-53. (canceled)

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