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(54) **Title:** EMULSIFIER COMPONENTS AND METHODS OF USING THE SAME

(57) **Abstract:** This invention relates to an additive comprising a functional group derived from a first hydrocarbyl-substituted acylating agent and a functional group derived from a second hydrocarbyl-substituted acylating agent, where the functional groups are coupled by a functional group derived from an alkylene glycol. The invention also relates to an emulsifier component prepared by a process that utilizes the described additive and converts it to an emulsifier component by reacting it with a neutralizing component. The invention also relates to a process of making the described emulsifier component, and a method of customizing an emulsifier component in a composition by using the described additive and the described process for converting it to the described emulsifier component.



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TITLE**EMULSIFIER COMPONENTS AND METHODS OF USING THE SAME**

[0001] This invention relates to an additive comprising a functional group derived from a first hydrocarbyl-substituted acylating agent and a functional group derived from a second hydrocarbyl-substituted acylating agent, where the functional groups are coupled by a functional group derived from an alkylene glycol, and in certain embodiments a linear alkylene glycol. The invention also relates to an emulsifier component prepared by a process that utilizes the described additive and converts it to an emulsifier component by reacting it with a neutralizing component. The invention also relates to a process of making the described emulsifier component, and a method of customizing an emulsifier component in a composition by using the described additive and the described process for converting it to the described emulsifier component.

15 BACKGROUND OF THE INVENTION

[0002] Hydrocarbyl-substituted carboxylic acylating agents having at least about 30 aliphatic carbon atoms in the substituent are known as additives in normally liquid fuels and lubricants. Examples of such acylating agents include the polyisobutenyl-substituted succinic acids and anhydrides. The use of such carboxylic acylating agents as additives in normally liquid fuels and lubricants is disclosed in U.S. Pat. Nos. 3,288,714 and 3,346,354.

[0003] These acylating agents are also useful as intermediates for preparing additives for use in normally liquid fuels and lubricants as described in U.S. Pat. Nos. 2,892,786; 3,087,936; 3,163,603; 3,172,892; 3,189,544; 3,215,707; 3,219,666; 3,231,587; 3,235,503; 3,272,746; 3,306,907; 3,306,908; 3,331,776; 3,341,542; 3,346,354; 3,374,174; 3,379,515; 3,381,022; 3,413,104; 3,450,715; 3,454,607; 3,455,728; 3,476,686; 3,513,095; 3,523,768; 3,630,904; 3,632,511; 3,697,428; 3,755,169; 3,804,763; 3,836,470; 3,862,981; 3,936,480; 3,948,909; 3,950,341; 4,234,435; and 4,471,091; and French Patent 2,223,415.

[0004] U.S. Pat. No. 3,216,936 describes nitrogen-containing dispersants for use in lubricants which are obtained by the reaction of an alkylene amine with an acidic mixture consisting of a hydrocarbon-substituted succinic acid having at least about

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50 aliphatic carbon atoms in the hydrocarbon substituent and an aliphatic monocarboxylic acid. The aliphatic monocarboxylic acids are described as including saturated and unsaturated acids such as acetic acid, dodecanoic acid, oleic acid, naphthenic acid, formic acid, etc. Acids having 12 or more aliphatic carbon atoms, particularly stearic acid and oleic acid, are described as being especially useful.

5 [0005] U.S. Pat. Nos. 3,639,242 and 3,708,522 describe compositions prepared by post-treating mono- and polycarboxylic acid esters with mono- or polycarboxylic acid acylating agents. The compositions thus obtained are reported to be useful as dispersants in lubricants and fuels.

10 [0006] U.S. Pat. No. 4,642,330 discloses dispersant salt compositions made by reacting phosphorus-free carboxylic solubilizers with sulfonic acid-free organic acids or mineral acids. The carboxylic solubilizer is the reaction product of a polycarboxylic acid acylating agent having at least one hydrocarbon-based substituent of at least 8 to 500 carbon atoms with at least one poly(alkyleneamine). The reference indicates that these dispersant salt compositions have good thermal stability when mixed with a surfactant or a hydrophilic organic solvent, and that they can be used with aqueous solutions to disperse various fillers including carbon black and to solubilize various fluids.

20 [0007] Nitrogen-containing, phosphorus-free carboxylic solubilizers useful in water based functional fluids are disclosed in U.S. Pat. Nos. 4,329,249; 4,368,133; 4,435,297; 4,447,348; and 4,448,703. These solubilizers are made by reacting (I) at least one carboxylic acid acylating agent having at least one hydrocarbyl substituent of from about 12 to about 500 carbon atoms with (II) at least one (a) N-(hydroxyl-substituted hydrocarbyl) amine, (b) hydroxyl-substituted poly(hydrocarbyloxy) analog of said amine (a), or (c) mixtures of (a) and (b). These patents indicate that preferred acylating agents include the substituted succinic acids or anhydrides, such as polyisobutenyl-substituted succinic anhydride, and that the amines that are useful include the primary, secondary and tertiary alkanol amines, such as diethylethanolamine and mixtures of diethylethanolamine and ethanolamine. These solubilizers are useful in dispersing oil-soluble, water-insoluble functional additives in water-based functional fluids.

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[0008] U.S. Pat. No. 5,047,175 discloses salt compositions comprising: (A) at least one salt moiety derived from (A)(I) at least one high-molecular weight polycarboxylic acylating agent, said acylating agent (A)(I) having at least one hydrocarbyl substituent having an average of from about 20 to about 500 carbon atoms, and (A)(II) ammonia, at least one amine, at least one alkali or alkaline earth metal, and/or at least one alkali or alkaline earth metal compound; (B) at least one salt moiety derived from (B)(I) at least one low-molecular weight polycarboxylic acylating agent, said acylating agent (B)(I) optionally having at least one hydrocarbyl substituent having an average of up to about 18 carbon atoms, and (B)(II) ammonia, at least one amine, at least one alkali or alkaline earth metal, and/or at least one alkali or alkaline earth metal compound; said components (A) and (B) being coupled together by (C) at least one compound having (i) two or more primary amino groups, (ii) two or more secondary amino groups, (iii) at least one primary amino group and at least one secondary amino group, (iv) at least two hydroxyl groups or (v) at least one primary or secondary amino group and at least one hydroxyl group. These salt compositions are useful as emulsifiers in water-in-oil explosive emulsions, particularly cap-sensitive explosive emulsions.

[0009] U.S. Pat. No. 4,828,633 discloses emulsion explosives based upon the emulsifier of U.S. Pat. No. 5,047,175.

[0010] U.S. Pat. No. 5,422,024 provides for aqueous oil-in-water emulsion functional fluids comprising water, an oil and an emulsifying quantity of a salt composition comprising: (A) at least one salt moiety derived from (A)(I) at least one high-molecular weight polycarboxylic acylating agent, said acylating agent (A)(I) having at least one hydrocarbyl substituent having an average of from about 20 to about 200 carbon atoms, and (A)(II) ammonia, at least one amine, at least one alkali or alkaline earth metal, and/or at least one alkali or alkaline earth metal compound; (B) at least one salt moiety derived from (B)(I) at least one low-molecular weight polycarboxylic acylating agent, said acylating agent (B)(I) optionally having at least one hydrocarbyl substituent having an average of average of up to about 18 carbon atoms, and (B)(II) ammonia, at least one amine, at least one alkali or alkaline earth metal, and/or at least one alkali or alkaline earth metal compound; said components (A) and (B) being coupled together by (C) least one

compound having (i) two or more primary amino groups, (ii) two or more secondary amino groups, (iii) at least one primary amino group and at least one secondary amino group, (iv) at least two hydroxyl groups or (v) at least one primary or secondary amino group at least one hydroxyl group.

5 [0011] These materials described above have proven to be useful emulsifiers however there is continued need for emulsifiers with improved performance, as well as emulsifier systems that are more easily customized for specific applications. There is a need to allow the fluid users and/or manufacturers the ability to easily adjust and/or adapt the emulsifier they are using based on the specific fluid and/or end use
10 they are dealing with. Thus there is a continued need for better performing and/or more customizable emulsifiers which can be customized by the fluid users and/or manufacturers.

SUMMARY OF THE INVENTION

[0012] The disclosed technology provides an additive comprising (i) a functional
15 group derived from a first hydrocarbyl-substituted acylating agent and (ii) a functional group derived from a second hydrocarbyl-substituted acylating agent, where the functional groups (i) and (ii) are coupled by a functional group derived from an alkylene glycol such as a linear alkylene glycol; wherein the first hydrocarbyl-substituted acylating agent comprises a hydrocarbyl substituent group
20 containing at least 20 carbon atoms; and wherein the second hydrocarbyl-substituted acylating agent comprises a hydrocarbyl substituent group containing less than 20 carbon atoms.

[0013] The invention further provides the described additive where the first hydrocarbyl-substituted acylating agent comprises the reaction product of a long
25 chain hydrocarbon with a monounsaturated carboxylic acid; wherein said long chain hydrocarbon has a number average molecular weight greater than 400. In some embodiments, long chain hydrocarbon has a number average molecular weight greater than 450, at least 500, at least 750, or even at least 800. (A “monounsaturated carboxylic acid” refers to a carboxylic acid that contains one
30 ethylenic unsaturation, that is, not counting the carbonyl double bond.)

[0014] The invention further provides the described additive where the first hydrocarbyl-substituted acylating agent comprises polyisobutylene succinic

anhydride having a number average molecular weight greater than 400. In some embodiments, the polyisobutylene succinic anhydride has a polyisobutylene group with a number average molecular weight greater than 450, at least 500, at least 750, or even at least 800.

5 [0015] The invention further provides the described additive wherein the second hydrocarbyl-substituted acylating agent comprises the reaction product of a long chain hydrocarbon with a monounsaturated carboxylic acid; wherein said long chain hydrocarbon has a number average molecular weight less than 400 or less than 280 or less than 250. In some embodiments, long chain hydrocarbon has a number
10 average molecular weight from 100 to 400, or from 200 to 400, or from 200 to 280, or from 200 to 250, or from 300 to 400, or even from 300 to 350, or even about 322.

[0016] The invention further provides the described additive wherein the second hydrocarbyl-substituted acylating agent comprises hexadecenyl succinic anhydride.

[0017] The invention further provides the described additive wherein the
15 alkylene glycol comprises a glycol having of the general formula $\text{HO}-\left[\text{C}(\text{R})_x-\text{O} \right]_m-\text{H}$ wherein each R is independently H or an alkyl group of 1 to 6 carbon atoms each x is independently an integer from 2 to 10 and m is an integer from 1 to 10. That is, some or all of the R groups may be H and the remainder (if any) of the R groups may be said alkyl groups. In certain embodiments disclosed
20 herein, one or more of the R groups may be methyl groups. In certain embodiments throughout this document, the number of carbon atoms in the glycol of the foregoing structure will be less than 400, or less than 200, or less than 100, or 2 to 50, or 2 to 10, or 2 or 3.

[0018] In some embodiments, the alkylene glycol is a linear alkylene glycol, and
25 in some embodiments it comprises ethylene glycol.

[0019] The invention further provides the described additive wherein the first hydrocarbyl-substituted acylating agent comprises polyisobutylene succinic anhydride having a number average molecular weight greater than 750; wherein the second hydrocarbyl-substituted acylating agent comprises hexadecenyl succinic
30 anhydride; and wherein the alkylene glycol comprises ethylene glycol.

[0020] The invention further provides an emulsifier component prepared by a process comprising the steps of: Step (I) reacting a first hydrocarbyl-substituted

acylating agent, a second hydrocarbyl-substituted acylating agent, and an (optionally linear) alkylene glycol; wherein the first hydrocarbyl-substituted acylating agent comprises a hydrocarbyl substituent group containing at least 20 carbon atoms; and wherein the second hydrocarbyl-substituted acylating agent
5 comprises a hydrocarbyl substituent group containing less than 20 carbon atoms; resulting in an additive comprising (i) a functional group derived from said first hydrocarbyl-substituted acylating agent and (ii) a functional group derived from said second hydrocarbyl-substituted acylating agent, where the functional groups (i) and (ii) are coupled by a functional group derived from said alkylene glycol; Step
10 (II) providing said additive for use as an emulsifier component precursor; and Step (III) converting said additive to an emulsifier component by reacting said additive with a neutralizing component. Any of the additives described herein may be prepared and used as described by this process.

[0021] The invention further provides the emulsifier component described above
15 where said neutralizing component comprises an alkali or alkaline earth-metal base or an amine. Suitable amines include NaOH, KOH, monoethanolamine, diethanolamine, triethanolamine, methyl diethanolamine, dimethylethanolamine, butylethanolamine, butyl diethanolamine, octyl diethanolamine, cyclohexyl diethanolamine, monoisopropanolamine, diisopropanolamine, triisopropanolamine,
20 diglycolamine, 1-amino-2-methyl-1-propanol, 3-amino-4-octanol, dicyclohexylamine, octylamine, and any combinations thereof.

[0022] The invention further provides a process of making an emulsifier component comprising the steps of: Step (I) reacting a first hydrocarbyl-substituted acylating agent, a second hydrocarbyl-substituted acylating agent, and an
25 (optionally linear) alkylene glycol; wherein the first hydrocarbyl-substituted acylating agent comprises a hydrocarbyl substituent group containing at least 20 carbon atoms; and wherein the second hydrocarbyl-substituted acylating agent comprises a hydrocarbyl substituent group containing less than 20 carbon atoms; resulting in an intermediate (which may also be referred to throughout this
30 document as an additive) comprising (i) a functional group derived from said first hydrocarbyl-substituted acylating agent and (ii) a functional group derived from said second hydrocarbyl-substituted acylating agent, where the functional groups (i)

and (ii) are coupled by a functional group derived from said alkylene glycol; Step (II) providing said additive for use as an emulsifier component precursor; and, typically thereafter, Step (III) converting said intermediate (or additive) to an emulsifier component by reacting said intermediate (additive) with a neutralizing component. Any of the additives described herein may be prepared and used as described by this process.

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[0023] The invention further provides the describe process wherein the first hydrocarbyl-substituted acylating agent comprises the reaction product of a long chain hydrocarbon with a monounsaturated carboxylic acid; wherein said long chain hydrocarbon has a number average molecular weight greater than 400; and wherein the second hydrocarbyl-substituted acylating agent comprises the reaction product of a long chain hydrocarbon with a monounsaturated carboxylic acid; wherein said long chain hydrocarbon has a number average molecular weight less than 400 or less than 280; wherein the (optionally linear) alkylene glycol comprises a glycol having of the general formula $\text{HO}-(\text{C}(\text{R}))_x-\text{O}-\text{H}$ wherein each R is independently H or an alkyl group of 1 to 6 carbon atoms, each x is independently an integer from 2 to 10 and m is an integer from 1 to 10.

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[0024] The invention further provides the describe process wherein the first hydrocarbyl-substituted acylating agent comprises polyisobutylene succinic anhydride having a number average molecular weight greater than 750; wherein the second hydrocarbyl-substituted acylating agent comprises hexadecenyl succinic anhydride; and wherein the alkylene glycol comprises ethylene glycol.

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[0025] The invention further provides a method of customizing an emulsifier component in a composition said method comprising the steps of: Step (I) preparing an additive by reacting a first hydrocarbyl-substituted acylating agent, a second hydrocarbyl-substituted acylating agent, and an (optionally linear) alkylene glycol; wherein the first hydrocarbyl-substituted acylating agent comprises a hydrocarbyl substituent group containing at least 20 carbon atoms; and wherein the second hydrocarbyl-substituted acylating agent comprises a hydrocarbyl substituent group containing less than 20 carbon atoms; resulting in an additive comprising (i) a functional group derived from said first hydrocarbyl-substituted acylating agent and (ii) a functional group derived from said second hydrocarbyl-substituted acylating

agent, where the functional groups (i) and (ii) are coupled by a functional group derived from said alkylene glycol; Step (II) supplying said additive into a composition that requires an emulsifier component; and, typically thereafter, Step (III) converting said additive, in said composition, to an emulsifier component by reacting said additive with a neutralizing component; resulting in a customized emulsifier component. Any of the additives described herein may be prepared and used as described by this method.

5 [0026] The invention further provides the described method wherein the first hydrocarbyl-substituted acylating agent comprises the reaction product of a long chain hydrocarbon with a monounsaturated carboxylic acid; wherein said long chain hydrocarbon has a number average molecular weight greater than 400; and wherein the second hydrocarbyl-substituted acylating agent comprises the reaction product of a long chain hydrocarbon with a monounsaturated carboxylic acid; wherein said long chain hydrocarbon has a number average molecular weight less than 400 or less than 280; and wherein the alkylene glycol comprises a glycol having of the general formula $\text{HO}-\left[(\text{CH}_2)_x-\text{O} \right]_m-\text{H}$ wherein each R is independently H or an alkyl group of 1 to 6 carbon atoms each x is independently an integer from 2 to 10 and m is an integer from 1 to 10.

DETAILED DESCRIPTION OF THE INVENTION

20 [0027] Various preferred features and embodiments will be described below by way of non-limiting illustration.

[0028] It has been found that using the described additive provides a benefit to emulsifier users, by allowing the user to optimize the Hydrophilic-Lipophilic Balance (HLB), buffering system and corrosion inhibition system of the additive resulting in an emulsifier customized for use in in the specific metalworking product and/or application relevant to the user. This approach involves the use of an additive that has never been used as an emulsifier itself, which may then be further modified by emulsifier users to achieve the specific emulsifier performance they desire.

30 The Additive

[0029] The disclosed technology provides an additive comprising (i) a functional group derived from a first hydrocarbyl-substituted acylating agent and (ii) a

functional group derived from a second hydrocarbyl-substituted acylating agent, where the functional groups (i) and (ii) are coupled by a functional group derived from an alkylene glycol which may be either a branched or a linear alkylene glycol; wherein the first hydrocarbyl-substituted acylating agent comprises a hydrocarbyl substituent group containing at least 20 carbon atoms; and wherein the second hydrocarbyl-substituted acylating agent comprises a hydrocarbyl substituent group containing less than 20 carbon atoms.

[0030] The first hydrocarbyl-substituted acylating agent and the second hydrocarbyl-substituted acylating agent, from which the functional groups (i) and (ii) are derived, may also be described as carboxylic acylating agents and may be aliphatic or aromatic, polycarboxylic acids or acid-producing compounds. As used herein, the term "carboxylic acylating agent" is intended to include carboxylic acids as well as acid-producing derivatives thereof such as anhydrides, esters, acyl halides and mixtures thereof, unless otherwise specifically stated.

[0031] The acylating agents may contain polar substituents provided that the polar substituents are not present in portions sufficiently large to alter significantly the hydrocarbon character of the acylating agent. Typical suitable polar substituents include halo, such as chloro and bromo, oxo, oxy, formyl, sulfenyl, sulfinyl, thio, nitro, etc. Such polar substituents, if present, preferably do not exceed about 10% by weight of the total weight of the hydrocarbon portion of the acylating agent, exclusive of the carboxyl groups.

[0032] Examples of low molecular weight polycarboxylic acids, (i.e., the second hydrocarbyl-substituted acylating agent which comprises a hydrocarbyl substituent group containing less than 20 carbon atoms), include dicarboxylic acids and derivatives such as maleic acid, maleic anhydride, chloromaleic anhydride, malonic acid, succinic acid, succinic anhydride, glutaric acid, glutaric anhydride, adipic acid, pimelic acid, azelaic acid, sebacic acid, glutaconic acid, citraconic acid, itaconic acid, allyl succinic acid, cetyl malonic acid, tetrapropylene-substituted succinic anhydride, etc. Lower alkyl esters of these acids can also be used.

[0033] In some embodiments, both the first hydrocarbyl-substituted acylating agent and the second hydrocarbyl-substituted acylating agents are hydrocarbyl substituted succinic acids and anhydrides.

[0034] The hydrocarbyl succinic acylating agents may contain polar substituents provided that the polar substituents are not present in portions sufficiently large to alter significantly the hydrocarbon character of the acylating agent. Typical suitable polar substituents include halo, such as chloro and bromo, oxo, oxy, formyl, sulfenyl, sulfinyl, thio, nitro, etc. Such polar substituents, if present, preferably do not exceed about 10% by weight of the total weight of the hydrocarbon portion of the acylating agent, exclusive of the carboxyl groups.

[0035] The high-molecular weight polycarboxylic acylating agents (i.e. the first hydrocarbyl-substituted acylating agent which comprises a hydrocarbyl substituent group containing at least 20 carbon atoms), are well known in the art and have been described in detail, for example, in U.S. Pat. Nos. 3,215,707; 3,231,587; 3,288,714; 3,346,354; 3,912,764; 4,110,349; and 4,234,435; and British Patent 1,492,337. These patents are incorporated herein by reference.

[0036] The hydrocarbyl groups of the first and second hydrocarbyl-substituted acylating agents are not overly limited so long as they meet the requirements described herein. Especially useful hydrocarbyl groups comprising polymers of 1-mono-olefins such as ethylene, propene, 1-butene, isobutene, 1-hexene, 1-octene, 2-methyl-1-heptene, 3-cyclohexyl-1-butene, and 2-methyl-5-propyl-1-hexene. Polymers of medial olefins, i.e., olefins in which the olefinic linkage is not at the terminal position, likewise are useful. These are exemplified by 2-butene, 3-pentene, and 4-octene. Interpolymers of 1-mono-olefins such as illustrated above with each other and with other interpolymerizable olefinic substances such as aromatic olefins, cyclic olefins, and polyolefins, are also useful. Such interpolymers include for example, those prepared by polymerizing isobutene with styrene, isobutene with butadiene, propene with isoprene, propene with isobutene, ethylene with piperylene, isobutene with chloroprene, isobutene with p-methyl-styrene, 1-hexene with 1,3-hexadiene, 1-octene with 1-hexene, 1-heptene with 1-pentene, 3-methyl-1-butene with 1-octene, 3,3-dimethyl-1-pentene with 1-hexene, isobutene with styrene and piperylene, etc.

[0037] For reasons of hydrocarbon solubility, the interpolymers contemplated for use in preparing the acylating agents of this invention are preferably substantially aliphatic and substantially saturated, that is, they should contain at

least about 80% and preferably about 95%, on a weight basis, of units derived from aliphatic mono-olefins. Preferably, they will contain no more than about 5% olefinic linkages based on the total number of the carbon-to-carbon covalent linkages present.

5 [0038] In one embodiment of the invention, the polymers are obtained by the polymerization of a C4 refinery stream having a butene content of about 35% to about 75% by weight and an isobutene content of about 30% to about 60% by weight. These polyisobutenes preferably contain predominantly (that is, greater than about 80% of the total repeat units) isobutene repeat units of the configuration
10 $-\text{CH}_2\text{C}(\text{CH}_3)_2-$. The hydrocarbons and ethylenically unsaturated hydrocarbons used in the preparation of the higher molecular weight succinic acylating agents may have up to about 200 carbon atoms per molecule. Some acylating agents are those containing hydrocarbyl groups of from about 20 to about 150, or from 30 to about 120, or from about 50 to about 80 carbon atoms. The hydrocarbyl-substituted
15 succinic acids and the anhydride may prepared by reacting maleic anhydride with a high molecular weight olefin. The hydrocarbyl-substituted succinic anhydrides may be hydrolyzed by treatment with water or steam to the corresponding acid and either the anhydride or the acid may be converted to the corresponding acid or ester.

[0039] The hydrocarbyl group of the first hydrocarbyl-substituted acylating
20 agent may contain from about 20 to about 200 carbon atoms, from about 30 to about 150 carbon atoms, from about 50 to about 200 carbon atoms, or even from about 70 to about 80 carbon atoms.

[0040] The second hydrocarbyl-substituted acylating agent, which may also be referred to as the low molecular weight succinic acylating agents can be prepared in
25 essentially the same manner as the high molecular weight materials. In some embodiments, its hydrocarbyl group is an aliphatic or alicyclic hydrocarbyl group with less than about 10% of its carbon-to-carbon bonds being unsaturated. Its hydrocarbyl can be derived from olefins of from 2 to about 18 carbon atoms with alpha-olefins being particularly useful. Examples of such olefins include ethylene, propylene, 1-butene, isobutene, 1-pentene, 2-methyl-1-butene, 3-methyl-1-butene, 1-hexene, 1-
30 heptene, 1-octene, styrene, 1-nonene, 1-decene, 1-undecene, 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene, 1-octadecene.

[0041] Commercially available alpha olefin fractions such as C12-18 alpha-olefins, C12-16 alpha-olefins, C14-14 16 alpha-olefins, C14-18 alpha-olefins, and C16-18 alpha-olefins, are particularly useful. These commercial alpha-olefin fractions also usually include minor amounts of alpha-olefins outside the given
5 ranges. As is the case for the high molecular weight materials, the unsaturated material or optionally chlorinated analog is reacted with maleic acid or maleic anhydride. The production of such substituted succinic acids and their derivatives is well known to those of skill in the art and need not be discussed in detail herein.

[0042] In some embodiments, the first hydrocarbyl-substituted acylating agent
10 comprises the reaction product of a long chain hydrocarbon with a monounsaturated carboxylic acid; wherein said long chain hydrocarbon has a number average molecular weight greater than 400. In some embodiments, long chain hydrocarbon has a number average molecular weight greater than 450, at least 500, at least 750, or even at least 800. In some embodiments, the first hydrocarbyl-substituted
15 acylating agent comprises polyisobutylene succinic anhydride having a number average molecular weight greater than 400. In some embodiments, the polyisobutylene succinic anhydride has a number average molecular weight greater than 450, at least 500, at least 750, or even at least 800.

[0043] In some embodiments, the second hydrocarbyl-substituted acylating
20 agent comprises the reaction product of a long chain hydrocarbon with a monounsaturated carboxylic acid; wherein said long chain hydrocarbon has a number average molecular weight less than 400 or less than 280. In some embodiments, long chain hydrocarbon has a number average molecular weight from 100 to 400, or from 200 to 400, or from 300 to 400, or even from 300 to 350, or
25 even about 322, or 100 to less than 280. In some embodiments, the second hydrocarbyl-substituted acylating agent comprises hexadecenyl succinic anhydride.

[0044] The functional groups (i) and (ii) described above are coupled by a
30 functional group derived from an alkylene glycol. This third functional group acts as a bridge between the low and the high molecular weight functional groups derived from the acylating agents described above. The low and high molecular weight agents may be mixed together, and are reacted with the bridging molecule. The reaction is such that the predominant species in the reaction mixture is the

product in which the alkylene glycol acts as a bridge between a first hydrocarbyl-substituted acylating agent and a second hydrocarbyl-substituted acylating agent. However, there may be some formation of molecules in which two low molecular weight succinic agents are linked as well as formation of species in which two high
5 molecular weight succinic agents are linked. In some embodiments low and high molecular weight agents may be reacted sequentially with the alkylene glycol. In this case, the species comprising a first hydrocarbyl-substituted acylating agent and a second hydrocarbyl-substituted acylating agent molecule linked by an alkylene glycol greatly predominates over the other species.

10 **[0045]** In general, any compound having (i) two or more primary amino groups, (ii) two or more secondary amino groups, (iii) at least one primary amino group and at least one secondary amino group, (iv) at least two hydroxyl groups, or (v) at least one primary or secondary amino group and at least one hydroxyl group may be used as a linking group. However, in the present invention, it has been found that using
15 an alkylene glycol, such as, in some embodiments, a linear alkylene glycol, provides the best results, i.e. the most customizable additive.

[0046] The alkylene glycols useful in the invention may also be referred to generally as polyols, and includes those compounds of the general formula: $R^1(OH)_m$ wherein R^1 is a divalent organic group joined to the $-OH$ groups through
20 carbon-to-oxygen bonds (that is, $-COH$ wherein the carbon is not part of a carbonyl group) and m is 2. These alcohols are be aliphatic and in some embodiments contain not more than about 40, or not more than about 20 carbon atoms.

[0047] Alcohols useful in this invention include alkylene glycols with the alkylene group containing from about 2 to 10 or 2 to 8 carbon atoms. They may also
25 include polyoxyalkylene glycol, that is, materials represented by $HO-[C(R)]_x-O-]_m-H$ where each R is independently H or an alkyl group of 1 to 6 carbon atoms each x is independently an integer from 2 to about 10 and m is an integer greater than 1, that is, 2 to 10. They are illustrated, for example, ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, dipropylene glycol, tripropylene glycol, dibutylene glycol, tributylene glycol, and other alkylene
30 glycols and polyoxyalkylene glycols in which the alkylene groups contain from 2 to about 8 carbon atoms. Polyoxyalkylene glycols which are copolymers of different

alkylene oxide units may also be used, such as copolymers of ethylene glycol and propylene glycols such as 1,2- or 1,3-propylene glycol. They may be referred to as alkylene glycols as an alternative to the nomenclature “polyalkylene glycol” – both such materials may be used. Such materials may also be referred to as oligomers, since the number of repeat units will typically not exceed 10. In one embodiment the linear alkylene glycol comprises a poly(ethylene glycol), a poly(1,3-propylene glycol) or a copolymer of ethylene glycol and 1,3-propylene glycol.

[0048] In some embodiments, one or more linking compounds is used in combination with linear alkylene glycols described herein. Such additional linker may include any compound having (i) two or more primary amino groups, (ii) two or more secondary amino groups, (iii) at least one primary amino group and at least one secondary amino group, (iv) at least two hydroxyl groups, or (v) at least one primary or secondary amino group and at least one hydroxyl group may be used as a linking group. In other embodiments, the linking compounds contains the alkylene glycols described herein, and is essentially free of, or even completely free of, any other linking compounds.

[0049] In some embodiments, the described additive wherein the alkylene glycol comprises a glycol having of the general formula $\text{HO}(\text{CH}_2)_x\text{OH}$ wherein x is an integer from 2 to 10. In some embodiments, the alkylene glycol comprises ethylene glycol.

[0050] The invention further provides the described additive wherein the first hydrocarbyl-substituted acylating agent comprises polyisobutylene succinic anhydride having a number average molecular weight greater than 750; wherein the second hydrocarbyl-substituted acylating agent comprises hexadecenyl succinic anhydride; and wherein the alkylene glycol comprises ethylene glycol.

[0051] In some embodiments, the first hydrocarbyl-substituted acylating agent comprises the reaction product of a long chain hydrocarbon with a monounsaturated carboxylic acid; wherein said long chain hydrocarbon has a number average molecular weight greater than 400; and the second hydrocarbyl-substituted acylating agent comprises the reaction product of a long chain hydrocarbon with a monounsaturated carboxylic acid; wherein said long chain hydrocarbon has a number average molecular weight less than 400 or less than 280; and the alkylene

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glycol comprises a glycol having of the general formula $\text{HO}-\left[\text{C}(\text{R})\right]_x-\text{O}-\left[\right]_m-\text{H}$ where each R is independently H or an alkyl group of 1 to 6 carbon atoms each x is independently an integer from 2 to about 10 and m is an integer from 1 to about 10.

5 [0052] In some embodiments, the first hydrocarbyl-substituted acylating agent comprises polyisobutylene succinic anhydride having a number average molecular weight greater than 750; the second hydrocarbyl-substituted acylating agent comprises hexadecenyl succinic anhydride; and the alkylene glycol comprises ethylene glycol.

10 The Emulsifier Component

[0053] The invention further provides an emulsifier component prepared by a process that allows for the customization of the emulsifier. The emulsifier component is prepared by: Step (I) reacting a first hydrocarbyl-substituted acylating agent, a second hydrocarbyl-substituted acylating agent, and an (optionally linear) alkylene glycol; wherein the first hydrocarbyl-substituted acylating agent comprises a hydrocarbyl substituent group containing at least 20 carbon atoms; and wherein the second hydrocarbyl-substituted acylating agent comprises a hydrocarbyl substituent group containing less than 20 carbon atoms; resulting in an additive comprising (i) a functional group derived from said first hydrocarbyl-substituted acylating agent and (ii) a functional group derived from said second hydrocarbyl-substituted acylating agent, where the functional groups (i) and (ii) are coupled by a functional group derived from said alkylene glycol; then Step (II) providing said additive for use as an emulsifier component precursor; and (typically thereafter) Step (III) converting said additive to an emulsifier component by reacting said additive with a neutralizing component. The emulsifier component described herein may be prepared using any of the additives described herein, where the additive is the emulsifier component precursor that is then converted into the emulsifier component.

30 [0054] In Step (II), by providing said additive for use as an emulsifier component precursor, it is meant that the emulsifier component precursor (which may also be referred to as the additive) is handled like a conventional emulsifier component would be. However, in the case of the emulsifier component precursor,

it is converted into the specific emulsifier component of a downstream party's choice, for example, a finished fluid blender and/or user, who follows Step (III) and convert the additive to an emulsifier component by reacting said additive with a neutralizing component.

5 [0055] In some embodiments, providing said additive for use as an emulsifier component precursor involves using, storing, transporting, selling, blending, and/or otherwise handing the additive before it is converted into the emulsifier component. In some embodiments, the emulsifier component precursor is transported and/or stored after the additive is formed, but before the additive is converted to the
10 emulsifier component.

[0056] The neutralizing components used to form the emulsifier components described above are not overly limited. Typically, the resulting emulsifier component is in the form of a salt. The emulsifier components may be formed from mixtures of one or more neutralizing components. In some embodiments, a single
15 kind of neutralizing component is used. In other embodiments, a mixture of two or more neutralizing components are used.

[0057] The metals useful as neutralizing components include the alkali and alkaline earth-metals that may be found in metal bases. The amines useful as neutralizing components in preparing the salt compositions of the invention include
20 ammonia, and the primary amines, secondary amines and hydroxyamines. In addition to ammonia, the primary amines, secondary amines and hydroxyamines, the amines useful as neutralizing components also include primary and secondary monoamines, and tertiary mono- and polyamines. Useful primary and secondary monoamines include aliphatic, cycloaliphatic and aromatic monoamines. The
25 tertiary amines are analogous to the primary amines, secondary amines and hydroxyamines with the exception that they can be either monoamines or polyamines and the hydrogen atoms in the H-N<or -NH₂ groups are replaced by hydrocarbyl groups.

[0058] Useful polyamines include are characterized by the presence within their
30 structure of at least two -NH₂ groups, at least two >NH groups, or at least one -NH₂ group and at least one >NH group. These polyamines can be aliphatic, cycloaliphatic, aromatic or heterocyclic, including aliphatic-substituted aromatic,

aliphatic-substituted cycloaliphatic, aliphatic-substituted heterocyclic, cycloaliphatic-substituted aliphatic, cycloaliphatic-substituted aromatic, cycloaliphatic-substituted heterocyclic, aromatic-substituted aliphatic, aromatic-substituted cycloaliphatic, aromatic-substituted heterocyclic, heterocyclic-substituted aliphatic, heterocyclic-substituted cycloaliphatic and heterocyclic-substituted aromatic amines. These amines may be saturated or unsaturated. If unsaturated, the amine is preferably free from acetylenic unsaturation. These amines may also contain non-hydrocarbon substituents or groups as long as these groups do not significantly interfere with the reaction. Such non-hydrocarbon substituents or groups include lower alkoxy, lower alkyl, mercapto, nitro, and interrupting groups such as -O- and -S-. The polyamines include aliphatic, cycloaliphatic and aromatic polyamines analogous to the aliphatic, cycloaliphatic and aromatic monoamines described below except for the presence within their structure of at least one additional >NH or -NH₂ group.

[0059] Aliphatic monoamines include mono-aliphatic and di-aliphatic-substituted amines wherein the aliphatic groups can be saturated or unsaturated and straight or branched chain. Thus, they are primary or secondary aliphatic amines. Such amines include, for example, mono- and di-alkyl-substituted amines, mono- and di-alkenyl-substituted amines, and amines having one N-alkenyl substituent and one N-alkyl substituent, and the like. The total number of carbon atoms in these aliphatic monoamines preferably does not exceed about 40 and usually does not exceed about 20 carbon atoms. Specific examples of such monoamines include ethylamine, diethylamine, n-butylamine, di-n-butylamine, allylamine, isobutylamine, cocoamine, stearylamine, laurylamine, methyl laurylamine, oleylamine, N-methyl-octylamine, dodecylamine, octadecylamine, and the like. Examples of cycloaliphatic-substituted aliphatic amines, aromatic-substituted aliphatic amines, and heterocyclic-substituted aliphatic amines, include 2-(cyclohexyl)-ethylamine, benzylamine, phenylethylamine, and 3-(furylpropyl) amine.

[0060] Cycloaliphatic monoamines are those monoamines wherein there is one cycloaliphatic substituent attached directly to the amino nitrogen through a carbon atom in the cyclic ring structure. Examples of cycloaliphatic monoamines include cyclohexylamines, cyclopentylamines, cyclohexenylamines, cyclopentenylamines,

N-ethyl-cyclohexylamines, dicyclohexylamines, and the like. Examples of aliphatic-substituted, aromatic-substituted, and heterocyclic-substituted cycloaliphatic monoamines include propyl-substituted cyclohexylamines, phenyl-substituted cyclopentylamines and pyranyl-substituted cyclohexylamine.

5 [0061] Aromatic monoamines include those monoamines wherein a carbon atom of the aromatic ring structure is attached directly to the amino nitrogen. The aromatic ring will usually be a mononuclear aromatic ring (i.e., one derived from benzene) but can include fused aromatic rings, especially those derived from naphthalene. Examples of aromatic monoamines include aniline, di(para-
10 methylphenyl) amine, naphthylamine, N-(n-butyl) aniline, and the like. Examples of aliphatic-substituted, cycloaliphatic-substituted, and heterocyclic-substituted aromatic monoamines include para-ethoxyaniline, paradodecylamine, cyclohexyl-substituted naphthylamine and thienyl-substituted aniline.

[0062] Heterocyclic polyamines can also be used. As used herein, the
15 terminology "heterocyclic polyamine" is intended to describe those heterocyclic amines containing at least two primary amino groups, at least two secondary amino groups, or at least one of each, and at least one nitrogen as a heteroatom in the heterocyclic ring. As long as there is present in the heterocyclic polyamines at least
20 two primary amino groups, at least two secondary amino groups, or at least one of each, the hetero-N atom in the ring can be a tertiary amino nitrogen; that is, one that does not have hydrogen attached directly to the ring nitrogen. The hetero-N atom can be one of the secondary amino groups; that is, it can be a ring nitrogen with hydrogen directly attached to it. Heterocyclic amines can be saturated or
25 unsaturated and can contain various substituents such as nitro, alkoxy, alkyl mercapto, alkyl, alkenyl, aryl, alkaryl, or aralkyl substituents. Generally, the total number of carbon atoms in the substituents will not exceed about 20. Heterocyclic amines can contain heteroatoms other than nitrogen, especially oxygen and sulfur. Obviously they can contain more than one nitrogen heteroatom. The 5- and 6-
30 membered heterocyclic rings are preferred.

[0063] Among the suitable heterocyclic polyamines are the aziridines, azetidines, azolidines, tetra- and di-hydro pyridines, pyrroles, indoles, piperidines, imidazoles, di- and tetrahydroimidazoles, piperazines, isoindoles, purines,

morpholines, thiomorpholines, N-aminoalkylmorpholines, N-aminoalkylthiomorpholines, N-aminoalkylpiperazines, N,N'-di-aminoalkylpiperazines, azepines, azocines, azonines, azecines and tetra-, di- and perhydro-derivatives of each of the above and mixtures of two or more of these heterocyclic amines. Useful
5 heterocyclic polyamines are the saturated 5- and 6-membered heterocyclic polyamines containing only nitrogen, oxygen and/or sulfur in the hetero ring, especially the piperidines, piperazines, thiomorpholines, morpholines, pyrrolidines, and the like. Usually the aminoalkyl substituents are substituted on a nitrogen atom forming part of the hetero ring. Specific examples of such heterocyclic amines
10 include N-aminoethylpiperazine and N,N'-diaminoethylpiperazine.

[0064] Hydrazine and substituted-hydrazines can also be used. The substituents which may be present on the hydrazine include alkyl, alkenyl, aryl, aralkyl, alkaryl, and the like. Usually, the substituents are alkyl, especially lower alkyl, phenyl, and substituted phenyl such as lower alkoxy-substituted phenyl or lower alkyl-
15 substituted phenyl. Specific examples of substituted hydrazines are methylhydrazine, N,N-dimethylhydrazine, N,N'-dimethylhydrazine, phenylhydrazine, N-phenyl-N'-ethylhydrazine, N-(para-tolyl)-N'-(n-butyl)-hydrazine, N-(para-nitrophenyl)-hydrazine, N-(para-nitrophenyl)-N-methylhydrazine, N,N'-di-(para-chlorophenyl)-hydrazine, N-phenyl-N'-cyclohexylhydrazine, and the like.

[0065] Another group of amines suitable for use in this invention are branched polyalkylene polyamines. The branched polyalkylene polyamines are polyalkylene polyamines wherein the branched group is a side chain containing on the average at least one nitrogen-bonded aminoalkylene group per nine amino units present on the main chain; for example, 1-4 of such branched chains per nine units on the main
20 chain, but preferably one side chain unit per nine main chain units. Thus, these polyamines contain at least three primary amino groups and at least one tertiary amino group. These amines may be expressed by the formula: $\text{NH}_2\text{-(R-NH)}_x\text{-[N(R)((R-NH)}_z\text{-R-NH}_2)]_y$ wherein R is an alkylene group such as ethylene, propylene, butylene and other homologs (both straight chained and
25 branched), etc., but preferably ethylene; and x, y and z are integers; x is in the range of from about 4 to about 24 or more, preferably from about 6 to about 18; y is in the range of from 1 to about 6 or more, preferably from 1 to about 3; and z is in the
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range of from zero to about 6, preferably from zero to about 1. The x and y units may be sequential, alternative, orderly or randomly distributed. A useful class of such polyamines includes those of the formula: $\text{NH}_2\text{-}[\text{-(R-N(H))}_5\text{-N(R)(R-NH}_2\text{)-(R-N(H))}_2\text{-}]_n\text{-H}$ wherein n is an integer in the range of from 1 to about 20 or more, preferably in the range of from 1 to about 3, and R is preferably ethylene, but may be propylene, butylene, etc. (straight chained or branched). U.S. Pat. Nos. 3,200,106 and 3,259,578 are incorporated herein by reference for their disclosures relative to said polyamines.

[0066] Suitable polyamines also include polyoxyalkylene polyamines, e.g., polyoxyalkylene diamines and polyoxyalkylene triamines, having average molecular weights ranging from about 200 to about 4000, preferably from about 400 to 2000. Examples of these polyoxyalkylene polyamines include those amines represented by the formula: $\text{NH}_2\text{-Alkylene-(O-Alkylene)}_m\text{-NH}_2$ wherein m has a value of from about 3 to about 70, preferably from about 10 to about 35. $\text{R-[-Alkylene-(O-Alkylene)}_n\text{-NH}_2\text{]}_{3-6}$ wherein n is a number in the range of from 1 to about 40, with the proviso that the sum of all of the n's is from about 3 to about 70 and generally from about 6 to about 35, and R is a polyvalent saturated hydrocarbyl group of up to about 10 carbon atoms having a valence of from about 3 to about 6. The alkylene groups may be straight or branched chains and contain from 1 to about 7 carbon atoms, and usually from 1 to about 4 carbon atoms. The various alkylene groups present within the above formulae may be the same or different.

[0067] Useful polyoxyalkylene polyamines include the polyoxyethylene and polyoxypropylene diamines and the polyoxypropylene triamines having average molecular weights ranging from about 200 to about 2000. The polyoxyalkylene polyamines are commercially available from the Texaco under the trade name "Jeffamine." U.S. Pat. Nos. 3,804,763 and 3,948,800 are incorporated herein by reference for their disclosure of such polyoxyalkylene polyamines.

[0068] Useful polyamines are the alkylene polyamines, including the polyalkylene polyamines, as described in more detail hereafter. The alkylene polyamines include those conforming to the formula: $(\text{R})(\text{R})\text{N-(Alkylene-N(R))}_n\text{-R}'$ wherein n is from 1 to about 10, preferably from 1 to about 7; each R and R' is independently a hydrogen atom, a hydrocarbyl group or a hydroxy-substituted

hydrocarbyl group having up to about 700 carbon atoms, preferably up to about 100 carbon atoms, more preferably up to about 50 carbon atoms, more preferably up to about 30 carbon atoms, with the proviso that at least one of R and at least one of R' are hydrogen; and the "Alkylene" group has from about 1 to about 18 carbon atoms, preferably from 1 to about 4 carbon atoms, with the preferred Alkylene being ethylene or propylene. Useful alkylene polyamines are those wherein each R and each R' is hydrogen with the ethylene polyamines, and mixtures of ethylene polyamines being particularly preferred. Such alkylene polyamines include methylene polyamines, ethylene polyamines, butylene polyamines, propylene polyamines, pentylene polyamines, hexylene polyamines, heptylene polyamines, etc. The higher homologs of such amines and related aminoalkyl-substituted piperazines are also included.

[0069] Alkylene polyamines that are useful include ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, propylene diamine, trimethylene diamine, hexamethylene diamine, decamethylene diamine, octamethylene diamine, di(heptamethylene) triamine, tripropylene tetramine, tetraethylene pentamine, trimethylene diamine, pentaethylene hexamine, di(trimethylene) triamine, N-(2-aminoethyl) piperazine, 1,4-bis(2-aminoethyl) piperazine, and the like. Higher homologs as are obtained by condensing two or more of the above-illustrated alkylene amines are useful as amines in this invention as are mixtures of two or more of any of the aforescribed polyamines.

[0070] Ethylene polyamines, such as those mentioned above, are described in detail under the heading "Diamines and Higher Amines, Aliphatic" in The Encyclopedia of Chemical Technology, Third Edition, Kirk-Othmer, Volume 7, pp. 580-602, a Wiley-Interscience Publication, John Wiley and Sons, 1979, these pages being incorporated herein by reference. Such compounds are prepared most conveniently by the reaction of an alkylene chloride with ammonia or by reaction of an ethylene imine with a ring-opening reagent such as ammonia, etc. These reactions result in the production of the somewhat complex mixtures of alkylene polyamines, including cyclic condensation products such as piperazines.

[0071] Alkoxyated alkylene polyamines (e.g., N,N-1(diethanol)-ethylene diamine) can be used. Such polyamines can be made by reacting alkylene amines

(e.g., ethylenediamine) with one or more alkylene oxides (e.g., ethylene oxide, octadecene oxide) of two to about 20 carbons. Similar alkylene oxide-alkanol amine reaction products can also be used such as the products made by reacting the
5 aforedescribed primary, secondary or tertiary alkanol amines with ethylene, propylene or higher epoxides in a 1:1 or 1:2 molar ratio. Reactant ratios and temperatures for carrying out such reactions are known to those skilled in the art.

[0072] Specific examples of alkoxyated alkylene polyamines include N-(2-hydroxyethyl) ethylene diamine, N,N-bis(2-hydroxyethyl)-ethylene-diamine, 1-(2-hydroxyethyl) piperazine, mono(hydroxypropyl)-substituted diethylene triamine,
10 di(hydroxypropyl)-substituted tetraethylene pentamine, N-(3-hydroxybutyl)-tetramethylene diamine, etc. Higher homologs obtained by condensation of the above-illustrated hydroxy alkylene polyamines through amino groups or through hydroxy groups are likewise useful. Condensation through amino groups results in a higher amine accompanied by removal of ammonia while condensation through the
15 hydroxy groups results in products containing ether linkages accompanied by removal of water. Mixtures of two or more of any of the aforesaid polyamines are also useful.

[0073] Useful hydroxyamines can be primary or secondary amines. They can also be tertiary amines provided said tertiary amines also contain at least two
20 hydroxyl groups. These hydroxyamines contain at least two >NH groups, at least two -NH₂ groups, at least one -OH group and at least one >NH or -NH₂ group, or at least two -OH groups. The terms "hydroxyamine" and "aminoalcohol" describe the same class of compounds and, therefore, can be used interchangeably.

[0074] The hydroxyamines can be primary or secondary alkanol amines or mixtures thereof. Such amines can be represented, respectfully, by the formulae:
25 (H)(R)N-R'-OH wherein R is a hydrocarbyl group of one to about eight carbon atoms or hydroxylsubstituted hydrocarbyl group of two to about eight carbon atoms and R' is a divalent hydrocarbyl group of about two to about 18 carbon atoms. The group -R'-OH in such formulae represents the hydroxyl-substituted hydrocarbyl
30 group. R' can be an acyclic, alicyclic or aromatic group. Typically, R' is an acyclic straight or branched alkylene group such as an ethylene, 1,2-propylene, 1,2-butylene, 1,2-octadecylene, etc. group. Typically, R is a lower alkyl group of up to

seven carbon atoms. The primary or secondary alkanol amines may contain slightly larger R and R' groups, and may contain up to about 40 carbon atoms.

[0075] The hydroxyamines can also be ether N-(hydroxy-substituted hydrocarbyl)amines. These are hydroxyl-substituted poly(hydrocarbyloxy) analogs of the above-described primary and secondary alkanol amines (these analogs also include hydroxyl-substituted oxyalkylene analogs). Such N-(hydroxyl-substituted hydrocarbyl) amines can be conveniently prepared by reaction of epoxides with
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aforedescribed amines and can be represented by the formulae: $H_2N-R'-OH$ and $(H)(R)_xN-R'-OH$ wherein x is a number from about 2 to about 15 and R and R' are as
10 described above.

[0076] Polyamine analogs of these hydroxy amines, particularly alkoxyated alkylene polyamines (e.g., N,N-(diethanol)-ethylene diamine) can also be used. Such polyamines can be made by reacting alkylene amines (e.g., ethylenediamine) with one or more alkylene oxides (e.g., ethylene oxide, octadecene oxide) of two to
15 about 20 carbons. Similar alkylene oxide-alkanol amine reaction products can also be used such as the products made by reacting the aforedescribed primary or secondary alkanol amines with ethylene, propylene or higher epoxides in a 1:1 or 1:2 molar ratio. Reactant ratios and temperatures for carrying out such reactions are known to those skilled in the art.

[0077] Specific examples of alkoxyated alkylene polyamines include N-(2-hydroxyethyl) ethylene diamine, N,N-bis(2-hydroxyethyl) ethylene diamine, 1-(2-hydroxyethyl) piperazine, mono(hydroxypropyl)-substituted diethylene triamine, di(hydroxypropyl)-substituted tetraethylene pentamine, N-(3-hydroxybutyl)-tetramethylene diamine, etc. Higher homologs obtained by condensation of the
25 above-illustrated hydroxyalkylene polyamines through amino groups or through hydroxy groups are likewise useful. Condensation through amino groups results in a higher amine accompanied by removal of ammonia, while condensation through the hydroxy groups results in products containing ether linkages accompanied by removal of water. Mixtures of two or more of any of the aforesaid mono- or
30 polyamines are also useful.

[0078] Examples of the N-(hydroxyl-substituted hydrocarbyl) amines include mono-, di-, and triethanol amine, diethylethanol amine, di-(3-hydroxyl propyl)

amine, N-(3-hydroxyl butyl) amine, N-(4-hydroxyl butyl) amine, N,N-di-(2-hydroxyl propyl) amine, N-(2-hydroxyl ethyl) morpholine and its thio analog, N-(2-hydroxyl ethyl) cyclohexyl amine, N-3-hydroxyl cyclopentyl amine, o-, m- and p-aminophenol, N-(hydroxyl ethyl) piperazine, N,N'-di(hydroxyl ethyl) piperazine, and the like.

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[0079] Further, hydroxyamines are the hydroxy-substituted primary amines described in U.S. Pat. No. 3,576,743 by the general formula R^a-NH_2 wherein R^a is a monovalent organic group containing at least one alcoholic hydroxy group. The total number of carbon atoms in R^a preferably does not exceed about 20. Hydroxy-substituted aliphatic primary amines containing a total of up to about 10 carbon atoms are useful. The polyhydroxy-substituted alkanol primary amines wherein there is only one amino group present (i.e., a primary amino group) having one alkyl substituent containing up to about 10 carbon atoms and up to about 6 hydroxyl groups are useful. These alkanol primary amines correspond to R^a-NH_2 wherein R^a is a mono- or polyhydroxy-substituted alkyl group. Specific examples of the hydroxy-substituted primary amines include 2-amino-1-butanol, 2-amino-2-methyl-1-propanol, p-(beta- hydroxyethyl)-aniline, 2-amino-1-propanol, 3-amino-1-propanol, 2-amino-2-methyl-1,3-propanediol, 2-amino-2-ethyl-1,3-propanediol, N-(beta-hydroxypropyl)-N'-(beta-aminoethyl)-piperazine, tris-(hydroxymethyl) amino methane (also known as trimethylolamino methane), 2-amino-1-butanol, ethanolamine, beta-(beta-hydroxyethoxy)-ethyl amine, glucamine, glusoamine, 4-amino-3-hydroxy-3-methyl-1-butene (which can be prepared according to procedures known in the art by reacting isoprene-oxide with ammonia), N-3-(aminopropyl)-4-(2-hydroxyethyl)piperidine, 2-amino-6-methyl-6-heptanol, 5-amino-1-pentanol, N-(beta-hydroxyethyl)1,3-diamino propane, 1,3-diamino-2-hydroxypropane, N-(beta-hydroxyethoxyethyl)ethylene diamine, trimethylolaminomethane and the like. U.S. Pat. No. 3,576,743 is incorporated herein by reference.

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[0080] Hydroxyalkyl alkylene polyamines having one or more hydroxyalkyl substituents on the nitrogen atoms, are also useful. Useful hydroxyalkyl-substituted alkylene polyamines include those in which the hydroxyalkyl group is a lower hydroxyalkyl group, i.e., having less than eight carbon atoms. Examples of such hydroxyalkyl-substituted polyamines include N-(2-hydroxyethyl) ethylene diamine,

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N,N-bis(2-hydroxyethyl) ethylene diamine, 1-(2-hydroxyethyl)-piperazine, monohydroxypropyl-substituted diethylene triamine, dihydroxypropylsubstituted tetraethylene pentamine, N-(3-hydroxybutyl) tetramethylene diamine, etc. Higher homologs as are obtained by condensation of the above-illustrated hydroxy alkylene polyamines through amino groups or through hydroxy groups are likewise useful. Condensation through amino groups results in a higher amine accompanied by removal of ammonia and condensation through the hydroxy groups results in products containing ether linkages accompanied by removal of water.

[0081] Useful tertiary amines include be aliphatic, cycloaliphatic, aromatic or heterocyclic, including aliphatic-substituted aromatic, aliphatic-substituted cycloaliphatic, aliphatic-substituted heterocyclic, cycloaliphatic-substituted aliphatic, cycloaliphatic substituted aromatic, cycloaliphatic-substituted heterocyclic, aromatic-substituted aliphatic, aromatic-substituted cycloaliphatic, aromatic-substituted heterocyclic, heterocyclic-substituted aliphatic, heterocyclic-substituted cycloaliphatic and heterocyclic-substituted aromatic amines. These tertiary amines may be saturated or unsaturated. If unsaturated, the amine is preferably free from acetylenic unsaturation. The tertiary amines may also contain non-hydrocarbon substituents or groups as long as these groups do not significantly interfere with the reaction. Such non-hydrocarbon substituents or groups include lower alkoxy, lower alkyl, mercapto, nitro, and interrupting groups such as -O- and -S- (e.g., as in such groups as -CH₂CH₂-X-CH₂CH₂- where X is -O- or -S-).

[0082] The monoamines can be represented by the formula N(R¹)(R²)(R³) wherein R¹, R², and R³ are the same or different hydrocarbyl groups. Preferably, R¹, R², and R³ are independently hydrocarbyl groups of from 1 to about 20 carbon atoms.

[0083] Examples of useful tertiary amines include trimethyl amine, triethyl amine, tripropyl amine, tributyl amine, monomethyldiethylamine, monoethyldimethyl amine, dimethylpropyl amine, dimethylbutyl amine, dimethylpentyl amine, dimethylhexyl amine, dimethylheptyl amine, dimethyloctyl amine, dimethylnonyl amine, dimethyldecyl amine, dimethylphenyl amine, N,N-dioctyl-1-octanamine, N,N-di-dodecyl-1-dodecanamine tricoco amine, trihydrogenated tallow amine, N-methyldihydrogenated tallow amine, N,N-dimethyl-1-dodecanamine, N,N-dimethyl-1-tetradecanamine, N,N-dimethyl-1-

hexadecanamine, N,N-dimethyl-1-octadecanamine, N,N-dimethylcocoamine, N,N-dimethylsoyaamine, N,N-dimethylhydrogenated tallow amine, etc.

[0084] Useful tertiary alkanol amines are represented by the formula (R)(R)N-R'-OH wherein each R is independently a hydrocarbyl group of one to about eight carbon atoms or hydroxyl-substituted hydrocarbyl group of two to about eight carbon atoms and R' is a divalent hydrocarbyl group of about two to about 18 carbon atoms. The group -R'-OH in such formula represents the hydroxyl-substituted hydrocarbyl group. R' can be an acyclic, alicyclic or aromatic group. Typically, R' is an acyclic straight or branched alkylene group such as an ethylene, 1,2-propylene, 1,2-butylene, 1,2-octadecylene, etc. group. Where two R groups are present in the same molecule they can be joined by a direct carbon-to-carbon bond or through a heteroatom (e.g., oxygen, nitrogen or sulfur) to form a 5-, 6-, 7- or 8-membered ring structure. Examples of such heterocyclic amines include N-(hydroxyl lower alkyl)-morpholines, thiomorpholines, -piperidines, -oxazolidines, -thiazolidines and the like. Typically, however, each R is a lower alkyl group of up to seven carbon atoms. The hydroxyamines can also be an ether N-(hydroxyl-substituted hydrocarbyl)amine. These are hydroxyl-substituted poly-(hydrocarbyloxy) analogs of the above described hydroxy amines (these analogs also include hydroxyl-substituted oxyalkylene analogs). Such N-(hydroxyl-substituted hydrocarbyl) amines can be conveniently prepared by reaction of epoxides with the amines described above and can be represented by the formula: (R)(R)N-(R'-O)_xH wherein x is a number from about 2 to about 15 and R and R' are as described above.

[0085] Useful polyamines include the alkylene polyamines discussed above as well as alkylene polyamines with only one or no hydrogens attached to the nitrogen atoms. Thus, the alkylene polyamines useful as neutralizing components include those conforming to the formula: (R)(R)N-(R'-O)_x-H wherein x is from 1 to about 10, from 1 to about 7; each R is independently a hydrogen atom, a hydrocarbyl group or a hydroxy-substituted hydrocarbyl group having up to about 700 carbon atoms, preferably up to about 100 carbon atoms, more preferably up to about 50 carbon atoms, more preferably up to about 30 carbon atoms; and the "Alkylene"

group has from about 1 to about 18 carbon atoms, preferably from 1 to about 4 carbon atoms, with the preferred Alkylene being ethylene or propylene.

[0086] The alkali and alkaline earth metals that are useful as neutralizing components can be any alkali or alkaline earth metal. The alkali metals are preferred. Sodium and potassium are particularly preferred. The alkali and alkaline earth metal compounds that are useful include, for example, the oxides, hydroxides and carbonates. Sodium hydroxide and potassium hydroxide are particularly preferred.

[0087] The invention further provides a process of making the described emulsifier component. The process comprises the steps of: Step (I) reacting a first hydrocarbyl-substituted acylating agent, a second hydrocarbyl-substituted acylating agent, and an (optionally linear) alkylene glycol; wherein the first hydrocarbyl-substituted acylating agent comprises a hydrocarbyl substituent group containing at least 20 carbon atoms; and wherein the second hydrocarbyl-substituted acylating agent comprises a hydrocarbyl substituent group containing less than 20 carbon atoms; resulting in an additive comprising (i) a functional group derived from said first hydrocarbyl-substituted acylating agent and (ii) a functional group derived from said second hydrocarbyl-substituted acylating agent, where the functional groups (i) and (ii) are coupled by a functional group derived from said alkylene glycol; Step (II) providing said additive for use as an emulsifier component precursor; Step (III) converting said additive to an emulsifier component by reacting said additive with a neutralizing component. Any of the emulsifier components described above may be prepared by this process.

[0088] In some embodiments, the process may be described as initially reacting the first hydrocarbyl-substituted acylating agent and the second hydrocarbyl-substituted acylating agent the alkylene glycol to form an additive, and thereafter providing the additive, as described above, to an end use who may then use the additive to form the emulsifier component of his/her choosing by reacting said intermediate with the neutralizing component to form the desired salt.

[0089] The ratio of reactants utilized in the preparation of either the additive (and/or the emulsifier component precursor) emulsifier component may be varied over a wide range. Generally, for each equivalent of each of the acylating agents, at

least about one equivalent of alkylene glycol is used. From about 0.1 to about 2 equivalents or more of neutralizing component are used for each equivalent of components acylating agents, respectively. The upper limit of alkylene glycol is about 2 equivalents of alkylene glycol for each equivalent of acylating agents.

5 Generally the ratio of equivalents of acylating agents is about 0.5 to about 2, with about 1:1 being preferred. Preferred amounts of the reactants are about 2 equivalents of the alkylene glycol and from about 0.1 to about 2 equivalents of each of neutralizing component for each equivalent of each acylating agent.

[0090] The number of equivalents of the acylating agents depends on the total number of carboxylic functions present in each. In determining the number of equivalents for each of the acylating agents, those carboxyl functions which are not capable of reacting as a carboxylic acid acylating agent are excluded. In general, however, there is one equivalent of acylating agent for each carboxy group in these acylating agents. For example, there would be two equivalents in an anhydride derived from the reaction of one mole of olefin polymer and one mole of maleic anhydride. Conventional techniques are readily available for determining the number of carboxyl functions (e.g., acid number, saponification number) and, thus, the number of equivalents of each of the acylating agents can be readily determined by one skilled in the art.

20 [0091] An equivalent weight of a polyamine is the molecular weight of the polyamine divided by the total number of nitrogens present in the molecule where tertiary amino groups are counted. Thus, ethylene diamine has an equivalent weight equal to one-half of its molecular weight; diethylene triamine has an equivalent weight equal to one-third its molecular weight. The equivalent weight of a commercially available mixture of polyalkylene polyamine can be determined by dividing the atomic weight of nitrogen (14) by the %N contained in the polyamine; thus, a polyamine mixture having a %N of 34 would have an equivalent weight of 41.2. An equivalent weight of ammonia or a monoamine is its molecular weight.

25 [0092] An equivalent weight of polyhydric alcohol is its molecular weight divided by the total number of hydroxyl groups present in the molecule. Thus, an equivalent weight of ethylene glycol is one-half its molecular weight.

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[0093] An equivalent weight of a hydroxyamine would be its molecular weight divided by the total number of nitrogen groups present in the molecule. Thus, dimethylethanolamine would have an equivalent weight equal to its molecular weight; ethanolamine would also have an equivalent weight equal to its molecular weight.

5 [0094] An equivalent weight of an alkali or alkaline earth metal is its molecular weight. An equivalent weight of an alkali or alkaline earth metal compound is its molecular weight divided by the number of alkali or alkaline earth metal atoms present in the molecule.

10 [0095] The acylating agents can be reacted with the alkylene glycol according to conventional ester and/or amide forming techniques. This normally involves heating acylating agents with the alkylene glycol optionally in the presence of a normally liquid, substantially inert, organic liquid solvent/diluent.

15 [0096] The reactions between the additive and the neutralizing component are carried out under salt forming conditions using conventional techniques. Typically, the components are mixed together and heated to a temperature in the range of about 20°C up to the decomposition temperature of the reaction component and/or product having the lowest such temperature, optionally, in the presence of a normally liquid, substantially inert organic liquid solvent/diluent, until the desired product has formed.

20 [0097] The invention further provides a method and/or use of the additive described above as part of a process of customizing an emulsifier component in a composition. This method and/or use includes the steps of: Step (I) preparing an additive by reacting a first hydrocarbyl-substituted acylating agent, a second hydrocarbyl-substituted acylating agent, and an (optionally linear) alkylene glycol; 25 wherein the first hydrocarbyl-substituted acylating agent comprises a hydrocarbyl substituent group containing at least 20 carbon atoms; and wherein the second hydrocarbyl-substituted acylating agent comprises a hydrocarbyl substituent group containing less than 20 carbon atoms; resulting in an additive comprising (i) a functional group derived from said first hydrocarbyl-substituted acylating agent and 30 (ii) a functional group derived from said second hydrocarbyl-substituted acylating agent, where the functional groups (i) and (ii) are coupled by a functional group derived from said alkylene glycol; Step (II) supplying said additive into a

composition that requires an emulsifier component; Step (III) converting said additive, in said composition, to an emulsifier component by reacting said additive with a neutralizing component; resulting in a customized emulsifier component.

Functional Fluid Composition

5 [0098] The emulsion components described herein may be used to make functional compositions such as oil-in-water emulsions which comprise a continuous water phase, a discontinuous organic phase, the emulsifying composition, and additives related to the function to be performed by the functional fluid. The discontinuous organic phase is preferably present at a level of at least
10 about 1% by weight, more preferably in the range of from about 1% to about 50% by weight, more preferably in the range of from about 1% to about 20% by weight based on the total weight of emulsion. The continuous water phase is preferably present at a level of about 99% by weight, more preferably at a level in the range of from about 50% to about 99% by weight, more preferably from about 80% to about
15 99% by weight based on the total weight of said emulsion. The salt compositions of the invention are preferably present at a level in the range of from about 1% to about 100% by weight, more preferably from about 20% to about 80% by weight based on the total weight of the organic phase. When the emulsifier is 100% of the organic phase, the emulsifier is acting to form an emulsion of itself in the water
20 phase, and the organic phase is the emulsifier.

[0099] The oil can include most liquid hydrocarbons, for example, paraffinic, olefinic, naphthenic, aromatic, saturated or unsaturated hydrocarbons. In general, the oil is a water-immiscible, emulsifiable hydrocarbon that is either liquid at room temperature. Oils from a variety of sources, including natural and synthetic oils and
25 mixtures thereof may be used.

[0100] Natural oils include animal oils and vegetable oils (e.g., castor oil, lard oil) as well as solvent-refined or acid-refined mineral oils of the paraffinic, naphthenic, or mixed paraffin-naphthenic types. Oils derived from coal or shale are also useful. Synthetic oils include hydrocarbon oils and halo-substituted
30 hydrocarbon oils such as polymerized and interpolymerized olefins e.g., polybutylenes, polypropylenes, propylene-isobutylene copolymers, chlorinated

polybutylenes; alkyl benzenes, e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di-(2-ethylhexyl) benzenes, and the like.

[0101] Another suitable class of synthetic oils that can be used comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acid, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkyl malonic acids, alkenyl malonic acids, etc.) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol, pentaerythritol, etc.). Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl)-sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid, and the like.

[0102] Esters useful as synthetic oils also include those made from C₅ to C₁₂ monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylol propane, pentaerythritol, dipentaerythritol, tripentaerythritol, etc.

[0103] Silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy-, or polyaryloxy-siloxane oils and silicate oils comprise another class of useful oils. These include tetraethyl-silicate, tetraisopropylsilicate, tetra-(2-ethylhexyl)-silicate, tetra-(4-methylhexyl)-silicate, tetra (p-tert-butylphenyl) -silicate, hexyl-(4-methyl-2-pentoxo)-di-siloxane, poly(methyl)-siloxanes, poly-(methylphenyl)-siloxanes, etc. Other useful synthetic oils include liquid esters of phosphorus-containing acid (e.g., tricresyl phosphate, trioctyl phosphate, diethyl ester of decane phosphonic acid, etc.), polymeric tetrahydrofurans, and the like.

[0104] Unrefined, refined and rerefined oils (and mixtures of each with each other) of the type disclosed hereinabove can be used. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. For example, a shale oil obtained directly from a retorting operation, a petroleum oil obtained directly from distillation or ester oil obtained directly from an esterification process and used without further treatment would be an unrefined oil. Refined oils are similar to the unrefined oils except that they have been further

treated in one or more purification steps to improve one or more properties. Many such purification techniques are known to those of skill in the art such as solvent extraction, distillation, acid or base extraction, filtration, percolation, etc. Rerefined oils are obtained by processes similar to those used to obtain refined oils applied to refined oils which have been already used in service. Such rerefined oils are also known as reclaimed or reprocessed oils and often are additionally processed by techniques directed toward removal of spent additives and oil breakdown products.

5

[0105] Examples of useful oils include a white mineral oil available from Witco Chemical Company under the trade designation KAYDOL; a white mineral oil available from Shell under the trade designation ONDINA; and a mineral oil available from Pennzoil under the trade designation N-750-HT.

10

[0106] Optional additional materials may be incorporated in the composition of the present invention. Typical finished compositions may include lubricity agents, anti-wear agents, dispersants, corrosion inhibitors, other surfactants, and the like. The emulsions of the present invention are shelf stable, which means they exhibit shelf stability of at least six months and typically one year or more.

15

[0107] A preferred method for making the emulsions of the invention comprises the steps of (1) mixing the emulsifier with the oil phase, (2) mixing the additives with the oil phase, (3) stirring the oil phase with the water phase to form a oil-in-water emulsion. Mixing of the oil with the appropriate additives may be conducted in any suitable mixing apparatus. Any type of apparatus capable of either low or high shear mixing may be used to mix the oil and water phases to prepare these oil-in-water emulsions.

20

[0108] The amount of each chemical component described is presented exclusive of any solvent or diluent oil, which may be customarily present in the commercial material, that is, on an active chemical basis, unless otherwise indicated. However, unless otherwise indicated, each chemical or composition referred to herein should be interpreted as being a commercial grade material which may contain the isomers, by-products, derivatives, and other such materials which are normally understood to be present in the commercial grade.

25

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[0109] As used herein, the term "hydrocarbyl substituent" or "hydrocarbyl group" is used in its ordinary sense, which is well-known to those skilled in the art. Specifi-

cally, it refers to a group having a carbon atom directly attached to the remainder of the molecule and having predominantly hydrocarbon character. Examples of hydrocarbyl groups include:

- 5 - hydrocarbon substituents, that is, aliphatic (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl, cycloalkenyl) substituents, and aromatic-, aliphatic-, and alicyclic-substituted aromatic substituents, as well as cyclic substituents wherein the ring is completed through another portion of the molecule (e.g., two substituents together form a ring);
- 10 - substituted hydrocarbon substituents, that is, substituents containing non-hydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbon nature of the substituent (e.g., halo (especially chloro and fluoro), hydroxy, alkoxy, mercapto, alkylmercapto, nitro, nitroso, and sulfoxy);
- 15 - hetero substituents, that is, substituents which, while having a predominantly hydrocarbon character, in the context of this invention, contain other than carbon in a ring or chain otherwise composed of carbon atoms and encompass substituents as pyridyl, furyl, thienyl and imidazolyl. Heteroatoms include sulfur, oxygen, and nitrogen. In general, no more than two, or no more than one, non-hydrocarbon substituent will be present for every ten carbon atoms
- 20 in the hydrocarbyl group; alternatively, there may be no non-hydrocarbon substituents in the hydrocarbyl group.

[0110] It is known that some of the materials described above may interact in the final formulation, so that the components of the final formulation may be different from those that are initially added. For instance, metal ions (of, e.g., a detergent) can

25 migrate to other acidic or anionic sites of other molecules. The products formed thereby, including the products formed upon employing the composition of the present invention in its intended use, may not be susceptible of easy description. Nevertheless, all such modifications and reaction products are included within the scope of the present invention; the present invention encompasses the composition

30 prepared by admixing the components described above.

[0111] The invention may be better understood with reference to the following non-limiting examples.

EXAMPLES

[0112] Several examples are prepared to demonstrate the invention.

Comparative Example 1

[0113] A preformed salt emulsifier component is prepared in a reaction vessel by
5 adding 33.33 pbw of 1000 Mn highly reacted polyisobutylene succinic anhydride,
28.41 pbw of hexadecenyl succinic anhydride, and 23.15 pbw ISO 22 mineral oil.
The mixture is heated to 99°C under a nitrogen purge. Then 3.87 pbw of ethylene
glycol is slowly added to the reaction vessel and the resulting mixture is held at
about 99°C for 4 hours. The reaction mixture is cooled to 68°C before adding 11.24
10 pbw dimethylethanolamine. The following reaction is held below 93°C. The amine
salted product is then cooled to ambient temperature.

Inventive Example 2

[0114] An unsalted ester acid emulsifier component is prepared in the lab. In a
reaction vessel, 40.45 parts by weight (pbw) of 1000 number average molecular
15 weight (Mn) highly reacted polyisobutylene succinic anhydride, 34.83 pbw of
hexadecenyl succinic anhydride, and 20.00 pbw ISO 22 mineral oil are mixed and
heated to 135°C under a nitrogen purge. Then 4.72 pbw of ethylene glycol is slowly
added to the reaction vessel and the resulting mixture is held at about 135°C for 4
hours. The resulting unsalted product is then cooled to ambient temperature and
20 collected.

[0115] Using the additives of Comparative Example 1 and Inventive Example 2, a
set of additive packages (Examples A-1 to G-1) are prepared and then used to prepare
emulsion samples (Examples A-2 to G-2) to evaluate the emulsion performance of
the additives. The formulations of the additive packages tested are summarized in the
25 table below, where all values are weight percent unless otherwise noted. The
additional additives used in each example are identical and include a low HLB
emulsifier, a fatty acid salt, a corrosion inhibitor, and a biocide.

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Table 1: Additive Packages:

| | Inv Ex A-1 | Inv Ex B-1 | Inv Ex C-1 | Comp Ex D-1 | Inv Ex E-1 | Inv Ex F-1 | Inv Ex G-1 |
|----------------------------|---------------|---------------|---------------|----------------|---------------|---------------|---------------|
| Comparative Ex 1 (DMEA) | 0 | 0 | 0 | 8.0 | 0 | 0 | 0 |
| Inventive Ex 2 | 7.30 | 6.47 | 7.00 | 0 | 4.56 | 4.04 | 4.37 |
| Amine (Type & wt%) | MEA 0.70 | TEA 1.53 | DMEA 1.00 | 0 | MEA 0.44 | TEA 0.96 | DMEA 0.63 |
| Additional Additives | 15.5 | 15.5 | 15.5 | 16.0 | 16.05 | 16.05 | 16.05 |
| ISO 22 Paraffinic oil | Balance | Balance | Balance | Balance | Balance | Balance | Balance |

[0116] All of the additive packages described in table above are prepared by blending the ingredients in the order listed and heating the mixtures to 50°C with moderate stirring for about one hour.

[0117] Each additive package is then used to prepare an emulsion. Each emulsion sample is prepared by adding water so that the concentration of the additive package is the same in each emulsion sample (5% by weight). Each emulsion sample is shaken vigorously shaken in a graduated cylinder and then allowed to stand for 24 hours before being rating for stability, by measuring the amount, or percent, of oil visible in the sample, and the amount, or percent, of cream visible in the sample. The less oil and cream visible, the more stable the emulsion, and so the more effective the additive package, and so the emulsifier additive. A formulation is considered acceptable for use if it has 0% or a trace of oil and no more than 0.5% cream after 24 hours.

[0118] An industry foam test was also conducted on some of the emulsion samples. In this test, 200 ml of the emulsion example is placed in a Sunbeam cake mixer and sheared at high speed for 300 seconds. Then the time, in seconds, for the foam to collapse after the mixer is turned off is recorded, and this time is reported as the foam break and/or collapse time. The shorter the time it takes for the foam to collapse, the better the result, but a result of 60 seconds or less is generally considered acceptable.

[0119] The results of the testing are summarized in the table below.

Table 2: Results

| | Inv Ex A-2 | Inv Ex B-2 | Inv Ex C-2 | Comp Ex D-2 | Inv Ex E-2 | Inv Ex F-2 | Inv Ex G-2 |
|---|------------------------|------------------------|-------------------------|----------------------------|------------------------|------------------------|-------------------------|
| Emulsifier Used in Additive Package | Inv Ex 2 and MEA | Inv Ex 2 and TEA | Inv Ex 2 and DMEA | Comp Ex 1 (DMEA) | Inv Ex 2 and MEA | Inv Ex 2 and TEA | Inv Ex 2 and DMEA |
| Concentration of Emulsifier in Emulsion | 0.4 wt% | 0.4 wt% | 0.4 wt% | 0.4 wt% | 0.25 wt% | 0.25 wt% | 0.25 wt% |
| Stability %oil/%cream 114 ppm water | O/O PASS | O/Trace PASS | O/Trace PASS | O/Trace PASS | O/Trace PASS | O/Trace PASS | O/Trace PASS |
| Stability %oil/%cream 600 ppm water | O/Trace PASS | O/Trace PASS | O/Trace PASS | O/0.5 FAIL | O/Trace PASS | O/Trace PASS | O/Trace PASS |
| Foam Break 114 ppm water | 132 sec | 7 sec | 9 sec | < 5 sec | 9 sec | < 5 sec | < 5 sec |

[0120] The results above show the additives of the present invention provide acceptable stability and emulsifier performance while also providing the adding flexibility of allowing in-situ salt formation.

[0121] Each of the documents referred to above is incorporated herein by reference, including any prior applications, whether or not specifically listed above, from which priority is claimed. The mention of any document is not an admission that such document qualifies as prior art or constitutes the general knowledge of the skilled person in any jurisdiction. Except in the Examples, or where otherwise explicitly indicated, all numerical quantities in this description specifying amounts of materials, reaction conditions, molecular weights, number of carbon atoms, and the like, are to be understood as modified by the word "about." It is to be understood that the upper and lower amount, range, and ratio limits set forth herein may be independently combined. Similarly, the ranges and amounts for each element of the invention can be used together with ranges or amounts for any of the other elements.

[0122] As used herein, the transitional term "comprising," which is synonymous with "including," "containing," or "characterized by," is inclusive or open-ended and does not exclude additional, un-recited elements or method steps. However, in each recitation of "comprising" herein, it is intended that the term also encompass, as

alternative embodiments, the phrases “consisting essentially of” and “consisting of,” where “consisting of” excludes any element or step not specified and “consisting essentially of” permits the inclusion of additional un-recited elements or steps that do not materially affect the basic and novel characteristics of the composition or method under consideration.

5

[0123] While certain representative embodiments and details have been shown for the purpose of illustrating the subject invention, it will be apparent to those skilled in this art that various changes and modifications can be made therein without departing from the scope of the subject invention. In this regard, the scope of the invention is to be limited only by the following claims.

10

What is claimed is:

1. An additive comprising (i) a functional group derived from a first hydrocarbyl-substituted acylating agent and (ii) a functional group derived from a second hydrocarbyl-substituted acylating agent, where the functional groups (i) and (ii) are
5 coupled by a functional group derived from an alkylene glycol;
wherein the first hydrocarbyl-substituted acylating agent comprises a hydrocarbyl substituent group containing at least about 20 carbon atoms; and
wherein the second hydrocarbyl-substituted acylating agent comprises a
hydrocarbyl substituent group containing less than about 20 carbon atoms.
10
2. The additive of claim 1 wherein the first hydrocarbyl-substituted acylating agent comprises the reaction product of a long chain hydrocarbon with a monounsaturated carboxylic acid; wherein said long chain hydrocarbon has a number average molecular weight greater than about 400.
15
3. The additive of claim 1 or claim 2 wherein the first hydrocarbyl-substituted acylating agent comprises polyisobutylene succinic anhydride, the polyisobutylene group having a number average molecular weight greater than about 400.
- 20 4. The additive of any one of claims 1 through 3 wherein the second hydrocarbyl-substituted acylating agent comprises the reaction product of a long chain hydrocarbon with a monounsaturated carboxylic acid; wherein said long chain hydrocarbon has a number average molecular weight less than about 280.
- 25 5. The additive of any one of claims 1 through 4 wherein the second hydrocarbyl-substituted acylating agent comprises hexadecenyl succinic anhydride.
6. The additive of any one of claims 1 through 5 wherein the alkylene glycol comprises a glycol having the general formula $\text{HO}-\left[\text{-(CH(R))}_x\text{-O-} \right]_m\text{-H}$ where each R is
30 independently H or an alkyl group of 1 to 6 carbon atoms, each x is independently an integer from 2 to about 10, and m is an integer from 1 to about 10.

7. The additive of any one of claims 1 through 6 wherein the alkylene glycol is a linear alkylene glycol.
8. The additive of any one of claims 1 through 7 wherein the alkylene glycol
5 comprises a poly(ethylene glycol), a poly(1,3-propylene glycol) or a copolymer of ethylene glycol and 1,3-propylene glycol.
9. The additive of any one of claims 1 through 8 wherein the alkylene glycol
10 comprises a glycol having the general formula $\text{HO}-(\text{CH}_2)_x-\text{OH}$ wherein x is an integer from 2 to about 10.
10. The additive of claim 9 wherein the alkylene glycol comprises ethylene glycol.
11. The additive of any one of claims 1 through 7 wherein the first hydrocarbyl-
15 substituted acylating agent comprises polyisobutylene succinic anhydride, the polyisobutylene group having a number average molecular weight greater than about 750;
wherein the second hydrocarbyl-substituted acylating agent comprises hexadecenyl succinic anhydride; and
20 wherein the alkylene glycol comprises ethylene glycol.
12. The additive of any of claims 1 through 11 which is reacted with a neutralizing component comprising an amine.
- 25 13. A process of making an emulsifier component comprising the steps of:
I. reacting a first hydrocarbyl-substituted acylating agent, a second hydrocarbyl-substituted acylating agent, and an alkylene glycol;
wherein the first hydrocarbyl-substituted acylating agent comprises a hydrocarbyl
substituent group containing at least about 20 carbon atoms; and
30 wherein the second hydrocarbyl-substituted acylating agent comprises a hydrocarbyl
substituent group containing less than about 20 carbon atoms;

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resulting in an intermediate comprising (i) a functional group derived from said first hydrocarbyl-substituted acylating agent and (ii) a functional group derived from said second hydrocarbyl-substituted acylating agent, where the functional groups (i) and (ii) are coupled by a functional group derived from said alkylene glycol;

5 II. providing said intermediate for use as an emulsifier component precursor; and thereafter

III. converting said intermediate to an emulsifier component by reacting said intermediate with a neutralizing component.

10 14. The process of claim 13 wherein the first hydrocarbyl-substituted acylating agent comprises the reaction product of a long chain hydrocarbon with a monounsaturated carboxylic acid; wherein said long chain hydrocarbon has a number average molecular weight greater than about 400; and

15 wherein the second hydrocarbyl-substituted acylating agent comprises the reaction product of a long chain hydrocarbon with a monounsaturated carboxylic acid; wherein said long chain hydrocarbon has a number average molecular weight less than about 280;

20 wherein the alkylene glycol comprises a glycol having of the general formula $\text{HO}-\left[\text{C}(\text{R})_x-\text{O} \right]_m-\text{H}$ wherein each R is independently H or an alkyl group of 1 to 6 carbon atoms, each x is independently an integer from 2 to about 10 and m is an integer from 1 to about 10.

25 15. The process of claim 13 or claim 14 wherein the alkylene glycol comprises a poly(ethylene glycol), a poly(1,3-propylene glycol) or a copolymer of ethylene glycol and 1,3-propylene glycol.

16. The process of claim 13 or claim 14 wherein the alkylene glycol comprises a glycol having the general formula $\text{HO}-(\text{CH}_2)_x-\text{OH}$ wherein x is an integer from 2 to about 10.

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17. The process of claim 14 wherein the first hydrocarbyl-substituted acylating agent comprises polyisobutylene succinic anhydride having a number average molecular weight greater than about 750;

5 wherein the second hydrocarbyl-substituted acylating agent comprises hexadecenyl succinic anhydride; and

wherein the alkylene glycol comprises ethylene glycol.

18. The process of any one of claims 13 through 17 wherein the neutralizing component comprises an amine.

10

19. A method of customizing an emulsifier component in a composition, said method comprising the steps of:

I. reacting a first hydrocarbyl-substituted acylating agent, a second hydrocarbyl-substituted acylating agent, and an alkylene glycol;

15 wherein the first hydrocarbyl-substituted acylating agent comprises a hydrocarbyl substituent group containing at least about 20 carbon atoms; and

wherein the second hydrocarbyl-substituted acylating agent comprises a hydrocarbyl substituent group containing less than about 20 carbon atoms;

20 resulting in an intermediate comprising (i) a functional group derived from said first hydrocarbyl-substituted acylating agent and (ii) a functional group derived from said second hydrocarbyl-substituted acylating agent, where the functional groups (i) and (ii) are coupled by a functional group derived from said alkylene glycol;

II. providing said intermediate for use as an emulsifier component precursor; and thereafter

25 III. converting said intermediate to an emulsifier component by reacting said intermediate with a neutralizing component;

resulting in a customized emulsifier component.

30 20. The method of claim 19 wherein the first hydrocarbyl-substituted acylating agent comprises the reaction product of a long chain hydrocarbon with a monounsaturated carboxylic acid; wherein said long chain hydrocarbon has a number average molecular weight greater than about 400; and

wherein the second hydrocarbyl-substituted acylating agent comprises the reaction product of a long chain hydrocarbon with a monounsaturated carboxylic acid; wherein said long chain hydrocarbon has a number average molecular weight less than about 280;

5 wherein the alkylene glycol comprises a glycol having of the general formula $\text{HO}-(\text{CH}_2)_x-\text{OH}$ wherein x is an integer from 2 to about 10.

21. The method of claim 19 or claim 20 wherein the neutralizing component comprises an amine.

10

22. An emulsifier component prepared by a process comprising the steps of:

I. reacting a first hydrocarbyl-substituted acylating agent, a second hydrocarbyl-substituted acylating agent, and an alkylene glycol;

15 wherein the first hydrocarbyl-substituted acylating agent comprises a hydrocarbyl substituent group containing at least about 20 carbon atoms; and

 wherein the second hydrocarbyl-substituted acylating agent comprises a hydrocarbyl substituent group containing less than about 20 carbon atoms;

20 resulting in an intermediate comprising (i) a functional group derived from said first hydrocarbyl-substituted acylating agent and (ii) a functional group derived from said second hydrocarbyl-substituted acylating agent, where the functional groups (i) and (ii) are coupled by a functional group derived from said alkylene glycol;

 II. providing said intermediate for use as an emulsifier component precursor; and thereafter

25 III. converting said intermediate to an emulsifier component by reacting said intermediate with a neutralizing component.

23. The emulsifier component of claim 22 where said neutralizing component comprises an amine.

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