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(54) Title: SALT COMPOSITIONS AND EXPLOSIVES USING THE SAME

(57) **Abrégé/Abstract:**

This invention relates to novel salt compositions and to explosive compositions comprising said salt compositions. The salt compositions are useful as emulsifiers in the explosive compositions. The explosive compositions are water-in-oil emulsion explosives.



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(54) **Title:** SALT COMPOSITIONS AND EXPLOSIVES USING THE SAME

(57) **Abstract:** This invention relates to novel salt compositions and to explosive compositions comprising said salt compositions. The salt compositions are useful as emulsifiers in the explosive compositions. The explosive compositions are water-in-oil emulsion explosives.



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TITLE

SALT COMPOSITIONS AND EXPLOSIVES USING THE SAME

FIELD OF THE INVENTION

[0001] This invention relates to novel salt compositions and to explosive compositions comprising said salt compositions. The salt compositions are useful as emulsifiers in the explosive compositions. The explosive compositions are water-in-oil emulsion explosives.

BACKGROUND OF THE INVENTION

[0002] Water-in-oil emulsion explosives typically comprise a continuous organic phase and a discontinuous oxidizer phase containing water and an oxygen-supplying source such as ammonium nitrate, the oxidizer phase being dispersed throughout the continuous organic phase. Examples of such water-in-oil emulsion explosives are disclosed, inter alia, in U.S. Pat. Nos. 3,447,978; 3,765,964; 3,985,593; 4,008,110; 4,097,316; 4,104,092; 4,218,272; 4,259,977; 4,357,184; 4,371,408; 4,391,659; 4,404,050; 4,409,044; 4,448,619; 4,453,989; and 4,534,809; U.K. Patent Application GB 2,050,340A; and European Application No. 0,156,572 and 0,155,800.

[0003] One type of surfactant and/or emulsifier used in conventional emulsion explosive comprises a salt of a mid molecular weight (as defined below) hydrocarbyl-substituted carboxylic acylating agent, i.e. polyisobutylene succinic anhydride (PIBSA), and a salted low molecular weight hydrocarbyl-substituted carboxylic acylating agent, i.e. a salted alkenyl succinic anhydride. These two moieties are coupled together by reacting them with a linking compound. Suitable linking compounds include compounds comprising: (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, (v) at least one primary or secondary amino group and at least one hydroxyl group, or combinations thereof. See US Patent 5047175 for additional background on these materials.

[0004] These coupled surfactants are often combined with a high molecular weight (as defined below) emulsifier, such as the reaction product of a high molecular weight PIBSA and an alkanolamine, such as dimethylethanolamine. The resulting mixture is then used as the surfactant formulations in emulsion explosive compositions. See US Patent 5920031 for additional background on these materials.

[0005] While these blends perform well, the surfactant packages are expensive and the requirement of blending the coupled surfactants with the additional high molecular weight surfactants adds complexity and expense to the compositions.

[0006] There is a need for a surfactant that can provide performance at least equivalent to that provided by the packages described above without the need to add one or more additional surfactants to the package.

[0007] In addition, the reactions used to prepare the coupled surfactants described above can be slow and difficult to drive to completion. This results in waste and inefficiency as well as additional cost. There is a need to develop reactions that produce effective surfactants for emulsion explosive compositions that proceeds to completion more quickly and without the need for expensive process modification, such as adding an expensive catalyst, increasing the reaction temperature and/or reaction time, etc.

[0008] Another problem with conventional surfactant packages is that the coupled surfactants described above have to be prepared with a mixture of a mid molecular weight hydrocarbyl-substituted carboxylic acylating agent, i.e. polyisobutylene succinic anhydride (PIBSA), and a salted low molecular weight hydrocarbyl-substituted carboxylic acylating agent, i.e. a salted alkenyl succinic anhydride. This need for both mid and low molecular weight acylating agents adds cost and complexity to the process. There is also a need for surfactants that perform well without the use of an additional high molecular weight surfactant while still providing at least comparable if not improved performance.

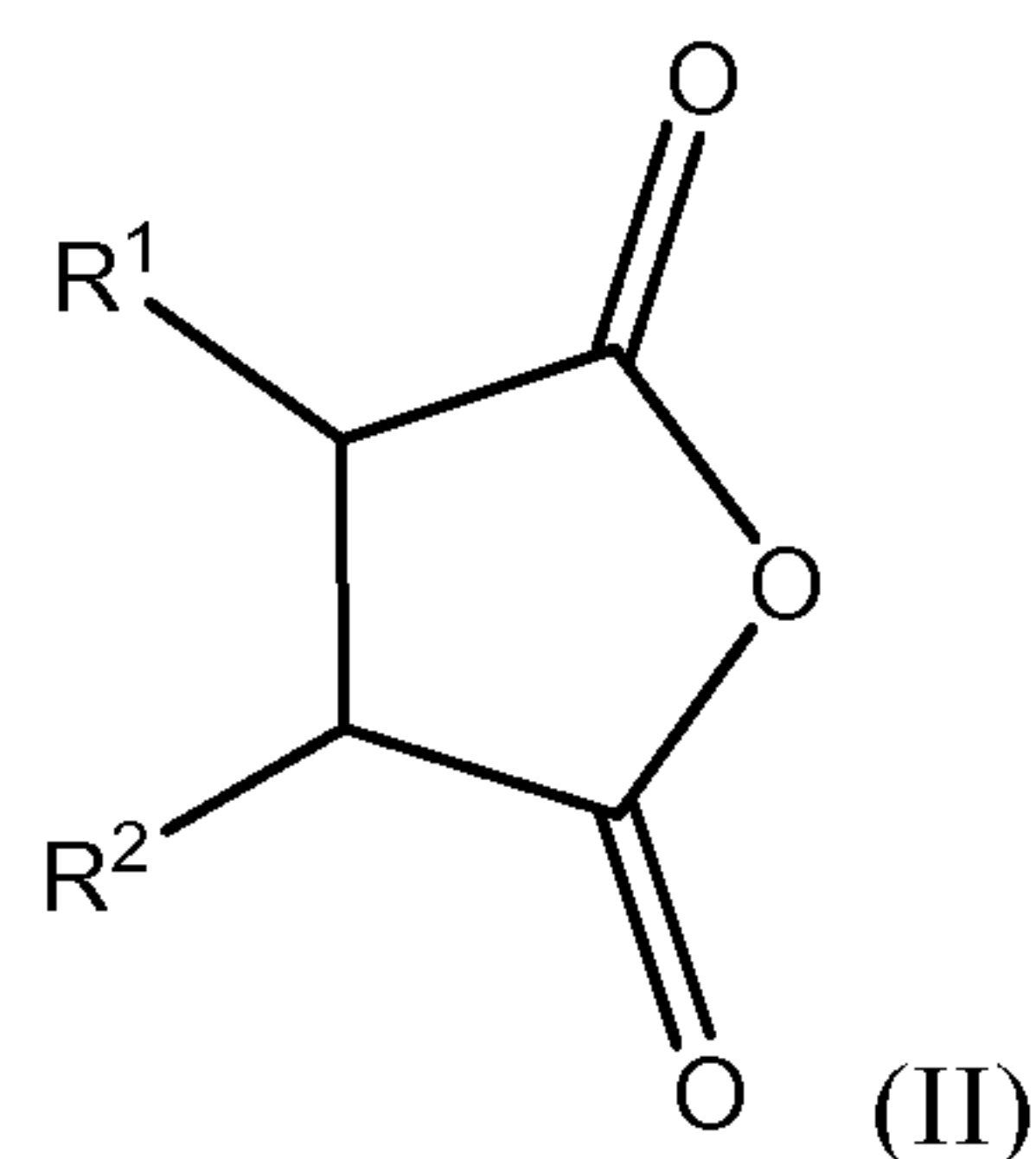
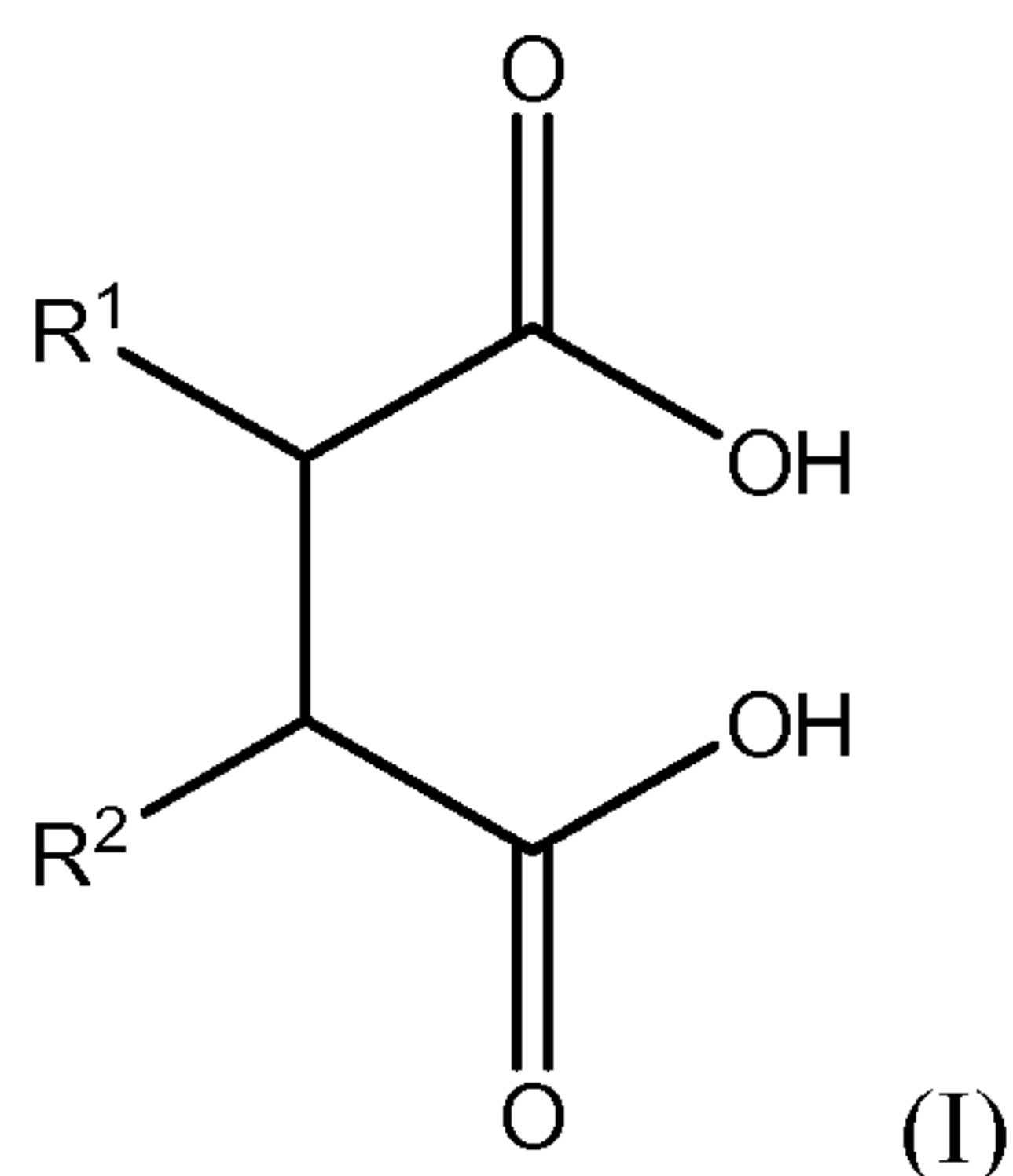
[0009] Still another problem with emulsion explosives is their stability, particularly during transportation. If a surfactant, and the emulsion it provides, has poor handling properties, the emulsion may crystallize during transportation and be unsuitable for use. Some premium surfactant packages that perform well in all

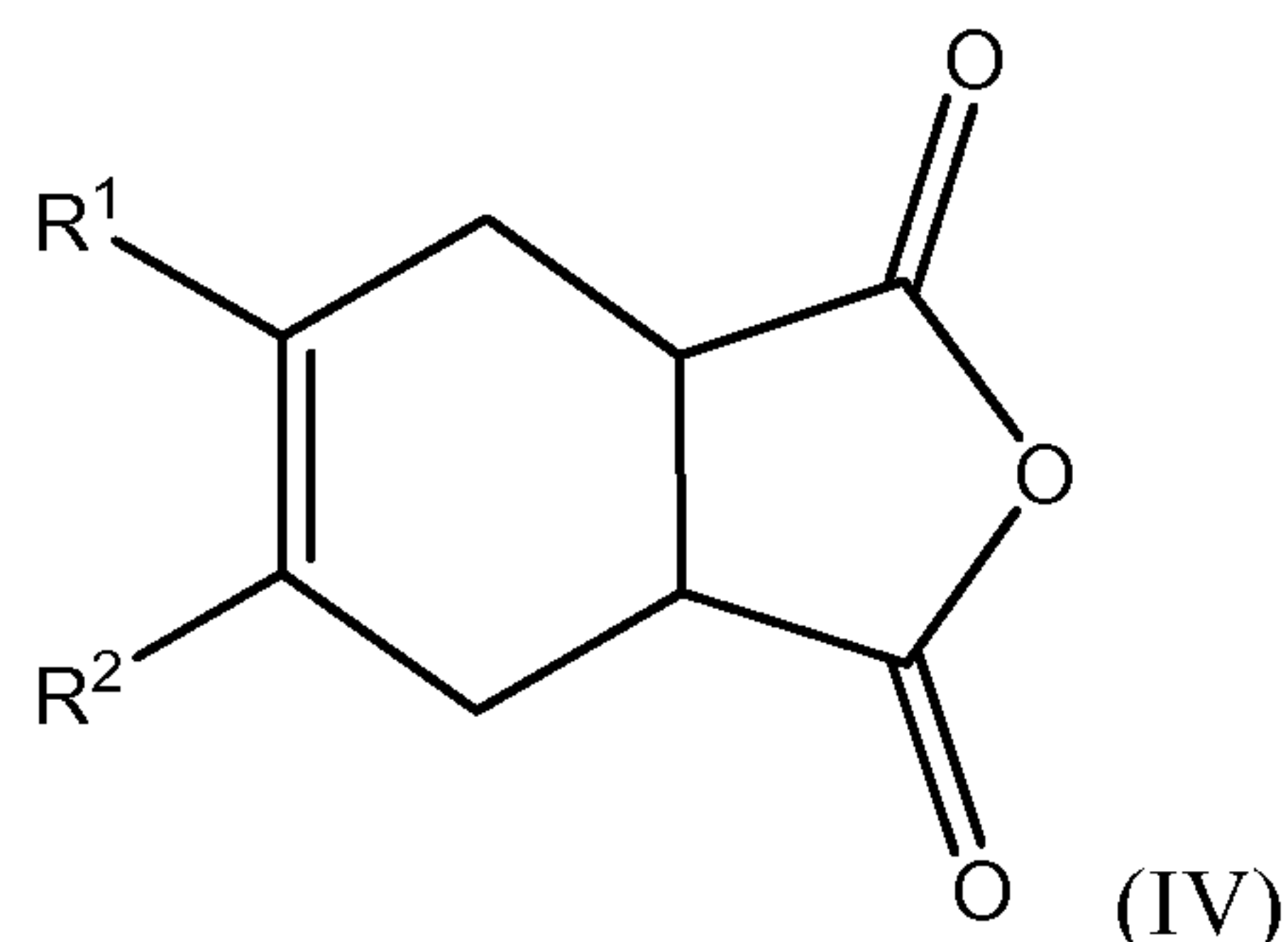
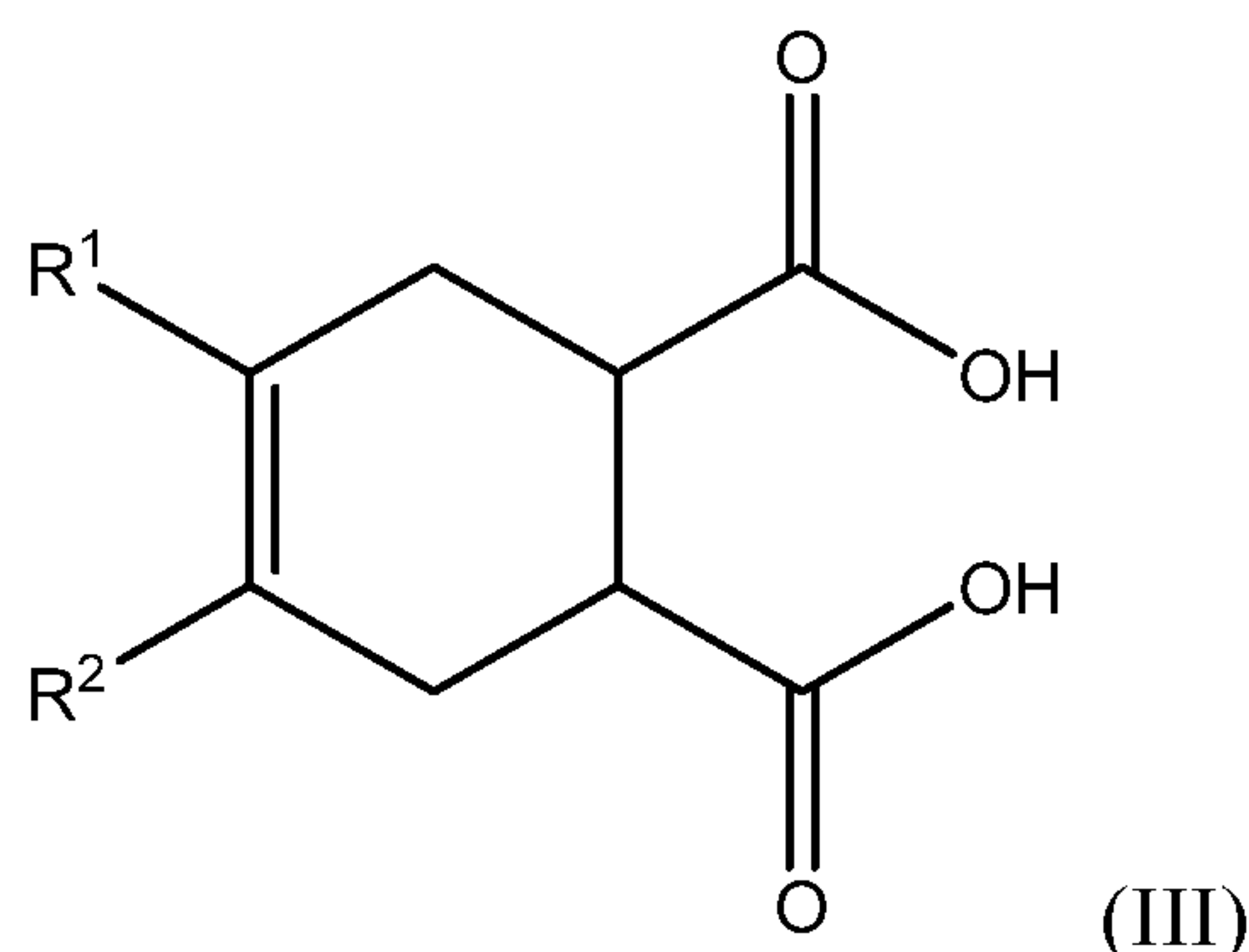
other areas have issues in this area. There is a need for surfactants that perform well and which provide emulsions that are more robust and avoid problems that can arise during transportation. Comparable performance, or even slightly worse performance in some areas, would be sufficient if the handling properties, particularly as it related to stability during storage and transportation could be improved. There is a need for surfactants, and the emulsion explosives they would provide, that address these issues.

SUMMARY OF THE INVENTION

[0010] The present invention provides for a novel salt composition comprising: (A) salt moieties derived from: (A)(I) at least one polycarboxylic acylating agent having at least one hydrocarbyl substituent having an average of from about 20 to about 500 carbon atoms (for example at least one mid-molecular weight polycarboxylic acylating agent having at least one hydrocarbyl substituent having an average of from about 20 to about 500 carbon atoms); and (A)(II) one or more members selected from the group consisting of ammonia, at least one amine, at least one alkali or alkaline earth metal, and at least one alkali or alkaline earth metal compound; where two of the described moieties (A) are coupled together by (B) at least one compound having at least two hydroxyls and at least one tertiary amino group.

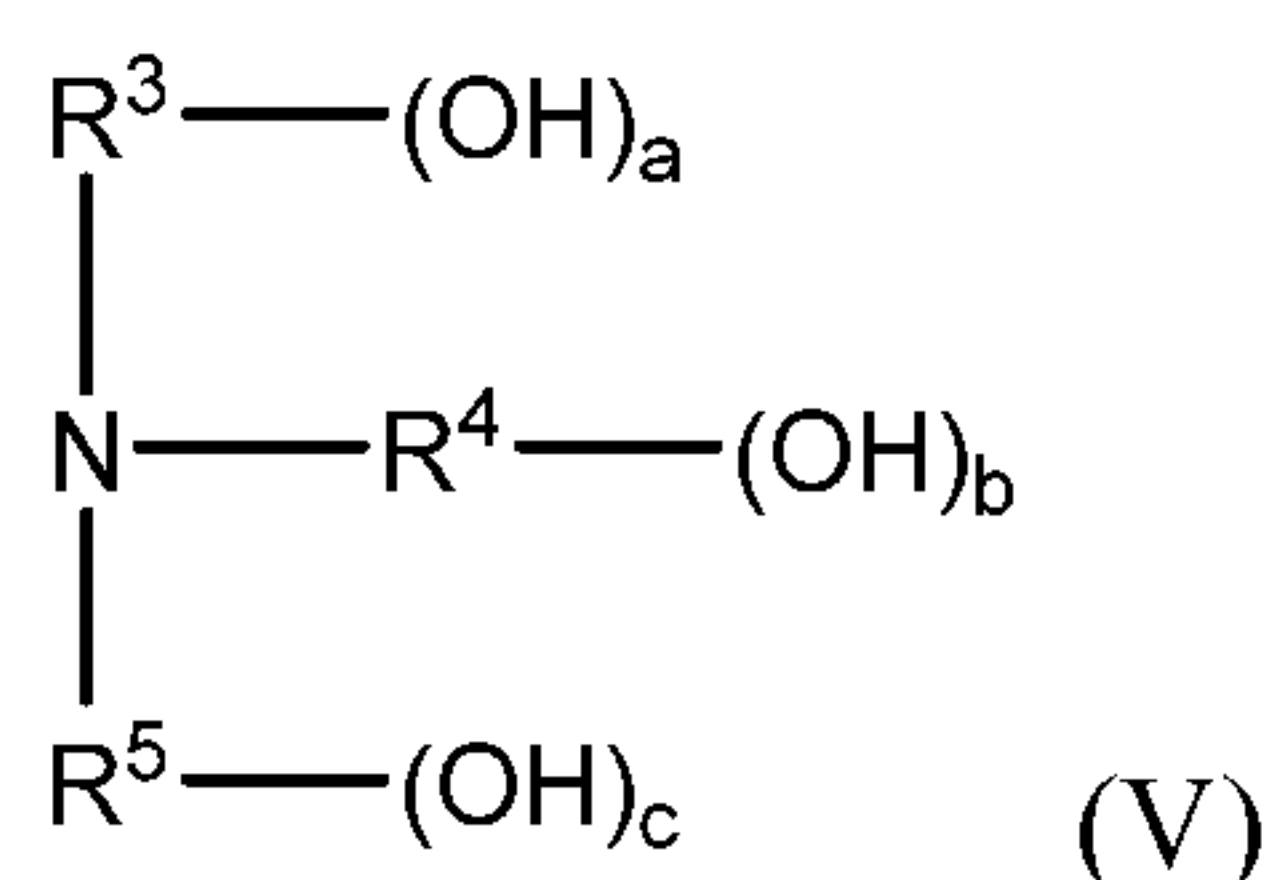
[0011] The polycarboxylic acylating agent of (A)(I) may be represented by any one or more of the following formulae:





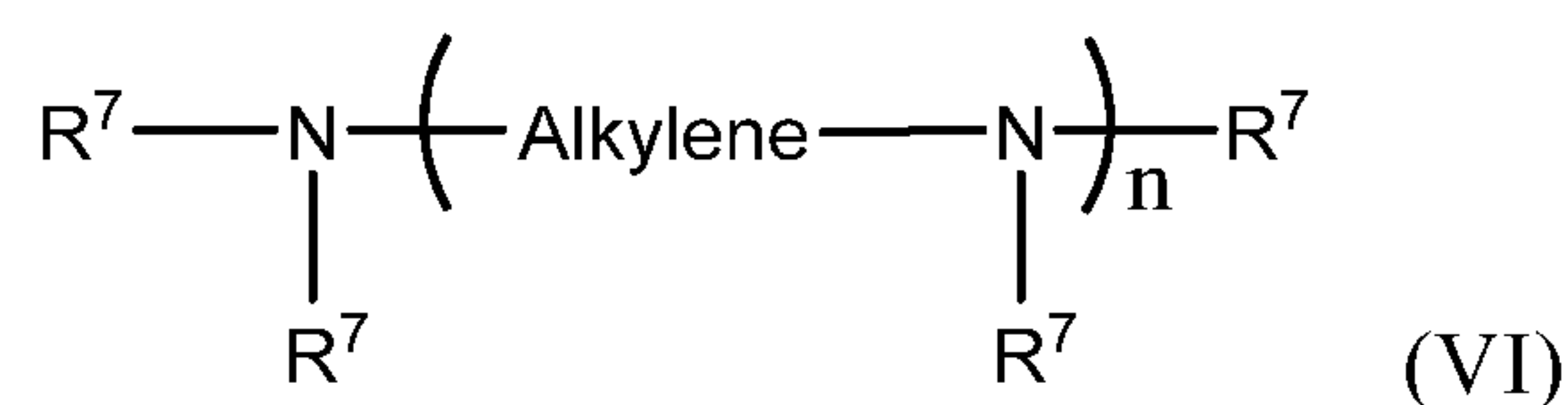
wherein each R^1 in each formula is independently said hydrocarbyl substituent of (A)(I) and wherein each R^2 in each formula is independently hydrogen or a methyl group. In some embodiments the hydrocarbyl substituent is a poly(isobutylene) group.

[0012] The a compound having at least two hydroxyls and at least one tertiary amino group, that is component (B), may be represented by the formula:



wherein each a, b, and c is independently 0 or 1 so long as the total of $a+b+c$ is at least 2, and wherein each R^3 , R^4 and R^5 is independently a hydrocarbon group containing from 1 to 50 carbon atoms or an $-(R^6-O-)_n-$ group wherein R^6 is a alkenyl group containing from 1 to 6 carbon atoms, and in some embodiments 2 carbon atoms, and n is an integer from 1 to 50 or from 1 to 20.

[0013] The (A)(II) may be represented by the formula:



wherein n is a number of from 0 to about 10 or from 1 to 10, each R^7 is independently a hydrogen atom or a hydrocarbyl group or a hydroxy-substituted hydrocarbyl group having up to about 700 carbon atoms, and the Alkylene group has from 1 to about 10 carbon atoms.

[0014] The present invention also provides either a booster-sensitive or cap-sensitive emulsion explosive comprising a discontinuous oxidizer phase comprising

at least one oxygen-supplying component, a continuous organic phase comprising at least one carbonaceous fuel. The carbonaceous fuel may include at least one wax, and an emulsifying amount of the surfactant compositions described herein.

[0015] The present invention further provides a cartridge casing containing at least one cap-sensitive emulsion explosive or booster sensitive explosive composition, said emulsion comprising a discontinuous oxidizer phase comprising at least one oxygen-supplying component, a continuous organic phase comprising at least one carbonaceous fuel, and an emulsifying amount of the surfactant compositions described herein.

[0016] The invention further provides surfactants, as described herein, where component (A)(I) is substantially free, or even free of, acylating agents containing fewer than 50, 40, 20 or even 15 carbon atoms in their hydrocarbyl groups.

DETAILED DESCRIPTION OF THE INVENTION

[0017] Various features and embodiments of the invention will be described below by way of non-limiting illustration.

[0018] The terms “low molecular weight”, “mid molecular weight”, and “high molecular weight” as used in this specification and in the appended claims are intended to provide a relative description when discussing the acylating agents used in the preparation of the coupled surfactants described herein as well as the acylating agents used in the preparation of the non-coupled surfactants sometimes used in combination with some conventional coupled surfactants. In some embodiments low molecular weight means less than half the molecular weight of the mid molecular weight materials and high molecular weight means at least twice the molecular weight of the mid molecular weight materials. In some embodiments low molecular weight means the material referred to contains less than 50 carbon atoms, or less than 40, 20 or even 15 carbon atoms. In some embodiments mid molecular weight means the material referred to contains less from 20 to 500 carbon atoms, or from 30, 40 or even 50 up to 500, 250, 150, 120 or even 100 carbon atoms. In some embodiments high molecular weight means the material referred to contains at least 120 carbon atoms, or from 100, 120 or 140 up to 500, 400 or even 300 carbon atoms. The number of carbon atoms listed above may be applied either as respective minimum or maximum values for a materials that contains a mixture

of hydrocarbons of varying sizes, or as defining the range that the average number of carbon atoms present in a mixture of hydrocarbons of varying sizes fall in. In some embodiments low molecular weight means the material referred to has a number average molecular weight (M_n) of less than 700 or even less than 500, or from 100 or 120 to 700 or 500 or even 450. In some embodiments mid molecular weight means the material referred to has an M_n of 500 to 1600 or from 800 or 900 to 1500, 1300, or even 1200. In some embodiments high molecular weight means the material referred to has an M_n of from 1300 to 5000, or from 1300, 1500 or even 1600 up to 5000, 3000, or even 2000.

[0019] The term "emulsion" as used in this specification and in the appended claims is intended to cover not only water-in-oil emulsions, but also compositions derived from such emulsions wherein at temperatures below that at which the emulsion is formed the discontinuous phase is solid or in the form of droplets of super-cooled liquid. This term also covers compositions derived from or formulated as such water-in-oil emulsions that are in the form of gelatinous or semi-gelatinous compositions.

[0020] The term "hydrocarbyl" is used herein to include: (1) hydrocarbyl groups, that is, aliphatic (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl, cycloalkenyl), aromatic, aliphatic- and alicyclicsubstituted aromatic groups and the like as well as cyclic groups wherein the ring is completed through another portion of the molecule (that is, any two indicated groups may together form an alicyclic group); (2) substituted hydrocarbyl groups, that is, those groups containing non-hydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbyl nature of the hydrocarbyl group; those skilled in the art will be aware of such groups, examples of which include ether, oxo, halo (e.g., chloro and fluoro), alkoxyl, mercapto, alkylmercapto, nitro, nitroso, sulfoxy, etc.; (3) hetero groups, that is, groups which, while having predominantly hydrocarbyl character within the context of this invention, contain other than carbon in a ring or chain otherwise composed of carbon atoms. Suitable heteroatoms will be apparent to those of skill in the art and include, for example, sulfur, oxygen, nitrogen and such substituents as pyridyl, furanyl, thiophenyl, imidazolyl, etc.

[0021] In general, no more than about three non-hydrocarbon groups or heteroatoms and preferably no more than one will be present for each ten carbon atoms in a hydrocarbyl group. Typically, there will be no such groups or heteroatoms in a hydrocarbyl group and it will, therefore, be purely hydrocarbyl.

[0022] The hydrocarbyl groups in some embodiments are free from acetylenic unsaturation; ethylenic unsaturation, when present will generally be such that there is no more than one ethylenic linkage present for every ten carbon to-carbon bonds.

[0023] The term "lower" as used herein in conjunction with terms such as alkyl, alkenyl, alkoxy, and the like, may be intended to describe such groups which contain a total of up to 30, 24 or even 16 or 8 or 7 carbon atoms.

[0024] The term "substantially free of" as used herein is intended to mean less than a significant amount that would impact the nature or character of the composition and/or compound being described. The term may also mean the material referred to is present at less than 10%, 5%, 2%, 1%, 0.5%, or even 0.1% by weight of the composition and/or component being described. In still other embodiments it may mean that less than 1,000 ppm, 500 ppm or even 100 ppm of the material in question is present. In other embodiments the term may mean no more than the amount unintentionally and/or unavoidably present due to the use of industrial materials that may contain byproducts and/or impurities.

Component (A)(I)

[0025] The carboxylic acylating agent of component (A)(I) may be aliphatic or aromatic, polycarboxylic acids or acid-producing compounds. Throughout this specification and in the appended claims, 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.

[0026] The acylating agent (A)(I) 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.

[0027] The polycarboxylic acylating agents (A)(I) are well known in the art and have been described in detail, for example, in the following U.S., British and Canadian patents: U.S. Pat. Nos. 3,024,237; 3,087,936; 3,163,603; 3,172,892; 3,215,707; 3,219,666; 3,231,587; 3,245,910; 3,254,025; 3,271,310; 3,272,743; 3,272,746; 3,278,550; 3,288,714; 3,306,907; 3,307,928; 3,312,619; 3,341,542; 3,346,354; 3,367,943; 3,373,111; 3,374,174; 3,381,022; 3,394,179; 3,454,607; 3,346,354; 3,470,098; 3,630,902; 3,652,616; 3,755,169; 3,868,330; 3,912,764; 4,234,435; and 4,368,133; British Patents 944,136; 1,085,903; 1,162,436; and 1,440,219; and Canadian Patent 956,397. These patents are incorporated herein by reference.

[0028] As disclosed in the foregoing patents, there are several processes for preparing these acylating agents (A)(I). Generally, these processes involve the reaction of (1) an ethylenically unsaturated carboxylic acid, acid halide, anhydride or ester reactant with (2) an ethylenically unsaturated hydrocarbon containing at least about 20 aliphatic carbon atoms or a chlorinated hydrocarbon containing at least about 20 aliphatic carbon atoms at a temperature within the range of about 100-300 degrees C. The chlorinated hydrocarbon or ethylenically unsaturated hydrocarbon reactant preferably contains at least about 30 carbon atoms, more preferably at least about 40 carbon atoms, more preferably at least about 50 carbon atoms, and may contain polar substituents, oil-solubilizing pendant groups, and be unsaturated within the general limitations explained hereinabove.

[0029] When preparing the carboxylic acid acylating agent, the carboxylic acid reactant usually corresponds to the formula $R_o-(COOH)_n$, where R_o is characterized by the presence of at least one ethylenically unsaturated carbon-to-carbon covalent bond and n is an integer from 2 to 6, and in some embodiments is 2. The acidic reactant can also be the corresponding carboxylic acid halide, anhydride, ester, or other equivalent acylating agent and mixtures of two or more of these. Ordinarily, the total number of carbon atoms in the acidic reactant will not exceed about 20, or about 10 or even about 6, exclusive of the carboxyl-based groups. In some embodiments the acidic reactant will have at least one ethylenic linkage in an alpha,

[0030] The ethylenically unsaturated hydrocarbon reactant and the chlorinated hydrocarbon reactant used in the preparation of these carboxylic acylating agents (A)(I) are in some embodiments of mid-molecular weight, as defined above, substantially saturated petroleum fractions and substantially saturated olefin polymers and the corresponding chlorinated products. Polymers and chlorinated polymers derived from mono-olefins having from 2 to about 30 carbon atoms are preferred. Especially useful polymers are the 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 internal 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

[0031] Interpolymers of 1-mono-olefins such as illustrated above with each other and with other interpolymers of olefinic substances such as aromatic olefins, cyclic olefins, and polyolefins, are also useful sources of the ethylenically unsaturated reactant. 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.

[0032] 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.

[0033] In one embodiment of the invention, the polymers and chlorinated 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 in the presence of a Lewis acid catalyst such as aluminum chloride or boron trifluoride. These polyisobutenes preferably contain predominantly (that is, greater than about 80% of the total repeat units) isobutene repeat units of the configuration: $[-CH_2-C(CH_3)_2-]$.

[0034] The chlorinated hydrocarbons and ethylenically unsaturated hydrocarbons used in the preparation of the carboxylic acylating agents in some embodiments have up to about 500 carbon atoms per molecule. Suitable acylating agents for use in component (A)(I) include those containing hydrocarbyl groups of from about 20 to about 500 carbon atoms, or from about 30, 40 or even 50 to about 500 carbon atoms.

[0035] The polycarboxylic acylating agents (A)(I) may also be prepared by halogenating a hydrocarbon such as the above described olefin polymers to produce a poly-halogenated product, converting the poly-halogenated product to a polynitrile, and then hydrolyzing the polynitrile. They may be prepared by oxidation of a polyhydric alcohol with potassium permanganate, nitric acid, or a similar oxidizing agent. Another method involves the reaction of an olefin or a polar-substituted hydrocarbon such as a chloropolyisobutene with an unsaturated polycarboxylic acid such as 2-pentene-1,3,5-tricarboxylic acid prepared by dehydration of citric acid.

[0036] The polycarboxylic acid acylating agents (A)(I) can also be obtained by reacting chlorinated polycarboxylic acids, anhydrides, acyl halides, and the like with ethylenically unsaturated hydrocarbons or ethylenically unsaturated substituted hydrocarbons such as the polyolefins and substituted polyolefins described hereinbefore in the manner described in U.S. Pat. No. 3340281, this patent being incorporated herein by reference.

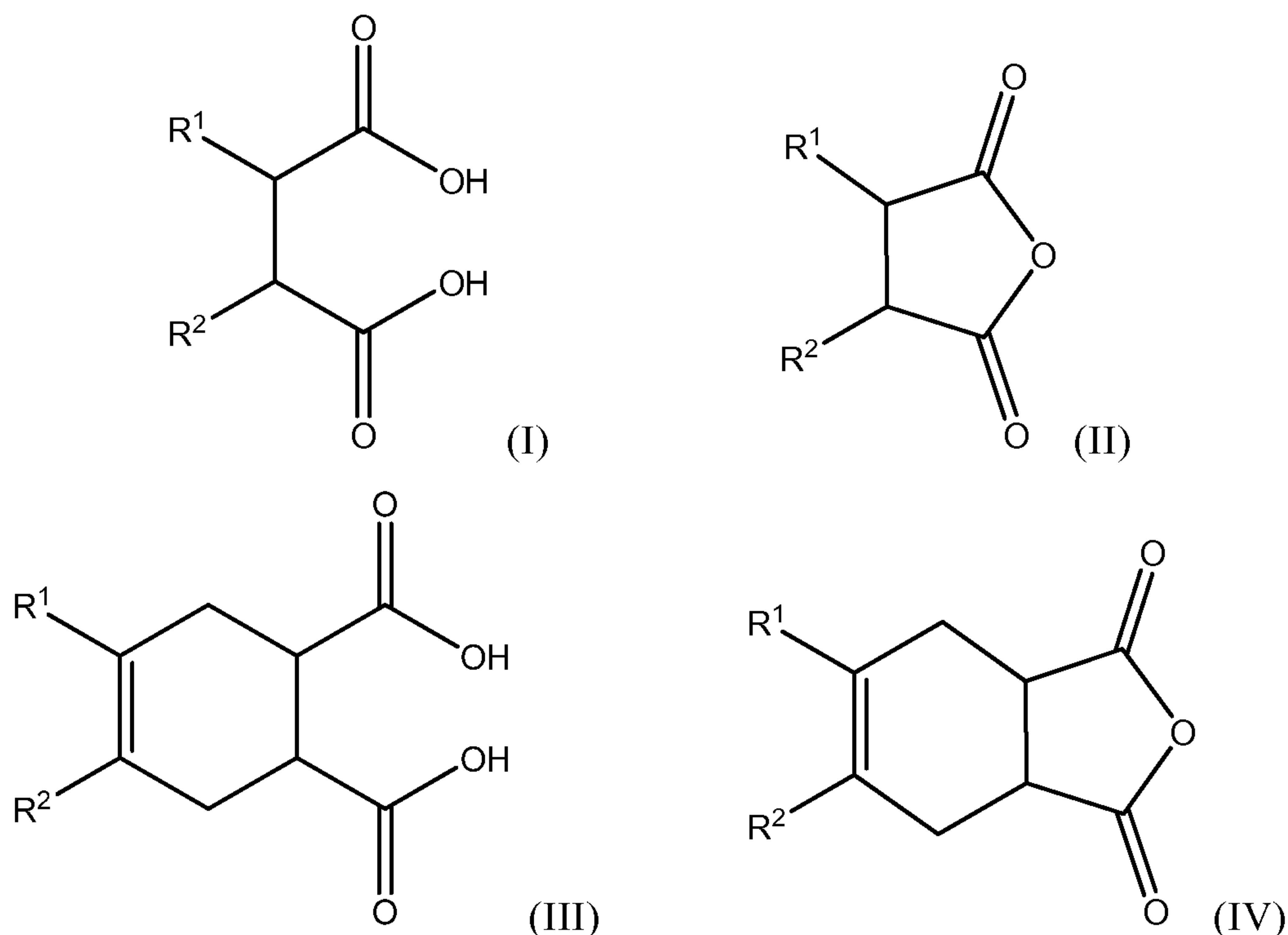
[0037] The polycarboxylic acid anhydrides (A)(I) can be obtained by dehydrating the corresponding acids. Dehydration is readily accomplished by heating the acid to a temperature above about 70.degree. C., preferably in the presence of a dehydration agent, e.g., acetic anhydride. Cyclic anhydrides are

usually obtained from polycarboxylic acids having acid groups separated by no more than three carbon atoms such as substituted succinic or glutaric acid, whereas linear anhydrides are usually obtained from polycarboxylic acids having the acid groups separated by four or more carbon atoms.

[0038] The acid halides of the polycarboxylic acids can be prepared by the reaction of the acids or their anhydrides with a halogenating agent such as phosphorus tribromide, phosphorus pentachloride, or thionyl chloride.

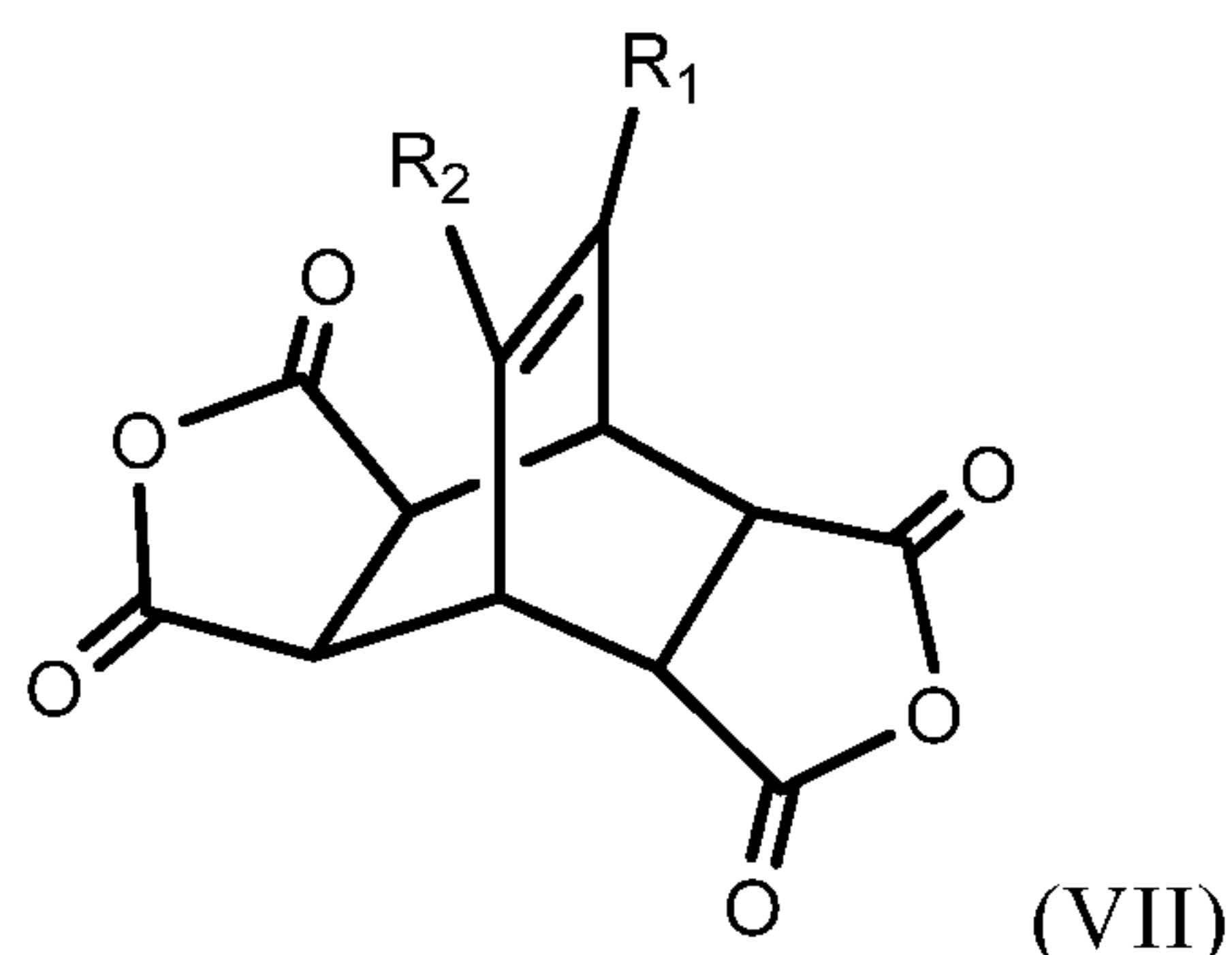
[0039] Hydrocarbyl-substituted succinic acids and the anhydride, acid halide and ester derivatives thereof are particularly preferred acylating agents (A)(I). These acylating agents may be prepared by reacting maleic anhydride with an olefin or a chlorinated hydrocarbon such as a chlorinated polyolefin. The reaction involves merely heating the two reactants at a temperature in the range of about 100 to 300 degrees C, or about 100 to 200 degrees C. The product from this reaction is a hydrocarbyl-substituted succinic anhydride wherein the substituent is derived from the olefin or chlorinated hydrocarbon. The product may be hydrogenated to remove all or a portion of any ethylenically unsaturated covalent linkages by standard hydrogenation procedures, if desired. 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 halide or ester by reacting with a phosphorus halide, phenol or alcohol. In some embodiments the hydrocarbyl group of component (A)(I) contains from 20, 30, 40 or even 50 carbon atoms up to 500 carbon atoms. In some embodiments the hydrocarbyl group is derived from polyisobutylene and has a number average molecular weight of 800 to 1500, 800 to 1200, 900 to 1100 or even about 1000.

[0040] As provided above, the hydrocarbyl-substituted succinic acids and anhydrides (A)(I) can be represented by formulas (I) through (IV):



wherein each R^1 in each formula is independently said hydrocarbyl substituent of (A)(I) and wherein each R^2 in each formula is independently hydrogen or a methyl group. In some embodiments the hydrocarbyl substituent is a poly(isobutylene) group. In some embodiments the succinic acids and anhydrides are in the form of formulas (I) and (II) and in other embodiments the succinic acids and anhydrides are in the form of formulas (III) and (IV). In formulas (I), (II), (III) and/or (IV), each R^1 in each formula is independently said hydrocarbyl substituent of (A)(I) and wherein each R^2 in each formula is independently hydrogen or a methyl group. In some embodiments the hydrocarbyl substituent is a poly(isobutylene) group. Each R^1 may independently contain from 20, 30, 40 or even 50 carbon atoms up to 500, 400, or even 350 carbon atoms.

[0041] Component (A)(I) may also include disuccans, such as those represented by the following formula:



where R^1 and R^2 are defined as provided above for formulas (I) to (IV).

[0042] In some embodiments the acylating agent (A)(I) is an aliphatic polycarboxylic acid, or a dicarboxylic acid. However (A)(I) may also be an aromatic polycarboxylic acid or acid-producing compound. The aromatic acids are preferably alkyl-substituted, dicarboxysubstituted benzene, naphthalene, anthracene, phenanthrene or like aromatic hydrocarbons. The alkyl groups may contain up to about 30 carbon atoms. The aromatic acid may also contain other substituents such as halo, hydroxy, lower alkoxy, etc.

Component (A)(II)

[0043] The amines useful as component (A)(II) in preparing the salt compositions of the invention include ammonia, and primary amines, secondary amines and hydroxyamines. Component (A)(II) may include monoamines, polyamines, and/or mixtures thereof. Suitable amines include primary, secondary, and/or tertiary; aliphatic, cycloaliphatic and/or aromatic amines.

[0044] Useful primary and secondary amines include aliphatic monoamines. 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 dialkenyl-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.

[0045] Suitable amines include cycloaliphatic monoamines which 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 pyranlyl-substituted cyclohexylamine.

[0046] Suitable amines include aromatic monoamines which are 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 naphthylene. Examples of aromatic monoamines include aniline, di(paramethylphenyl) 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 thienylsubstituted aniline.

[0047] Heterocyclic polyamines can also be used. As used herein, the 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 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

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-membered heterocyclic rings are preferred.

[0048] Among the suitable heterocyclic polyamines are the aziridines, azetidines, azolidines, tetra- and di-hydro pyridines, pyrroles, indoles, piperadines, imidazoles, di- and tetra-hydroimidazoles, 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 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 include N-aminoethylpiperazine and N,N'-diaminoethylpiperazine.

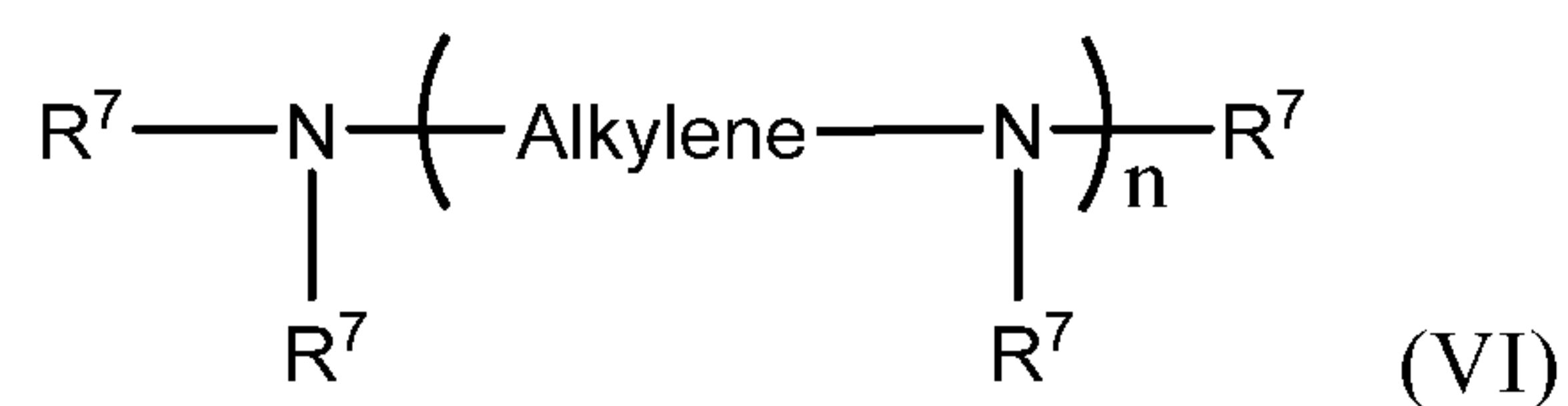
[0049] Hydrazine and substituted-hydrazines can also be used. The substituents which may be present on the hydrazine include alkyl, alkenyl, aryl, aralkyl, alkaryl, and the like. Usually, the substituents are alkyl, especially lower alkyl, phenyl, and substituted phenyl such as lower alkoxy-substituted phenyl or lower alkyl-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-chlorophenol)-hydrazine, N-phenyl-N'-cyclohexylhydrazine, and the like.

[0050] 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, (i.e. $\text{NH}_2\text{-R-}[\text{-N(H)-R-}]_x\text{-}$), per nine amino units present on the main chain; for example, 1-4 of such branched chains per nine units on the main 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.

[0051] 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 Jefferson Chemical Company, Inc. 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.

[0052] As noted above, useful polyamines alkylene polyamines conforming to formula (VI):



wherein n may be from 1 to 10 or even 7; each R and R' is independently a hydrogen atom, a hydrocarbyl group or a hydroxy-substituted hydrocarbyl group having up to about 700, 100, 50 or even 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 1 up to 18, or even 4 carbon atoms, and in some embodiments the Alkylene group is 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.

[0053] Alkylene polyamines that are useful include ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine,

propylene diamine, trimethylene diamine, hexamethylene 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 afore-described polyamines.

[0054] 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.

[0055] Alkoxylated alkylene polyamines (e.g., N,N-(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 afore-described 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.

[0056] Specific examples of alkoxylated alkylene polyamines include N-(2-hydroxyethyl) ethylene diamine, N,Nbis(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 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

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.

[0057] Suitable hydroxyamines include primary or secondary amines. They can also be tertiary amines provided said tertiary amines also contain at least two 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.

[0058] The hydroxyamines can be primary or secondary alkanol amines or mixtures thereof. Such amines can be represented, respectfully, by the formulae: H₂N-R'-OH and (H)(R)N-R'-OH wherein R is 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 formulae 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. Typically, R is a lower alkyl group of up to seven carbon atoms.

[0059] 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 afore-described amines and can be represented by the formulae: H₂N-(R'O)_x-H and (H)(R)N-(R'O)_x-H wherein x is a number from about 2 to about 15 and R and R' are as described above.

[0060] Polyamine analogs of these hydroxy amines, particularly alkoxylated alkylene polyamines (e.g., N,N-(di-ethanol)-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 about 20 carbons. Similar alkylene oxide-alkanol amine reaction products can also

be used such as the products made by reacting the afore-described 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.

[0061] 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 hydroxy-alkyl-substituted polyamines include N-(2-hydroxyethyl) ethylene diamine, 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.

[0062] 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.

[0063] 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 poly hydroxy-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 trismethylolamino methane), 2-amino-1-butanol, ethanolamine, beta-(beta-hydroxyethoxy)-ethyl amine, glucamine, glusoamine, 4-amino-3-hydroxy-3-methyl-1-buten (which can be prepared according to procedures known in the art by reacting isopreneoxide with ammonia), N-3-(aminopropyl)-4-(2-hydroxyethyl)-piperadine, 2-amino-6-methyl-6-heptanol, 5-amino-1-pentanol, N-(beta-hydroxyethyl)-1,3-diamino propane, 1,3-diamino-2-hydroxypropane, N-(beta-hydroxy ethoxyethyl)-ethylenediamine and the like. U.S. Pat. No. 3,576,743 is incorporated herein by reference.

[0064] In addition to ammonia, the primary amines, secondary amines and hydroxyamines discussed above, the amines useful as components (A)(II) also include tertiary mono- and polyamines. The tertiary amines are analogous to the primary amines, secondary amines and hydroxyamines discussed above 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.

[0065] The tertiary amines 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 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 of component (B) with component (A). 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-).

[0066] The monoamines can be represented by the formula (R¹)(R²)(R³)N wherein R¹, R² and R³ are the same or different hydrocarbyl groups. In some embodiments R¹, R² and R³ independently hydrocarbyl groups of from 1 to about 20 carbon atoms.

[0067] 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-didodecyl-1-dodecanamine tricoco amine, trihydrogenated-tallow amine, N-methyl-dihydrogenated 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.

[0068] Useful tertiary alkanol amines are represented by the formula (R)(R')N-R¹-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 R¹ is a divalent hydrocarbyl group of about two to about 18 carbon atoms. The group -R¹-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-(hydroxy-substituted hydrocarbyl)amine. These are hydroxyl-substituted poly(hydrocarbyloxy) analogs of the above-described hydroxy amines (these

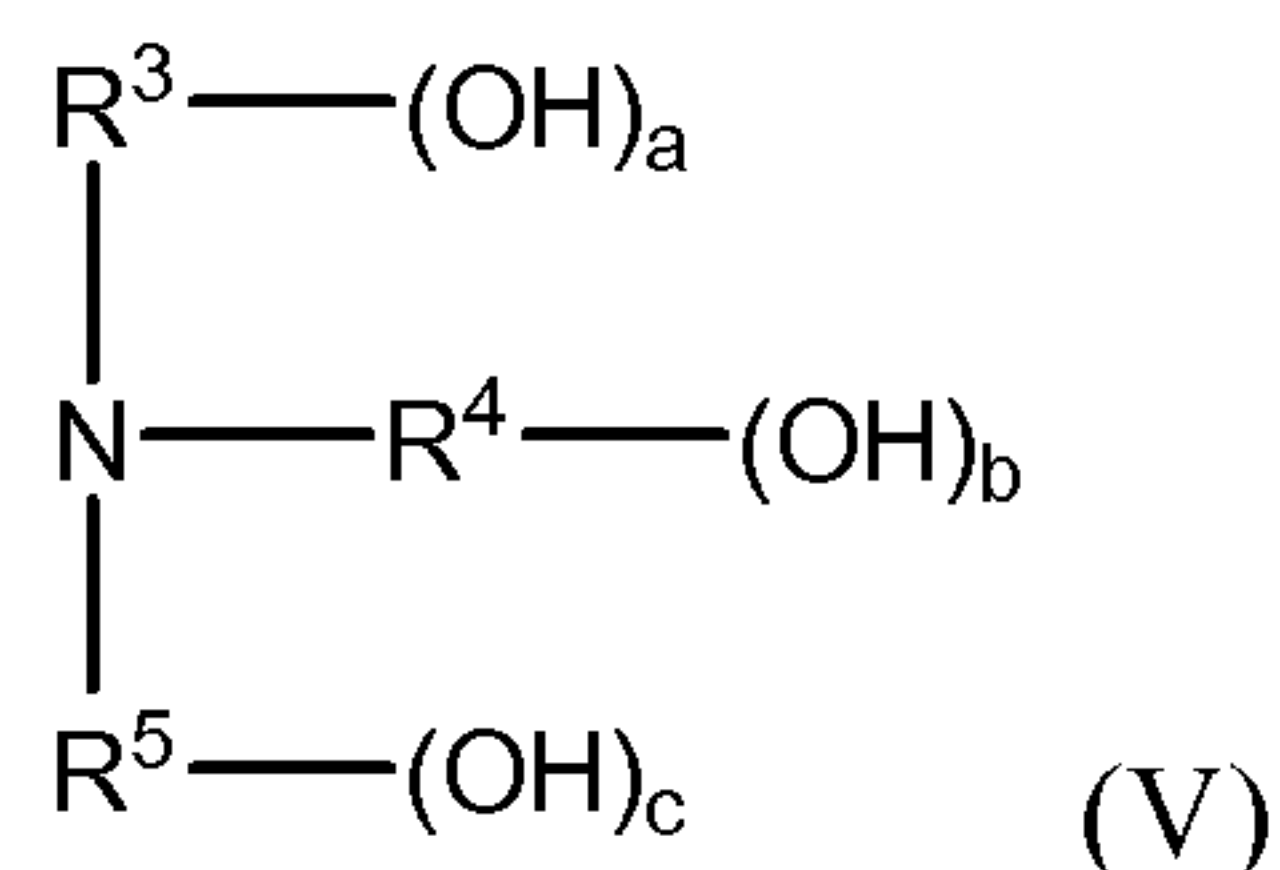
analogues also include hydroxyl-substituted oxyalkylene analogues). Such N-(hydroxyl-substituted hydrocarbyl) amines can be conveniently prepared by reaction of epoxides with afore-described amines and can be represented by the formula: $(R)(R)N-(-R^1O-)_x-H$ wherein x is a number from about 2 to about 15 and R and R^1 are as described above.

[0069] The alkali and alkaline earth metals that are useful as component (A)(II) 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.

Component B

[0070] Component (B) of the present invention is a compound having at least two hydroxyls and at least one tertiary amino group. This compound serves as the linking bridge between two of the component (A) moieties described above. Compounds suitable for use as component (B) can be described as di-hydroxy tertiary amines.

[0071] As noted above, in some embodiments component (B) includes at least one tertiary amine of the formula:

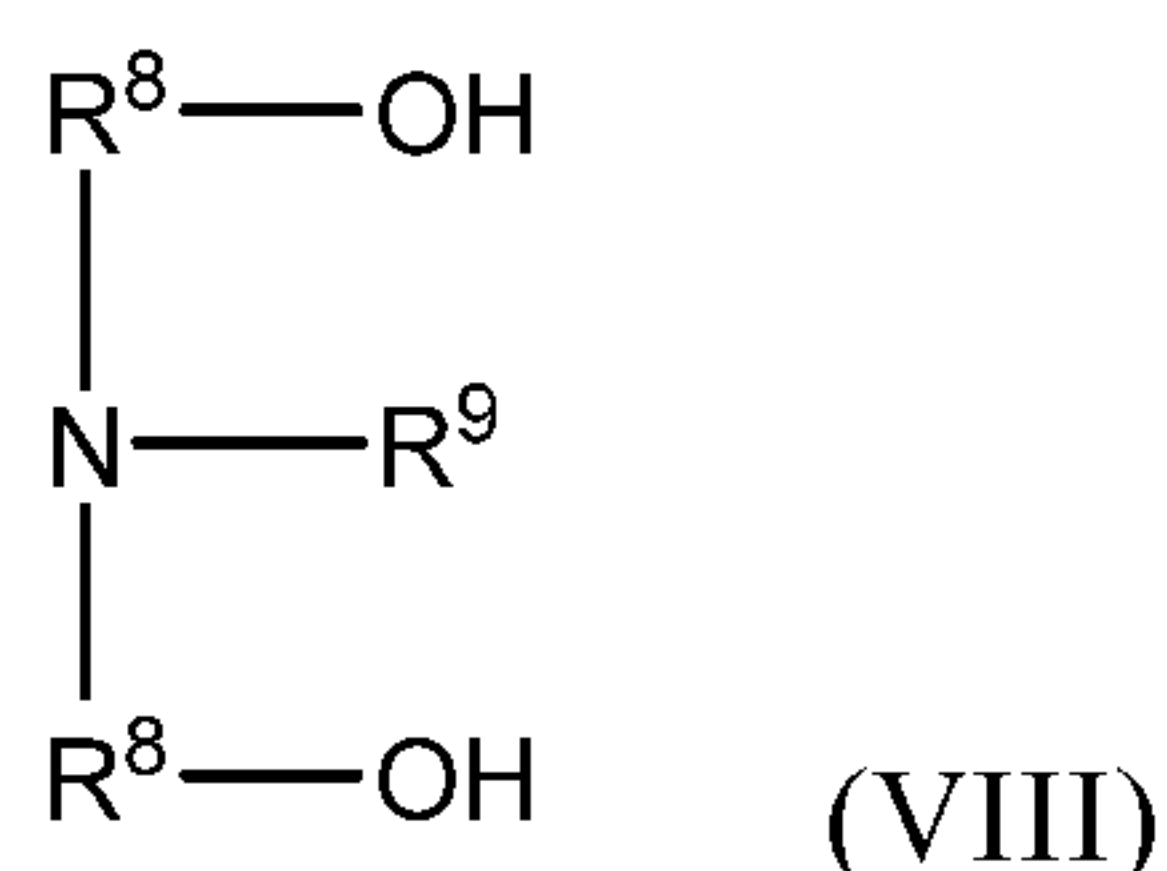


wherein each a , b , and c is independently 0 or 1 so long as the total of $a+b+c$ is at least 2, and wherein each R^3 , R^4 and R^5 is independently a hydrocarbon group containing from 1 to 50 carbon atoms or an $-(-R^6-O-)_n-$ group wherein R^6 is a alkenyl group containing from 1 to 6 carbon atoms, and in some embodiments 2 carbon atoms, and n is an integer from 1 to 50 or from 1 to 20.

[0072] In other words, so long as the compound contains two hydroxy groups, it may be suitable. In some embodiments R^3 , R^4 and/or R^5 in formula (V) are hydrocarbyl groups, or even alkenyl groups. In such embodiments, each $-OH$ shown in formula (V) above may be attached anywhere along the hydrocarbyl or

alkenyl group and are not necessarily present at the end of the group. In some embodiments the –OH groups are located at the end of the hydrocarbyl or alkenyl chain that serves as the individual R group. In some embodiments two –OH groups are attached to the same hydrocarbyl or alkenyl group, which may be branched. For example, the group $-R_1-(OH)_a$, or any of the other groups, may include $-CH_2-CH(OH)-CH_2-OH$. In other embodiments, the group $-R_1-(OH)_a$, or any of the other corresponding groups, may include, for example, $-CH_2-CH_2-OH$.

[0073] In some embodiments component (B) includes at least one tertiary amine of the formula:

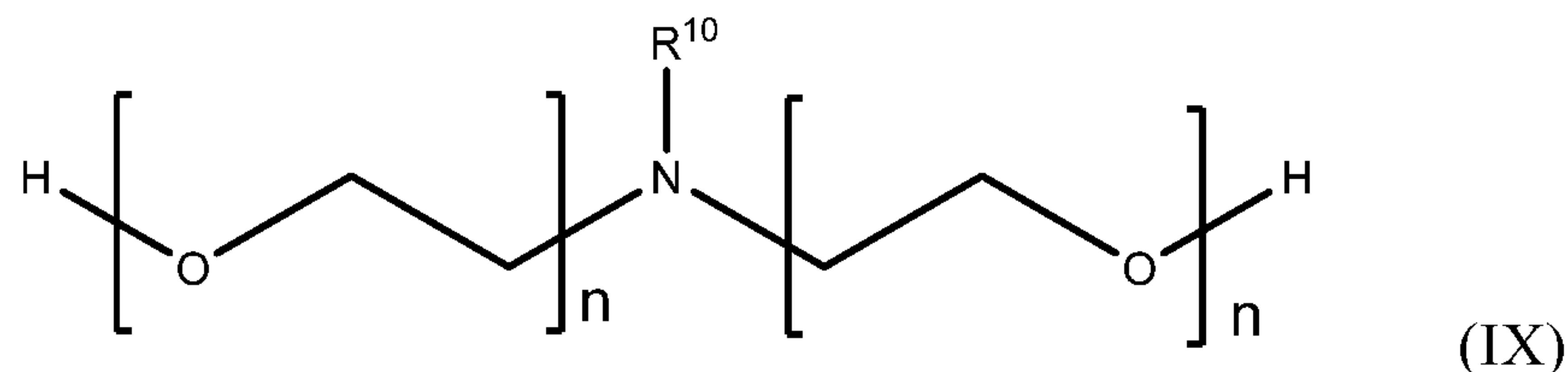


[0074] wherein each R^8 is independently a hydrocarbon group containing from 1 to 10 carbon atoms and where R^9 is a hydrocarbon group containing from 1 to 50 carbon atoms.

[0075] Suitable compounds include 3-(didodecylamino)propane-1,2-diol, N-methyldiethanolamine, N-ethyldiethanolamine, N-propyldiethanolamine, N-n-butyldiethanolamine, N-tert-butyldiethanolamine, N-cyclohexyldiethanolamine, N-2-ethylhexyldiethanolamine, N-amyldiethanolamine, N-isobutyldiethanolamine, N-sec-butyldiethanolamine, N-dodecyldiethanolamine, N-hexadecyldiethanolamine, , N-hydrogenated rapeseed alkyl diethanolamine, N-hydrogenated tallowalkyldiethanolamine, N-phenyldiethanolamine, N-m-tolyldiethanolamine.

[0076] Suitable tertiary amines also include Bis(2-hydroxyethyl)octadecylamine (also known as N-octadecyldiethanolamine), Bis(2-hydroxyethyl)cocoalkylamines (also known as N-cocoalkyldiethanolamine), Bis(2-hydroxyethyl)oleylamine (also known as N-oleyldiethanolamine), Bis(2-hydroxyethyl)soyaalkylamines (also known as N-soyaalkyldiethanolamine), Bis(2-hydroxyethyl)tallowalkylamines (also known as N-tallowalkyldiethanolamine), which are all commercially available from Akzo Nobel under Ethomeen™ trade names.

[0077] The materials above may be prepared by ethoxylating a primary amine. Further ethoxylation is also possible. Such materials, which are also suitable for use as component (B), may be represented by the formula:



wherein each n is independently an integer having the value of 1 to 50 or even 1 to 20 and R¹⁰ is a hydrocarbyl group containing from 1 to 50 or even from 1 to 20 carbon atoms. In some embodiments, both n's in formula (IX) have the same value.

[0078] Examples of such materials include Polyoxyethylene (5) octadecylamine, Polyoxyethylene (15) octadecylamine, Polyoxyethylene (5) cocoalkylamines, Polyoxyethylene (15) cocoalkylamines, Polyoxyethylene (5) soyaalkylamines, Polyoxyethylene (15) soyaalkylamines, Polyoxyethylene (5) tallowalkylamines, Polyoxyethylene (15) tallowalkylamines, Polyoxyethylene (20) tallowalkylamine, all of which are available commercially from Akzo Nobel under Ethomeen™ trade names.

[0079] Suitable materials may also be made by reacting a dialkylamine with either glycidol or chloroglycerin (3-chloro-1,2-propanediol). Examples of these materials include 3-(dimethylamino)-1,2-propanediol, 3-(diethylamino)-1,2-propanediol, 3-(dipropylamino)-1,2-propanediol, 3-(diisopropylamino)-1,2-propanediol, 3-(dioctadecylamino)-1,2-propanediol, 3-(dicocylalkylamino)-1,2-propanediol.

[0080] Combinations of any of the materials described above may also be used. In some embodiments component (B) includes 3-(didodecylamino)propane-1,2-diol, tallow-bis-(2-hydroxyethyl)amine, N-methyldiethanolamine, or combinations thereof, which may also be used in combination with any of the materials described above.

[0081] In some embodiments component (B) may further comprise one or more polyols, such as ethylene glycol. Such materials may also serve as the linking compound. However, to obtain the benefits of the present invention a substantial

portion of component (B) must be made up of one or more compounds having at least two hydroxyls and at least one tertiary amino group, as described above.

[0082] In some embodiments, component (B), and even all of the materials used to make the surfactant, are substantially free to free of non-amine containing polyols (which may also be described as nitrogen-free polyols). In other embodiments, component (B) may be no more than 40%, 25%, 10% or even 5% by weight non-amine containing polyols, thus allowing for some use of conventional polyols as the linking compound yet still obtaining at least a portion of the benefits of the present invention derived from the use of compounds having at least two hydroxyls and at least one tertiary amino group, as described above.

[0083] When the optional polyol is present useful materials include those compounds of the general formula: $R(OH)_m$ wherein R is a monovalent or polyvalent organic group joined to the -OH groups through carbon-to-oxygen bonds (that is, -COH wherein the carbon is not part of a carbonyl group) and m is an integer of from 2 to about 10, or from 2 to about 6. These alcohols can be aliphatic, cycloaliphatic, aromatic, and heterocyclic, including aliphatic-substituted cycloaliphatic alcohols, aliphatic-substituted aromatic alcohols, aliphatic-substituted heterocyclic alcohols, cycloaliphatic-substituted aliphatic alcohols, cycloaliphatic-substituted heterocyclic alcohols, heterocyclic-substituted aliphatic alcohols, heterocyclic-substituted cycloaliphatic alcohols, and heterocyclic-substituted aromatic alcohols. The polyhydric alcohols corresponding to the formula $R(OH)_m$ preferably contain not more than about 40 carbon atoms, more preferably not more than about 20 carbon atoms. The alcohols may contain non-hydrocarbon substituents or groups which do not interfere with the reaction of the alcohols with the hydrocarbyl-substituted carboxylic acids or anhydrides of this invention. 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 $-CH_2CH_2-X-CH_2CH_2$ where X is -O- or -S-).

[0084] Specific hydrocarbyl groups include methyl, butyl, dodecyl, tolyl, phenyl, naphthyl, dodecylphenyl, p-octylphenyl ethyl, cyclohexyl, and the like. Carboxylic acids useful in preparing the ester derivatives are mono- or polycarboxylic acids such as acetic acid, valeric acid, lauric acid, stearic acid,

succinic acid, and alkyl or alkenyl-substituted succinic acids wherein the alkyl or alkenyl group contains up to about 20 carbon atoms. Members of this class of alcohols are commercially available from various sources; e.g., PLURONICS, polyols available from Wyandotte Chemicals Corporation; POLYGLYCOL 112-2, a liquid triol derived from ethyleneoxide and propylene-oxide available from Dow Chemical Co.; polyalkylene glycols and various derivatives thereof, both available from Union Carbide Corporation. However, the alcohols used must have an average of at least two free alcoholic hydroxyl group per molecule of polyoxyalkylene alcohol. For purposes of describing these polyoxyalkylene alcohols, an alcoholic hydroxyl group is one attached to a carbon atom that does not form part of an aromatic nucleus.

[0085] Alcohols useful in this invention also include alkylene glycols and polyoxyalkylene alcohols such as polyoxyethylene alcohols, polyoxypropylene alcohols, polyoxybutylene alcohols, and the like. These polyoxyalkylene alcohols (sometimes called polyglycols) can contain up to about 150 oxyalkylene groups, with the alkylene group containing from about 2 to about 8 carbon atoms. Such polyoxyalkylene alcohols are generally dihydric alcohols. That is, each end of the molecule terminates with an OH group. In order for such polyoxyalkylene alcohols to be useful, there must be at least two OH groups.

[0086] The polyhydric alcohols useful in this invention include polyhydroxy aromatic compounds. Polyhydric phenols and naphthols are useful hydroxyaromatic compounds. These hydroxy-substituted aromatic compounds may contain other substituents in addition to the hydroxy substituents such as halo, alkyl, alkenyl, alkoxy, alkylmercapto, nitro and the like. Usually, the hydroxy aromatic compound will contain from 2 to about 4 hydroxy groups. The aromatic hydroxy compounds are illustrated by the following specific examples: resorcinol, catechol, p,p'-dihydroxy-biphenyl, hydroquinone, pyrogallol, phloroglucinol, hexylresorcinol, orcinol, etc.

[0087] The polyhydric alcohols preferably contain from 2 to about 10 hydroxy groups. They are illustrated, for example, by the alkylene glycols and polyoxyalkylene glycols mentioned above such as ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, dipropylene glycol, tripropylene

glycol, dibutylene glycol, tributylene glycol, and other alkylene glycols and polyoxyalkylene glycols in which the alkylene groups contain from 2 to about 8 carbon atoms.

[0088] Other useful polyhydric alcohols include glycerol, monooleate of glycerol, monostearate of glycerol, monomethyl ether of glycerol, pentaerythritol, n-butyl ester of 9,10-dihydroxy stearic acid, methyl ester of 9,10-dihydroxy stearic acid, 1,2-butanediol, 2,3-hexanediol, 2,4-hexanediol, pinacol, erythritol, arabitol, sorbitol, mannitol, 1,2-cyclohexanediol, and xylene glycol. Carbohydrates such as sugars, starches, celluloses, and so forth likewise can be used. The carbohydrates may be exemplified by glucose, fructose, sucrose, rhamose, mannose, glyceraldehyde, and galactose.

[0089] Polyhydric alcohols having at least 3 hydroxyl groups, some, but not all of which have been esterified with an aliphatic monocarboxylic acid having from about 8 to about 30 carbon atoms such as octanoic acid, oleic acid, stearic acid, linoleic acid, dodecanoic acid or tall oil acid are useful. Further specific examples of such partially esterified polyhydric alcohols are the monooleate of sorbitol, distearate of sorbitol, monooleate of glycerol, monostearate of glycerol, didodecanoate of erythritol, and the like.

[0090] Useful alcohols also include those polyhydric alcohols containing up to about 12 carbon atoms, and especially those containing from about 3 to about 10 or 6 carbon atoms. This class of alcohols includes glycerol, erythritol, pentaerythritol, dipentaerythritol, gluconic acid, mannitol, sorbitol, glyceraldehyde, glucose, arabinose, 1,7-heptanediol, 2,4-heptanediol, 1,2,3-hexanetriol, 1,2,4-hexanetriol, 1,2,5-hexanetriol, 2,3,4-hexanetriol, 1,2,3-butanetriol, 1,2,4-butanetriol, quinic acid, 2,2,6,6-tetrakis-(hydroxymethyl)cyclohexanol, 1,10-decanediol, digitalose, 2-hydroxy-methyl-2-methyl-1,3-propanediol-(trimethylolethane), 2-hydroxymethyl-2-ethyl-1,3-propanediol(trimethylopropane), and the like. Aliphatic alcohols containing at least about 3 hydroxyl groups and up to about 10 carbon atoms are useful.

[0091] In some embodiments, where component (B) contains a mixture of (i) one or more compounds having at least two hydroxyls and at least one tertiary amino group and (ii) one or more polyols or polyhydric alcohols, the ratio of (i) to

(ii), on a molar basis can be from 1:0.5 to 10:1 or from 1:1 to 5:1, or from 2:1 to 3:1 or even from 2.5:1 to 3:1 or even about 2.7:1. Not wishing to be bound by theory, it is believed that having at least an equal mix, or even at least some excess of compounds having at least two hydroxyls and at least one tertiary amino group over nitrogen-free polyols, is necessary to obtain the primary benefits of the invention.

Formation of the Salt Compositions

[0092] The salt compositions of the invention can be prepared by initially reacting the acylating agents (A)(I) with component (B) to form an intermediate, and thereafter reacting said intermediate with component (A)(II) to form the desired salt. An alternative, though less efficient method of preparing these salt compositions involves reacting components (A)(I) and (A)(II) with each other to form the salt moieties, and then reacting the salt moieties with component (B).

[0093] The ratio of reactants utilized in the preparation of the inventive salt compositions may be varied. Generally, for each equivalent of acylating agents (A)(I) at least about one-half equivalent of component (B) is used. From about 0.1 to about 2 equivalents or more of component (A)(II) is used for each equivalent of component (A)(I) respectively. The upper limit of component (B) is about 1 equivalent, based on -OH groups, of component (B) for each equivalent of component (A)(I), based on carboxyl groups.

[0094] In some embodiments the reactants are used such that from 0.2 to 1.0 or even 0.4 to 0.6 equivalents of the component (B), and from 0.2 to about 2.0, or from 0.2 to 1.0, or even from 0.4 to 0.6 equivalents of component (A)(II). are used for each equivalent of component (A)(I).

[0095] The number of equivalents of the acylating agent (A)(I) depends on the total number of carboxylic functions present in each. In determining the number of equivalents for each of the acylating agents present in (A)(I) 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 (A)(I) 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 in (A)(I) can be readily determined by one skilled in the art.

[0096] The acylating agent (A)(I) can be reacted with component (B) according to conventional ester- and/or amide-forming techniques. This normally involves heating acylating agent (A)(I) with component (B), optionally in the presence of a normally liquid, substantially inert, organic liquid solvent/diluent. Temperatures of at least about 30 degrees C up to the decomposition temperature of the reaction component and/or product having the lowest such temperature can be used. This temperature is preferably in the range of about 50 to about 130 degrees C, more preferably about 80 to about 100 degrees C when the acylating agent (A)(I) is an anhydride. On the other hand, when the acylating agent (A)(I) is an acids, this temperature is preferably in the range of about 100 to about 300 degrees C with temperatures in the range of about 125 to 250 degrees C often being employed.

[0097] The reactions between components (A)(I) and (A)(II) are carried out under salt forming conditions using conventional techniques. Typically, components (A)(I) and (A)(II) are mixed together and heated to a temperature in the range of about 20 degrees C up to the decomposition temperature of the reaction component and/or product having the lowest such temperature about 20 to 130 degrees C, or about 40 to 110 degrees C; optionally, in the presence of a normally liquid, substantially inert organic liquid solvent/diluent, until the desired product has formed.

[0098] The product of the reaction between components (A)(I) and (A)(II) must contain at least some salt linkage to permit said product to be effective as an emulsifier in accordance with the invention. In some embodiments at least about 10%, at least about 30%, at least about 50%, or even at least about 70%, and advantageously up to about 100% of component (A)(II) that reacts with the acylating agents (A)(I), respectively, form a salt linkage.

Explosive Compositions

[0099] The explosive compositions of the invention are water-in-oil emulsions which, in one embodiment, are cap-sensitive water-in-oil emulsion explosives and in another embodiment are booster-sensitive water-in oil emulsion explosives. These emulsion explosives employ the salt compositions of the invention as

emulsifiers. The explosive emulsions comprise a discontinuous oxidizer phase comprising at least one oxygen-supplying component, a continuous organic phase comprising at least one carbonaceous fuel, and an emulsifying amount of at least one of the salt compositions of the invention.

[0100] The continuous organic phase may be present at a level of at least about 2% by weight, or in the range of from about 2% to about 15% by weight, or from about 3.5% to about 8% by weight based on the total weight of explosive emulsion. The discontinuous oxidizer phase may be present at a level of at least about 85% by weight, or in the range of from about 85% to about 98% by weight, or from about 92% to about 96.5% by weight based on the total weight of said explosive emulsion. The salt compositions of the invention may be present at a level in the range of from about 4% to about 40% by weight, or from about 12% to about 20% by weight based on the total weight of the organic phase. An oxygen-supplying component may be present at a level in the range of from about 70% to about 95% by weight, or from about 85% to about 92% by weight, or from about 87% to about 90% by weight based on the total weight of the oxidizer phase. The water may be present at a level in the range of about 5% to about 30% by weight, or from about 8% to about 15% by weight, or from about 10% to about 13% by weight based on the weight of the oxidizer phase.

[0101] The carbonaceous fuel that is useful in the explosive emulsions of the invention can include most hydrocarbons, for example, paraffinic, olefinic, naphthenic, aromatic, saturated or unsaturated hydrocarbons, and is typically in the form of an oil or a wax or a mixture thereof. In general, the carbonaceous fuel is a water-immiscible, emulsifiable hydrocarbon that is either liquid or liquefiable at a temperature of up to about 95.degree. C., and preferably between about 40.degree. C. and about 75.degree. C. Oils from a variety of sources, including natural and synthetic oils and mixtures thereof can be used as the carbonaceous fuel.

[0102] 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 hydrocarbon oils such as polymerized and interpolymers of olefins (e.g.,

polybutylenes, polypropylenes, propylene-isobutylene copolymers, chlorinated polybutylenes, etc.); alkyl benzenes (e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di-(2-ethylhexyl) benzenes, etc.); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenyls, etc.); and the like.

[0103] 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-ethyl-hexanoic acid, and the like.

[0104] 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.

[0105] 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-methyl-hexyl)-silicate, tetra(p-tert-butylphenyl)-silicate, hexyl-(4-methyl-2-pentoxy)-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.

[0106] 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.

[0107] 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.

[0108] The carbonaceous fuel can be any wax having melting point of at least about 25.degree. C., such as petrolatum wax, microcrystalline wax, and paraffin wax, mineral waxes such as ozocerite and montan wax, animal waxes such as spermacetic wax, and insect waxes such as beeswax and Chinese wax. Useful waxes include waxes identified by the trade designation MOBILWAX 57 which is available from Mobil Oil Corporation; D02764 which is a blended wax available from Astor Chemical Ltd.; and VYBAR which is available from Petrolite Corporation. Preferred waxes are blends of microcrystalline waxes and paraffin.

[0109] In one embodiment, the carbonaceous fuel includes a combination of a wax and an oil. In this embodiment, the wax content is at least about 25% and preferably ranges from about 25% to about 90% by weight of the organic phase, and the oil content is at least about 10% and preferably ranges from about 10% to about 75% by weight of the organic phase. These mixtures are particularly suitable for use in cap-sensitive explosive emulsions.

[0110] While its presence is not necessary, the explosive emulsions can also contain up to about 15% by weight of an auxiliary fuel, such as aluminum, aluminum alloys, magnesium, and the like. Particulate aluminum is a preferred auxiliary fuel.

[0111] The oxygen-supplying component is preferably at least one inorganic oxidizer salt such as ammonium, alkali or alkaline earth metal nitrate, chlorate or perchlorate. Examples include ammonium nitrate, sodium nitrate, calcium nitrate, ammonium chlorate, sodium perchlorate and ammonium perchlorate. Ammonium nitrate is especially preferred. Mixtures of ammonium nitrate and sodium or calcium nitrate are also preferred. In one embodiment, inorganic oxidizer salt comprises principally ammonium nitrate, although up to about 25% by weight of the oxidizer phase can comprise either another inorganic nitrate (e.g., alkali or alkaline earth metal nitrate) or an inorganic perchlorate (e.g., ammonium perchlorate or an alkali or alkaline earth metal perchlorate) or a mixture thereof.

[0112] In one embodiment of the invention, closed cell, void-containing materials are used as sensitizing components. The term "closed-cell, void-containing material" is used herein to mean any particulate material which comprises closed cell, hollow cavities. Each particle of the material can contain one or more closed cells, and the cells can contain a gas, such as air, or can be evacuated or partially evacuated. In one embodiment of the invention, sufficient closed cell void containing material is used to yield a density in the resulting emulsion of from about 0.8 to about 1.35 g/cc, more preferably about 0.9 to about 1.3 g/cc, more preferably about 1.1 to about 1.3 g/cc. In general, the emulsions of the subject invention can contain up to about 15% by weight, preferably from about 0.25% to about 15% by weight of the closed cell void containing material. Preferred closed cell void containing materials are discrete glass spheres having a particle size within the range of about 10 to about 175 microns. In general, the bulk density of such particles can be within the range of about 0.1 to about 0.4 g/cc. Useful glass microbubbles which can be used are the microbubbles sold by 3M Company and which have a particle size distribution in the range of from about 10 to about 160 microns and a nominal size in the range of about 60 to 70 microns, and densities in the range of from about 0.1 to about 0.4 g/cc.; these include microbubbles distributed under the trade designation B15/250. Other useful glass microbubbles are sold under the trade designation of ECCOSPHERES by Emerson & Cumming, Inc., and generally have a particle size range from about 44 to about 175 microns and a bulk density of about 0.15 to about 0.4 g/cc. Other suitable microbubbles

include the inorganic microspheres sold under the trade designation of Q-CEL by Philadelphia Quartz Company. The closed cell void containing material can be made of inert or reducing materials. For example, phenol-formaldehyde microbubbles can be utilized within the scope of this invention. If the phenol-formaldehyde microbubbles are utilized, the microbubbles themselves are a fuel component for the explosive and their fuel value should be taken into consideration when designing a water-in-oil emulsion explosive composition. Another closed cell void containing material which can be used within the scope of the subject invention is the saran microspheres sold by Dow Chemical Company. The saran microspheres have a diameter of about 30 microns and a particle density of about 0.032 g/cc. Because of the low bulk density of the saran microspheres, it is preferred that only from about 0.25 to about 1% by weight thereof be used in the water-in-oil emulsions of the subject invention.

[0113] Gas bubbles which are generated in-situ by adding to the composition and distributing therein a gas generating material such as, for example, an aqueous solution of sodium nitrite, can also be used can be used to sensitize the explosive emulsions. Other suitable sensitizing components which may be employed alone or in addition to the foregoing include insoluble particulate solid self-explosives such as, for example, grained or flaked TNT, DNT, RDX and the like and water-soluble and/or hydrocarbon-soluble organic sensitizers such as, for example, amine nitrates, alkanolamine nitrates, hydroxyalkyl nitrates, and the like. The explosive emulsions of the present invention may be formulated for a wide range of applications. Any combination of sensitizing components may be selected in order to provide an explosive composition of virtually any desired density, weight-strength or critical diameter. The quantity of solid self-explosive ingredients and of water-soluble and/or hydrocarbon-soluble organic sensitizers may comprise up to about 40% by weight of the total explosive composition. The volume of the occluded gas component may comprise up to about 50% of the volume of the total explosive composition.

[0114] Optional additional materials may be incorporated in the explosive emulsions of the invention in order to further improve sensitivity, density, strength, rheology and cost of the final explosive. Typical of materials found useful as

optional additives include, for example, particulate non-metal fuels such as sulfur, gilsonite and the like, particulate inert materials such as sodium chloride, barium sulphate and the like, water phase or hydrocarbon phase thickeners such as guar gum, polyacrylamide, carboxymethyl or ethyl cellulose, biopolymers, starches, elastomeric materials, and the like, crosslinkers for the thickeners such as potassium pyroantimonate and the like, buffers or pH controllers such as sodium borate, zinc nitrate and the like, crystals habit modifiers such as alkyl naphthalene sodium sulphonate and the like, liquid phase extenders such as formamide, ethylene glycol and the like and bulking agents and additives of common use in the explosives art. The quantities of optional additional materials used may comprise up to about 50% by weight of the total explosive emulsion.

[0115] One method for making the explosive emulsions of the invention comprises the steps of (1) mixing water, inorganic oxidizer salts (e.g., ammonium nitrate) and, in certain cases, some of the supplemental water-soluble compounds, in a first premix, (2) mixing the carbonaceous fuel, the emulsifying salt compositions of the invention and any other optional oil-soluble compounds, in a second premix and (3) adding the first premix to the second premix in a suitable mixing apparatus, to form a water-in-oil emulsion. The first premix is heated until all the salts are completely dissolved and the solution may be filtered if needed in order to remove any insoluble residue. The second premix is also heated to liquefy the ingredients. Any type of apparatus capable of either low or high shear mixing can be used to prepare these water-in-oil emulsions. Closed cell void containing materials, gas-generating materials, solid self-explosive ingredients such as particulate TNT, solid fuels such as aluminum or sulfur, inert materials such as barytes or sodium chloride, undissolved solid oxidizer salts and other optional materials, if employed, are added to the emulsion and simply blended until homogeneously dispersed throughout the composition.

[0116] The water-in-oil explosive emulsions of the invention can also be prepared by adding the second premix liquefied organic solution phase to the first premix hot aqueous solution phase with sufficient stirring to invert the phases. However, this method usually requires substantially more energy to obtain the desired dispersion than does the preferred reverse procedure. Alternatively, these

water-in-oil explosive emulsions are particularly adaptable to preparation by a continuous mixing process where the two separately prepared liquid phases are pumped through a mixing device wherein they are combined and emulsified.

[0117] The salt compositions of this invention can be added directly to the inventive explosive emulsions. They can also be diluted with a substantially inert, normally liquid organic diluent such as mineral oil, naphtha, benzene, toluene or xylene, to form an additive concentrate. These concentrates usually contain from about 10% to about 90% by weight of the salt composition of this invention and may contain, in addition, one or more other additives known in the art or described hereinabove.

[0118] 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. The products formed thereby, including the products formed upon employing the composition of the present invention in its intended use, may not be susceptible of easy description. Nevertheless, all such modifications and reaction products are included within the scope of the present invention; the present invention encompasses the composition prepared by admixing the components described above.

EXAMPLES

[0119] The following examples illustrate the preparation of the salt compositions of this invention. Unless otherwise indicated, in the following examples and elsewhere in the specification and claims, all parts and percentages are by weight, and all temperatures are in degrees centigrade (C). While the examples are provided to illustrate the present invention, they are not intended to limit it.

Comparative Example 1.

[0120] A surfactant is prepared by reacting, in a 3 liter reaction flask under a nitrogen blanket, 1033 grams of mid-molecular weight polyisobutylene succinic anhydride (PIBSA), which itself is derived from 1000 number average molecular weight (Mn) polyisobutylene (PIB) and 31 grams of ethylene glycol. The reaction is carried out in diluent oil at a temperature of about 85 degrees C. The ethylene glycol is added to the PIBSA over time and the reaction is given three hours to

complete. The reaction results in a diol coupled diester with a calculated yield of 99%. 402 grams (on an actives basis) of the resulting coupled diester is charged to a 1 liter reaction flask and reacted with 44 grams of diethylethanolamine. The reaction is carried out in diluent oil at a temperature of about 45 to 50 degrees C. The amine is charged over time and the reaction is given 2 hours to complete. The resulting surfactant is a diol coupled salt with a calculated yield of 99% and a total acid number (TAN) of 28.6 compared to a theory TAN of 31.7. This is a comparative example.

Example 2.

[0121] A surfactant is prepared by reacting, in a 5 liter reaction flask under a nitrogen blanket, 2008 grams of the PIBSA described in Example 1 above and 344 grams of tallow-bis(2-hydroxyethyl) amine. The reaction is carried out in diluent oil at a temperature of about 85 degrees C. The amine diol is added to the PIBSA over time and the reaction is given three hours to complete. The reaction results in a diol amine coupled diester with a calculated yield of 100%. 402 grams (on an actives basis) of the resulting coupled diester is charged to a 1 liter reaction flask and reacted with 39 grams of diethylethanolamine. The reaction is carried out in diluent oil at a temperature of about 45 to 50 degrees C. The amine is charged over time and the reaction is given 2 hours to complete. The resulting surfactant is a diol amine coupled salt with a calculated yield of 100% and a TAN of 28.3 compared to a theory TAN of 28.2.

Example 3.

[0122] A surfactant is prepared by reacting, in a 1 liter reaction flask under a nitrogen blanket, 450 grams of the PIBSA described in Example 1 above and 26 grams of N-methyldiethanolamine. The reaction is carried out in diluent oil at a temperature of about 92 degrees C. The amine diol is added to the PIBSA over time and the reaction is given three hours to complete. The reaction results in a diol amine coupled diester that immediately salted. 39 grams of dimethylethanolamine is added to the salt from the first step. The reaction is carried out in diluent oil at a temperature of about 45 to 50 degrees C. The amine is charged over time and the reaction is given 2 hours to complete. The resulting surfactant is a diol amine

coupled salt with a calculated yield of 91% and a TAN of 33.3 compared to a theory TAN of 31.7.

Example 4.

[0123] A surfactant is prepared by reacting, in a 2 liter reaction flask under a nitrogen blanket, 900 grams of the PIBSA described in Example 1 above and 112 grams of tallow-bis(2-hydroxyethyl) amine. The reaction is carried out in diluent oil at a temperature of about 85 to 90 degrees C. The amine diol is added to the PIBSA over time and the reaction is given one hour and then 7.3 grams of ethylene glycol is added over time, maintaining the reaction at a temperature of about 85 to 90 degrees C. The reaction results in a diol amine coupled diester that also include some diol coupling. The product immediately salted. 102 grams of diethylethanolamine is added to the salt from the first step. The reaction is carried out in diluent oil at a temperature of about 45 to 50 degrees C. The amine is charged over time and the reaction is given 2 hours to complete. The resulting surfactant is a diol amine coupled salt with a calculated yield of 94% and a TAN of 29.5 compared to a theory TAN of 29.1.

Example 5.

[0124] A surfactant is prepared by reacting, in a 1 liter reaction flask, 335 grams (on an actives basis, that is oil and/or solvent free) a coupled diester prepared according to the first part of Example 2 above, with 16 grams of diethylethanolamine. The reaction is carried out in diluent oil at a temperature of about 45 to 50 degrees C. The amine is charged over time and the reaction is given 2 hours to complete. The resulting surfactant is a diol amine coupled salt with a calculated yield of 99% and a TAN of 34.4 compared to a theory TAN of 29.5, and was achieved with a reduced amine charge relative to Example 2.

Example 6.

[0125] A surfactant is prepared by reacting, in a 1 liter reaction flask, 335 grams (on an actives basis) of the resulting coupled diester prepared in the first step of Example 2 above, with 24 grams of diethylethanolamine. The reaction is carried out in diluent oil at a temperature of about 45 to 50 degrees C. The amine is charged over time and the reaction is given 2 hours to complete. The resulting surfactant is a diol amine coupled salt with a calculated yield of 99% and a TAN of

34.0 compared to a theory TAN of 28.8, and was achieved with an intermediate amine charge relative to Examples 2 and 5.

Emulsion Evaluations

[0126] Examples 1 to 6 are used to prepare emulsions with an aqueous ammonium nitrate oxidizer phase and an organic fuel phase. The same aqueous ammonium nitrate oxidizer phase is used in each of the samples. The organic fuel phase is either 100N diluent oil or diesel fuel, as marked. Emulsions are characterized by examination under a microscope. The emulsions are then subjected to a series of stress and stability tests, detailed below.

[0127] Two shear tests were employed. A low shear paint shaker test is used, which simulates transportation of the emulsion explosive, from the production site to the work site where it would be used. For this test the emulsion explosive composition is placed in a paint shaker for four hours. A high shear syringe test simulates pumping the emulsion explosive, for example from a storage container into a bore hole where it will be detonated. In this test the emulsion is injected through a small orifice of a syringe under pressure. Testing is conducted at 30 and 50 psi injection pressure.

[0128] Two stability tests are employed. In the ambient storage test in the emulsion is stored for 30 days at ambient temperature and then evaluated. In the thermal cycling test the emulsion is held at -30°C for six hours and then held at +50°C for six hours. The emulsion is then evaluated after five and ten of these cycles in this accelerated aging test.

[0129] Fresh (untested) and stressed/aged (tested) emulsions were evaluated under a microscope, in order to evaluate each sample's performance. The evaluation using the microscope includes measuring the amount of ammonium nitrate crystallisation, with lower crystallization being desired. The lower the % coverage (crystal count) the more stable the emulsion. Generally, crystal counts below 5% are classed as a good pass; borderline emulsions have between 5 and 10% crystal count and fails have more than 10% crystallisation. The results of this testing are summarized in the tables below:

Table A – Percent Crystallization in Diesel Fuel Emulsions, Run 1⁵.

Sample ID	Surfactant ID	Fresh Emulsion	After 50 PSI Syringe Test	After 4 HR Shaker Test	After 10 Cycle Thermal Test	After 30 Day Ambient Test
A-1	Comp 1 ¹	0.00	0.25	0.01	1.17	0.02
A-2	Comp 2 ²	0.06	0.11	0.05	0.54	0.02
A-3	Comp 3 ³	0.02	0.09	CRYST ⁴	0.26	0.01
A-4	Example 3	0.05	0.15	0.05	0.37	0.04

1 – Comparative Surfactant 1 is a salt formed from a high molecular weight hydrocarbyl substituted succinic anhydride and a tertiary alkanolamine, and does not have a coupled structure.

2 – Comparative Surfactant 2 is an ethylene glycol coupled surfactant prepared from a 1:1 mixture of mid molecular weight hydrocarbyl substituted succinic anhydride and a low molecular weight hydrocarbyl substituted succinic anhydride where the two anhydrides are linked by ethylene glycol and the resulting compound is salted with a tertiary alkanolamine.

3 – Comparative Surfactant 3 is premium surfactant package that mixes Comparative Surfactants 1 and 2, making it more complex to produce and more expensive.

4 – This indicates the sample crystallized during the test, which is a severe failure.

5 – Each of the emulsions in Table A has the same formulation but differ in the surfactant used. Each emulsion uses the same aqueous phase and the same diesel fuel in the same amounts, and each sample uses its specific surfactant at a 0.8% by weight actives level.

Table B – Percent Crystallization in Diesel Fuel Emulsions, Run 2⁴.

Sample ID	Surfactant ID	Fresh Emulsion	After 50 PSI Syringe Test	After 4 HR Shaker Test	After 10 Cycle Thermal Test	After 30 Day Ambient Test
B-1	Comp 1 ¹	0.02	0.03	0.01	0.31	0.01
B-2	Comp 2 ²	0.01	0.02	0.05	0.45	0.01
B-3	Example 1 ³	0.04	0.38	0.20	1.25	0.20
B-4	Example 2	0.03	0.02	0.06	0.77	0.02

1 – Comparative Surfactant 1 is the same as that defined in Table A above.

2 – Comparative Surfactant 2 is the same as that defined in Table A above.

3 – Example 1 is a comparative example as it does not contain a tertiary amine diol linkage.

4 – Each of the emulsions in Table B has the same formulation but differ in the surfactant used. Each emulsion uses the same aqueous phase and the same diesel fuel in the same amounts, and each sample uses its specific surfactant at a 0.8% by weight actives level.

Table C – Percent Crystallization in 100N Oil Emulsions, Run 3⁵.

Sample ID	Surfactant ID	Fresh Emulsion	After 50 PSI Syringe Test	After 4 HR Shaker Test	After 10 Cycle Thermal Test	After 30 Day Ambient Test
C-1	Comp 1 ¹	0.03	87.96	0.07	0.1	0.01
C-2	Comp 2 ²	0.01	2.23	0.01	0.06	0.01
C-3	Comp 3 ³	0.01	24.61	15.56	0.02	0.01
C-4	Example 1 ⁴	0.09	25.73	0.06	0.38	0.13
C-5	Example 2	0.03	35.85	0.02	0.24	0.03

1 – Comparative Surfactant 1 is the same as that defined in Table A above.

2 – Comparative Surfactant 2 is the same as that defined in Table A above.

3 – Comparative Surfactant 3 is the same as that defined in Table A above.

4 – Example 1 is a comparative example as it does not contain a tertiary amine diol linkage.

5 – Each of the emulsions in Table C has the same formulation but differ in the surfactant used. Each emulsion uses the same aqueous phase and the same 100N oil in the same amounts, and each sample uses its specific surfactant at a 0.8% by weight actives level.

Table D – Percent Crystallization in 100N Oil Emulsions, Run 4³.

Sample ID	Surfactant ID	Fresh Emulsion	After 50 PSI Syringe Test	After 4 HR Shaker Test	After 10 Cycle Thermal Test	After 30 Day Ambient Test
D-1	Comp 3 ¹	0.01	92.42	CRYST ²	0.08	NOT TESTED
D-2	Example 4	0.02	86.69	0.05	0.19	NOT TESTED

1 – Comparative Surfactant 3 is the same as that defined in Table A above.

2 – This indicates the sample crystallized during the test, which is a severe failure.

3 – Each of the emulsions in Table D has the same formulation but differ in the surfactant used. Each emulsion uses the same aqueous phase and the same 100N oil in the same amounts, and each sample uses its specific surfactant at a 0.8% by weight actives level.

[0130] Two stability tests are employed. In the ambient storage test in the emulsion is stored for 30 days at ambient temperature and then evaluated. In the thermal cycling test the emulsion is held at -30°C for six hours and then held at +50°C for six hours. The emulsion is then evaluated after five and ten of these cycles in this accelerated aging test.

[0131] The results show that the surfactants of the present invention, and the emulsion made from the same, address one or more of the problems described above. For example, the data shows that the compositions of the present invention can provide at least comparable performance in a less complex and less expensive surfactant package. The data also shows that the compositions of the present invention can provide improved stability performance, specifically with regards to stability during transportation of the emulsion, while maintaining sufficient performance in other areas.

[0132] Each of the documents referred to above is incorporated herein by reference. 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." Unless otherwise indicated, all percent values, ppm values and parts values are on a weight basis. 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. However, the amount of each chemical component is presented exclusive of any solvent or diluent oil, which may be customarily present in the commercial material, unless otherwise indicated. 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. As used herein, the expression "consisting essentially of" permits the inclusion of substances that do not materially affect the basic and novel characteristics of the composition under consideration.

We claim:

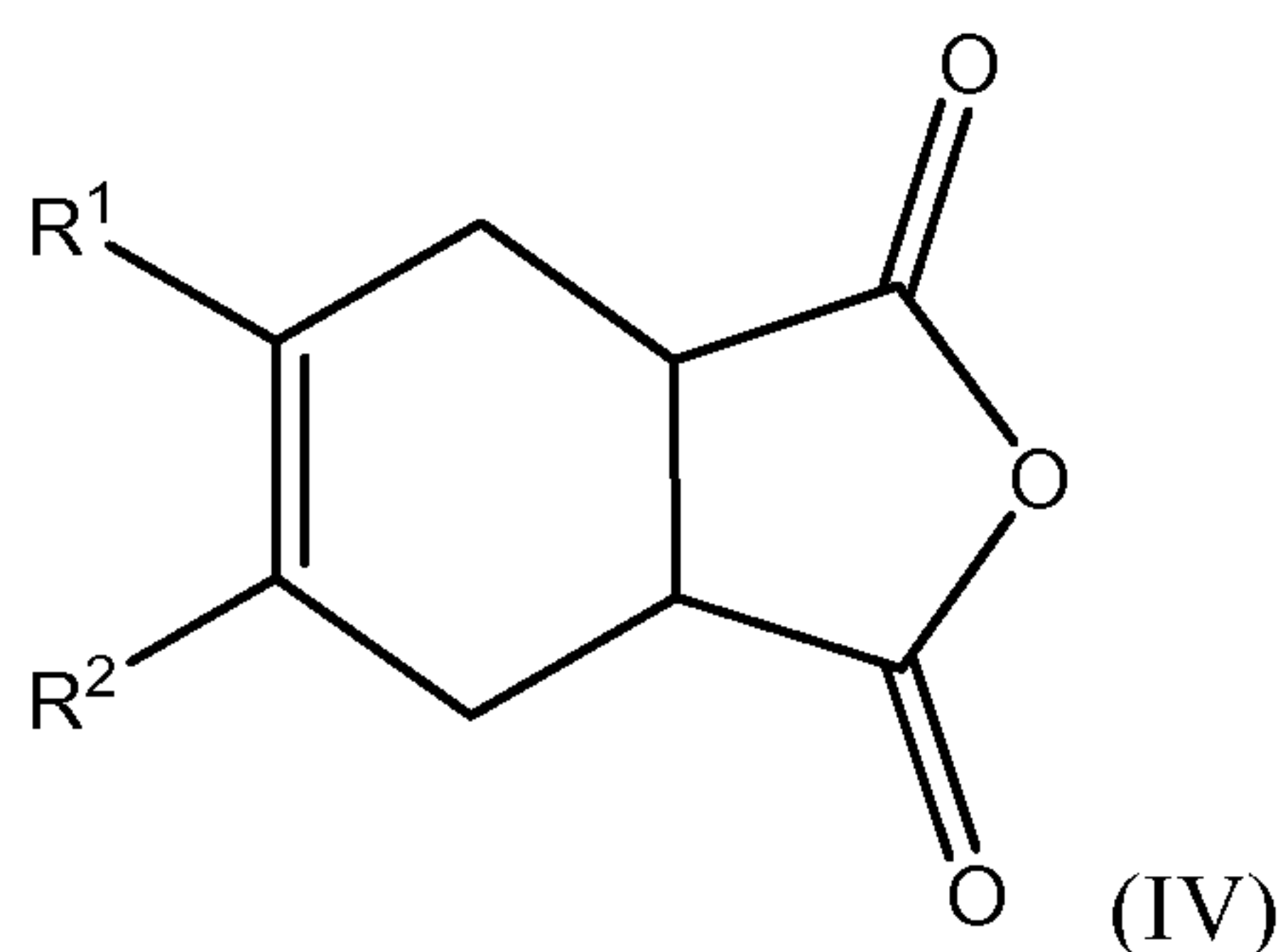
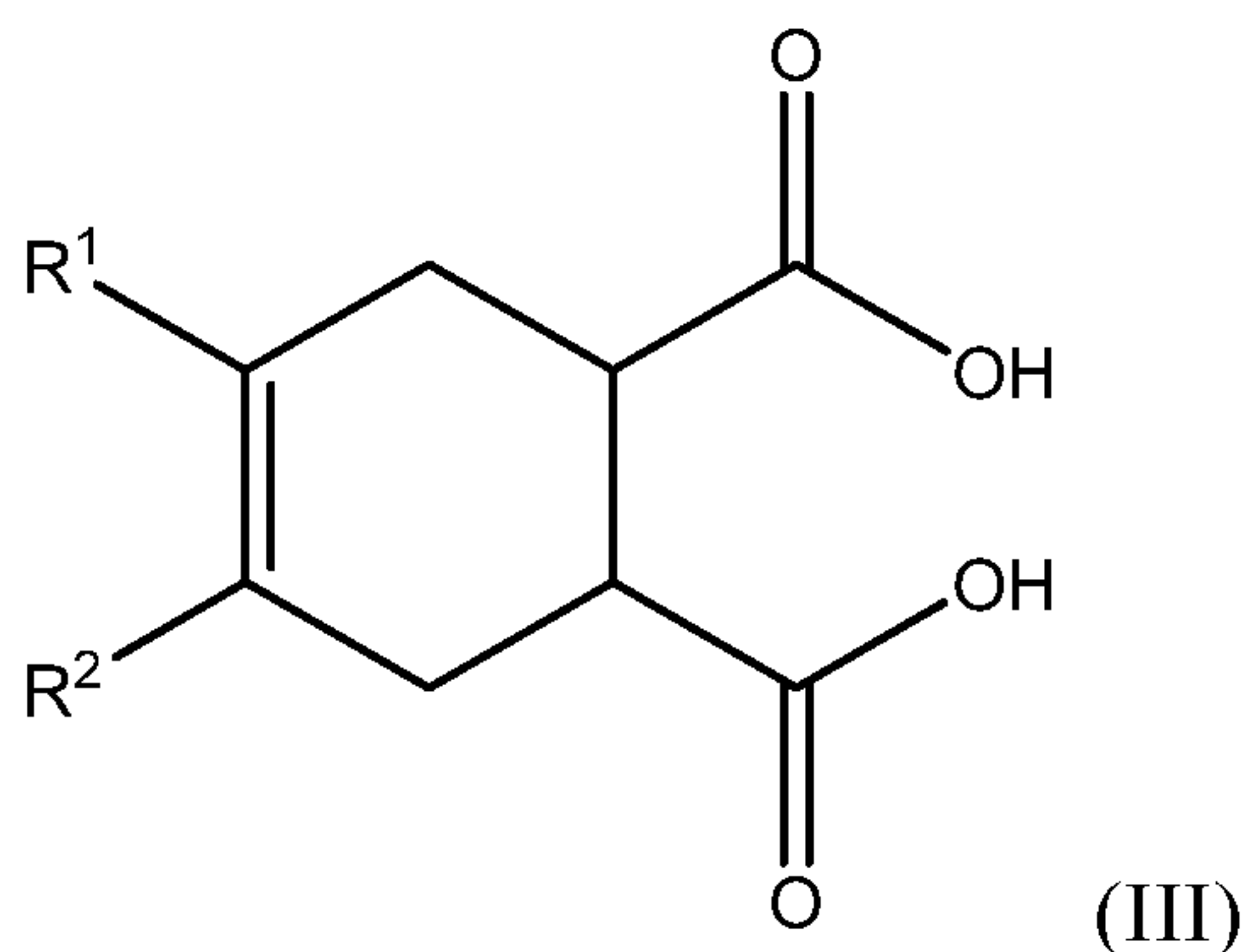
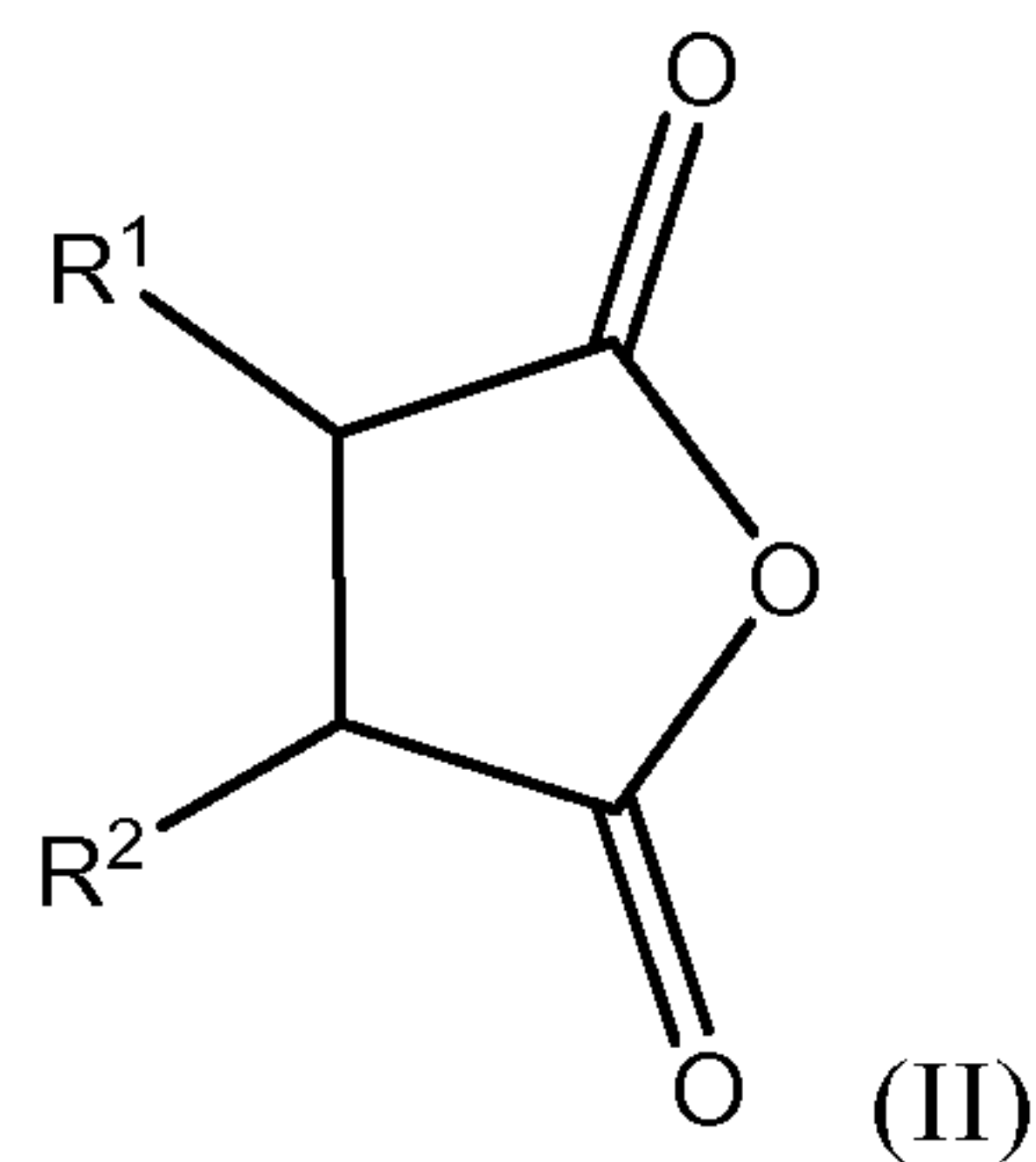
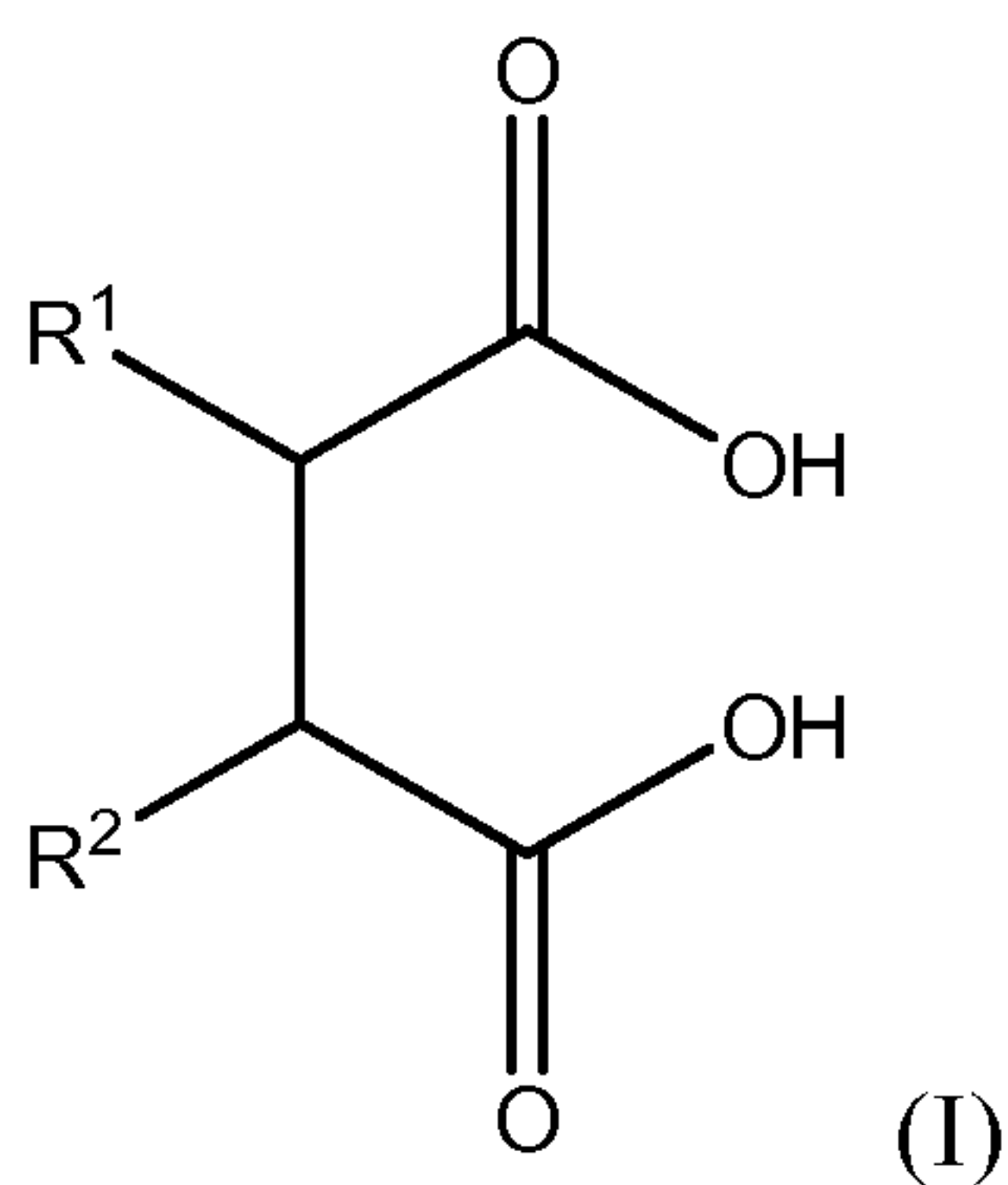
1. A composition comprising: (A) salt moieties derived from (A)(I) at least one polycarboxylic acylating agent, said acylating agent (A)(I) having at least one hydrocarbyl substituent having an average of from about 20 to about 500 carbon atoms, and

(A)(II) one or more members selected from the group consisting of ammonia, at least one amine, at least one alkali or alkaline earth metal, and at least one alkali or alkaline earth metal compound;

where two of said moieties (A) are coupled together by (B) at least one compound having at least two hydroxyls and at least one tertiary amino group.

2. The composition of claim 1 wherein (A)(I) is derived from at least one alpha-beta olefinically unsaturated carboxylic acid or acid-producing compound, said acid or acid-producing compound containing no less than 20 carbon atoms exclusive of the carboxyl groups.

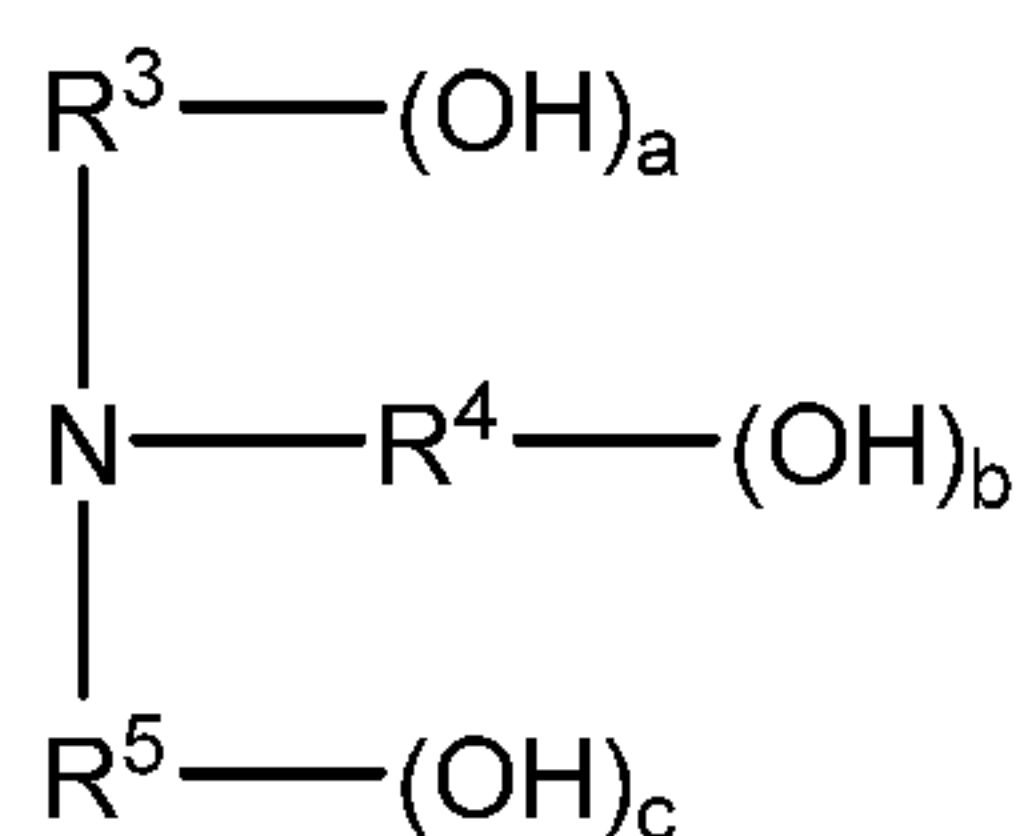
3. The composition of claim 1 wherein (A)(I) is represented by any one or more of the following formulae:



wherein each R^1 in each formula is independently said hydrocarbyl substituent of (A)(I) and wherein each R^2 in each formula is independently hydrogen or a methyl group.

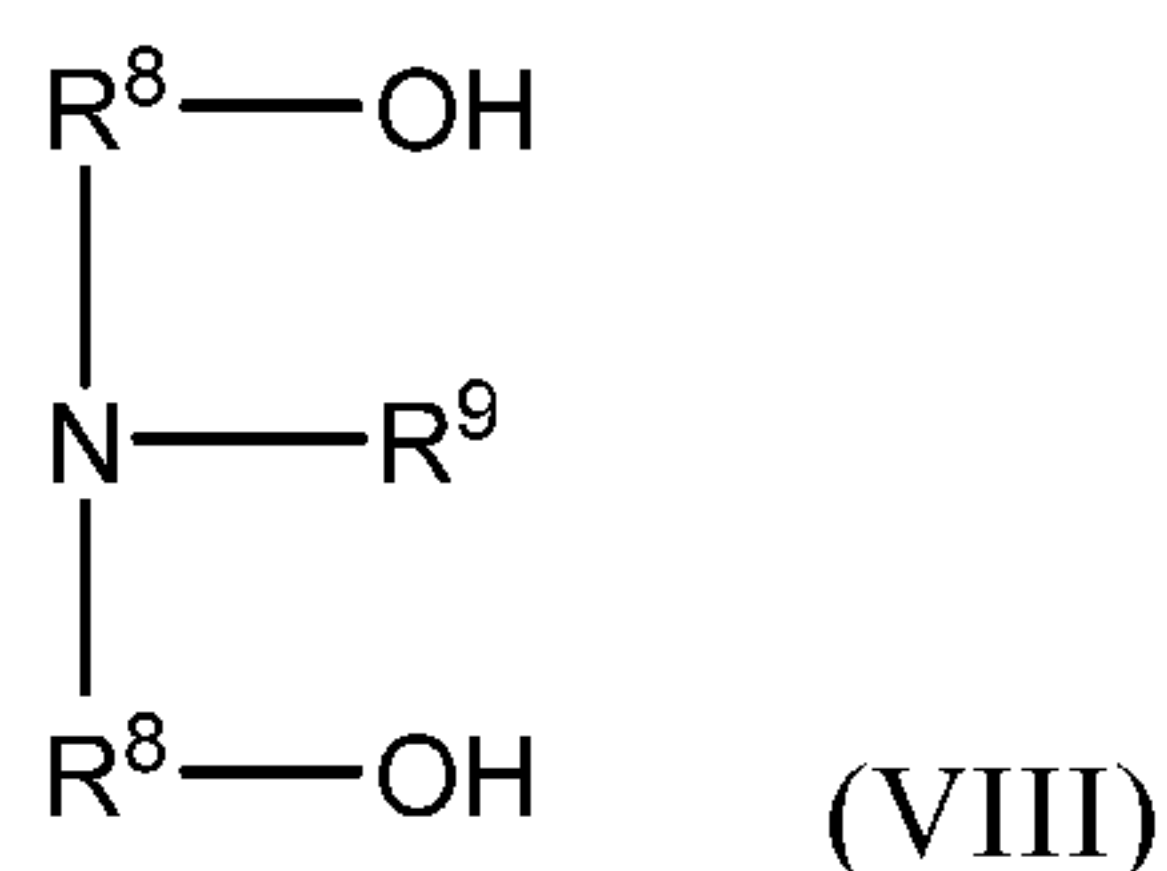
4. The composition of claim 1 wherein said hydrocarbyl substituent of (A)(I) is a poly(isobutylene) group.

5. The composition of claim 1 wherein component (B) comprises at least one tertiary amine of the formula:



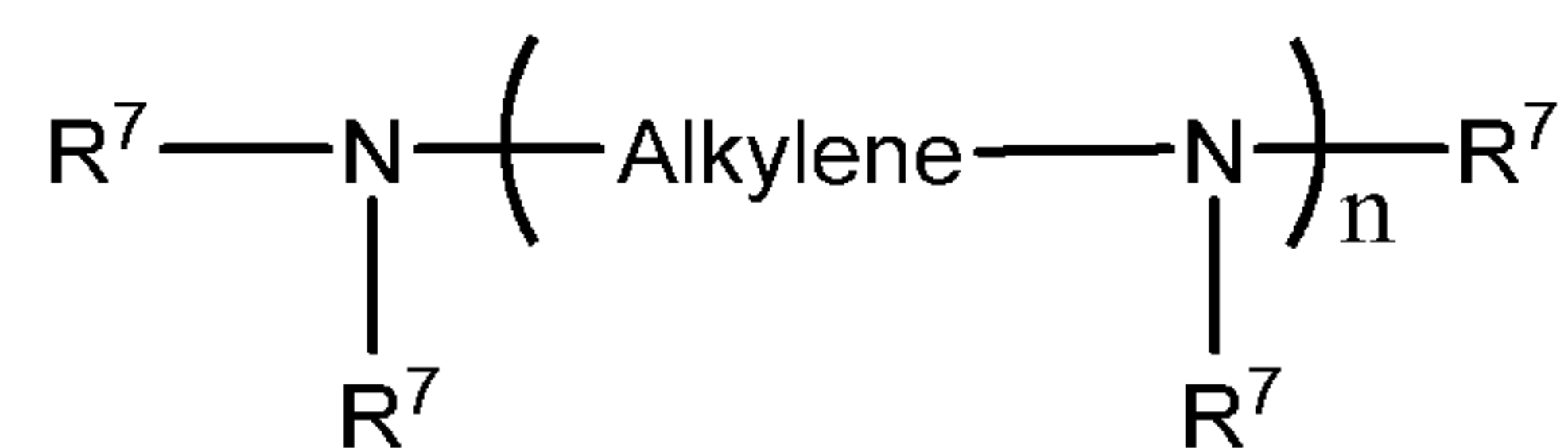
wherein each a, b, and c is independently 0 or 1 so long as the total of a+b+c is at least 2, and wherein each R^3 , R^4 and R^5 is independently a hydrocarbon group containing from 1 to 50 carbon atoms or an $-(R^6-O-)_n-$ group wherein R^6 is a alkenyl group containing from 1 to 6 carbon atoms, and n is an integer from 1 to 50 or from 1 to 20.

6. The composition of claim 1 wherein component (B) comprises at least one tertiary amine of the formula:



wherein each R^8 is independently a hydrocarbon group containing from 1 to 10 carbon atoms and where R^9 is a hydrocarbon group containing from 1 to 50 carbon atoms.

7. The composition of claim 1 wherein component (A)(II) comprises at least one alkylene polyamine of the formula



wherein n is a number of from 1 to about 10, each R⁷ is independently a hydrogen atom or a hydrocarbyl group or a hydroxy-substituted hydrocarbyl group having up to about 700 carbon atoms, and the Alkylene group has from 1 to about 10 carbon atoms.

8. The composition of claim 1 wherein component (B) comprises: 3-(didodecylamino)propane-1,2-diol, tallow-bis-(2-hydroxyethyl)amine, N-methyldiethanolamine, N-ethyldiethanolamine, N-propyldiethanolamine N-n-butyldiethanolamine N-tert-butyldiethanolamine N-cyclohexyldiethanolamine N-2-ethylhexyldiethanolamine, N-amyldiethanolamine, N-isobutyldiethanolamine, N-sec-butyldiethanolamine, N-dodecyldiethanolamine, N-hexadecyldiethanolamine, , N-hydrogenated rapeseed alkyldiethanolamine, N-hydrogenated tallowalkyldiethanolamine, N-phenyldiethanolamine, N-m-tolyldiethanolamine, bis(2-hydroxyethyl)octadecylamine, bis(2-hydroxyethyl)cocoalkylamines, bis(2-hydroxyethyl)oleylamine, bis(2-hydroxyethyl)soyaalkylamines, bis(2-hydroxyethyl)tallowalkylamines, polyoxyethylene (5) octadecylamine, polyoxyethylene (15) octadecylamine, polyoxyethylene (5) cocoalkylamines, polyoxyethylene (15) cocoalkylamines, polyoxyethylene (5) soyaalkylamines, polyoxyethylene (15) soyaalkylamines, polyoxyethylene (5) tallowalkylamines, polyoxyethylene (15) tallowalkylamines, polyoxyethylene (20) tallowalkylamine, 3-(dimethylamino)-1,2-propanediol, 3-(diethylamino)-1,2-propanediol, 3-(dipropylamino)-1,2-propanediol, 3-(diisopropylamino)-1,2-propanediol, 3-(dioctadecylamino)-1,2-propanediol, 3-(dicocylalkylamino)-1,2-propanediol, or combinations thereof.

9. The composition of claim 1 wherein component (B) further comprises at least one polyol.

10. The composition of claim 9 wherein the molar ratio of tertiary amine to polyol in component (B) is from 1:0.5 to 10:1.
11. The composition of claim 1 further comprising diluent such that the composition of claim 1 is present in the composition from about 10% to about 90% by weight, resulting in a concentrate composition.
12. The composition of claim 1 further comprising an oxidizer phase comprising at least one oxygen-supplying component with an organic phase comprising at least one carbonaceous fuel, resulting in an explosive composition.
13. An emulsion explosive composition comprising a discontinuous oxidizer phase comprising at least one oxygen-supplying component, a continuous organic phase comprising at least one carbonaceous fuel, said carbonaceous fuel comprising at least one wax, and an emulsifying amount of the composition of claim 1.
14. A cartridge comprising a cartridge casing containing either a cap-sensitive or booster sensitive emulsion explosive, said emulsion comprising a discontinuous oxidizer phase comprising at least one oxygen-supplying component, a continuous organic phase comprising at least one carbonaceous fuel, and an emulsifying amount of the composition of claim 1.
15. The composition of claim 1 wherein said hydrocarbyl substituent of (A)(I) is substantially free of hydrocarbon groups containing less than 20 carbon atoms.