

MOLECULES HAVING ONE HYDROPHOBIC GROUP AND TWO IDENTICAL HYDROPHILIC IONIC GROUPS AND COMPOSITIONS THEREOF

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CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims priority and is related to U.S. Provisional Application Ser. 62/552,108, filed on August 30, 2017 and entitled "MOLECULES HAVING ONE HYDROPHOBIC AND TWO IDENTICAL HYDROPHILIC GROUPS AND COMPOSITIONS THEREOF AND METHODS OF PREPARATION THEREOF." The entire contents of this patent application are hereby expressly incorporated herein by reference including, without limitation, the specification, claims, and abstract, as well as any figures, tables, or drawings thereof.

15 FIELD OF THE INVENTION

The present disclosure relates generally to the field of surfactant compounds, methods of making the same, method of using the same as corrosion control agents, and corrosion control compositions. In particular, the present disclosure is related to a new class of compounds that comprise two identical hydrophilic cationic or anionic groups and one hydrophobic group. The disclosed compounds share some structural features with conventional or Gemini surfactants but are structurally distinguishable from existing surfactants. The disclosed compounds are useful as a surfactant alone or together with other conventional or Gemini surfactant(s) in various applications. The compounds disclosed herein are also found to be effective corrosion inhibitors.

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BACKGROUND OF THE INVENTION

A surfactant compound usually contains a hydrophilic group and hydrophobic group. Because of its unique structure, a surfactant has various applications in different fields. As the understanding of the relationship between a surfactant compound's structure and its function and mode of operation improves, the need for surfactant compounds having new or improved properties, such as surface tension properties, is increasing.

Although structures of surfactants are diverse and numerous, the existing surfactants can be classified into two broad categories; one of conventional surfactants and another of Gemini surfactants.

5 A conventional surfactant usually has a hydrophobic group and a hydrophilic group. Depending on the characteristics of the hydrophilic group, a conventional surfactant can be one of nonionic, anionic, cationic, amphoteric, or zwitterionic surfactants.

A Gemini surfactant, on the other hand, has two hydrophobic groups and two hydrophilic groups. Gemini surfactants can be further divided similar subcategories based on the characteristics of the hydrophobic group(s), in an analogous manner as used for
10 classifying a conventional surfactant.

Accordingly, it is an objective to develop novel surfactant compounds having properties distinguishable from conventional and/or Gemini surfactants. In both conventional and Gemini surfactants, the ratio of hydrophilic group to hydrophobic group is 1:1, while the disclosed compounds have a ratio of hydrophilic group to hydrophobic
15 group of 2:1. This difference in the ratio of hydrophilic group to hydrophobic group provides for unique applications of the disclosed compounds, not only as surfactants, but also as antimicrobials, sanitizers, fabric softeners, antistatic agents, corrosion inhibitors, foaming agents, floatation collectors, dispersants, , surfactants assisted enhanced oil recovery (EOR), cleaners, etc..

20 It is a further objective of the disclosure to develop a method to make the novel compounds efficiently and effectively.

It is a further objective of the disclosure to use the novel compounds in an article, product, and/or composition.

Furthermore, quaternary ammonium compounds comprise an important
25 subcategory of surfactants because they contain unique properties. A main distinction between quaternary ammonium compounds and other surfactants is their unique structure. Quaternary ammonium compounds consist mainly of two moieties, a hydrophobic group, e.g., long alkyl group, and a quaternary ammonium salt group. The unique positive charge of the ammonium plays a key role, e.g., electrostatic interactions, between the surfactant
30 and surface.

Industrial water systems employ process water to serve many different purposes but may be prone to microbial contamination and fouling. Metal surfaces in any water system are prone to corrosion, partly due to microbial contamination and fouling.

Corrosion inhibitors are often added into a water system to protect its metal surfaces infrastructure, such as carbon steel pipelines, from corrosion. However, the quaternary ammonium compounds used for such purposes are often *bis* quaternary species or species quaternized with benzyl chloride and are known to be very hazardous. In addition, governmental regulations exist to release any water containing single quaternary compounds into the environment.

Therefore, there is a continuing need for different or alternative quaternary ammonium compounds that are better and safer corrosion control agents.

Accordingly, it is also an objective of the present disclosure to develop novel corrosion control agents having improved corrosion control properties.

It is a further objective of the disclosure to develop methods and corrosion control compositions to make the corrosion in a water system more efficient and effective.

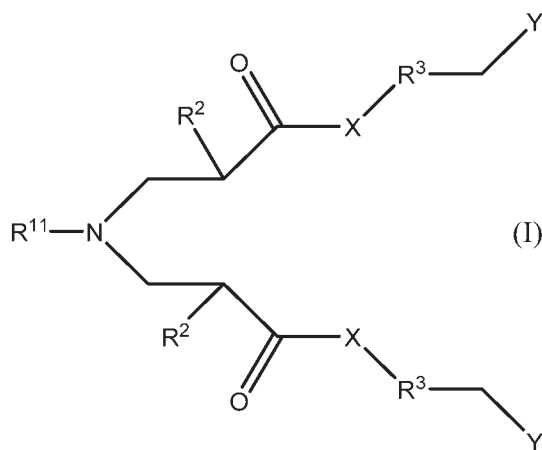
These and other objects, advantages and features of the present disclosure will become apparent from the following specification taken in conjunction with the claims set forth herein.

BRIEF SUMMARY OF THE INVENTION

Disclosed herein are novel compounds, including surfactant compounds, compositions comprising the disclosed compounds and methods of making the disclosed compounds. More particularly, disclosed herein are the compounds comprising two identical hydrophilic groups and a single hydrophobic group. In a disclosed compound, each hydrophilic group includes or ends in a quaternary amine or a negatively charged species, and the hydrophobic group includes a long hydrophobic chain. The disclosed compounds are different from conventional or Gemini surfactants, because the ratio of hydrophilic groups to hydrophobic group in the disclosed compounds is 2:1, while in conventional or Gemini surfactants the ratio is 1:1. This difference in structure provides unique applications for the disclosed compounds, not only as surfactants, but also for other purposes, such as antimicrobial sanitizers, fabric softeners, antistatic agents, corrosion

inhibitors, foaming agents, floatation collectors, dispersants, surfactants assisted enhanced oil recovery (EOR), cleaners, etc.

In one aspect, a compound according to Formula I is provided:



5 wherein

X is NH, or O;

R¹¹ is R¹ or R¹-Z-(CH₂)_m;

R¹ is an unsubstituted or substituted, linear or branched C₁-C₃₀ alkyl, cyclic alkyl, alkenyl, or alkynyl group;

10 Z is NH or O;

R² is H, CH₃, or an unsubstituted, linear or branched C₁-C₁₀ alkyl, alkenyl, or alkynyl group;

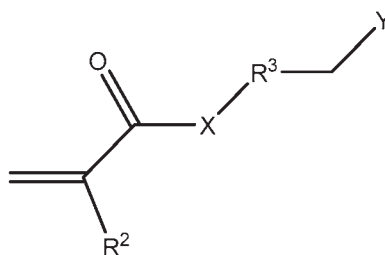
m is an integer of 1 to 4;

R³ is absent or an unsubstituted, linear C₁-C₃₀ alkylene group;

15 Y is -NR₄R₅R₆⁽⁺⁾ or a salt thereof; and

R⁴, R⁵, and R⁶ are independently C₁-C₁₀ alkyl group.

In other aspect, disclosed herein is a method to synthesize the disclosed compounds. The method comprises contacting a primary amine with an activated olefin containing at least one cationic group to generate any compound disclosed herein; wherein
20 the primary amine is R¹¹-NH₂, R¹¹ is R¹ or R¹-Z-(CH₂)_m; the activated olefin is



X is NH, or O;

R^{11} is R^1 or $R^1-Z-(CH_2)_m$;

R^1 is an unsubstituted or substituted, linear or branched C_1 - C_{30} alkyl, cyclic alkyl,
5 alkenyl, or alkynyl group;

Z is NH or O;

R^2 is H, CH_3 , or an unsubstituted, linear or branched C_2 - C_{10} alkyl, alkenyl, or
alkynyl group;

m is an integer of 1 to 4;

10 R^3 is absent or an unsubstituted, linear C_1 - C_{30} alkylene group;

Y is $-NR_4R_5R_6^{(+)}$ or a salt thereof; and

R^4 , R^5 , and R^6 are independently C_1 - C_{10} alkyl group.

In yet another aspect, provided herein is an article, product, or composition that
comprises one or more compounds disclosed herein.

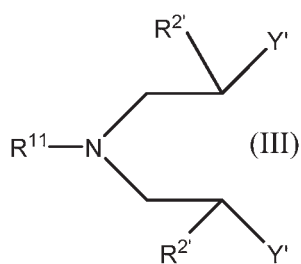
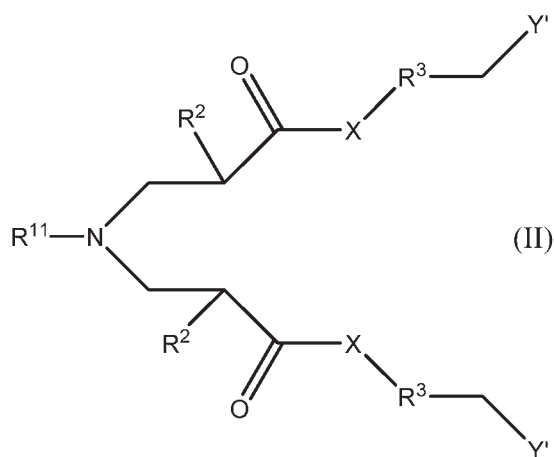
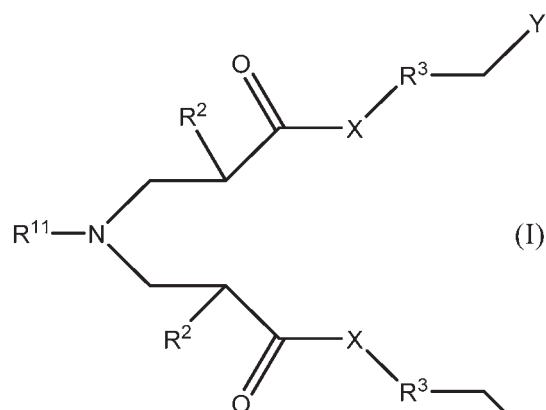
15 In yet another aspect, provided herein is a composition comprising one or more
compounds disclosed herein.

Disclosed also herein are the methods and compositions for corrosion control for a
metal surface in a water system. Specifically, the disclosed methods and compositions for
corrosion control for a water system use one or more water soluble di-cationic or di-
20 anionic compounds derived from water soluble primary amines (Michael donor) by an aza-
Michael addition reaction with an activated olefin (Michael acceptor).

The exemplary di-cationic or di-anionic compounds disclosed herein have a
superior performance than the conventional single quaternary ammonium compounds used
for mitigating corrosion for metal surfaces in water systems. The exemplary di-cationic or
25 di-anionic compounds disclosed herein also show improved performance when they are
used as a fouling control agent in a water system. Therefore, the disclosed corrosion
control compositions or methods have an advantage of not only preventing corrosion of

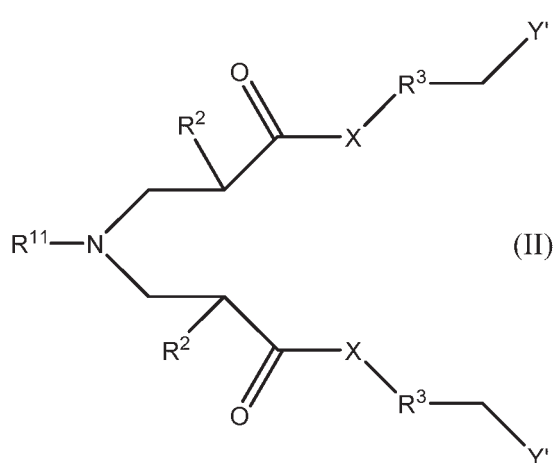
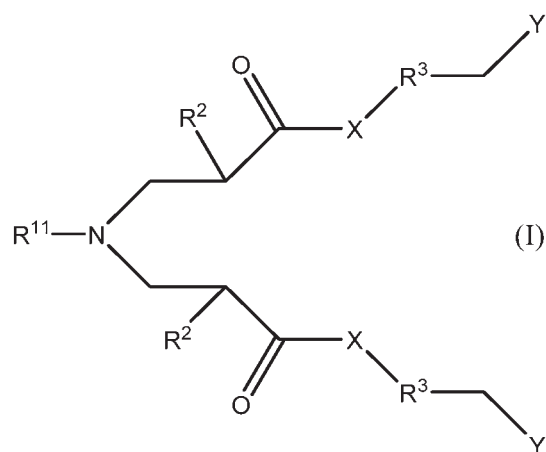
surfaces but also preventing microbial/biofilm growth, leading to overall reduction in chemical uses, cost, and operation complexity for operating a water system.

In one aspect, disclosed herein is a method for inhibiting corrosion at a surface in a water system, the method comprises providing a corrosion control composition or a use
 5 solution of the corrosion control composition into a water system to generate a treated water system or onto a surface of the water system, wherein the corrosion control composition comprises one or more compounds according to one of Formula I, Formula II, and Formula III and one or more additional corrosion control composition agents,

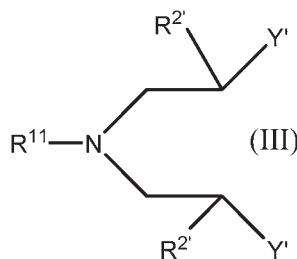


wherein X is NH or O; R^{11} is R^1 or $R^1-Z-(CH_2)_m$; R^1 is an unsubstituted or substituted, linear or branched C_1 - C_{30} alkyl, cyclic alkyl, alkenyl, or alkynyl group; Z is NH or O; R^2 is H, CH_3 , or an unsubstituted, linear or branched C_2 - C_{10} alkyl, alkenyl, or alkynyl group; m is an integer of 1 to 4; R^3 is absent or an unsubstituted, linear C_1 - C_{30} alkylene group; Y is -
 5 $NR_4R_5R_6^{(+)}$; Y' is $-COOH$, $-SO_3H$, $-PO_3H$, $-OSO_3H$, $-OPO_3H$, or a salt thereof; R^4 , R^5 , and R^6 are independently a C_1 - C_{10} alkyl group; $R^{2'}$ is H, CH_3 , or an unsubstituted or substituted, linear or branched C_1 - C_{10} alkyl, alkenyl, alkynyl group, $-COOH$, $-CH_2COOH$, Y' , or $-(CH_2)_m-Y'$, and wherein the corrosion control composition mitigates corrosion on the surface in the water system.

10 In other aspect, disclosed herein is a corrosion control composition, the corrosion control composition comprises one or more compounds according to one of Formula I, Formula II, and Formula III and one or more additional corrosion control composition agents,



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wherein X is NH or O; R^{11} is R^1 or $R^1-Z-(CH_2)_m$; R^1 is an unsubstituted or substituted, linear or branched C_1 - C_{30} alkyl, cyclic alkyl, alkenyl, or alkynyl group; Z is NH or O; R^2 is H, CH_3 , or an unsubstituted, linear or branched C_2 - C_{10} alkyl, alkenyl, or alkynyl group; m is an integer of 1 to 4; R^3 is absent or an unsubstituted, linear C_1 - C_{30} alkylene group; Y is $-NR_4R_5R_6^{(+)}$; Y' is $-COOH$, $-SO_3H$, $-PO_3H$, $-OSO_3H$, $-OPO_3H$, or a salt thereof; R^4 , R^5 , and R^6 are independently a C_1 - C_{10} alkyl group; $R^{2'}$ is H, CH_3 , or an unsubstituted or substituted, linear or branched C_1 - C_{10} alkyl, alkenyl, alkynyl group, $-COOH$, $-CH_2COOH$, Y' , or $-(CH_2)_m-Y'$, and wherein the corrosion control composition mitigates corrosion on the surface in the water system.

The forgoing summary is illustrative only and is not intended to be in any way limiting. In addition to the illustrative aspects, embodiments and features described above, further aspects, embodiments, and features of the present technology will become apparent to those skilled in the art from the following drawings and the detailed description, which shows and describes illustrative embodiments of the present technology. Accordingly, the figures and detailed description are also to be regarded as illustrative in nature and not in any way limiting.

BRIEF DESCRIPTION OF DRAWINGS

FIG. 1A, FIG. 1B, and FIG. 1C show a representation of an exemplary compound of the disclosure (**FIG. 1C**), together with comparative representations for a conventional surfactant (**FIG. 1A**) and Gemini surfactant (**FIG. 1B**).

FIG. 2 shows a generic reaction scheme between a primary amine (Michael donor) and activated olefin including a cationic group (Michael acceptor).

FIG. 3 shows the corrosion rate in mils per year (mpy) during the bubble test period (18 hour). For the blank sample, no 2-mercaptoethanol (2ME) was added.

Various embodiments of the present invention will be described in detail with reference to the drawings, wherein like reference numerals represent like parts throughout

the several views. Reference to various embodiments does not limit the scope of the invention. Figures represented herein are not limitations to the various embodiments according to the invention and are presented for exemplary illustration of the invention.

5 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

Disclosed herein are novel compounds and methods of making these novel compounds or surfactant compositions. More particularly, compounds comprising two identical hydrophilic groups and one hydrophobic group in the molecule, and methods of synthesizing such surfactants are disclosed. For example, each hydrophilic group includes
10 or ends with a quaternary amine and the hydrophobic group includes a long aliphatic chain.

The embodiments of this invention are not limited to particular compositions and methods of use which can vary and are understood by skilled artisans. It is further to be understood that all terminology used herein is for the purpose of describing particular
15 embodiments only and is not intended to be limiting in any manner or scope. For example, as used in this specification and the appended claims, the singular forms "a," "an" and "the" can include plural referents unless the content clearly indicates otherwise. Further, all units, prefixes, and symbols may be denoted in its SI accepted form.

Numeric ranges recited within the specification are inclusive of the numbers within the defined range. Throughout this disclosure, various aspects of this invention are
20 presented in a range format. The description in range format is merely for convenience and brevity and should not be construed as an inflexible limitation on the scope of the invention. Accordingly, the description of a range should be considered to have specifically disclosed all the possible sub-ranges as well as individual numerical values within that range (*e.g.* 1 to 5 includes 1, 1.5, 2, 2.75, 3, 3.80, 4, and 5).

25 So that the present invention may be more readily understood, certain terms are first defined. Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which embodiments of the invention pertain. Many methods and materials similar, modified, or equivalent to those described herein can be used in the practice of the embodiments of the
30 present invention without undue experimentation, the preferred materials and methods are described herein. In describing and claiming the embodiments of the present invention, the following terminology will be used in accordance with the definitions set out below.

The term "about," as used herein, refers to variation in the numerical quantity that can occur, for example, through typical measuring and liquid handling procedures used for making concentrates or use solutions in the real world; through error in these procedures; through differences in the manufacture, source, or purity of the ingredients used to make the compositions or carry out the methods; and the like. The term "about" also encompasses amounts that differ due to novel equilibrium conditions for a composition resulting from a particular initial mixture. Whether or not modified by the term "about", the claims include equivalents to the quantities.

As used herein, "substituted" refers to an organic group as defined below (*e.g.*, an alkyl group) in which one or more bonds to a hydrogen atom contained therein are replaced by a bond to non-hydrogen or non-carbon atoms. Substituted groups also include groups in which one or more bonds to carbon(s) or hydrogen(s) atom replaced by one or more bonds, including double or triple bonds, to a heteroatom. Thus, a substituted group is substituted with one or more substituents, unless otherwise specified. A substituted group can be substituted with 1, 2, 3, 4, 5, or 6 substituents.

Substituted ring groups include rings and ring systems in which a bond to a hydrogen atom is replaced with a bond to a carbon atom. Therefore, substituted cycloalkyl, aryl, heterocyclyl, and heteroaryl groups may also be substituted with substituted or unsubstituted alkyl, alkenyl, and alkynyl groups are defined herein.

As used herein, the term "alkyl" or "alkyl groups" refers to saturated hydrocarbons having one or more carbon atoms, including straight-chain alkyl groups (*e.g.*, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, etc.), cyclic alkyl groups (or "cycloalkyl" or "alicyclic" or "carbocyclic" groups) (*e.g.*, cyclopropyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, etc.), branched-chain alkyl groups (*e.g.*, isopropyl, tert-butyl, sec-butyl, isobutyl, etc.), and alkyl-substituted alkyl groups (*e.g.*, alkyl-substituted cycloalkyl groups and cycloalkyl-substituted alkyl groups).

Unless otherwise specified, the term "alkyl" includes both "unsubstituted alkyls" and "substituted alkyls." As used herein, the term "substituted alkyls" refers to alkyl groups having substituents replacing one or more hydrogens on one or more carbons of the hydrocarbon backbone. Such substituents may include, for example, alkenyl, alkynyl, halogeno, hydroxyl, alkylcarbonyloxy, arylcarbonyloxy, alkoxy carbonyloxy, aryloxy, aryloxy carbonyloxy, carboxylate, alkylcarbonyl, arylcarbonyl, alkoxy carbonyl,

aminocarbonyl, alkylaminocarbonyl, dialkylaminocarbonyl, alkylthiocarbonyl, alkoxyl, phosphate, phosphonato, phosphinato, cyano, amino (including alkyl amino, dialkylamino, arylamino, diarylamino, and alkylarylamino), acylamino (including alkylcarbonylamino, arylcarbonylamino, carbamoyl and ureido), imino, sulfhydryl, alkylthio, arylthio, thiocarboxylate, sulfates, alkylsulfinyl, sulfonates, sulfamoyl, sulfonamido, nitro, trifluoromethyl, cyano, azido, heterocyclic, alkylaryl, or aromatic (including heteroaromatic) groups.

In some embodiments, substituted alkyls can include a heterocyclic group. As used herein, the term "heterocyclic group" includes closed ring structures analogous to carbocyclic groups in which one or more of the carbon atoms in the ring is an element other than carbon, for example, nitrogen, sulfur or oxygen. Heterocyclic groups may be saturated or unsaturated. Exemplary heterocyclic groups include, but are not limited to, aziridine, ethylene oxide (epoxides, oxiranes), thiirane (episulfides), dioxirane, azetidine, oxetane, thietane, dioxetane, dithietane, dithiete, azolidine, pyrrolidine, pyrroline, oxolane, dihydrofuran, and furan.

Alkenyl groups or alkenes are straight chain, branched, or cyclic alkyl groups having two to about 30 carbon atoms, and further including at least one double bond. In some embodiments, an alkenyl group has from 2 to about 30 carbon atoms, or typically, from 2 to 10 carbon atoms. Alkenyl groups may be substituted or unsubstituted. For a double bond in an alkenyl group, the configuration for the double bond can be a *trans* or *cis* configuration. Alkenyl groups may be substituted similarly to alkyl groups.

Alkynyl groups are straight chain, branched, or cyclic alkyl groups having two to about 30 carbon atoms, and further including at least one triple bond. In some embodiments, an alkynyl group has from 2 to about 30 carbon atoms, or typically, from 2 to 10 carbon atoms. Alkynyl groups may be substituted or unsubstituted. Alkynyl groups may be substituted similarly to alkyl or alkenyl groups.

As used herein, the terms "alkylene", "cycloalkylene", "alkynylides", and "alkenylene", alone or as part of another substituent, refer to a divalent radical derived from an alkyl, cycloalkyl, or alkenyl group, respectively, as exemplified by $-\text{CH}_2\text{CH}_2\text{CH}_2-$. For alkylene, cycloalkylene, alkynylene, and alkenylene groups, no orientation of the linking group is implied.

The term “ester” as used herein refers to $-R^{30}COOR^{31}$ group. R^{30} is absent, a substituted or unsubstituted alkylene, cycloalkylene, alkenylene, alkynylene, arylene, aralkylene, heterocyclalkylene, or heterocyclylene group as defined herein. R^{31} is a substituted or unsubstituted alkyl, cycloalkyl, alkenyl, alkynyl, aryl, aralkyl, heterocyclalkyl, or heterocycl group as defined herein.

The term “amine” (or “amino”) as used herein refers to $-R^{32}NR^{33}R^{34}$ groups. R^{32} is absent, a substituted or unsubstituted alkylene, cycloalkylene, alkenylene, alkynylene, arylene, aralkylene, heterocyclalkylene, or heterocyclylene group as defined herein. R^{33} and R^{34} are independently hydrogen, or a substituted or unsubstituted alkyl, cycloalkyl, alkenyl, alkynyl, aryl, aralkyl, heterocyclalkyl, or heterocycl group as defined herein.

The term “amine” as used herein also refers to an independent compound. When an amine is a compound, it can be represented by a formula of $R^{32'}NR^{33'}R^{34'}$ groups, wherein $R^{32'}$, $R^{33'}$, and $R^{34'}$ are independently hydrogen, or a substituted or unsubstituted alkyl, cycloalkyl, alkenyl, alkynyl, aryl, aralkyl, heterocyclalkyl, or heterocycl group as defined herein.

The term “alcohol” as used herein refers to $-R^{35}OH$ groups. R^{35} is absent, a substituted or unsubstituted alkylene, cycloalkylene, alkenylene, alkynylene, arylene, aralkylene, heterocyclalkylene, or heterocyclylene group as defined herein.

The term “carboxylic acid” as used herein refers to $-R^{36}COOH$ groups. R^{36} is absent, a substituted or unsubstituted alkylene, cycloalkylene, alkenylene, alkynylene, arylene, aralkylene, heterocyclalkylene, or heterocyclylene group as defined herein.

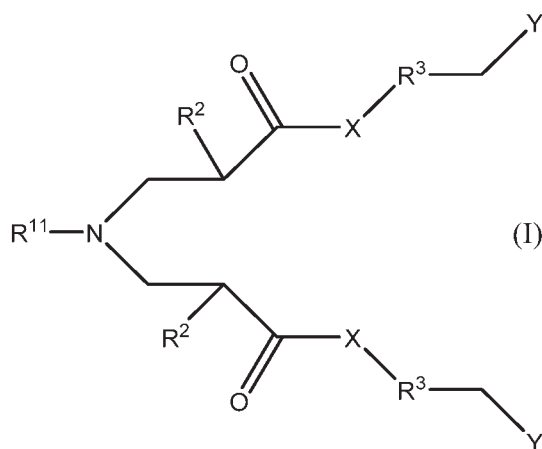
The term “ether” as used herein refers to $-R^{37}OR^{38}$ groups. R^{37} is absent, a substituted or unsubstituted alkylene, cycloalkylene, alkenylene, alkynylene, arylene, aralkylene, heterocyclalkylene, or heterocyclylene group as defined herein. R^{38} is a substituted or unsubstituted alkyl, cycloalkyl, alkenyl, alkynyl, aryl, aralkyl, heterocyclalkyl, or heterocycl group as defined herein.

The term “solvent” as used herein refers to any inorganic or organic solvent. Solvents are useful in the disclosed method or article, product, or composition as reaction solvent or carrier solvent. Suitable solvents include, but are not limited to, oxygenated solvents such as lower alkanols, lower alkyl ethers, glycols, aryl glycol ethers and lower alkyl glycol ethers. Examples of other solvents include, but are not limited to, methanol, ethanol, propanol, isopropanol and butanol, isobutanol, ethylene glycol, diethylene glycol,

triethylene glycol, propylene glycol, dipropylene glycol, hexylene glycol, mixed ethylene-propylene glycol ethers, ethylene glycol phenyl ether, and propylene glycol phenyl ether. Water is a solvent too. The solvent used herein can be of a single solvent or a mixture of many different solvents.

5 Glycol ethers include, but are not limited to, diethylene glycol n-butyl ether, diethylene glycol n-propyl ether, diethylene glycol ethyl ether, diethylene glycol methyl ether, diethylene glycol t-butyl ether, dipropylene glycol n-butyl ether, dipropylene glycol methyl ether, dipropylene glycol ethyl ether, dipropylene glycol propyl ether, dipropylene glycol tert-butyl ether, ethylene glycol butyl ether, ethylene glycol propyl ether, ethylene glycol ethyl ether, ethylene glycol methyl ether, ethylene glycol methyl ether acetate, propylene glycol n-butyl ether, propylene glycol ethyl ether, propylene glycol methyl ether, propylene glycol n-propyl ether, tripropylene glycol methyl ether and tripropylene glycol n-butyl ether, ethylene glycol phenyl ether, propylene glycol phenyl ether, and the like, or mixtures thereof.

15 In one aspect, disclosed herein is a compound according to Formula I



wherein

X is NH, or O;

R¹¹ is R¹ or R¹-Z-(CH₂)_m;

20 R¹ is an unsubstituted or substituted, linear or branched C₁-C₃₀ alkyl, cyclic alkyl, alkenyl, or alkynyl group;

Z is NH or O;

R² is H, CH₃, or an unsubstituted, linear or branched C₂-C₁₀ alkyl, alkenyl, or alkynyl group;

m is an integer of 1 to 4;

R³ is absent or an unsubstituted, linear C₁-C₃₀ alkylene group;

Y is -NR₄R₅R₆⁽⁺⁾ or a salt thereof; and

R⁴, R⁵, and R⁶ are independently C₁-C₁₀ alkyl group.

5 In some embodiments of the disclosed compounds herein, X is NH. In some other embodiments, X is O.

In some embodiments, R¹¹ is R¹. In some other embodiments, R¹¹ is R¹-Z-(CH₂)_m-. In some embodiments, R¹¹ is R¹-Z-(CH₂)_m-, and Z is NH. In some other embodiments, R¹¹ is R¹-Z-(CH₂)_m-, and Z is O. In yet some other embodiments, R¹¹ is R¹-Z-(CH₂)_m-, Z is
10 NH, m is 2.

In some embodiments, R² is H. In some embodiments, R² is CH₃. In yet some other embodiments, R² is CH₃CH₃, CH₂CH₂CH₃, or CH(CH₃)₂.

In some embodiments, Y is -NR₄R₅R₆⁽⁺⁾. In some other embodiments, Y is -NR₄R₅R₆⁽⁺⁾, and R⁴, R⁵, and R⁶ are independently CH₃. In yet some other embodiments, Y is -NR₄R₅R₆⁽⁺⁾, and R⁴ and R⁵, independently CH₃, and R⁶ is a C₆-C₁₂ aromatic alkyl. In
15 some other embodiments, Y is -NR₄R₅R₆⁽⁺⁾, and R⁴ and R⁵, independently CH₃, and R⁶ is -CH₂-C₆H₆.

In some embodiments, Y is -NR₄R₅R₆⁽⁺⁾ and the counter ion for Y is any negative charged ion or species. In some other embodiments, the counter ion for Y is chloride,
20 bromide, fluoride, iodide, acetate, aluminate, cyanate, cyanide, dihydrogen phosphate, dihydrogen phosphite, formate, carbonate, hydrogen carbonate, hydrogen oxalate, hydrogen sulfate, hydroxide, nitrate, nitrite, thiocyanate, or a combination thereof.

In some embodiments, R³ is CH₂. In some other embodiments, R³ is CH₂CH₂. In other embodiments, R³ is C(CH₃)₂. In yet some other embodiments, R³ is an unsubstituted,
25 linear, and saturated C₂-C₁₀ alkylene group. In some embodiments, R³ is an unsubstituted, linear, and unsaturated C₂-C₁₀ alkylene group.

In some embodiments, R¹ is a linear C₁-C₃₀ alkyl, alkenyl, or alkynyl group. In some other embodiments, R¹ is a branched C₁-C₃₀ alkyl, alkenyl, or alkynyl group. In yet some other embodiments, R¹ is a linear and saturated C₅-C₃₀ alkyl group. In some other
30 embodiments, R¹ is a branched and saturated C₅-C₃₀ alkyl group.

In some embodiments, R^1 is a linear C_1 - C_{30} alkenyl group with one or more double bonds. In some other embodiments, wherein R^1 is a branched C_1 - C_{30} alkenyl group with one or more double bonds.

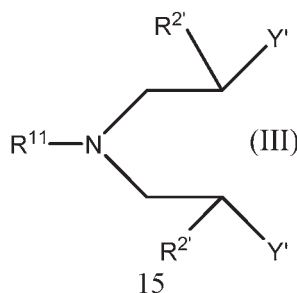
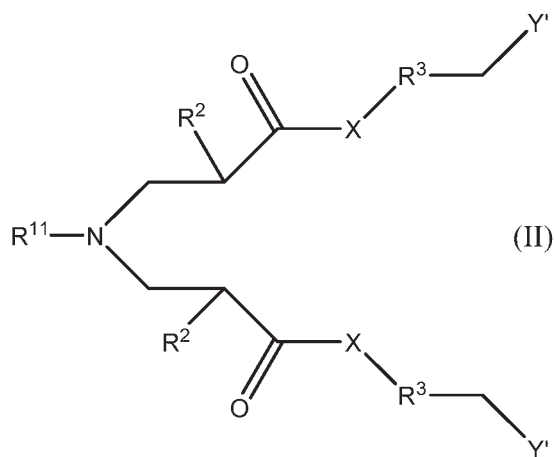
In some embodiments, R^1 is a linear C_1 - C_{30} alkynyl group with one or more triple bonds. In some other embodiments, R^1 is a branched C_1 - C_{30} alkynyl group with one or more triple bonds.

In some embodiments, R^{11} is a linear and saturated C_2 - C_{20} alkyl group. In some other embodiments, R^{11} is a *trans* C_2 - C_{20} alkenyl group with at least one double bond. In some other embodiments, R^{11} is a C_2 - C_{20} alkenyl group with at least one double bond of *trans* configuration. In some embodiments, R^{11} is a *cis* C_2 - C_{20} alkenyl group with at least one double bond. In some other embodiments, R^{11} is a C_2 - C_{20} alkenyl group with at least one double bond of *cis* configuration.

In some embodiments, R^{11} is R^1 -NH-CH₂CH₂CH₂ group and R^1 is a linear and saturated C_2 - C_{20} alkyl, a *trans* alkenyl, or a *cis* alkenyl group.

In some other embodiments, R^2 is H, X is NH, R^3 is CH₂CH₂, Y is CH₂-N⁺(CH₃)₃Cl⁻.

In another aspect, disclosed herein is a compound according to Formula II or Formula III



wherein X is NH, or O; R¹¹ is R¹ or R¹-Z-(CH₂)_m; R¹ is an unsubstituted or substituted, linear or branched C₁-C₃₀ alkyl, cyclic alkyl, alkenyl, or alkynyl group; Z is NH or O; R² is H, CH₃, or an unsubstituted, linear or branched C₁-C₁₀ alkyl, alkenyl, or alkynyl group; R^{2'} is H, CH₃, or an unsubstituted or substituted, linear or branched C₁-C₁₀ alkyl, alkenyl, alkynyl group, -COOH, -CH₂COOH, Y', or -(CH₂)_m-Y'; m is an integer of 1 to 4; R³ is absent or an unsubstituted, linear C₁-C₃₀ alkylene group; Y' is -COOH, -PO₃H, -OPO₃H, -SO₃H, -OSO₃H or salt thereof.

In some embodiments, Y' is -COOH or salt thereof. In some embodiments, Y' is -PO₃H, -OPO₃H, or salt thereof. In some other embodiments, Y' is -SO₃H, -OSO₃H, or salt thereof.

In some embodiments of the disclosed compounds herein, X is NH. In some other embodiments, X is O.

In some embodiments, R¹¹ is R¹. In some other embodiments, R¹¹ is R¹-Z-(CH₂)_m. In some embodiments, R¹¹ is R¹-Z-(CH₂)_m, and Z is NH. In some other embodiments, R¹¹ is R¹-Z-(CH₂)_m, and Z is O. In yet some other embodiments, R¹¹ is R¹-Z-(CH₂)_m, Z is NH, m is 2.

In some embodiments, R² is H. In some embodiments, R² is CH₃. In yet some other embodiments, R² is CH₃CH₃, CH₂CH₂CH₃, or CH(CH₃)₂.

In some embodiments, R^{2'} is H. In some embodiments, R^{2'} is CH₃. In yet some other embodiments, R^{2'} is CH₃CH₃, CH₂CH₂CH₃, or CH(CH₃)₂. In some other embodiments, R^{2'} is -COOH. In some other embodiments, R^{2'} is -CH₂COOH.

In some embodiments, R³ is CH₂. In some other embodiments, R³ is CH₂CH₂. In other embodiments, R³ is C(CH₃)₂. In yet some other embodiments, R³ is an unsubstituted, linear, and saturated C₂-C₁₀ alkylene group. In some embodiments, R³ is an unsubstituted, linear, and unsaturated C₂-C₁₀ alkylene group.

In some embodiments, R¹ is a linear C₁-C₃₀ alkyl, alkenyl, or alkynyl group. In some other embodiments, R¹ is a branched C₁-C₃₀ alkyl, alkenyl, or alkynyl group. In yet some other embodiments, R¹ is a linear and saturated C₅-C₃₀ alkyl group. In some other embodiments, R¹ is a branched and saturated C₅-C₃₀ alkyl group.

In some embodiments, R¹ is a linear C₁-C₃₀ alkenyl group with one or more double bonds. In some other embodiments, wherein R¹ is a branched C₁-C₃₀ alkenyl group with one or more double bonds.

In some embodiments, R^1 is a linear C_1 - C_{30} alkynyl group with one or more triple bonds. In some other embodiments, R^1 is a branched C_1 - C_{30} alkynyl group with one or more triple bonds.

In some embodiments, R^{11} is a linear and saturated C_2 - C_{20} alkyl group. In some other embodiments, R^{11} is a *trans* C_2 - C_{20} alkenyl group with at least one double bond. In some other embodiments, R^{11} is a C_2 - C_{20} alkenyl group with at least one double bond of *trans* configuration. In some embodiments, R^{11} is a *cis* C_2 - C_{20} alkenyl group with at least one double bond. In some other embodiments, R^{11} is a C_2 - C_{20} alkenyl group with at least one double bond of *cis* configuration.

In some embodiments, R^{11} is R^1 -NH-CH₂CH₂CH₂ group and R^1 is a linear and saturated C_1 - C_{20} alkyl, a *trans* alkenyl, or a *cis* alkenyl group.

In some other embodiments, R^2 is H, X is NH, R^3 is CH₂CH₂, Y' is -COOH or -PO₃H. In some embodiments, the compound is one by Formula II. In some other embodiments, the compound is one by Formula III.

In some embodiments, the compound is one with formula III, $R^{2'}$ is H, X is NH, Y' is -COOH or -PO₃H. In some other embodiments, the compound is one with formula III, $R^{2'}$ is -CH₃, X is NH, Y' is -COOH or -PO₃H. In yet some other embodiments, the compound is one with formula III, $R^{2'}$ is Y' or -CH₂Y', X is NH, Y' is -COOH or -PO₃H.

In yet some other embodiments, when the compound is one with formula III and the Y' group is negatively charged, the counter positive ions for the negative charges include, but are not limited to, alkali metal ions, Li⁺, Na⁺, K⁺, NH₄⁺, a quaternary ammonium ion, etc.

Without being limited to a particular mechanism of action or definition of structure and function of the compounds, the compounds disclosed herein have two hydrophilic groups associated with one hydrophobic group. Accordingly, the compounds disclosed herein have a ratio of hydrophilic groups to hydrophobic group of 2:1 as compared to both a conventional surfactant and Gemini surfactant, which exhibit a 1:1 ratio. **FIG. 1A, FIG. 1B, and FIG. 1C** shows a representation of an exemplary compound disclosed herein (**FIG. 1C**), together with ones for a conventional (**FIG. 1A**) and Gemini surfactant (**FIG. 1B**). Due to the higher ratio of hydrophilic groups to hydrophobic group, the disclosed compounds are particularly well suited for use as antimicrobial sanitizers, fabric softeners,

antistatic agents, corrosion inhibitors, foaming agents, floatation collectors, dispersants, , surfactants assisted enhanced oil recovery (EOR), cleaners, etc.

In this disclosure, the term "hydrophobic group" can be used interchangeable with the term "hydrophobic tail or head." Similarly, the term "hydrophilic group" can be used interchangeably with the term "polar head or tail", or "hydrophilic group", or "polar group." The term "a molecule" can also be used interchangeably with the term "a compound."

Methods of Making

In another aspect, disclosed herein is a method to synthesize the compounds disclosed herein. The disclosed method comprises contacting a primary amine (Michael donor) with an activated olefin containing a hydrophilic group (Michael acceptor) at a temperature of from about -20°C to about 200°C, in some embodiments, for from about 10 minutes to about 48 hours, to generate the compounds disclosed herein. The reaction leading to the compounds disclosed herein is aza-Michael addition between a primary amine (Michael donor) and an activated olefin containing a hydrophilic group (Michael acceptor).

An aliphatic amine group may undergo an aza-Michael Addition reaction when in contact with an unsaturated hydrocarbon moiety (e.g., carbon-carbon double bond) that is in proximity of an electron withdrawing group such as carbonyl, cyano, or nitro group. Specifically, the Michael addition is a reaction between nucleophiles and activated olefin and alkyne functionalities, wherein the nucleophile adds across a carbon-carbon multiple bond that is adjacent to an electron withdrawing and resonance stabilizing activating group, such as a carbonyl group. The Michael addition nucleophile is known as the "Michael donor", the activated electrophilic olefin is known as the "Michael acceptor", and reaction product of the two components is known as the "Michael adduct." Examples of Michael donors include, but are not restricted to, amines, thiols, phosphines, carbanions, and alkoxides. Examples of Michael acceptors include, but are not restricted to, acrylate esters, alkyl methacrylates, acrylonitrile, acrylamides, maleimides, cyanoacrylates and vinyl sulfones, vinyl ketones, nitro ethylenes, α , β -unsaturated aldehydes, vinyl phosphonates, acrylonitrile, vinyl pyridines, azo compounds, beta-keto acetylenes and acetylene esters.

As used herein, an "activated olefin" refers to a substituted alkene in which at least one of the double-bond carbon has a conjugated electron withdrawing group. Examples of

activated olefins include, but not limited to, α , β -unsaturated carbonyl compounds (such as $\text{CH}_2=\text{CHCO-NH-CH}_3$, alkyl- $\text{CH}=\text{CH-CO-alkyl}$, $\text{CH}_2=\text{CH}_2\text{C(O)-O-CH}_3$), $\text{CH}_2=\text{CH-COOH}$, $\text{CH}_2=\text{CH(CH}_3\text{)-COOH}$, $\text{CH}_2=\text{CH-SO}_3\text{H}$, and like.

As used herein, “contacting” is referred to any way to bring the primary amine
5 (Michael donor) and the activated olefin containing at least one cationic or anionic group (Michael acceptor) together as one skilled in the art would do to conduct a chemical reaction in a controlled and practical manner. For example, in some embodiments, the primary amine or a solution comprising the primary amine can be added into a container or vessel containing the activated olefin or a solution comprising the activated olefin, in
10 batches or drops. In some other embodiments, the activated olefin or a solution comprising the activated olefin can be added into a container or vessel containing the primary amine or a solution comprising the primary amine, in batches or drops. In yet some other embodiments, both the activated olefin or a solution comprising the activated olefin and the primary amine or a solution comprising the primary amine are added to a container or
15 vessel in batches or drops, simultaneously, sequentially, or alternatively.

The chemical reaction used to synthesize the disclosed compounds is Aza-Michael addition reaction. It was found that the Aza-Michael addition can be used to synthesize the disclosed compounds under mild conditions and a high yield for the disclosed compounds in a reasonable reaction time.

20 Aza-Michael addition reaction can be catalyzed by a strong acid or base. In some cases, some ionic liquids can function both as reaction media and catalyst. The preferred catalyst for the Aza-Michael addition reaction to synthesize the disclosed compounds is a base. The base catalyst can be any or a combination of an alkalinity source or primary alkalinity source. Exemplary base catalyst can be an alkali metal, hydroxide, alkali metal
25 carbonate, alkali metal silicate, alkali metal silicate, or amine. Exemplary base catalyst can be hydroxide and amines. Because the reaction to synthesize the disclosed compounds uses a primary amine, the primary amine itself can function as a catalyst for the reaction. In such embodiments, no additional catalyst is necessary, or an additional catalyst is optional. Other preferred catalysts include amidine and guanidine bases.

30 The use of solvent and/or diluent for the reaction is optional. When employed, a wide range of non-acidic solvents are suitable, such as, for example, water, ethers (e.g., tetrahydrofuran (THF)), aromatic hydrocarbons (e.g., toluene and xylene), alcohols (e.g., n-

butanol), esters (e.g., ethyl 3-ethoxypropionate), and the like. A wide range of solvents can be used for the reaction because the synthesis process is relatively insensitive to solvent. When solvent (or diluent) is employed, loading levels can range from about 0wt-% up to about 80 wt-% and higher. The solvent loading level can be about 0 wt-%, from about 1
5 wt-% to about 10 wt-%, from about 10 wt-% to about 20 wt-%, from about 20 wt-% to about 30 wt-%, from about 30 wt-% to about 40 wt-%, from about 40 wt-% to about 50 wt-%, from about 50 wt-% to about 60 wt-%, from about 60 wt-% to about 70 wt-%, from about 70 wt-% to about 80 wt-%, from about 1 wt-% to about 20 wt-%, from about 20 wt-% to about 40 wt-%, from about 40 wt-% to about 60 wt-%, from about 60 wt-% to about
10 80 wt-%, from about 40 wt-% to about 70 wt-%, about 5 wt-%, about 15 wt-%, about 25 wt-%, about 35 wt-%, about 45 wt-%, about 55 wt-%, about 65 wt-%, about 75 wt-%, or any value there between of the final reaction mixture.

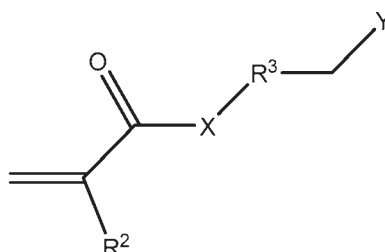
Generally, the contacting step of the method can be carried out at a temperature over a wide range of temperatures. The contacting, or reaction temperature can range from
15 about -20°C to about 200°C, from about 0°C to about 150°C, more preferably from about 50°C to about 80°C. The contacting temperature can be from about 10°C to about 140°C, about 20°C to about 130°C, about 30°C to about 120°C, about 40°C to about 110°C, about 50°C to about 100°C, about 60°C to about 90°C, about 70°C to about 80°C, about 0°C to about 20°C, about 20°C to about 40°C, about 40°C to about 60°C, about 60°C to about
20 80°C, about 80°C to about 100°C, about 100°C to about 120°C, about 120°C to about 150°C, about 5°C, about 25°C, about 45°C, about 65°C, about 85°C, about 105°C, about 125°C, about 145°C, or any value there between. The reaction temperature can be about the same from starting of the reaction to end of the reaction and can be changed from one temperature to another while the reaction is going on.

25 The contacting or reaction time for the synthesis of the compounds disclosed herein can vary widely, depending on such factors as the reaction temperature, the efficacy and amount of the catalyst, the presence or absence of diluent (solvent), and the like. The preferred reaction time can be from about 10 minutes to about 48 hours, from about 0.5 hours to about 48 hours, from about 1 hour to 40 hours, from about 2 hours to 38 hours,
30 from about 4 hours to about 36 hours, from 6 hours to about 34 hours, from about 8 hours to about 32 hours, from about 10 hours to about 30 hours, from about 12 hours to about 28 hours, from about 14 hours to 26 hours, from about 16 hours to 24 hours, from about 18

hours to 20 hours, from about 1 hour to 8 hours, from 8 hours to 16 hours, from 8 hours to about 24 hours, about 2 hours, about 4 hours, about 6 hours, about 8 hours, about 10 hours, about 14 hours, about 16 hours, about 18 hours, about 24 hours, about 30 hours, about 36 hours, or any values there between.

5 The reaction for the synthesis of the compounds disclosed herein can go to completion when one mole of the primary amine and at least two moles of the activated olefin, are mixed together for a sufficient of time at a temperature described above. Typically, if the reaction is carried out at a room temperature, the reaction can have a product yield of more than 98%.

10 In some embodiments of the disclosed methods, the primary amine is $R^{11}-NH_2$, R^{11} is R^1 or $R^1-Z-(CH_2)_m$; the activated olefin is



X is NH, or O;

R^{11} is R^1 or $R^1-Z-(CH_2)_m$;

15 R^1 is an unsubstituted or substituted, linear or branched C_1 - C_{30} alkyl, cyclic alkyl, alkenyl, or alkynyl group;

Z is NH or O;

R^2 is H, CH_3 , or an unsubstituted, linear or branched C_1 - C_{10} alkyl, alkenyl, or alkynyl group;

20 m is an integer of 1 to 4;

R^3 is absent or an unsubstituted, linear C_1 - C_{30} alkylene group;

Y is $-NR_4R_5R_6^{(+)}$ or a salt thereof; and

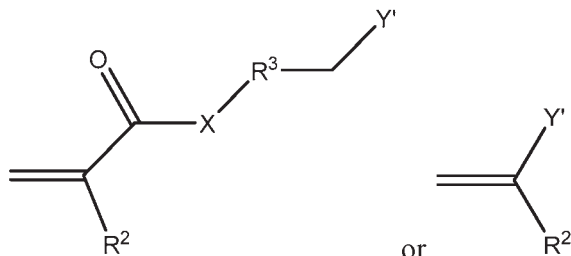
R^4 , R^5 , and R^6 are independently C_1 - C_{10} alkyl group.

In some embodiments, the activated olefin is (3-

25 Acrylamidopropyl)trimethylammonium chloride (APTAC), [3-(Methacryloylamino)propyl]trimethylammonium chloride (MAPTAC), 2-(acryloyloxy)-N,N,N-trimethylethanaminium chloride (DMAEA-MCQ), N,N-dimethylaminoethyl acrylate benzyl chloride quaternary salt (DMAEA-BCQ), 2-(methacryloyloxy)-N,N,N-

trimethylethan-1-aminium methyl sulfate (DMAEA-MSQ), 2-(acryloyloxy)-N,N,N-trimethylethanaminium chloride (DMAEA-MSQ), or mixture thereof.

In some embodiments of the disclosed methods, the primary amine is R^{11} -NH₂, R^{11} is R^1 or R^1 -Z-(CH₂)_m; the activated olefin is



X is NH, or O;

R^{11} is R^1 or R^1 -Z-(CH₂)_m;

R^1 is an unsubstituted or substituted, linear or branched C₁-C₃₀ alkyl, cyclic alkyl, alkenyl, or alkynyl group;

10 Z is NH or O;

R^2 is H, CH₃, or an unsubstituted, linear or branched C₁-C₁₀ alkyl, alkenyl, or alkynyl group;

$R^{2'}$ is H, CH₃, or an unsubstituted or substituted, linear or branched C₁-C₁₀ alkyl, alkenyl, alkynyl group, -COOH, -CH₂COOH, Y', or -(CH₂)_m-Y';

15 m is an integer of 1 to 4;

R^3 is absent or an unsubstituted, linear C₁-C₃₀ alkylene group; and

Y' is -COOH, -PO₃H, -SO₃H, or a salt thereof.

In some embodiments, the activated olefin is acrylic acid, methacrylic acid, itaconic acid, maleic acid, vinylsulfonic acid, vinylphosphonic acid, or mixture thereof.

20 In some other embodiments, the activated olefin is 2-acrylamido-2-methylpropane sulfonic acid (AMPS), 3-(allyloxy)-2-hydroxypropane-1-sulfonate, or mixture thereof.

In yet some other embodiments, when the activated olefin contains anionic group that can bear negative charge at an alkaline pH, the counter positive ions for the negative charges include, but are not limited to, alkali metal ions, Li⁺, Na⁺, K⁺, NH₄⁺, a quaternary ammonium ion, etc.

In some embodiments of the disclosed methods, the contacting step is done in the presence of a reaction solvent. The reaction solvent can be any inorganic or organic solvent commonly used in chemical synthesis. The reaction solvent used in the disclosed

method can be introduced into the reaction between the primary amine and the activated olefin including a cationic or anionic group by any way known by one skilled in the art. For example, the solvent can be added into the container or vessel for reaction before, at the same, with one or both reactants, or after the primary amine, the activated olefin, or both are added.

In some embodiments, the reaction solvent is water, methanol, ethanol, propanol, glycol, PEG, or a mixture thereof. In some other embodiments, the reaction solvent is water.

In some other embodiments of the disclosed methods, the contacting step is done in the presence of a catalyst, base, or acid. The catalyst, base, or acid can be introduced into the reaction between the primary amine and activated olefin by any way known by one skilled in the art.

In some embodiments, the contacting step is done without the presence of any additional base. In some other embodiments, the contacting step is done in the presence of an alkalinity source. In some other embodiments, the contacting step is done in the presence of an organic base, such as alkanolamines. In yet some other embodiments, the contacting step is done in the presence of an alkali metal hydroxide, carbonate, imidazole/pyridine based base, or combination thereof, such as NaOH, Na₂CO₃, aminoethyl pyridine, aminopropyl imidazole, or a combination thereof. In some other embodiments, the contacting step is done with the presence of benzyltrimethylammonium hydroxide. In some embodiments, the catalyst base is an amidine or guanidine base, or mixtures thereof. In some other embodiments, the catalyst is a ionic liquid, such as 1,8-diazabicyclo[5.4.0]-undec-7-en-8-ium acetate, for the reaction under a solvent free condition at room temperatures.

In yet some other embodiments of the disclosed methods, the contacting step is done in the presence of an acid. In some other embodiments, the contacting step is done in the presence of a catalyst. The catalyst can any one or more of the catalysts known for the Michael addition reaction by one skilled in the art.

In yet some other embodiments of the disclosed methods, the contacting step is done free of a catalyst, base, or acid. In some other embodiments, the contacting step is done free of an alkali metal hydroxide, carbonate, silicate, metasilicate, imidazole/pyridine-based base, or all thereof. In some embodiments, the contact step is done free of a base.

In yet another aspect, disclosed herein is an article, product, or composition comprising one or more compounds disclosed here or produced by the methods disclosed herein.

In some embodiments, the article, product or composition further comprises a carrier solvent or a carrier. As used herein, a “carrier solvent” or carrier is a solvent or solvent system in which the disclosed compound can be distributed evenly and stable.

As used herein, “stable” means that compounds disclosed herein does not precipitate from or separated from the carrier solvent or other ingredients in the composition in about 1 hour, from about 1 hour to about 12 hours, about 12 hours, about 1 day, about 5 days, about 10 days, about 20 days, about 1 month, from about 1 month to about 1 year, or from about 1 year to about 2 year after the compounds disclosed herein and carrier solvent or any other ingredients are mixed homogenously.

In some embodiments, the carrier solvent can be any inorganic or organic solvent commonly used in industry or in laboratory. In some other embodiments of the article, product, or composition, the carrier solvent is water, an alcohol, an alkylene glycol, an alkylene glycol alkyl ether, or a combination thereof. In some other embodiments, the carrier solvent is methanol, ethanol, propanol, isopropanol, butanol, isobutanol, monoethyleneglycol, ethyleneglycol monobutyl ether, or a combination thereof.

In some embodiments, the articles, products, or compositions are solid. In some other embodiments, the articles, products, or compositions are liquid.

In some embodiments, the article, product or composition can further comprise an additional surfactant. The additional surfactant is a nonionic, semi-nonionic, anionic, cationic, amphoteric, zwitterionic, Gemini surfactant, or combinations thereof.

In some embodiments, the additional surfactant is a nonionic, semi-nonionic, anionic, cationic, amphoteric, zwitterionic, Gemini surfactant, or combinations thereof. In some embodiments, the composition disclosed here includes a normal surfactant but is free of a Gemini surfactant. In some other embodiments, the composition includes a Gemini surfactant, but is free of a normal surfactant. In yet some other embodiments, the surfactant composition includes one kind of nonionic, semi-nonionic, anionic, cationic, amphoteric, and zwitterionic surfactants, but is free of the rest of the surfactants. For example, a disclosed composition can include one or more compounds disclosed herein

and one or more nonionic surfactants, but is free of a semi-nonionic, anionic, cationic, amphoteric, zwitterionic, or Gemini surfactant.

In some embodiments, the article, product or composition disclosed here comprises one or more compounds disclosed herein, an acid, and carrier solvent. In some
5 embodiments, the article, product or composition disclosed here comprises one or more compounds disclosed herein, an acid, carrier solvent, and a peroxycarboxylic acid or peroxycarboxylic acid composition.

In some embodiments, the article, product or composition can further comprise a primary alkalinity source. In some embodiments, the article, product or composition
10 disclosed here is a detergent composition that comprises one or more compounds disclosed herein and primary alkalinity sources. A detergent composition, as used herein, refers to a composition that contains more primary alkalinity source than the compounds disclosed herein in weight percentage and can generate an alkaline use solution having a use solution pH of from about 8 to about 13.

15 In some embodiments, the article, product or composition disclosed here is a detergent composition that comprises one or more compounds disclosed herein, primary alkalinity sources, and chelants. In some embodiments, the article, product or composition disclosed here is a detergent composition that comprises one or more compounds disclosed herein, primary alkalinity sources, chelants, and surfactants. In some embodiments, the
20 article, product or composition disclosed here is a detergent composition that comprises one or more compounds disclosed herein, primary alkalinity sources, and chelants, but is free of a surfactant.

In some embodiments, the compositions are solid compositions. In some other embodiments, the compositions are liquid.

25 In some embodiments, the article, product or composition disclosed here is a detergent composition that comprises one or more compounds disclosed herein, primary alkalinity sources, and enzymes. In some embodiments, the article, product or composition disclosed here is a detergent composition that comprises one or more compounds disclosed herein, primary alkalinity sources, chelants, enzymes, and surfactants. In some
30 embodiments, the article, product or composition disclosed here is a detergent composition that comprises one or more compounds disclosed herein, primary alkalinity sources, and enzymes, but is free of a surfactant, chelant, or both.

In some embodiments, the primary alkalinity source comprises an alkali metal hydroxide, alkali metal carbonate, alkali metal silicate, alkali metal silicate, amine, or mixture thereof. In some other embodiments, the primary alkalinity source comprises an alkali metal hydroxide, alkali metal carbonate, or mixture thereof.

5 In some embodiments, the detergent composition disclosed herein include a builder. In some embodiments, the detergent composition disclosed herein is free of a builder but includes a part of the primary alkalinity source as builder.

In some embodiments, the detergent composition disclosed herein include an enzyme, wherein the enzyme is amylase, protease, lipase, cellulase, cutinase, gluconase, peroxidase, and/or mixtures thereof. In some embodiments, the enzyme is a protease enzyme. In some other embodiments, the enzyme is a protease and amylase. In some other embodiments, the enzyme is a protease, amylase, and a lipase. In yet some other embodiments, the detergent composition or composition disclosed herein is free of an enzyme.

15 In some embodiments, the detergent composition or composition disclosed here include a chelant, wherein the chelant is methylglycinediacetic acid (MGDA), glutamic acid-N,N-diacetic acid (GLDA), N-hydroxyethylaminodiacetic acid, ethylenediaminetetraacetic acid (EDTA) (including tetra sodium EDTA), hydroxyethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, N-hydroxyethyl-ethylenediaminetriacetic acid (HEDTA), diethylenetriaminepentaacetic acid (DTPA), ethylenediaminesuccinic acid (EDDS), 2-hydroxyethyliminodiacetic acid (HEIDA), iminodisuccinic acid (IDS), 3-hydroxy-2'-iminodisuccinic acid (HIDS), or a mixture thereof.

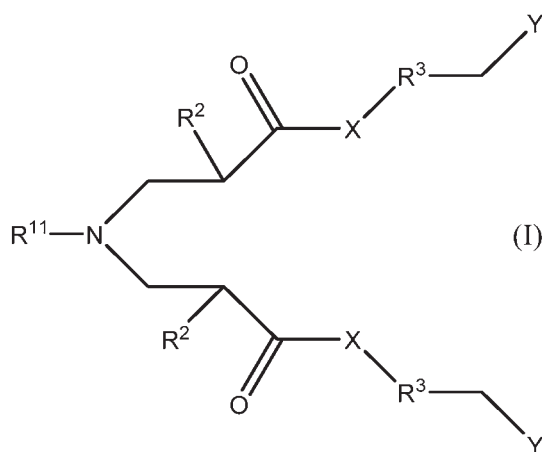
25 In other embodiments, the detergent composition disclosed herein further include one or more addition detergent composition agents.

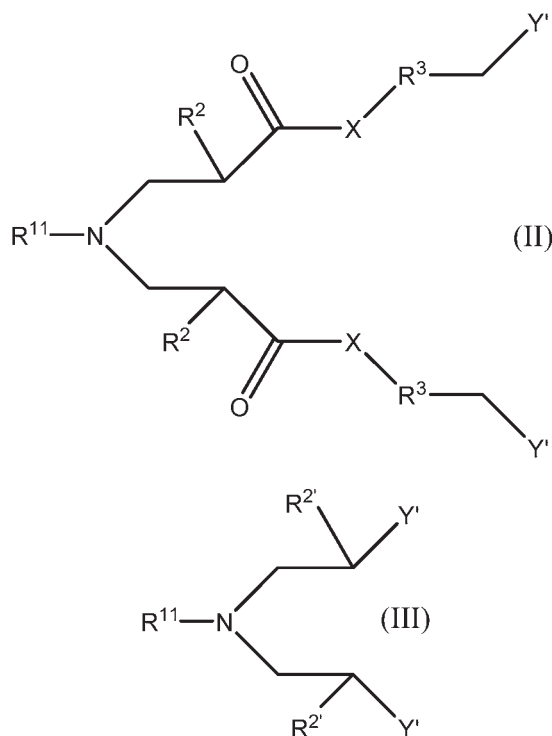
In some embodiments, the detergent compositions disclosed herein are solid compositions. In some other embodiments, the detergent compositions are liquid. In some embodiments, the solid detergent compositions disclosed herein are any pressed, extruded, or cast solid compositions, or in loose powder forms. In some other embodiments, the solid detergent composition is pressed and/or extruded blocks. In some other embodiments, the detergent compositions are multiple-use pressed solid block compositions.

A multi-use solid block detergent composition is preferred because the solid block detergent composition provides solid state stability and can be used in a dispenser. The use of solidification technology and solid block detergents for institutional and industrial operations is set forth for example with respect to the **SOLID POWER®** brand technology such as disclosed in U.S. Reissue Patent Nos. 32,762 and 32,818. In some embodiments, the detergent compositions disclosed herein include sodium carbonate hydrate cast solid products as disclosed by Heile et al., U.S. Patent Nos. 4,595,520 and 4,680,134. Each of these references are herein incorporated by reference in its entirety. Without being limited according to a mechanism of action, the solidification mechanism is ash hydration or the interaction of the sodium carbonate with water.

Disclosed also herein are methods of using a new class of di-cationic or di-anionic compounds for controlling corrosion on surfaces in a water system and corresponding corrosion control compositions comprising this new class of di-cationic or di-anionic compounds. Specifically, using one or more di-cationic or di-anionic compounds, which comprise two identical hydrophilic groups and one hydrophobic group and are derived from an aza-Michael addition reaction between a primary amine (Michael donor) and activated olefin (Michael acceptor), as corrosion control agents are disclosed.

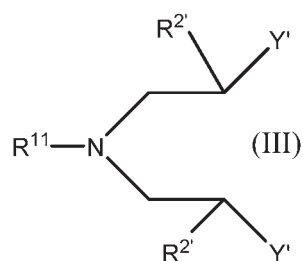
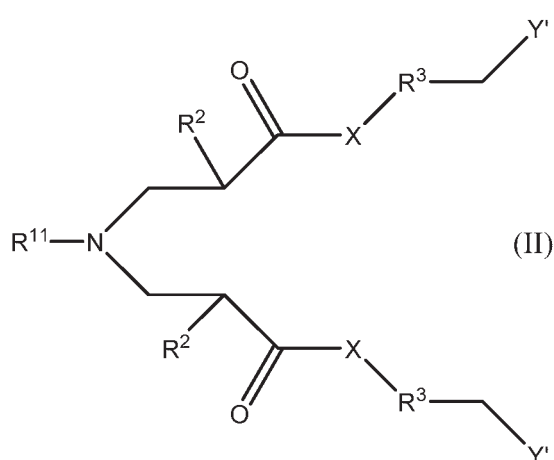
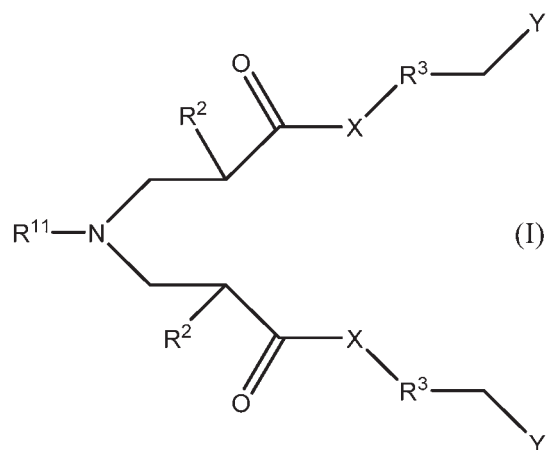
In one aspect, disclosed herein is a corrosion control composition, the composition comprises one or more compounds according to one of Formula **I**, Formula **II**, Formula **III** and one or more additional corrosion control composition agents,





wherein X is NH or O; R¹¹ is R¹ or R¹-Z-(CH₂)_m-; R¹ is an unsubstituted or substituted, linear or branched C₁-C₃₀ alkyl, cyclic alkyl, alkenyl, or alkynyl group; Z is NH or O; R² is H, CH₃, or an unsubstituted, linear or branched C₂-C₁₀ alkyl, alkenyl, or alkynyl group; m is an integer of 1 to 4; R³ is absent or an unsubstituted, linear C₁-C₃₀ alkylene group; Y is -NR₄R₅R₆⁽⁺⁾; Y' is -COOH, -SO₃H, -PO₃H, -OSO₃H, -OPO₃H, or a salt thereof; R^{2'} is H, CH₃, or an unsubstituted or substituted, linear or branched C₁-C₁₀ alkyl, alkenyl, alkynyl group, -COOH, -CH₂COOH, Y', or -(CH₂)_m-Y'; and R⁴, R⁵, and R⁶ are independently a C₁-C₁₀ alkyl group, and wherein the corrosion control composition mitigates corrosion on the surface in the water system.

In another aspect, disclosed herein is a method for inhibiting corrosion at a surface in a water system, the method comprises providing a corrosion control composition or a use solution of the corrosion control composition into a water system to generate a treated water system or onto a surface of the water system, wherein the corrosion control composition comprises one or more compounds according to one of Formula I, Formula II, Formula III and one or more additional corrosion control composition corrosion control composition agents,



wherein X is NH or O; R¹¹ is R¹ or R¹-Z-(CH₂)_m-; R¹ is an unsubstituted or substituted,
 5 linear or branched C₅-C₃₀ alkyl, cyclic alkyl, alkenyl, or alkynyl group; Z is NH or O; R² is
 H, CH₃, or an unsubstituted, linear or branched C₂-C₁₀ alkyl, alkenyl, or alkynyl group; m
 is an integer of 1 to 4; R³ is absent or an unsubstituted, linear C₁-C₃₀ alkylene group; Y is -
 NR₄R₅R₆⁽⁺⁾; Y' is -COOH, -SO₃H, -PO₃H, -OSO₃H, -OPO₃H, or a salt thereof; R^{2'} is H,
 CH₃, or an unsubstituted or substituted, linear or branched C₁-C₁₀ alkyl, alkenyl, alkynyl
 10 group, -COOH, -CH₂COOH, Y', or -(CH₂)_m-Y'; and R⁴, R⁵, and R⁶ are independently a

C₁-C₁₀ alkyl group, and wherein the corrosion control composition mitigates corrosion on the surface in the water system.

In some embodiments, the corrosion control composition can mitigate corrosion on a metal surface to about 280 mpy, about 265, about 250 mpy, about 225 mpy, about 200
 5 mpy, about 175 mpy, about 150 mpy, about 175 mpy, about 100 mpy, or any value there between, when the di-cation or di-anionic compound is at about 2 ppm and corrosion rate is measured by a bubble test.

In some embodiments, the one or more compounds are one or more of Formula **I**. In some other embodiments, the one or more compounds are one or more of Formula **II**.
 10 In yet some other embodiments, the one or more compounds are one or more of Formula **III**. In some other embodiments, the one or more compounds are one or more of Formula **II** and Formula **III**.

In some embodiments of the disclosed compounds herein, X is NH. In some other embodiments, X is O.

15 In some embodiments, R¹¹ is R¹. In some other embodiments, R¹¹ is R¹-Z-(CH₂)_m-. In some embodiments, R¹¹ is R¹-Z-(CH₂)_m-, and Z is NH. In some other embodiments, R¹¹ is R¹-Z-(CH₂)_m-, and Z is O. In yet some other embodiments, R¹¹ is R¹-Z-(CH₂)_m-, Z is NH, m is 2.

In some embodiments, R² is H. In some embodiments, R² is CH₃. In yet some
 20 other embodiments, R² is CH₃CH₃, CH₂CH₂CH₃, or CH(CH₃)₂.

In some embodiments, Y is -NR₄R₅R₆⁽⁺⁾. In some other embodiments, Y is -NR₄R₅R₆⁽⁺⁾, and R⁴, R⁵, and R⁶ are independently CH₃. In yet some other embodiments, Y is -NR₄R₅R₆⁽⁺⁾, and R⁴ and R⁵, independently CH₃, and R⁶ is a C₂-C₁₂ aromatic alkyl. In
 25 some other embodiments, Y is -NR₄R₅R₆⁽⁺⁾, and R⁴ and R⁵, independently CH₃, and R⁶ is -CH₂-C₆H₆.

In some embodiments, Y is -NR₄R₅R₆⁽⁺⁾ and the counter ion for Y any negative charged ion or species. In some other embodiments, the counter ion for Y is chloride, bromide, fluoride, iodide, acetate, aluminate, cyanate, cyanide, dihydrogen phosphate, dihydrogen phosphite, formate, carbonate, hydrogen carbonate, hydrogen oxalate,
 30 hydrogen sulfate, hydroxide, nitrate, nitrite, thiocyanate, or a combination thereof.

In some embodiments, Y is -COOH or salt thereof. In some other embodiments, Y is -SO₃H or salt thereof. In yet some other embodiments, Y is -PO₃H or salt thereof. In some other embodiments, Y is an acidic species or salt thereof.

In some embodiments, R³ is CH₂. In some other embodiments, R³ is CH₂CH₂. In other embodiments, R³ is C(CH₃)₂. In yet some other embodiments, R³ is an unsubstituted, linear, and saturated C₂-C₁₀ alkylene group. In some embodiments, R³ is an unsubstituted, linear, and unsaturated C₂-C₁₀ alkylene group.

In some embodiments, R¹ is a linear C₅-C₃₀ alkyl, alkenyl, or alkynyl group. In some other embodiments, R¹ is a branched C₅-C₃₀ alkyl, alkenyl, or alkynyl group. In yet some other embodiments, R¹ is a linear and saturated C₅-C₃₀ alkyl group. In some other embodiments, R¹ is a branched and saturated C₅-C₃₀ alkyl group.

In some embodiments, R¹ is a linear C₁-C₃₀ alkenyl group with one or more double bonds. In some other embodiments, wherein R¹ is a branched C₃-C₃₀ alkenyl group with one or more double bonds.

In some embodiments, R¹ is a linear C₃-C₃₀ alkynyl group with one or more triple bonds. In some other embodiments, R¹ is a branched C₃-C₃₀ alkynyl group with one or more triple bonds.

In some embodiments, R¹¹ is a linear and saturated C₁-C₂₀ alkyl group. In some other embodiments, R¹¹ is a *trans* C₃-C₂₀ alkenyl group with at least one double bond. In some other embodiments, R¹¹ is a C₃-C₂₀ alkenyl group with at least one double bond of *trans* configuration. In some embodiments, R¹¹ is a *cis* C₃-C₂₀ alkenyl group with at least one double bond. In some other embodiments, R¹¹ is a C₃-C₂₀ alkenyl group with at least one double bond of *cis* configuration.

In some embodiments, R¹¹ is R¹-NH-CH₂CH₂CH₂ group and R¹ is a linear and saturated C₆-C₂₀ alkyl, a *trans* alkenyl, or a *cis* alkenyl group.

In some other embodiments, R² is H, X is NH, R³ is CH₂CH₂, Y is CH₂-N⁺(CH₃)₃Cl⁻.

In some embodiments, the compound is a mixture of two or more di-cationic or anionic compounds. In some other embodiments, the compound is a single or mixture of di-cationic compounds. In some other embodiments, the compound is a single or mixture of di-anionic compounds. The two or more di-cationic or anionic compounds are different

from each other by molecular or average molecular weight, structure or combination thereof.

In some embodiments, the compound is a mixture of at least two different dicationic compounds derived from the same primary amine and activated olefin or from
5 different primary amines and activated olefins.

In some embodiments, the compound is derived from a primary amine and (3-Acrylamidopropyl)trimethylammonium chloride (APTAC). In some other embodiments, the compound is derived from a primary amine and [3-(methacryloylamino)propyl]trimethylammonium chloride (MAPTAC).

10 In some embodiments, the compound is derived from a primary amine and an activated olefin. In some embodiments, the activated olefin is (3-Acrylamidopropyl)trimethylammonium chloride (APTAC), [3-(Methacryloylamino)propyl]trimethylammonium chloride (MAPTAC), 2-(acryloyloxy)-N,N,N-trimethylethanaminium chloride (DMAEA-MCQ), N,N-dimethylaminoethyl
15 acrylate benzyl chloride quaternary salt (DMAEA-BCQ), 2-(methacryloyloxy)-N,N,N-trimethylethan-1-aminium methyl sulfate (DMAEA-MSQ), or 2-(acryloyloxy)-N,N,N-trimethylethanaminium chloride (DMAEA-MSQ).

In some other embodiments, the activated olefin is (3-Acrylamidopropyl)trimethylammonium chloride (APTAC), [3-(Methacryloylamino)propyl]trimethylammonium chloride (MAPTAC), or mixture thereof.
20

In some other embodiments, the activated olefin is 2-(acryloyloxy)-N,N,N-trimethylethanaminium chloride (DMAEA-MCQ), N,N-dimethylaminoethyl acrylate benzyl chloride quaternary salt (DMAEA-BCQ), 2-(methacryloyloxy)-N,N,N-trimethylethan-1-aminium methyl sulfate (DMAEA-MSQ), 2-(acryloyloxy)-N,N,N-trimethylethanaminium chloride (DMAEA-MSQ), or mixture thereof.
25

In In some embodiments, the compound is derived from a primary amine and an activated olefin. In some embodiments, the activated olefin is acrylic acid, methacrylic acid, itaconic acid, maleic acid, vinylsulfonic acid, vinylphosphonic acid, or mixture thereof.

30 In some other embodiments, the activated olefin is 2-acrylamido-2-methylpropane sulfonic acid (AMPS), 3-(allyloxy)-2-hydroxypropane-1-sulfonate, or mixture thereof.

In yet some other embodiments, when the activated olefin contains anionic group that can bear negative charge at an alkaline pH, the counter positive ions for the negative charges include, but are not limited to, alkali metal ions, Li^+ , Na^+ , K^+ , NH_4^+ , a quaternary ammonium ion, etc.

5 In some embodiments, the compound is soluble or dispersible in water or the corrosion control composition.

In some embodiments, the corrosion control composition comprises a carrier, wherein the carrier is water, an organic solvent, or a mixture thereof.

10 In some embodiments, the corrosion control composition further comprises an organic solvent. In some other embodiments, the corrosion control composition further comprises an organic solvent and water.

In some embodiments, the organic solvent is an alcohol, a hydrocarbon, a ketone, an ether, an alkylene glycol, a glycol ether, an amide, a nitrile, a sulfoxide, an ester, or any combination thereof. In some other embodiments, the organic solvent is an alcohol, an alkylene glycol, an alkylene glycol alkyl ether, or a combination thereof. In yet some
15 embodiments, the organic solvent is methanol, ethanol, propanol, isopropanol, butanol, isobutanol, monoethyleneglycol, ethyleneglycol monobutyl ether, or a combination thereof.

In some embodiments, the organic solvent is methanol, ethanol, propanol, isopropanol, butanol, 2-ethylhexanol, hexanol, octanol, decanol, 2-butoxyethanol, methylene glycol, ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, diethyleneglycol monomethyl ether, diethylene glycol monoethyl ether, ethylene glycol monobutyl ether, ethylene glycol dibutyl ether, pentane, hexane, cyclohexane, methylcyclohexane, heptane, decane, dodecane, diesel, toluene, xylene, heavy aromatic
20 naphtha, cyclohexanone, diisobutylketone, diethyl ether, propylene carbonate, N-methylpyrrolidinone, N,N-dimethylformamide, a mixture thereof with water, or any combination thereof.

In some embodiments, wherein the corrosion control composition further comprises one or more of additional corrosion inhibitors. In some embodiments, wherein the
30 corrosion control composition further comprises one or more of additional corrosion inhibitors and a carrier. In some embodiments, the corrosion inhibitor is an imidazoline compound, a pyridinium compound, or a combination thereof.

In some embodiments, the corrosion control composition further comprises a fouling control agent. In some embodiments, the fouling control agent is a single quat compound.

5 In some embodiments, the corrosion control composition further comprises a biocide. In some embodiments, the corrosion control composition further comprises a biocide and carrier. In some other embodiments, the corrosion control composition further comprises a biocide, corrosion inhibitor, and carrier.

10 In some embodiments, the biocide is an oxidizing biocide. In some other embodiments, the biocide is a non-oxidizing biocide. In some other embodiments, the biocide is chlorine, hypochlorite, ClO_2 , bromine, ozone, hydrogen peroxide, peracetic acid, peroxy sulphate, peroxy carboxylic acid, peroxy carboxylic acid composition, or mixture thereof. In some other embodiments, the biocide is glutaraldehyde, dibromonitrilopropionamide, isothiazolone, terbutylazine, polymeric biguanide, methylene bithiocyanate, tetrakis hydroxymethyl phosphonium sulphate, and combination thereof.

15 In some embodiments, the corrosion control composition further comprises an organic sulfur compound. In some other embodiments, wherein the organic sulfur compound is a mercaptoalkyl alcohol, mercaptoacetic acid, thioglycolic acid, 3,3'-dithiodipropionic acid, sodium thiosulfate, thiourea, L-cysteine, tert-butyl mercaptan, sodium thiosulfate, ammonium thiosulfate, sodium thiocyanate, ammonium thiocyanate, 20 sodium metabisulfite, or a combination thereof.

In some embodiments, the corrosion control composition further comprises an acid. In some embodiments, the corrosion control composition further comprises an inorganic acid, mineral acid, organic acid, or mixture thereof. In some embodiments, the corrosion control composition comprises from about 1 wt-% to about 20 wt-% of the acid.

25 In some embodiments, the acid is hydrochloric acid, hydrofluoric acid, citric acid, formic acid, acetic acid, or mixture thereof.

In some embodiments, the corrosion control composition further comprises a hydrogen sulfide scavenger. In some other embodiments, the hydrogen sulfide scavenger is an oxidant, inorganic peroxide, sodium peroxide, chlorine dioxide; a $\text{C}_1\text{-C}_{10}$ aldehyde, 30 formaldehyde, glyoxal, glutaraldehyde, acrolein, or methacrolein, a triazine, monoethanolamine triazine, monomethylamine triazine, or a mixture thereof.

In some embodiments, the corrosion control composition further comprises a surfactant. In some embodiments, the corrosion control composition further comprises a surfactant, biocide, and carrier.

In some embodiments, the surfactant is a nonionic, semi-nonionic, cationic, anionic, amphoteric, zwitterionic, Gemini, di-cationic, di-anionic surfactant, or mixtures thereof.

In some embodiments, the surfactant is an alkyl phenol, fatty acid, or mixture thereof.

In some embodiments, the corrosion control composition further comprises an asphaltene inhibitor, a paraffin inhibitor, a scale inhibitor, a gas hydrate inhibitor, a pH modifier, or any combination thereof.

In some embodiments, the corrosion control composition further comprises an emulsion breaker, reverse emulsion breaker, coagulant/flocculant agent, a water clarifier, a dispersant, antioxidant, polymer degradation prevention agent, permeability modifier, foaming agent, antifoaming agent, emulsifying agent, scavenger agent for CO₂, and/or O₂, gelling agent, lubricant, friction reducing agent, salt, or mixture thereof.

In some embodiments, the corrosion control composition is a liquid, gel, or a mixture comprising liquid/gel and solid.

In some embodiments, the corrosion control composition or a use solution thereof has a pH of from about 1 to about 11, from about 1 to about 3, from about 3 to about 5, from about 5 to about 7, from about 7 to about 9, from about 9 to about 11, about 2, about 4, about 6, about 8, about 10, or any value there between.

In some embodiments, the corrosion control composition comprises from about 10 wt-% to about 80 wt-% of a di-cationic compound or mixture thereof. In some other embodiments, the corrosion control composition comprise from about 10 wt-% to about 30 wt-%, from about 30 wt-% to about 50 wt-%, from about 50 wt-% to about 70 wt-%; from about 10 wt-% to about 40 wt-%, from about 20 wt-% to about 50 wt-%; from about 30 wt-% to about 60 wt-%; from about 40 wt-% to about 80 wt-%, about 15 wt-%, about 25 wt-%, about 35 wt-%, about 45 wt-%, about 55 wt-%, about 65 wt-%, about 75 wt-%, or any value there between of a di-cationic compound or mixture thereof.

In some embodiments, the corrosion control composition comprises from about 20 wt-% to about 60 wt-% of a di-anionic compound or mixture thereof. In some other

embodiments, the corrosion control composition comprise from about 10 wt-% to about 30 wt-%, from about 30 wt-% to about 50 wt-%, from about 50 wt-% to about 70 wt-%; from about 10 wt-% to about 40 wt-%, from about 20 wt-% to about 50 wt-%; from about 30 wt-% to about 60 wt-%; from about 40 wt-% to about 80 wt-%, about 15 wt-%, about 25 wt-%, about 35 wt-%, about 45 wt-%, about 55 wt-%, about 65 wt-%, about 75 wt-%, or any value there between of a di-anionic compound or mixture thereof.

In some embodiments, the di-cationic or di-anionic compound or mixture thereof has a concentration of from about 1 ppm to about 1000 ppm in the treated water system. In some embodiments, the di-cationic or di-anionic compound or mixture thereof has a concentration of from about 1 ppm to about 5 ppm, from about 5 ppm to about 10 ppm, from about 1 ppm to about 10 ppm, from about 1 ppm to about 20 ppm, from about 1 ppm to about 25 ppm, from about 5 ppm to about 15 ppm, from about 15 ppm to about 50 ppm, from about 50 ppm to about 100 ppm, from about 100 ppm to about 200 ppm, from about 200 ppm to about 300 ppm, from about 300 ppm to about 400 ppm, from about 400 ppm to about 500 ppm, from about 500 ppm to about 600 ppm, from about 600 ppm to about 700 ppm, from about 700 ppm to about 800 ppm, from about 800 ppm to about 900 ppm, or any value there between in the treated water system.

In some embodiments, the corrosion control composition is provided to the water system independently, simultaneously, or sequentially with an additional functional ingredient.

In some embodiments, the water system comprises fresh water, recycled water, salt water, surface water, produced water, or mixture thereof. In some embodiments, the water system comprises water, oil, and solid, as those found in oil and gas operations. In some embodiments, the water system comprises water and hydrocarbon or oil.

In some embodiments, the water system is a cooling water system, boiler water system, petroleum wells, downhole formations, geothermal wells, mineral washing, flotation and benefaction, papermaking, gas scrubbers, air washers, continuous casting processes in the metallurgical industry, air conditioning and refrigeration, water reclamation, water purification, membrane filtration, food processing, clarifiers, municipal sewage treatment, municipal water treatment, or potable water system.

In some embodiments, the corrosion control composition or di-cationic or di-anionic compounds disclosed herein can prevent corrosion on a surface in a water system

as indicated by a bubble cell test described in the Examples section of this disclosure, when the treated water system has a di-cationic or di-anionic concentration of from about 1 ppm to about 1,000 ppm, from about 1 to about 900 ppm, from about 1 ppm to about 800 ppm, from about 1 ppm to about 700 ppm, from about 1 ppm to about 600 ppm, from about 1 ppm to about 500 ppm, from about 1 ppm to about 400 ppm, from about 1 ppm to about 300 ppm, from about 1 ppm to about 250 ppm, from about 1 ppm to about 200 ppm, from about 1 ppm to about 150 ppm, from about 1 ppm to about 100 ppm, from about 1 ppm to about 50 ppm, from about 1 ppm to about 25 ppm, from about 1 ppm to about 10 ppm, from about 0.5 ppm to about 2 ppm, about 950 ppm, about 850 ppm, about 750 ppm, about 650 ppm, about 550 ppm, about 450 ppm, about 350, about 250 ppm, about 150 ppm, about 50 ppm, about 25 ppm, about 10 ppm, about 5 ppm, about 2 ppm, about 1 ppm, about 0.5 ppm, or any range or value there between, after dosing the water system with the di-cationic or di-anionic, or the corrosion control composition.

The methods and compositions of the present disclosure may comprise, consist essentially of, or consist of the components and ingredients of the disclosed compositions or methods as well as other ingredients described herein. As used herein, "consisting essentially of" means that the methods and compositions may include additional steps, components or ingredients, but only if the additional steps, components or ingredients do not materially alter the basic and novel characteristics of the claimed methods and compositions.

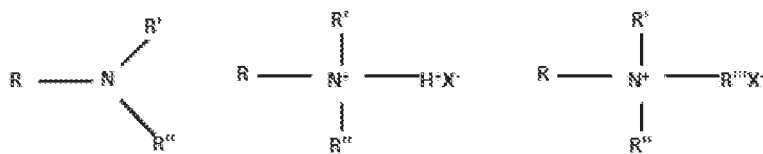
Alkalinity Source

The disclosed methods of preparation may include using an effective amount of an alkalinity source as a catalyst. The disclosed corrosion control compositions or methods of using thereof may also include using an effective amount of an alkalinity source. The alkalinity source can be added to the reaction mixture in the form of solid, liquid, or solution thereof.

In general, an effective amount of the alkalinity source should be considered as an amount that provides a reaction mixture having a pH of at least about 8. When the solution has a pH of between about 8 and about 10, it can be considered mildly alkaline, and when the pH is greater than about 12, the solution can be considered caustic.

The alkalinity source can include an alkali metal carbonate, an alkali metal hydroxide, alkaline metal silicate, alkaline metal metasilicate, or a mixture thereof. Suitable metal carbonates that can be used include, for example, sodium or potassium carbonate, bicarbonate, sesquicarbonate, or a mixture thereof. Suitable alkali metal hydroxides that can be used include, for example, sodium, lithium, or potassium hydroxide. Examples of useful alkaline metal silicates include sodium or potassium silicate (with $M_2O:SiO_2$ ratio of 2.4 to 5:1, M representing an alkali metal) or metasilicate. A metasilicate can be made by mixing a hydroxide and silicate. The alkalinity source may also include a metal borate such as sodium or potassium borate, and the like.

The alkalinity source may also include ethanolamines, urea sulfate, amines, amine salts, and quaternary ammonium. The simplest cationic amines, amine salts and quaternary ammonium compounds can be schematically drawn thus:



in which, R represents a long alkyl chain, R', R'', and R''' may be either long alkyl chains or smaller alkyl or aryl groups or hydrogen and X represents an anion.

In some embodiments, the methods of preparation is free of the alkalinity source because the reactants contain a primary amine or primary amine group to catalyze the reaction.

20 **Primary Alkalinity Source**

The disclosed composition can include a primary alkalinity source, especially when the disclosed composition is a detergent composition.

The primary alkalinity source of the composition or detergent composition disclosed herein can include, for example, an alkali metal hydroxide, alkali metal carbonate, alkali metal silicate, alkali metal metasilicate or mixture thereof. Examples of suitable alkalinity sources include, but are not limited to, sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, sodium silicate, sodium metasilicate, potassium silicate, or a mixture thereof. The alkalinity source is preferably an alkali

hydroxide, alkali carbonate, or mixture thereof. The alkalinity source controls the pH of the resulting use solution of the composition disclosed when water or other diluent is added to the composition to form a use solution.

When the disclosed composition is a detergent composition, the pH of the use
5 solution must be maintained in the alkaline range to provide sufficient detergency properties. Therefore, the disclosed detergent composition comprises more primary alkalinity source than the disclosed compounds disclosed herein in term of weight percentage.

A use solution of a composition disclosed herein as used herein refers to a diluted
10 solution for the composition or compounds by a diluent. A diluent as used herein refers to water, city water, distilled water, or carrier solvents defined herein. The composition or the compounds can be diluted by a factor of 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11-1,000,000, or any value there between to generate a use solution and then use the use solution for this application. In this disclosure, when a composition or di-cationic compounds are applied,
15 either the composition/compounds or use solution thereof is applied.

When the disclosed composition is a detergent composition, the pH of a use solution of the detergent composition is defined as the pH that is determined at room temperature when the use solution is obtained by diluting the detergent composition with distilled water and contains from 0.1 g/L to about 3 g/L of the primary alkalinity source. In
20 some embodiments, the concentration of the alkalinity source is from about 0.1 g/L to about 0.5 g/L, from about 0.5 g/L to about 1 g/L, from about 1 g/L to about 3 g/L, from about 1 g/L to about 2 g/L, from about 2 g/L to about 3 g/L, about 0.1 g/L, about 0.2 g/L, about 0.3 g/L, about 0.4 g/L, about 0.5 g/L, about 1.0 g/L, about 1.5 g/L, about 2.0 g/L, about 2.5 g/L, about 3.0 g/L, or any value there between in the use solution.

Alternatively, when the disclosed composition is a detergent composition, the pH of
25 a use solution of the detergent composition is defined as the pH that is determined at room temperature when the use solution is obtained by diluting the detergent composition with distilled water and contains from 0.5 g/L to about 5 g/L of the composition. In some embodiments, the concentration of the composition is from about from about 0.5 g/L to
30 about 1 g/L, from about 1 g/L to about 2 g/L, from about 2 g/L to about 3 g/L, from about 3 g/L to about 4 g/L, from about 4 g/L to about 5 g/L, about 0.5 g/L, about 1.0 g/L, about

1.5 g/L, about 2.0 g/L, about 2.5 g/L, about 3.0 g/L, about 3.5 g/L, about 4.0 g/L, about 4.5 g/L, about 5.0 g/L or any value there between in the use solution.

In some embodiments, a use solution of the detergent composition therefore provides a pH of at least about 8, preferably a pH of from about 9.5 to about 12, more preferably from about 10 to about 11 or from about 11 to about 12, when its primary alkalinity source is at a concentration of about 0.1 g/L, about 0.2 g/L, about 0.5 g/L, about 0.8 g/L, or about 1 gram per liter (g/L). In some embodiments, a use solution of the detergent composition therefore provides a pH of at least 8, preferably a pH of 9.5 to 11, more preferably 10 to 11, from about 11 to about 12, when its primary alkalinity source in distilled water is at a concentration of about 1 g/L, about 1.5 g/L, about 2.0 g/L, about 2.5 g/L, about 3 g/L, or any value there between.

In some other embodiments, a use solution of the detergent composition therefore provides a pH of at least about 8, preferably a pH of from about 9.5 to about 12, more preferably from about 10 to about 11 or from about 11 to about 12, when the composition itself is at a concentration of about 0.5 g/L, about 0.8 g/L, about 1 g/L, about 1.5 g/L, about 2.0 g/L, about 2.5 g/L, about 3.0 g/L, about 3.5 g/L, about 4.0 g/L, about 4.5 g/L, or about 5.0 g/L. In some embodiments, a use solution of the detergent composition therefore provides a pH of at least 8, preferably a pH of 9.5 to 11, more preferably 10 to 11, from about 11 to about 12, when the composition itself is at a concentration of about 1 g/L, about 1.5 g/L, about 2.0 g/L, about 2.5 g/L, about 3 g/L, about 3.5 g/L, about 4.0 g/L, about 4.5 g/L, about 5.0 g/L, or any value there between.

In some embodiments, the pH of the use solution is between about 10 and about 13. In some embodiments, the pH of the use solution is between about 8 and about 10. Particularly, the pH of the use solution is about 11-12. If the pH of the use solution is too low, for example, below approximately 10, the use solution may not provide adequate detergency properties. Further, at lower pH levels, the silicate species become unstable and may precipitate out of solution. If the pH of the use solution is too high, for example, above approximately 13, the use solution may be too alkaline and attack or damage the surface to be cleaned. A further consideration for the pH is that if the composition is too alkaline, a user would be required to wear PPE. However, if the pH of the composition is at or below about 11.5 pH, PPE is not required. Therefore, it is desirable for the pH of the

detergent composition disclosed herein in diluted use form to be between about 11 and about 12 for the composition to be effective, but not corrosive to human skin.

Preferably, the primary alkalinity source is an alkali metal hydroxide. Preferred alkali metal hydroxides include sodium hydroxide and potassium hydroxide. More preferably, the primary alkalinity source is sodium hydroxide. Sodium carbonate can be of light density or heavy density.

When a carbonate is included in the disclosed detergent composition, an effective amount of the alkali metal carbonate is an amount that provides a use solution having a pH of at least 8, preferably a pH of 9.5 to 11, more preferably 10 to 10.3.

In general, when the primary alkalinity source is present in the disclosed detergent composition at a concentration of at least about 1 wt-%, the composition or a use solution of the composition can emulsify fats and oils present. When the primary alkalinity source is present in a concentration of about 3 wt-% or greater, the composition or a use solution of the composition can emulsify, suspend, and separate oils and fats after treatment.

In some embodiments where the disclosed composition is not a detergent composition, the composition is free of a primary alkalinity source.

Acids

Generally, acids, as used in this disclosure, include both organic and inorganic acids. Organic acids include, but not limited to, hydroxyacetic (glycolic) acid, formic acid, acetic acid, propionic acid, butyric acid, valeric acid, caproic acid, gluconic acid, itaconic acid, trichloroacetic acid, urea hydrochloride, and benzoic acid. Organic acids also include dicarboxylic acids such as oxalic acid, malonic acid, succinic acid, glutaric acid, maleic acid, fumaric acid, adipic acid, and terephthalic acid. Combinations of these organic acids can also be used. Inorganic acids include, but are not limited to, mineral acids, such as phosphoric acid, sulfuric acid, sulfamic acid, methylsulfamic acid, hydrochloric acid, hydrobromic acid, hydrofluoric acid, and nitric acid. Inorganic acids can be used alone, in combination with other inorganic acid(s), or in combination with one or more organic acid. Acid generators can be used to form a suitable acid, including for example generators such as potassium fluoride, sodium fluoride, lithium fluoride, ammonium fluoride, ammonium bifluoride, sodium silicofluoride, etc.

Examples of particularly suitable acids in this the methods or compositions disclosed herein include inorganic and organic acids. Exemplary inorganic acids include

phosphoric, phosphonic, sulfuric, sulfamic, methylsulfamic, hydrochloric, hydrobromic, hydrofluoric, and nitric. Exemplary organic acids include hydroxyacetic (glycolic), citric, lactic, formic, acetic, propionic, butyric, valeric, caproic, gluconic, itaconic, trichloroacetic, urea hydrochloride, and benzoic. Organic dicarboxylic acids can also be used such as oxalic, maleic, fumaric, adipic, and terephthalic acid.

Percarboxylic acids and peroxydicarboxylic acid compositions

A peroxydicarboxylic acid (*i.e.* peracid) or peroxydicarboxylic acid composition can be included in the articles, products, or compositions disclosed herein. As used herein, the term “peracid” may also be referred to as a “percarboxylic acid,” “peroxydicarboxylic acid” or “peroxyacid.” Sulfoperoxydicarboxylic acids, sulfonated peracids and sulfonated peroxydicarboxylic acids are also included within the terms “peroxydicarboxylic acid” and “peracid” as used herein. As one of skill in the art appreciates, a peracid refers to an acid having the hydrogen of the hydroxyl group in carboxylic acid replaced by a hydroxy group. Oxidizing peracids may also be referred to herein as peroxydicarboxylic acids.

A peracid includes any compound of the formula $R-(COOOH)_n$ in which R can be hydrogen, alkyl, alkenyl, alkyne, acyclic, alicyclic group, aryl, heteroaryl, or heterocyclic group, and n is 1, 2, or 3, and named by prefixing the parent acid with peroxy. Preferably R includes hydrogen, alkyl, or alkenyl. The terms "alkyl," "alkenyl," "alkyne," "acyclic," "alicyclic group," "aryl," "heteroaryl," and "heterocyclic group" are as defined herein.

A peroxydicarboxylic acid composition, as used herein, refers to any composition that comprises one or more peracids, their corresponding acids, and hydrogen peroxide or other oxidizing agents. A peroxydicarboxylic acid composition can also include a stabilizer, fluorescent active tracer or compound, or other ingredients, as one skilled in the other would know.

As used herein, the terms “mixed” or “mixture” when used relating to “percarboxylic acid composition,” “percarboxylic acids,” “peroxydicarboxylic acid composition” or “peroxydicarboxylic acids” refer to a composition or mixture including more than one percarboxylic acid or peroxydicarboxylic acid. Peracids such as peroxyacetic acid and peroxyoctanoic acid may also be used. Any combination of these acids may also be used.

In some embodiments, however, the articles, products, or compositions are free of a peroxydicarboxylic acid or peroxydicarboxylic acid composition.

Builder

The detergent compositions disclosed herein include one or more builders. In some embodiments, a builder may also serve as a part of the primary alkalinity source in the detergent compositions. In some embodiments, the builder includes a carbonate, hydroxide, metasilicate, or mixture thereof. In some embodiments, a carbonate can assist in providing solid detergent compositions, as the carbonate can act as a hydratable salt.

Examples of suitable builders include, but are not limited to alkali metal carbonates, alkali metal hydroxides, and alkali metal silicates. Exemplary alkali metal carbonates that can be used include, but are not limited to, sodium or potassium carbonate, bicarbonate, sesquicarbonate, and mixtures thereof. Exemplary alkali metal hydroxides that can be used include, but are not limited to, sodium or potassium hydroxide. The alkali metal hydroxide may be added to the composition in any form known in the art, including as solid beads, dissolved in an aqueous solution, or a combination thereof. Examples of alkali metal silicates include, but are not limited to, sodium or potassium silicate or polysilicate, sodium or potassium metasilicate and hydrated sodium or potassium metasilicate or a combination thereof.

In some embodiments, the composition is free of a builder.

Chelant

The detergent composition disclosed herein may also include a chelant. Chelants include, but are not limited to, chelating agents (chelators), sequestering agents (sequestrants), detergent builders, and the like. Examples of chelants include, but are not limited to, phosphonates, phosphates, aminocarboxylates and their derivatives, pyrophosphates, polyphosphates, ethylenediamine and ethylenetriamine derivatives, hydroxyacids, and mono-, di-, and tri-carboxylates and their corresponding acids. Other exemplary chelants include aluminosilicates, nitroloacetates and their derivatives, and mixtures thereof.

Suitable aminocarboxylic acids according to the invention include, but are not limited to, methylglycinediacetic acid (MGDA), glutamic acid-N,N-diacetic acid (GLDA), N-hydroxyethylaminodiacetic acid, ethylenediaminetetraacetic acid (EDTA) (including tetra sodium EDTA), hydroxyethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, N-hydroxyethyl-ethylenediaminetriacetic acid (HEDTA), diethylenetriaminepentaacetic acid (DTPA), ethylenediaminesuccinic acid

(EDDS), 2-hydroxyethyliminodiacetic acid (HEIDA), iminodisuccinic acid (IDS), 3-hydroxy-2-2'-iminodisuccinic acid (HIDS) and other similar acids or salts thereof having an amino group with a carboxylic acid substituent. Additional description of suitable aminocarboxylates suitable for use as chelating agents and/or sequestrants is set forth in
5 Kirk-Othmer, Encyclopedia of Chemical Technology, Third Edition, volume 5, pages 339-366 and volume 23, pages 319-320, the disclosure of which is incorporated by reference herein.

Chelants can be water soluble, and/or biodegradable. Other exemplary chelants include TKPP (tetrapotassium pyrophosphate), PAA (polyacrylic acid) and its salts,
10 phosphonobutane carboxylic acid, Alanine,N,N-bis(carboxymethyl)-,trisodium salt, and sodium gluconate.

In some embodiments, the chelant is free of phosphorus. In some embodiments, the chelant may also serve as a solidifying agent to help form the solid composition, such as sodium salts of citric acid.

15 Preferably, the chelant is a sodium salt of aminocarboxylates. More preferably, the chelant is methyl glycine diacetic acid (MGDA). Synergistic water conditioning is achieved when using methyl glycine diacetic acid (MGDA) in combination with polyacrylic acids and its salts.

In some embodiments, the composition disclosed herein is free of a chelant,
20 detergent builder, or both. In some embodiments, the composition disclosed herein is free of a chelant, detergent builder, or both that contain phosphorus.

Scale Inhibitor

The reverse emulsion breaker composition can further comprise a scale inhibitor. Suitable scale inhibitors include, but are not limited to, phosphates, phosphate esters,
25 phosphoric acids, phosphonates, phosphonic acids, polyacrylamides, salts of Sacrylamidomethyl propane sulfonate/acrylic acid copolymer (AMPS/AA), phosphinated maleic copolymer (PHOS/MA), mono-, bis- and oligomeric phosphinosuccinic acid (PSO) derivatives, polycarboxylic acid, hydrophobically modified polycarboxylic acid, and salts of a polymaleic acid/acrylic acid/acrylamidomethyl propane sulfonate terpolymer
30 (PMA/AA/AMPS).

In some embodiments, the composition disclosed herein is free of a scale inhibitor.

Enzyme

The compositions or detergent compositions disclosed herein can include an enzyme. An enzyme in the detergent compositions enhances removal of soils, prevents re-deposition, and/or reduces foam during applications of the detergent compositions or their use solutions. The function of an enzyme is to break down adherent soils, such as starch or proteinaceous materials, typically found in soiled surfaces and removed by a detergent composition into a wash water source.

Exemplary types of enzymes which can be incorporated into the detergent compositions disclosed herein include, but are not limited to, amylase, protease, lipase, cellulase, cutinase, gluconase, peroxidase, and/or mixtures thereof. A composition disclosed herein may employ more than one enzyme, from any suitable origin, such as vegetable, animal, bacterial, fungal or yeast origin. In some embodiments, the enzyme is a protease. As used herein, the terms "protease" or "proteinase" refer enzymes that catalyze the hydrolysis of peptide bonds.

As one skilled in the art shall ascertain, enzymes are designed to work with specific types of soils. For example, according to an embodiment of the invention, ware wash applications may use a protease enzyme as it is effective at the high temperatures of the ware wash machines and is effective in reducing protein-based soils. Protease enzymes are particularly advantageous for cleaning soils containing protein, such as blood, cutaneous scales, mucus, grass, food (e.g., egg, milk, spinach, meat residue, tomato sauce), or the like. Protease enzymes are capable of cleaving macromolecular protein links of amino acid residues and convert substrates into small fragments that are readily dissolved or dispersed into the aqueous use solution. Proteases are often referred to as deterative enzymes due to the ability to break soils through the chemical reaction known as hydrolysis. Protease enzymes can be obtained, for example, from *Bacillus subtilis*, *Bacillus licheniformis* and *Streptomyces griseus*. Protease enzymes are also commercially available as serine endoproteases.

Examples of commercially-available protease enzymes are available under the following trade names: Esperase, Purafect, Purafect L, Purafect Ox, Everlase, Liquanase, Savinase, Prime L, Prosperase and Blap.

The enzyme to be included into the detergent composition may be an independent entity and/or may be formulated in combination with the detergent composition. In some embodiments, the enzyme may be formulated into a detergent composition in either liquid

or solid formulations. In addition, enzyme compositions may be formulated into various delayed or controlled release formulations. For example, a solid molded detergent composition may be prepared without the addition of heat. As a skilled artisan will appreciate, enzymes tend to become denatured by the application of heat and therefore use
5 of enzymes within detergent compositions require methods of forming detergent compositions that does not rely upon heat as a step in the formation process, such as solidification.

The enzyme composition may further be obtained commercially in a solid (*i.e.*, puck, powder, etc.) or liquid formulation. Commercially-available enzymes are generally
10 combined with stabilizers, buffers, cofactors and inert vehicles. The actual active enzyme content depends upon the method of manufacture, which is well known to a skilled artisan and such methods of manufacture are not critical to the present invention.

Alternatively, the enzyme composition may be provided separate from the detergent composition, such as added directly to a use solution of a detergent composition
15 or a wash liquor, or wash water of an application, *e.g.* dishwasher.

Other Additional Detergent Composition Agent

The detergent composition disclosed herein may include one or more additional detergent composition agents. Exemplary additional detergent composition agents include, but are not limited to, a threshold agent; crystal modifier; hardening agent; bleaching
20 agent; peroxycarboxylic acid, peroxycarboxylic acid composition, filler; defoaming agent; anti-redeposition agent; stabilizing agent; dispersant; fragrance and dye; and thickener.

In some embodiments, the detergent composition disclosed herein is free of one, more, or all the additional detergent composition agents.

Additional Corrosion Control Composition Agent in a Corrosion Control Composition

25 In addition to one or more di-cationic di-anionic compounds derived from primary amines as described herein, a corrosion control composition in the present disclosure comprises one or more additional corrosion control composition agents.

The additional corrosion control composition agent in the disclosed corrosion control compositions can include, but is not limited to, a carrier, acid, dispersant, biocide,
30 additional corrosion inhibitor, fouling control agent, antioxidant, polymer degradation prevention agent, permeability modifier, foaming agent, antifoaming agent, fracturing

proppant, scavenger for H₂S, CO₂, and/or O₂, gelling agent, lubricant, and friction reducing agent, salt, or mixture thereof.

The additional corrosion control composition agent in the disclosed corrosion control compositions can also include, but not be limited to, an organic sulfur compound, asphaltene inhibitor, paraffin inhibitor, scale inhibitor, water clarifier, emulsion breaker, 5 reverse emulsion breaker, gas hydrate inhibitor, a pH modifier, a surfactant, or a combination thereof.

Furthermore, the additional corrosion control composition agent can be a sequestrant, solubilizer, lubricant, buffer, cleaning agent, rinse aid, preservative, binder, 10 thickener or other viscosity modifier, processing aid, carrier, water-conditioning agent, or foam generator, threshold agent or system, aesthetic enhancing agent (e.g., dye, odorant, perfume), or other additive suitable for formulation with a reverse emulsion breaker, or mixtures thereof.

The additional corrosion control composition agent in a corrosion control 15 composition disclosed herein will vary according to the specific corrosion control composition being manufactured and its intended use as one skilled in the art will appreciate.

Alternatively, the corrosion control composition does not contain or is free of one or more of the additional corrosion control composition agents.

When one or more additional corrosion control composition agents are used in the 20 corrosion control compositions disclosed herein, they can be formulated together with the di-cationic or di-anionic compounds as described here in the same corrosion control compositions. Alternatively, some or all the additional corrosion control composition agents can be formulated into one or more different formulations and be supplied to the water systems or surfaces. In other words, the additional corrosion control composition 25 agents can be provided into a water system or onto a surface independently, simultaneously, or sequentially.

Biocide and Carrier

In some embodiments, the corrosion control compositions disclosed herein further include a biocide, in addition to the di-cationic or di-anionic compounds. In some other 30 embodiments, the disclosed corrosion control compositions herein further include a carrier. In some other embodiments, the disclosed corrosion control compositions herein further include a biocide and carrier. In some embodiments, the disclosed methods or corrosion

control compositions herein may consist of one or more di-cationic or di-anionic compounds disclosed herein and carrier. In some embodiments, the corrosion control compositions disclosed herein consist of one or more di-cationic or di-anionic compounds disclosed herein, a carrier, and a biocide.

5 Biocides suitable for use may be oxidizing or non-oxidizing biocides. Oxidizing biocides include, but are not limited to, bleach, chlorine, bromine, chlorine dioxide, and materials capable of releasing chlorine and bromine. Non-oxidizing biocides include, but are not limited to, glutaraldehyde, isothiazolin, 2,2-dibromo-3-nitrilopropionamide, 2-bromo-2-nitropropane-1,3 diol, 1-bromo-1-(bromomethyl)-1,3-propanedicarbonitrile, 10 tetrachloroisophthalonitrile, alkyl dimethyl benzyl ammonium chloride, dimethyl dialkyl ammonium chloride, didecyl dimethyl ammonium chloride, poly(oxyethylene(dimethyliminio)ethylene(dimethyliminio)ethylene dichloride, methylene bithiocyanate, 2-decylthioethanamine, tetrakis(hydroxymethyl) phosphonium sulfate, dithiocarbamate, cyanodithioimidocarbonate, 2-methyl-5-nitroimidazole-1-ethanol, 2-(2-bromo-2-nitroethenyl)furan, beta-bromo-beta-nitrostyrene, beta-nitrostyrene, beta-nitrovinyl furan, 2-bromo-2-bromomethyl glutaronitrile, bis(trichloromethyl) sulfone, S-(2-hydroxypropyl)thiomethanesulfonate, tetrahydro-3,5-dimethyl-2H-1,3,5-hydrazine-2-thione, 2-(thiocyanomethylthio)benzothiazole, 2-bromo-4'-hydroxyacetophenone, 1,4-bis(bromoacetoxy)-2-butene, bis(tributyltin)oxide, 2-(tert-butylamino)-4-chloro-6- 15 (ethylamino)-s-triazine, dodecylguanidine acetate, dodecylguanidine hydrochloride, coco alkyl dimethylamine oxide, n-coco alkyl trimethylenediamine, tetra-alkyl phosphonium chloride, 7-oxabicyclo[2.2.1]heptane-2,3-dicarboxylic acid, 4,5-dichloro-2-n-octyl-4-isothiazoline-3-one, 5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one.

25 Suitable non-oxidizing biocides also include, for example, aldehydes (e.g., formaldehyde, glutaraldehyde, and acrolein), amine-type compounds (e.g., quaternary amine compounds and cocodiamine), halogenated compounds (e.g., 2-bromo-2-nitropropane-3-diol (Bronopol) and 2,2-dibromo-3-nitrilopropionamide (DBNPA)), sulfur compounds (e.g., isothiazolone, carbamates, and metronidazole), and quaternary 30 phosphonium salts (e.g., tetrakis(hydroxymethyl)-phosphonium sulfate (THPS)).

Suitable oxidizing biocides include, for example, sodium hypochlorite, trichloroisocyanuric acids, dichloroisocyanuric acid, calcium hypochlorite, lithium

hypochlorite, chlorinated hydantoins, stabilized sodium hypobromite, activated sodium bromide, brominated hydantoins, chlorine dioxide, ozone, peroxy carboxylic acid, peroxy carboxylic acid composition, and peroxides.

5 The corrosion control composition can comprise from about 0.1 wt-% to about 10 wt-%, from about 0.5 wt-% to about 5 wt-%, or from about 0.5 wt-% to about 4 wt-% of a biocide, based on total weight of the composition. In some embodiments, the corrosion control composition is free of a biocide. In some embodiments, the corrosion control composition is free of an oxidizing biocide. In some other embodiments, the corrosion control composition is free of a non-oxidizing biocide.

10 A carrier in the disclosed corrosion control composition can be water, an organic solvent, or a combination of water and an organic solvent. The organic solvent can be an alcohol, a hydrocarbon, a ketone, an ether, an alkylene glycol, a glycol ether, an amide, a nitrile, a sulfoxide, an ester, or a combination thereof. Examples of suitable organic solvents include, but are not limited to, methanol, ethanol, propanol, isopropanol, butanol, 15 2-ethylhexanol, hexanol, octanol, decanol, 2-butoxyethanol, methylene glycol, ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, diethyleneglycol monomethyl ether, diethylene glycol monoethyl ether, ethylene glycol monobutyl ether, ethylene glycol dibutyl ether, pentane, hexane, cyclohexane, methylcyclohexane, heptane, decane, dodecane, diesel, toluene, xylene, heavy aromatic naphtha, cyclohexanone, 20 diisobutylketone, diethyl ether, propylene carbonate, N-methylpyrrolidinone, N,N-dimethylformamide, or a combination thereof.

The corrosion control composition can comprise from about 1 wt-% to about 80 wt-%, from about 1 wt-% to about 70 wt-%, from about 1 wt-% to about 60 wt-%, from about 1 wt-% to about 50 wt-%, from about 1 wt-% to about 40 wt-%, from about 1 wt-% 25 to about 30 wt-%, from about 1 wt-% to about 20 wt-%, from about 1 wt-% to about 10 wt-%, from about 5 wt-% to about 10 wt-%, from about 5 wt-% to about 20 wt-%, from about 5 wt-% to about 30 wt-%, from about 5 wt-% to about 40 wt-%, from about 5 wt-% to about 50 wt-%, from about 10 wt-% to about 20 wt-%, from about 10 wt-% to about 30 wt-%, from about 10 to about 40 wt-%, from about 10 wt-% to about 50 wt-%, about 10 30 wt-%, about 20 wt-%, about 30 wt-%, about 40-%, about 50 wt-%, about 60 wt-%, about 70 wt-%, about 80 wt-%, about 90 wt-%, or any value there between of the one or more carrier, based on total weight of the composition.

Anionic Surfactants

Anionic surfactants are surface active substances in which the charge on the hydrophobe is negative; or surfactants in which the hydrophobic section of the molecule carries no charge unless the pH is elevated to neutrality or above (*e.g.*, carboxylic acids).

5 Carboxylate, sulfonate, sulfate and phosphate are the polar (hydrophilic) solubilizing groups found in anionic surfactants. Of the cations (counter ions) associated with these polar groups, sodium, lithium and potassium impart water solubility; ammonium and substituted ammonium ions provide both water and oil solubility; and, calcium, barium, and magnesium promote oil solubility. As those skilled in the art understand, anionic
10 surfactants are excellent deterative surfactants and are therefore favored additions to heavy duty detergent compositions.

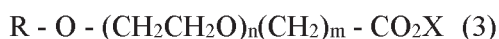
Anionic sulfate surfactants suitable for use in the present compositions include alkyl ether sulfates, alkyl sulfates, the linear and branched primary and secondary alkyl sulfates, alkyl ethoxysulfates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide
15 ether sulfates, the C₅-C₁₇ acyl-N-(C₁-C₄ alkyl) and -N-(C₁-C₂ hydroxyalkyl) glucamine sulfates, and sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside, and the like. Also included are the alkyl sulfates, alkyl poly(ethyleneoxy) ether sulfates and aromatic poly(ethyleneoxy) sulfates such as the sulfates or condensation products of ethylene oxide and nonyl phenol (usually having 1 to 6 oxyethylene groups per molecule).

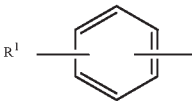
20 Anionic sulfonate surfactants suitable for use in the present compositions also include alkyl sulfonates, the linear and branched primary and secondary alkyl sulfonates, and the aromatic sulfonates with or without substituents.

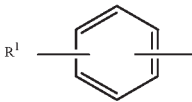
Anionic carboxylate surfactants suitable for use in the present compositions include carboxylic acids (and salts), such as alkanoic acids (and alkanoates), ester carboxylic acids
25 (*e.g.*, alkyl succinates), ether carboxylic acids, sulfonated fatty acids, such as sulfonated oleic acid, and the like. Such carboxylates include alkyl ethoxy carboxylates, alkyl aryl ethoxy carboxylates, alkyl polyethoxy polycarboxylate surfactants and soaps (*e.g.*, alkyl carboxyls). Secondary carboxylates useful in the present compositions include those which contain a carboxyl unit connected to a secondary carbon. The secondary carbon can
30 be in a ring structure, *e.g.*, as in p-octyl benzoic acid, or as in alkyl-substituted cyclohexyl carboxylates. The secondary carboxylate surfactants typically contain no ether linkages, no ester linkages and no hydroxyl groups. Further, they typically lack nitrogen atoms in

the group-group (amphiphilic portion). Suitable secondary soap surfactants typically contain 11-13 total carbon atoms, although more carbons atoms (*e.g.*, up to 16) can be present. Suitable carboxylates also include acylamino acids (and salts), such as acylglutamates, acyl peptides, sarcosinates (*e.g.*, N-acyl sarcosinates), taurates (*e.g.*, N-acyl taurates and fatty acid amides of methyl tauride), and the like.

Suitable anionic surfactants include alkyl or alkylaryl ethoxy carboxylates of the following formula:



in which R is a C₈ to C₂₂ alkyl group or , in which R¹ is a C₄-C₁₆ alkyl group; n is an integer of 1-20; m is an integer of 1-3; and X is a counter ion, such as hydrogen, sodium, potassium, lithium, ammonium, or an amine salt such as monoethanolamine, diethanolamine or triethanolamine. In some embodiments, n is an integer of 4 to 10 and m is 1. In some embodiments, R is a C₈-C₁₆ alkyl group. In some embodiments, R is a C₁₂-C₁₄ alkyl group, n is 4, and m is 1.

In other embodiments, R is  and R¹ is a C₆-C₁₂ alkyl group. In still yet other embodiments, R¹ is a C₉ alkyl group, n is 10 and m is 1.

Such alkyl and alkylaryl ethoxy carboxylates are commercially available. These ethoxy carboxylates are typically available as the acid forms, which can be readily converted to the anionic or salt form. Commercially available carboxylates include, Neodox 23-4, a C₁₂₋₁₃ alkyl polyethoxy (4) carboxylic acid (Shell Chemical), and Emcol CNP-110, a C₉ alkylaryl polyethoxy (10) carboxylic acid (Witco Chemical). Carboxylates are also available from Clariant, *e.g.*, the product Sandopan[®] DTC, a C₁₃ alkyl polyethoxy (7) carboxylic acid.

In some embodiments, the composition or detergent composition disclosed herein is free of an anionic surfactant.

Nonionic Surfactants

Useful nonionic surfactants are generally characterized by the presence of an organic hydrophobic group and an organic hydrophilic group and are typically produced by the condensation of an organic aliphatic, alkyl aromatic or polyoxyalkylene hydrophobic

compound with a hydrophilic alkaline oxide moiety which in common practice is ethylene oxide or a polyhydration product thereof, polyethylene glycol. Practically any hydrophobic compound having a hydroxyl, carboxyl, amino, or amido group with a reactive hydrogen atom can be condensed with ethylene oxide, or its polyhydration adducts, or its mixtures with alkoxylenes such as propylene oxide to form a nonionic surface-active agent. The length of the hydrophilic polyoxyalkylene moiety which is condensed with any particular hydrophobic compound can be readily adjusted to yield a water dispersible or water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic properties. Useful nonionic surfactants include:

Block polyoxypropylene-polyoxyethylene polymeric compounds based upon propylene glycol, ethylene glycol, glycerol, trimethylolpropane, and ethylenediamine as the initiator reactive hydrogen compound. Examples of polymeric compounds made from a sequential propoxylation and ethoxylation of initiator are commercially available from BASF Corp. One class of compounds are difunctional (two reactive hydrogens) compounds formed by condensing ethylene oxide with a hydrophobic base formed by the addition of propylene oxide to the two hydroxyl groups of propylene glycol. This hydrophobic portion of the molecule weighs from about 1,000 to about 4,000. Ethylene oxide is then added to sandwich this hydrophobe between hydrophilic groups, controlled by length to constitute from about 10% by weight to about 80% by weight of the final molecule. Another class of compounds are tetra-flinctional block copolymers derived from the sequential addition of propylene oxide and ethylene oxide to ethylenediamine. The molecular weight of the propylene oxide hydrotype ranges from about 500 to about 7,000; and, the hydrophile, ethylene oxide, is added to constitute from about 10% by weight to about 80% by weight of the molecule.

Condensation products of one mole of alkyl phenol wherein the alkyl chain, of straight chain or branched chain configuration, or of single or dual alkyl constituent, contains from about 8 to about 18 carbon atoms with from about 3 to about 50 moles of ethylene oxide. The alkyl group can, for example, be represented by diisobutylene, di-amy, polymerized propylene, iso-octyl, nonyl, and di-nonyl. These surfactants can be polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols. Examples of commercial compounds of this chemistry are available on the market under

the trade names Igepal[®] manufactured by Rhone-Poulenc and Triton[®] manufactured by Union Carbide.

Condensation products of one mole of a saturated or unsaturated, straight or branched chain alcohol having from about 6 to about 24 carbon atoms with from about 3 to about 50 moles of ethylene oxide. The alcohol moiety can consist of mixtures of alcohols in the above delineated carbon range or it can consist of an alcohol having a specific number of carbon atoms within this range. Examples of like commercial surfactant are available under the trade names Lutensol[™], Dehydol[™] manufactured by BASF, Neodol[™] manufactured by Shell Chemical Co. and Alfonic[™] manufactured by Vista Chemical Co.

Condensation products of one mole of saturated or unsaturated, straight or branched chain carboxylic acid having from about 8 to about 18 carbon atoms with from about 6 to about 50 moles of ethylene oxide. The acid moiety can consist of mixtures of acids in the above defined carbon atoms range or it can consist of an acid having a specific number of carbon atoms within the range. Examples of commercial compounds of this chemistry are available on the market under the trade names Disponil or Agnique manufactured by BASF and Lipopeg[™] manufactured by Lipo Chemicals, Inc.

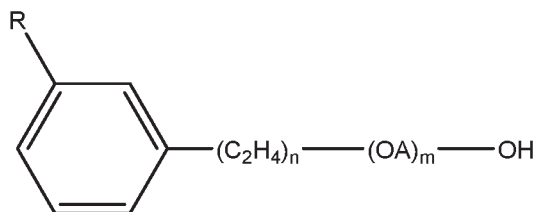
In addition to ethoxylated carboxylic acids, commonly called polyethylene glycol esters, other alkanolic acid esters formed by reaction with glycerides, glycerin, and polyhydric (saccharide or sorbitan/sorbitol) alcohols have application in this invention for specialized embodiments, particularly indirect food additive applications. All of these ester moieties have one or more reactive hydrogen sites on their molecule which can undergo further acylation or ethylene oxide (alkoxide) addition to control the hydrophilicity of these substances. Care must be exercised when adding these fatty esters or acylated carbohydrates to compositions of the present invention containing amylase and/or lipase enzymes because of potential incompatibility.

Examples of nonionic low foaming surfactants include, but are not limited to, compounds which are modified, essentially reversed, by adding ethylene oxide to ethylene glycol to provide a hydrophile of designated molecular weight; and, then adding propylene oxide to obtain hydrophobic blocks on the outside (ends) of the molecule. The hydrophobic portion of the molecule weighs from about 1,000 to about 3,100 with the central hydrophile including 10% by weight to about 80% by weight of the final molecule. These reverse Pluronics[™] are manufactured by BASF Corporation under the trade name

Pluronic™ R surfactants. Likewise, the Tetronic™ R surfactants are produced by BASF Corporation by the sequential addition of ethylene oxide and propylene oxide to ethylenediamine. The hydrophobic portion of the molecule weighs from about 2,100 to about 6,700 with the central hydrophile including 10% by weight to 80% by weight of the final molecule.

Compounds which are modified by "capping" or "end blocking" the terminal hydroxy group or groups (of multi-functional moieties) to reduce foaming by reaction with a small hydrophobic molecule such as propylene oxide, butylene oxide, benzyl chloride; and, short chain fatty acids, alcohols or alkyl halides containing from 1 to about 5 carbon atoms; and mixtures thereof. Also included are reactants such as thionyl chloride which convert terminal hydroxy groups to a chloride group. Such modifications to the terminal hydroxy group may lead to all-block, block-heteric, heteric-block or all-heteric nonionics.

Additional examples of effective low foaming nonionic surfactants include, but are not limited to the alkylphenoxypolyethoxyalkanols of U.S. Pat. No. 2,903,486 issued Sep. 8, 1959 to Brown et al. and represented by the formula



in which R is an alkyl group of 8 to 9 carbon atoms, A is an alkylene chain of 3 to 4 carbon atoms, n is an integer of 7 to 16, and m is an integer of 1 to 10.

The polyalkylene glycol condensates of U.S. Pat. No. 3,048,548 issued Aug. 7, 1962 to Martin et al. having alternated hydrophilic oxyethylene chains and hydrophobic oxypropylene chains where the weight of the terminal hydrophobic chains, the weight of the middle hydrophobic unit and the weight of the linking hydrophilic units each represent about one-third of the condensate.

The defoaming nonionic surfactants disclosed in U.S. Pat. No. 3,382,178 issued May 7, 1968 to Lissant et al. having the general formula $Z[(\text{OR})_n\text{OH}]_z$ wherein Z is alkoxylatable material, R is a radical derived from an alkylene oxide which can be ethylene and propylene and n is an integer from, for example, 10 to 2,000 or more and z is an integer determined by the number of reactive oxyalkylatable groups.

The conjugated polyoxyalkylene compounds described in U.S. Pat. No. 2,677,700, issued May 4, 1954 to Jackson et al. corresponding to the formula $Y(C_3H_6O)_n(C_2H_4O)_mH$ wherein Y is the residue of organic compound having from about 1 to 6 carbon atoms and one reactive hydrogen atom, n has an average value of at least about 6.4, as determined by hydroxyl number and m has a value such that the oxyethylene portion constitutes about 10% to about 90% by weight of the molecule.

The conjugated polyoxyalkylene compounds described in U.S. Pat. No. 2,674,619, issued Apr. 6, 1954 to Lundsted et al. having the formula $Y[(C_3H_6O)_n(C_2H_4O)_mH]_x$ wherein Y is the residue of an organic compound having from about 2 to 6 carbon atoms and containing x reactive hydrogen atoms in which x has a value of at least about 2, n has a value such that the molecular weight of the polyoxypropylene hydrophobic base is at least about 900 and m has value such that the oxyethylene content of the molecule is from about 10% to about 90% by weight. Compounds falling within the scope of the definition for Y include, for example, propylene glycol, glycerine, pentaerythritol, trimethylolpropane, ethylenediamine and the like. The oxypropylene chains optionally, but advantageously, contain small amounts of ethylene oxide and the oxyethylene chains also optionally, but advantageously, contain small amounts of propylene oxide.

Additional conjugated polyoxyalkylene surface-active agents which are advantageously used in the compositions of this invention correspond to the formula: $P[(C_3H_6O)_n(C_2H_4O)_mH]_x$ wherein P is the residue of an organic compound having from about 8 to 18 carbon atoms and containing x reactive hydrogen atoms in which x has a value of 1 or 2, n has a value such that the molecular weight of the polyoxyethylene portion is at least about 44 and m has a value such that the oxypropylene content of the molecule is from about 10% to about 90% by weight. In either case the oxypropylene chains may contain optionally, but advantageously, small amounts of ethylene oxide and the oxyethylene chains may contain also optionally, but advantageously, small amounts of propylene oxide.

Polyhydroxy fatty acid amide surfactants suitable for use in the present compositions include those having the structural formula R_2CONR_1Z in which: R₁ is H, C₁-C₄ hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl, ethoxy, propoxy group, or a mixture thereof; R₂ is a C₅-C₃₁ hydrocarbyl, which can be straight-chain; and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls

directly connected to the chain, or an alkoxylated derivative (preferably ethoxylated or propoxylated) thereof. Z can be derived from a reducing sugar in a reductive amination reaction; such as a glycityl moiety.

The alkyl ethoxylate condensation products of aliphatic alcohols with from about 0
5 to about 25 moles of ethylene oxide are suitable for use in the present compositions. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from 6 to 22 carbon atoms.

The ethoxylated C₆-C₁₈ fatty alcohols and C₆-C₁₈ mixed ethoxylated and propoxylated fatty alcohols are suitable surfactants for use in the present compositions,
10 particularly those that are water soluble. Suitable ethoxylated fatty alcohols include the C₆-C₁₈ ethoxylated fatty alcohols with a degree of ethoxylation of from 3 to 50.

Suitable nonionic alkylpolysaccharide surfactants, particularly for use in the present compositions include those disclosed in U.S. Pat. No. 4,565,647, Llenado, issued Jan. 21, 1986. These surfactants include a hydrophobic group containing from about 6 to about 30
15 carbon atoms and a polysaccharide, *e.g.*, a polyglycoside, hydrophilic group containing from about 1.3 to about 10 saccharide units. Any reducing saccharide containing 5 or 6 carbon atoms can be used, *e.g.*, glucose, galactose and galactosyl moieties can be substituted for the glucosyl moieties. (Optionally the hydrophobic group is attached at the 2-, 3-, 4-, etc. positions thus giving a glucose or galactose as opposed to a glucoside or
20 galactoside). The inter-saccharide bonds can be, *e.g.*, between the one position of the additional saccharide units and the 2-, 3-, 4-, and/or 6-positions on the preceding saccharide units.

Fatty acid amide surfactants suitable for use the present compositions include those having the formula: R₆CON(R₇)₂ in which R₆ is an alkyl group containing from 7 to 21
25 carbon atoms and each R₇ is independently hydrogen, C₁- C₄ alkyl, C₁- C₄ hydroxyalkyl, or --(C₂H₄O)_xH, where x is in the range of from 1 to 3.

A useful class of non-ionic surfactants include the class defined as alkoxylated amines or, most particularly, alcohol alkoxylated/aminated/alkoxylated surfactants. These non-ionic surfactants may be at least in part represented by the general formulae: R²⁰--
30 (PO)_sN--(EO)_tH, R²⁰--(PO)_sN--(EO)_tH(EO)_uH, and R²⁰--N(EO)_tH; in which R²⁰ is an alkyl, alkenyl or other aliphatic group, or an alkyl-aryl group of from 8 to 20, preferably 12 to 14 carbon atoms, EO is oxyethylene, PO is oxypropylene, s is 1 to 20, preferably 2-5, t

is 1-10, preferably 2-5, and u is 1-10, preferably 2-5. Other variations on the scope of these compounds may be represented by the alternative formula: $R^{20}-(PO)_v-N[(EO)_wH][(EO)_zH]$ in which R^{20} is as defined above, v is 1 to 20 (e.g., 1, 2, 3, or 4 (preferably 2)), and w and z are independently 1-10, preferably 2-5. These compounds are represented

commercially by a line of products sold by Huntsman Chemicals as nonionic surfactants. A preferred chemical of this class includes SurfonicTM PEA 25 Amine Alkoxylate. Preferred nonionic surfactants for the compositions of the invention include alcohol alkoxylates, EO/PO block copolymers, alkylphenol alkoxylates, and the like.

The treatise *Nonionic Surfactants*, edited by Schick, M. J., Vol. 1 of the Surfactant Science Series, Marcel Dekker, Inc., New York, 1983 is an excellent reference on the wide variety of nonionic compounds generally employed in the practice of the present invention. A typical listing of nonionic classes, and species of these surfactants, is given in U.S. Pat. No. 3,929,678 issued to Laughlin and Heuring on Dec. 30, 1975. Further examples are given in "Surface Active Agents and detergents" (Vol. I and II by Schwartz, Perry and Berch).

Suitable nonionic surfactants suitable for use with the compositions of the present invention include alkoxylated surfactants. Suitable alkoxylated surfactants include EO/PO copolymers, fully capped or partially EO/PO copolymers, alcohol alkoxylates, capped alcohol alkoxylates, mixtures thereof, or the like. Suitable alkoxylated surfactants for use as solvents include EO/PO block copolymers, such as the Pluronic and reverse Pluronic surfactants; alcohol alkoxylates, such as Dehypon LS-54 ($R-(EO)_5(PO)_4$) and Dehypon LS-36 ($R-(EO)_3(PO)_6$); and capped alcohol alkoxylates, such as Plurafac LF221 and Tegoten EC11; mixtures thereof, or the like.

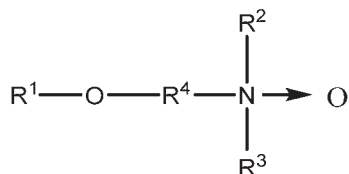
In some embodiments that are not detergent compositions, the composition disclosed herein is free of a nonionic surfactant.

Semi-Polar Nonionic or Semi-Nonionic Surfactants

The semi-polar type of nonionic surfactants is another class of nonionic surfactants useful in compositions disclosed herein. Generally, semi-polar nonionic (semi-nonionic) surfactants are high foaming agents and foam stabilizers, which can limit their application in CIP systems. However, in some embodiments designed for high foaming composition or detergent composition, semi-polar nonionic surfactants would have immediate utility.

The semi-polar nonionic surfactants include, but are not limited to, the amine oxides, phosphine oxides, sulfoxides and their alkoxyated derivatives.

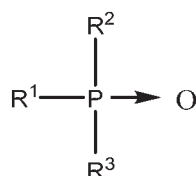
Amine oxides are tertiary amine oxides corresponding to the general formula:



- 5 wherein the arrow is a conventional representation of a semi-polar bond; and, R^1 , R^2 , and R^3 may be aliphatic, aromatic, heterocyclic, alicyclic, or combinations thereof. Generally, for amine oxides of detergent interest, R^1 is an alkyl radical of from about 8 to about 24 carbon atoms; R^2 and R^3 are alkyl or hydroxyalkyl of 1-3 carbon atoms or a mixture thereof; R^2 and R^3 can be attached to each other, *e.g.* through an oxygen or nitrogen atom,
10 to form a ring structure; R^4 is an alkylene or a hydroxyalkylene group containing 2 to 3 carbon atoms; and n ranges from 0 to about 20.

- Useful water soluble amine oxide surfactants are selected from the coconut or tallow alkyl di-(lower alkyl) amine oxides, specific examples of which are dodecyldimethylamine oxide, tridecyldimethylamine oxide, etradeyldimethylamine oxide,
15 pentadecyldimethylamine oxide, hexadecyldimethylamine oxide, heptadecyldimethylamine oxide, octadecyldimethylamine oxide, dodecyldipropylamine oxide, tetradecyldipropylamine oxide, hexadecyldipropylamine oxide, tetradecyldibutylamine oxide, octadecyldibutylamine oxide, bis(2-hydroxyethyl)dodecylamine oxide, bis(2-hydroxyethyl)-3-dodecoxy-1-
20 hydroxypropylamine oxide, dimethyl-(2-hydroxydodecyl)amine oxide, 3,6,9-trioctadecyldimethylamine oxide and 3-dodecoxy-2-hydroxypropyl-di-(2-hydroxyethyl)amine oxide.

Useful semi-polar nonionic surfactants also include the water-soluble phosphine oxides having the following structure:

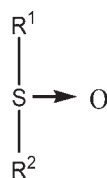


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wherein the arrow is a conventional representation of a semi-polar bond; and, R^1 is an alkyl, alkenyl or hydroxyalkyl moiety ranging from 10 to about 24 carbon atoms in chain length; and, R^2 and R^3 are each alkyl moieties separately selected from alkyl or hydroxyalkyl groups containing 1 to 3 carbon atoms.

5 Examples of useful phosphine oxides include dimethyldodecylphosphine oxide, dimethyltetradecylphosphine oxide, methylethyltetradecylphosphine oxide, dimethylhexadecylphosphine oxide, diethyl-2-hydroxyoctyldodecylphosphine oxide, bis(2-hydroxyethyl)dodecylphosphine oxide, and bis(hydroxymethyl)tetradecylphosphine oxide.

10 Semi-polar nonionic surfactants useful herein also include the water-soluble sulfoxide compounds which have the structure:



15 wherein the arrow is a conventional representation of a semi-polar bond; and, R^1 is an alkyl or hydroxyalkyl moiety of about 8 to about 28 carbon atoms, from 0 to about 5 ether linkages and from 0 to about 2 hydroxyl substituents; and R^2 is an alkyl moiety consisting of alkyl and hydroxyalkyl groups having 1 to 3 carbon atoms.

Useful examples of these sulfoxides include dodecyl methyl sulfoxide; 3-hydroxy tridecyl methyl sulfoxide; 3-methoxy tridecyl methyl sulfoxide; and 3-hydroxy-4-dodecoxybutyl methyl sulfoxide.

20 Semi-polar nonionic surfactants for the compositions of the invention include dimethyl amine oxides, such as lauryl dimethyl amine oxide, myristyl dimethyl amine oxide, cetyl dimethyl amine oxide, combinations thereof, and the like. Useful water soluble amine oxide surfactants are selected from the octyl, decyl, dodecyl, isododecyl, coconut, or tallow alkyl di-(lower alkyl) amine oxides, specific examples of which are octyldimethylamine oxide, nonyldimethylamine oxide, decyldimethylamine oxide, 25 undecyldimethylamine oxide, dodecyldimethylamine oxide, iso-dodecyldimethyl amine oxide, tridecyldimethylamine oxide, tetradecyldimethylamine oxide, pentadecyldimethylamine oxide, hexadecyldimethylamine oxide, heptadecyldimethylamine oxide, octadecyldimethylamine oxide, dodecyldipropylamine oxide, tetradecyldipropylamine oxide, hexadecyldipropylamine oxide,

tetradecyldibutylamine oxide, octadecyldibutylamine oxide, bis(2-hydroxyethyl)dodecylamine oxide, bis(2-hydroxyethyl)-3-dodecoxy-1-hydroxypropylamine oxide, dimethyl-(2-hydroxydodecyl)amine oxide, 3,6,9-trioctadecyldimethylamine oxide and 3-dodecoxy-2-hydroxypropyl-di-(2-hydroxyethyl)amine oxide.

In some embodiments, the composition or detergent composition disclosed herein is free of a semi-polar nonionic surfactant.

Cationic Surfactants

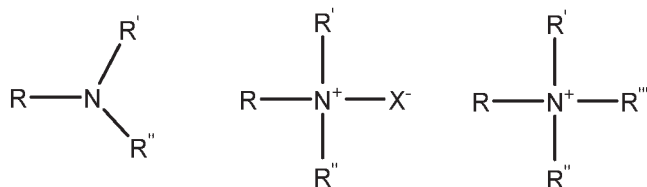
Surface active substances are classified as cationic if the charge on the hydrotrope portion of the molecule is positive. Surfactants in which the hydrotrope carries no charge unless the pH is lowered close to neutrality or lower, but which are then cationic (*e.g.* alkyl amines), are also included in this group. In theory, cationic surfactants may be synthesized from any combination of elements containing an "onium" structure $R_nX^+Y^{--}$ and could include compounds other than nitrogen (ammonium) such as phosphorus (phosphonium) and sulfur (sulfonium). In practice, the cationic surfactant field is dominated by nitrogen containing compounds, probably because synthetic routes to nitrogenous cationics are simple and straightforward and give high yields of product, which can make them less expensive.

Cationic surfactants preferably include, more preferably refer to, compounds containing at least one long carbon chain hydrophobic group and at least one positively charged nitrogen. The long carbon chain group may be attached directly to the nitrogen atom by simple substitution; or more preferably indirectly by a bridging functional group or groups in so-called interrupted alkylamines and amido amines. Such functional groups can make the molecule more hydrophilic and/or more water dispersible, more easily water solubilized by co-surfactant mixtures, and/or water soluble. For increased water solubility, additional primary, secondary or tertiary amino groups can be introduced, or the amino nitrogen can be quaternized with low molecular weight alkyl groups. Further, the nitrogen can be a part of branched or straight chain moiety of varying degrees of unsaturation or of a saturated or unsaturated heterocyclic ring. In addition, cationic surfactants may contain complex linkages having more than one cationic nitrogen atom.

The surfactant compounds classified as amine oxides, amphoterics and zwitterions are themselves typically cationic in near neutral to acidic pH solutions and can overlap

surfactant classifications. Polyoxyethylated cationic surfactants generally behave like nonionic surfactants in alkaline solution and like cationic surfactants in acidic solution.

The simplest cationic amines, amine salts and quaternary ammonium compounds can be schematically drawn thus:



in which, R represents an alkyl chain, R', R'', and R''' may be either alkyl chains or aryl groups or hydrogen and X represents an anion. The amine salts and quaternary ammonium compounds are preferred for practical use in this invention due to their high degree of water solubility.

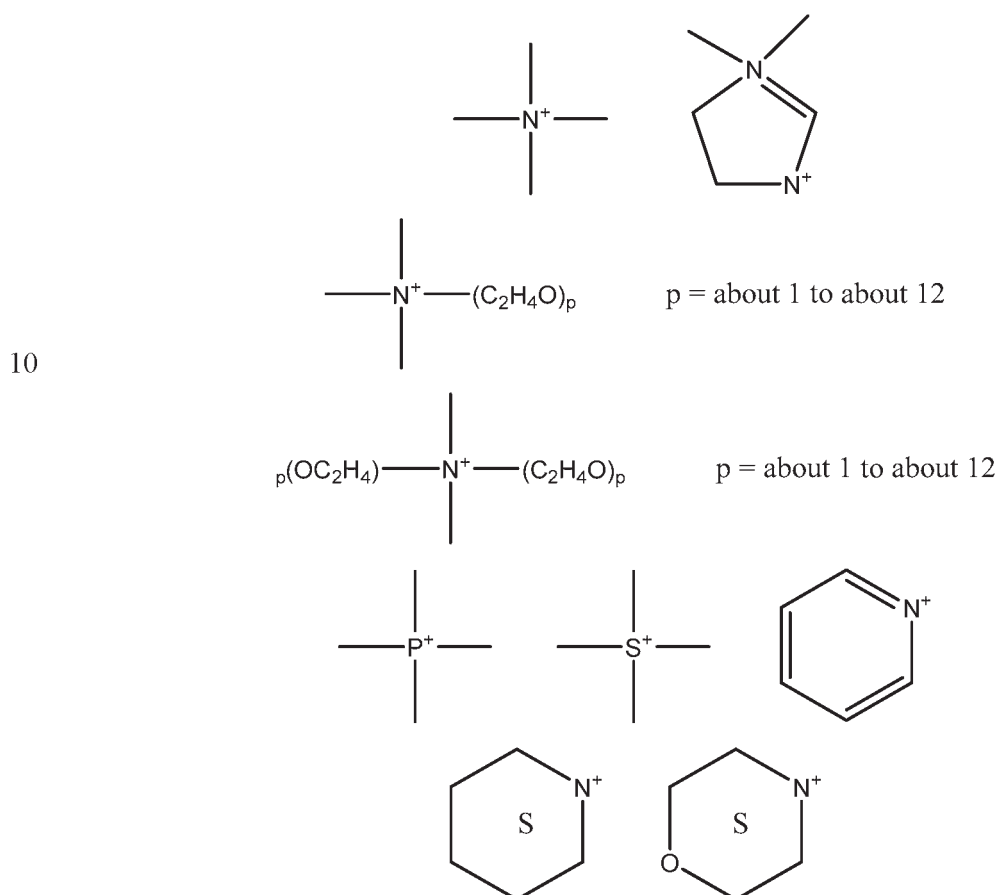
Most large volume commercial cationic surfactants can be subdivided into four major classes and additional sub-groups known to those skilled in the art and described in "Surfactant Encyclopedia", *Cosmetics & Toiletries*, Vol. 104 (2) 86-96 (1989). The first class includes alkylamines and their salts. The second class includes alkyl imidazolines. The third class includes ethoxylated amines. The fourth class includes quaternaries, such as alkylbenzyltrimethylammonium salts, alkyl benzene salts, heterocyclic ammonium salts, tetra alkylammonium salts, and the like. Cationic surfactants are known to have a variety of properties that can be beneficial in the present compositions. These desirable properties can include detergency in compositions of or below neutral pH, antimicrobial efficacy, thickening or gelling in cooperation with other agents, and the like.

Cationic surfactants useful in the compositions disclosed herein include those having the formula $\text{R}^1_m\text{R}^2_x\text{Y}_L\text{Z}$ wherein each R^1 is an organic group containing a straight or branched alkyl or alkenyl group optionally substituted with up to three phenyl or hydroxy groups and optionally interrupted by up to four of the following structures:



- or an isomer or mixture of these structures, and which contains from about 8 to 22 carbon atoms. The R^1 groups can additionally contain up to 12 ethoxy groups. m is a number from 1 to 3. Preferably, no more than one R^1 group in a molecule has 16 or more carbon atoms when m is 2 or more than 12 carbon atoms when m is 3. Each R^2 is an alkyl or hydroxyalkyl group containing from 1 to 4 carbon atoms or a benzyl group with no more than one R^2 in a molecule being benzyl, and x is a number from 0 to 11, preferably from 0 to 6. The remainder of any carbon atom positions on the Y group are filled by hydrogens.

Y is can be a group including, but not limited to:



- or a mixture thereof. Preferably, L is 1 or 2, with the Y groups being separated by a moiety selected from R^1 and R^2 analogs (preferably alkylene or alkenylene) having from 1 to about 22 carbon atoms and two free carbon single bonds when L is 2. Z is a water-soluble anion, such as a halide, sulfate, methylsulfate, hydroxide, or nitrate anion, particularly preferred being chloride, bromide, iodide, sulfate or methyl sulfate anions, in a number to give electrical neutrality of the cationic component.

In some embodiments, the composition or detergent composition disclosed herein is free of a cationic surfactant.

Amphoteric Surfactants

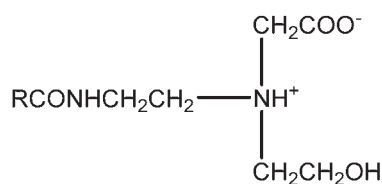
Amphoteric, or ampholytic, surfactants contain both a basic and an acidic hydrophilic group and an organic hydrophobic group. These ionic entities may be any of anionic or cationic groups described herein for other types of surfactants. A basic nitrogen and an acidic carboxylate group are the typical functional groups employed as the basic and acidic hydrophilic groups. In a few surfactants, sulfonate, sulfate, phosphonate or phosphate provide the negative charge.

Amphoteric surfactants can be broadly described as derivatives of aliphatic secondary and tertiary amines, in which the aliphatic radical may be straight chain or branched and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and one contains an anionic water solubilizing group, *e.g.*, carboxy, sulfo, sulfato, phosphato, or phosphono. Amphoteric surfactants are subdivided into two major classes known to those of skill in the art and described in "Surfactant Encyclopedia" Cosmetics & Toiletries, Vol. 104 (2) 69-71 (1989), which is herein incorporated by reference in its entirety. The first class includes acyl/dialkyl ethylenediamine derivatives (*e.g.* 2-alkyl hydroxyethyl imidazoline derivatives) and their salts. The second class includes N-alkylamino acids and their salts. Some amphoteric surfactants can be envisioned as fitting into both classes.

Amphoteric surfactants can be synthesized by methods known to those of skill in the art. For example, 2-alkyl hydroxyethyl imidazoline is synthesized by condensation and ring closure of a long chain carboxylic acid (or a derivative) with dialkyl ethylenediamine. Commercial amphoteric surfactants are derivatized by subsequent hydrolysis and ring-opening of the imidazoline ring by alkylation -- for example with chloroacetic acid or ethyl acetate. During alkylation, one or two carboxy-alkyl groups react to form a tertiary amine and an ether linkage with differing alkylating agents yielding different tertiary amines.

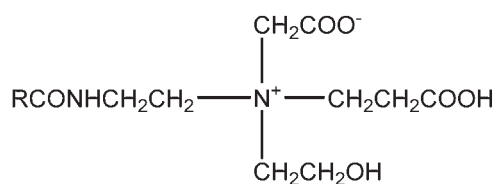
Long chain imidazole derivatives having application in the present invention generally have the general formula:

(MONO)ACETATE

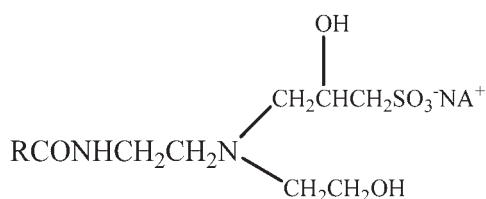


Neutral pH Zwitterion

(DI)PROPIONATE



AMPHOTERIC SULFONATE



5

wherein R is an acyclic hydrophobic group containing from about 8 to 18 carbon atoms and M is a cation to neutralize the charge of the anion, generally sodium.

Commercially prominent imidazoline-derived amphoterics that can be employed in the present compositions include for example: Cocoamphopropionate, Cocoamphocarboxy-
 10 propionate, Cocoamphoglycinate, Cocoamphocarboxy-glycinate, Cocoamphopropyl-sulfonate, and Cocoamphocarboxy-propionic acid. Amphocarboxylic acids can be produced from fatty imidazolines in which the dicarboxylic acid functionality of the amphodicarboxylic acid is diacetic acid and/or dipropionic acid.

The carboxymethylated compounds (glycinates) described herein above frequently
 15 are called betaines. Betaines are a special class of amphoteric discussed herein below in the section entitled, Zwitterion Surfactants.

Long chain N-alkylamino acids are readily prepared by reaction RNH_2 , in which $\text{R}=\text{C}_8\text{-C}_{18}$ straight or branched chain alkyl, fatty amines with halogenated carboxylic acids. Alkylation of the primary amino groups of an amino acid leads to secondary and tertiary
 20 amines. Alkyl substituents may have additional amino groups that provide more than one reactive nitrogen center. Most commercial N-alkylamine acids are alkyl derivatives of beta-alanine or beta-N(2-carboxyethyl) alanine. Examples of commercial N-alkylamino acid ampholytes having application in this invention include alkyl beta-amino dipropionates, $\text{RN}(\text{C}_2\text{H}_4\text{COOM})_2$ and $\text{RNHC}_2\text{H}_4\text{COOM}$. In an embodiment, R can be an
 25 acyclic hydrophobic group containing from about 8 to about 18 carbon atoms, and M is a cation to neutralize the charge of the anion.

Suitable amphoteric surfactants include those derived from coconut products such as coconut oil or coconut fatty acid. Additional suitable coconut derived surfactants include as part of their structure an ethylenediamine moiety, an alkanolamide moiety, an amino acid moiety, *e.g.*, glycine, or a combination thereof; and an aliphatic substituent of
5 from about 8 to 18 (*e.g.*, 12) carbon atoms. Such a surfactant can also be considered an alkyl amphodicarboxylic acid. These amphoteric surfactants can include chemical structures represented as: $C_{12}\text{-alkyl-C(O)-NH-CH}_2\text{-CH}_2\text{-N}^+(\text{CH}_2\text{-CH}_2\text{-CO}_2\text{Na})_2\text{-CH}_2\text{-CH}_2\text{-OH}$ or $C_{12}\text{-alkyl-C(O)-N(H)-CH}_2\text{-CH}_2\text{-N}^+(\text{CH}_2\text{-CO}_2\text{Na})_2\text{-CH}_2\text{-CH}_2\text{-OH}$. Disodium cocoampho dipropionate is one suitable amphoteric surfactant and is commercially
10 available under the tradename Miranol™ FBS from Rhodia Inc., Cranbury, N.J. Another suitable coconut derived amphoteric surfactant with the chemical name disodium cocoampho diacetate is sold under the tradename Mirataine™ JCHA, also from Rhodia Inc., Cranbury, N.J.

A typical listing of amphoteric classes, and species of these surfactants, is given in
15 U.S. Pat. No. 3,929,678 issued to Laughlin and Heuring on Dec. 30, 1975. Further examples are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). Each of these references are herein incorporated by reference in their entirety.

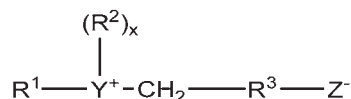
In some embodiments, the composition or detergent composition disclosed herein is
20 free of an amphoteric surfactant.

Zwitterionic Surfactants

Zwitterionic surfactants can be thought of as a subset of the amphoteric surfactants and can include an anionic charge. Zwitterionic surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and
25 tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. Typically, a zwitterionic surfactant includes a positive charged quaternary ammonium or, in some cases, a sulfonium or phosphonium ion; a negative charged carboxyl group; and an alkyl group. Zwitterionic surfactants generally contain cationic and anionic groups which ionize to a nearly equal degree in the isoelectric
30 region of the molecule and which can develop strong "inner-salt" attraction between positive-negative charge centers. Examples of such zwitterionic synthetic surfactants include derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium

compounds, in which the aliphatic radicals can be straight chain or branched, and wherein one of the aliphatic substituents contains from 8 to 18 carbon atoms and one contains an anionic water solubilizing group, *e.g.*, carboxy, sulfonate, sulfate, phosphate, or phosphonate.

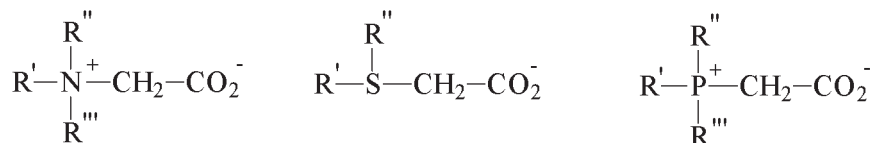
- 5 Betaine and sultaine surfactants are exemplary zwitterionic surfactants for use herein. A general formula for these compounds is:



- wherein R¹ contains an alkyl, alkenyl, or hydroxyalkyl radical of from 8 to 18 carbon atoms having from 0 to 10 ethylene oxide moieties and from 0 to 1 glyceryl moiety; Y is
10 selected from the group consisting of nitrogen, phosphorus, and sulfur atoms; R² is an alkyl or monohydroxy alkyl group containing 1 to 3 carbon atoms; x is 1 when Y is a sulfur atom and 2 when Y is a nitrogen or phosphorus atom, R³ is an alkylene or hydroxy
alkylene or hydroxy alkylene of from 1 to 4 carbon atoms and Z is a radical selected from the group consisting of carboxylate, sulfonate, sulfate, phosphonate, and phosphate groups.

- 15 Examples of zwitterionic surfactants having the structures listed above include: 4-[N,N-di(2-hydroxyethyl)-N-octadecylammonio]-butane-1-carboxylate; 5-[S-3-hydroxypropyl-S-hexadecylsulfonio]-3-hydroxypentane-1-sulfate; 3-[P,P-diethyl-P-3,6,9-trioxatetracosanephosphonio]-2-hydroxypropane-1-phosphate; 3-[N,N-dipropyl-N-3-dodecoxy-2-hydroxypropyl-ammonio]-propane-1-phosphonate; 3-(N,N-dimethyl-N-hexadecylammonio)-propane-1-sulfonate; 3-(N,N-dimethyl-N-hexadecylammonio)-2-hydroxy-propane-1-sulfonate; 4-[N,N-di(2(2-hydroxyethyl)-N(2-hydroxydodecyl)ammonio)-butane-1-carboxylate; 3-[S-ethyl-S-(3-dodecoxy-2-hydroxypropyl)sulfonio]-propane-1-phosphate; 3-[P,P-dimethyl-P-dodecylphosphonio]-propane-1-phosphonate; and S[N,N-di(3-hydroxypropyl)-N-hexadecylammonio]-2-
20 hydroxy-pentane-1-sulfate. The alkyl groups contained in said detergent surfactants can be straight or branched and saturated or unsaturated.

The zwitterionic surfactant suitable for use in the present compositions includes a betaine of the general structure:



These surfactant betaines typically do not exhibit strong cationic or anionic characters at pH extremes nor do they show reduced water solubility in their isoelectric range. Unlike "external" quaternary ammonium salts, betaines are compatible with anionics. Examples of suitable betaines include coconut acylamidopropyldimethyl betaine; hexadecyl dimethyl betaine; C₁₂₋₁₄ acylamidopropylbetaine; C₈₋₁₄ acylamidohexyldiethyl betaine; 4-C₁₄₋₁₆ acylmethylamidodiethylammonio-1-carboxybutane; C₁₆₋₁₈ acylamidodimethylbetaine; C₁₂₋₁₆ acylamidopentanedithylbetaine; and C₁₂₋₁₆ acylmethylamidodimethylbetaine.

Sultaines useful in the present invention include those compounds having the formula (R(R¹)₂ N⁺ R²SO³⁻), in which R is a C₆-C₁₈ hydrocarbyl group, each R¹ is typically independently C₁-C₃ alkyl, *e.g.*, methyl, and R² is a C₁-C₆ hydrocarbyl group, *e.g.*, a C₁-C₃ alkylene or hydroxyalkylene group.

A typical listing of zwitterionic classes, and species of these surfactants, is given in U.S. Pat. No. 3,929,678 issued to Laughlin and Heuring on Dec. 30, 1975. Further examples are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). Each of these references are herein incorporated in their entirety.

In some embodiments, the composition or detergent composition disclosed herein is free of a zwitterionic surfactant.

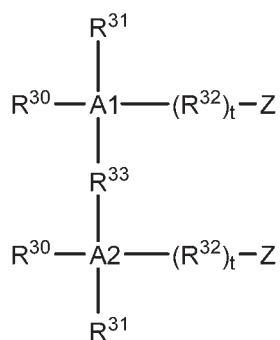
Gemini Surfactants

While conventional surfactants generally have one hydrophilic group and one hydrophobic group, a Gemini surfactant has at least two hydrophobic groups and at least two hydrophilic groups. These surfactants have the general formula: A1-G-A2 and get their name because they comprise two surfactant moieties (A1, A2) joined by a spacer (G), wherein each surfactant moiety (A1, A2) has a hydrophilic group and a hydrophobic group. Generally, the two surfactant moieties (A1, A2) are the same, but they can be different.

The Gemini surfactants may be anionic, nonionic, cationic or amphoteric. The hydrophilic and hydrophobic groups of each surfactant moiety (A1, A2) may be any of those known to be used in conventional surfactants having one hydrophilic group and one

hydrophobic group. For example, a typical nonionic Gemini surfactant, e.g., a bis-polyoxyethylene alkyl ether, would contain two polyoxyethylene alkyl ether moieties. Each moiety would contain a hydrophilic group, e.g., polyethylene oxide, and a hydrophobic group, e.g., an alkyl chain.

- 5 Anionic and nonionic Gemini surfactants include those of the formula:

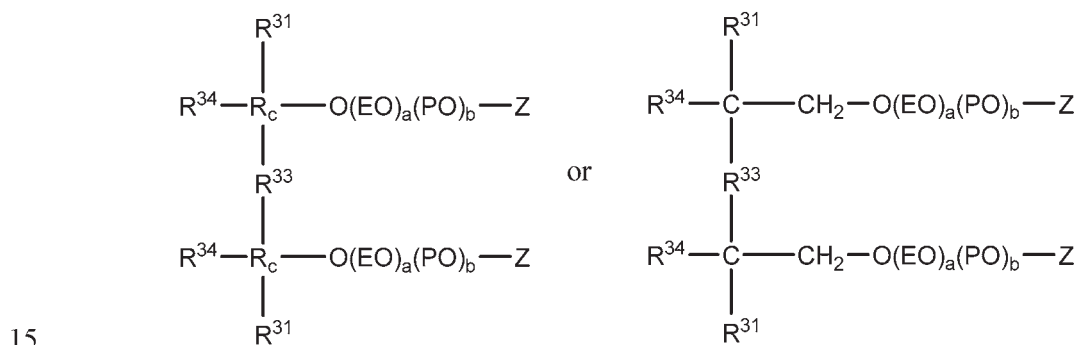


- wherein R^{30} is independently C_1 to C_{22} alkyl, $R^{34}-C(O)-$, or $R^{34}-B-R^{35}-$, wherein R^{34} is C_1 to C_{22} alkyl, R^{35} is C_1 to C_{12} alkyl, and B is an amide group, $-C(O)N(R^{36})-$, an amino group $-N(R^{36})-$, a carboxyl group $-C(O)-O-$, a carbonyl group, or a polyether group $-(EO)_a(PO)_b-$, wherein EO represents ethyleneoxy radicals, PO represents propyleneoxy radicals, a and b are numbers of from 0 to 100, a is preferably from about 0 to about 30 and b is preferably from about 0 to 10, wherein a plus b is at least one, and the EO and PO radicals can be randomly mixed or in discrete blocks, and R^{36} is hydrogen or C_1 to C_6 alkyl.
- 15 R^{31} is independently hydrogen or C_1 to C_{22} alkyl; R^{32} is independently a C_1 - C_{10} alkyl, $-O-$, an amide group $-C(O)N(R^6)-$, a polyether group $-O(EO)_a(PO)_b-$, $-R^{37}-D-R^{37}-$, or $-D-R^{37}-D-$, wherein R^{37} is independently a C_1 - C_6 alkyl and D is $-O-$, $-S-$, an amide group $-C(O)N(R^{36})-$, or an amino group $-N(R^{36})-$, wherein R^{36} , a and b are as defined above, and t is independently 0 or 1.
- 20 Z is independently hydrogen, $-SO_3Y$, $-P(O)(OY)_2$, $-COOY$, $-CH_2COOY$, $-CH_2CH(OH)CH_2SO_3Y$ and when R^{32} is not a polyether, Z is also $-OSO_3Y$, and $-OP(O)(OY)_2$; wherein Y is hydrogen, alkali metal such as sodium and potassium; alkaline earth metal such as magnesium and calcium; ammonium; or organic base salt such as monoethanolamine, diethanolamine, triethanolamine, triethylamine, trimethylamine, N-hydroxyethyl morpholine, and the like.
- 25

A1 or A2 is independently a straight chain or branched C₁ to C₆ alkyl, an O--R₅--O-- group or aryl; preferably phenyl; R³³ is a bond, an aryl group such as a phenyl or diphenyl group, a C₁ to C₁₀ alkyl group, preferably a C₁ to C₄ alkyl group, most preferably methylene, --C≡C--, --O--, --S--, --S--S--, --N(R³⁶)--, --R³⁵O--, --R³⁵O(EO)_a(PO)_b--, --D₁---
 5 R³⁸--D₁-- or --R³⁸--D₁---R³⁸--, wherein R³⁸ is independently a C₁-C₁₀ alkyl group, --C(O)--, --R³⁵O(EO)_a(PO)_b--, --O--R³⁵--O--, or aryl, e.g. phenyl, and D₁ is independently --O--, --S--, --S--S--, --SO₂--, --C(O)--, a polyether group --O(EO)_a(PO)_b--, an amide group --C(O)N(R³⁶)--, an amino group --N(R³⁶)-, --O--R₅--O--, or aryl wherein R³⁵, R³⁶, a and b are as defined above.

10 On the formulae of this disclosure, the term "alkali" includes substituted alkali, especially the hydroxy substituted derivatives thereof and straight as well as branched chains. When Z is hydrogen, the gemini surfactants are nonionic.

Other Gemini surfactants specifically useful in the present disclosure include gemini anionic or nonionic surfactants of the formulae:



wherein R_c represents aryl, preferably phenyl. R³¹, R³³, R³⁴, and Z are as defined above. a and b are numbers of from 0 to 100, a is preferably from about 0 to about 30 and b is preferably from about 0 to 10, wherein a plus b is at least one, and the EO and PO radicals can be randomly mixed or in discrete blocks.

20 The primary hydroxyl group of these surfactants can be readily phosphated, sulfated or carboxylated by standard techniques.

In some embodiments, the composition or detergent composition disclosed herein is free of a Gemini surfactant.

Additional Corrosion Inhibitor

25 In some embodiments, the corrosion control compositions disclosed herein further include an additional corrosion inhibitor. In some other embodiments, the disclosed

corrosion control compositions herein further include an additional corrosion inhibitor and carrier. In some other embodiments, the disclosed corrosion control compositions herein further include an additional corrosion inhibitor, biocide, and carrier. In some embodiments, the disclosed control compositions herein may consist of one or more di-cationic or di-anionic compounds disclosed herein, one or more additional corrosion inhibitors, and carrier. In some embodiments, the corrosion control compositions disclosed herein consist of one or more di-cationic or di-anionic compounds disclosed herein, a carrier, additional corrosion inhibitor, and biocide.

The corrosion control composition can comprise from about 0.1 wt-% to about 20 wt-%, from about 0.1 wt-% to about 10 wt-%, or from 0.1 to about 5 wt-% of the one or more additional corrosion inhibitors, based on total weight of the composition. A composition of the disclosure can comprise from 0 wt-% to 10 percent by weight of the one or more additional corrosion inhibitors, based on total weight of the composition. The composition can comprise about 1.0 wt-%, about 1.5 wt-%, about 2.0 wt-%, about 2.5 wt-%, about 3.0 wt-%, about 3.5 wt-%, about 4.0 wt-%, about 4.5 wt-%, about 5.0 wt-%, about 5.5 wt-%, about 6.0 wt-%, about 6.5 wt-%, about 7.0 wt-%, about 7.5 wt-%, about 8.0 wt-%, about 8.5 wt-%, about 9.0 wt-%, about 9.5 wt-%, about 10.0 wt-%, about 10.5 wt-%, about 11.0 wt-%, about 11.5 wt-%, about 12.0 wt-%, about 12.5 wt-%, about 13.0 wt-%, about 13.5 wt-%, about 14.0 wt-%, about 14.5 wt-%, or about 15.0 wt-% of or any value or range there between of the one or more additional corrosion inhibitors, based on total weight of the composition. A specific water system can have its own requirements for using one or more additional corrosion inhibitors, and the weight percent of one or more additional corrosion inhibitors in the composition can vary with the water system in which it is used.

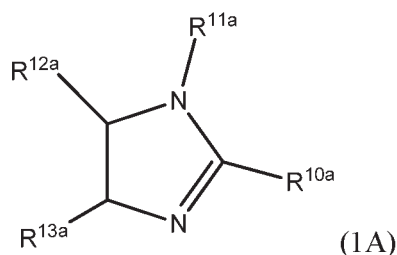
Additional corrosion inhibitors for multi-metal protection are typically triazoles, such as, but not limited to, benzotriazole, halogenated triazoles, and nitro-substituted azoles.

The one or more additional corrosion inhibitors can be an imidazoline compound, a quaternary ammonium compound, a pyridinium compound, or a combination thereof.

The one or more additional corrosion inhibitors can be an imidazoline. The imidazoline can be, for example, imidazoline derived from a diamine, such as ethylene diamine (EDA), diethylene triamine (DETA), triethylene tetraamine (TETA) etc. and a

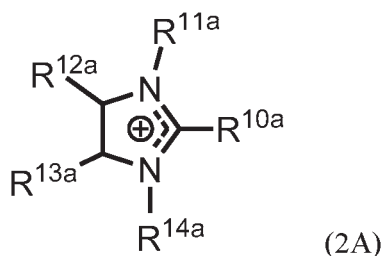
long chain fatty acid such as tall oil fatty acid (TOFA). The imidazoline can be an imidazoline of Formula (1A) or an imidazoline derivative. Representative imidazoline derivatives include an imidazolinium compound of Formula (2A) or a bis-quaternized compound of Formula (3A).

- 5 The one or more additional corrosion inhibitors can include an imidazoline of Formula (1A):



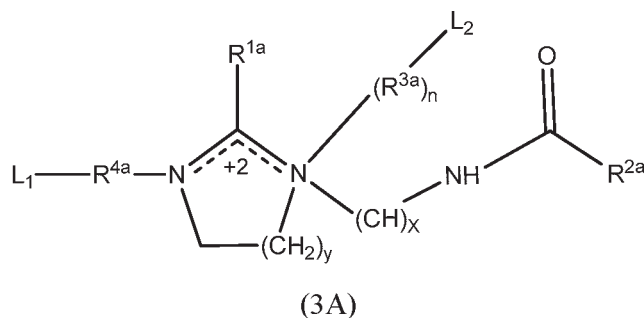
- wherein R^{10a} is a C_1 - C_{20} alkyl or a C_1 - C_{20} alkoxyalkyl group; R^{11a} is hydrogen, C_1 - C_6 alkyl, C_1 - C_6 hydroxyalkyl, or C_1 - C_6 arylalkyl; and R^{12a} and R^{13a} are independently
 10 hydrogen or a C_1 - C_6 alkyl group. Preferably, the imidazoline includes an R^{10a} which is the alkyl mixture typical in tall oil fatty acid (TOFA), and R^{11a} , R^{12a} and R^{13a} are each hydrogen.

The one or more additional corrosion inhibitors can be an imidazolinium compound of Formula (2A):



- 15 wherein R^{10a} is a C_1 - C_{20} alkyl or a C_1 - C_{20} alkoxyalkyl group; R^{11a} and R^{14a} are independently hydrogen, C_1 - C_6 alkyl, C_1 - C_6 hydroxyalkyl, or C_1 - C_6 arylalkyl; R^{12a} and R^{13a} are independently hydrogen or a C_1 - C_6 alkyl group; and X^- is a halide (such as chloride, bromide, or iodide), carbonate, sulfonate, phosphate, or the anion of an organic carboxylic
 20 acid (such as acetate). Preferably, the imidazolinium compound includes 1-benzyl-1-(2-hydroxyethyl)-2-tall-oil-2-imidazolinium chloride.

The one or more additional corrosion inhibitors can be a bis-quaternized compound having the formula (3A):



wherein R^{1a} and R^{2a} are each independently unsubstituted branched, chain or ring alkyl or alkenyl having from 1 to about 29 carbon atoms; partially or fully oxygenized, sulfurized, and/or phosphorylated branched, chain, or ring alkyl or alkenyl having from 1 to about 29 carbon atoms; or a combination thereof; R^{3a} and R^{4a} are each independently unsubstituted branched, chain or ring alkylene or alkenylene having from 1 to about 29 carbon atoms; partially or fully oxygenized, sulfurized, and/or phosphorylated branched, chain, or ring alkylene or alkenylene having from 1 to about 29 carbon atoms; or a combination thereof;

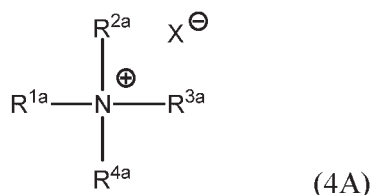
L_1 and L_2 are each independently absent, H, $-\text{COOH}$, $-\text{SO}_3\text{H}$, $-\text{PO}_3\text{H}$, $-\text{COOR}^{5a}$, $-\text{CONH}_2$, $-\text{CONHR}^{5a}$, or $-\text{CON}(\text{R}^{5a})_2$; R^{5a} is each independently a branched or unbranched alkyl, aryl, alkylaryl, alkylheteroaryl, cycloalkyl, or heteroaryl group having from 1 to about 10 carbon atoms; n is 0 or 1, and when n is 0, L_2 is absent or H; x is from 1 to about 10; and y is from 1 to about 5. Preferably, R^{1a} and R^{2a} are each independently C_6 - C_{22} alkyl, C_8 - C_{20} alkyl, C_{12} - C_{18} alkyl, C_{16} - C_{18} alkyl, or a combination thereof; R^{3a} and R^{4a} are C_1 - C_{10} alkylene, C_2 - C_8 alkylene, C_2 - C_6 alkylene, or C_2 - C_3 alkylene; n is 0 or 1; x is 2; y is 1; R_3 and R_4 are $-\text{C}_2\text{H}_2-$; L_1 is $-\text{COOH}$, $-\text{SO}_3\text{H}$, or $-\text{PO}_3\text{H}$; and L_2 is absent, H, $-\text{COOH}$, $-\text{SO}_3\text{H}$, or $-\text{PO}_3\text{H}$. For example, R^{1a} and R^{2a} can be derived from a mixture of tall oil fatty acids and are predominantly a mixture of $\text{C}_{17}\text{H}_{33}$ and $\text{C}_{17}\text{H}_{31}$ or can be C_{16} - C_{18} alkyl; R^{3a} and R^{4a} can be C_2 - C_3 alkylene such as $-\text{C}_2\text{H}_2-$; n is 1 and L_2 is $-\text{COOH}$ or n is 0 and L_2 is absent or H; x is 2; y is 1; R^{3a} and R^{4a} are $-\text{C}_2\text{H}_2-$; and L_1 is $-\text{COOH}$.

It should be appreciated that the number of carbon atoms specified for each group of formula (3A) refers to the main chain of carbon atoms and does not include carbon atoms that may be contributed by substituents.

The one or more additional corrosion inhibitors can be a bis-quaternized imidazoline compound having the formula (3A) wherein R^{1a} and R^{2a} are each independently C_6 - C_{22} alkyl, C_8 - C_{20} alkyl, C_{12} - C_{18} alkyl, or C_{16} - C_{18} alkyl or a combination thereof; R^{4a} is C_1 - C_{10} alkylene, C_2 - C_8 alkylene, C_2 - C_6 alkylene, or C_2 - C_3 alkylene; x is 2; y

is 1; n is 0; L₁ is -COOH, -SO₃H, or -PO₃H; and L₂ is absent or H. Preferably, a bis-quaternized compound has the formula (3A) wherein R^{1a} and R^{2a} are each independently C₁₆-C₁₈ alkyl; R^{4a} is -C₂H₂-; x is 2; y is 1; n is 0; L₁ is -COOH, -SO₃H, or -PO₃H and L₂ is absent or H.

- 5 The one or more additional corrosion inhibitors can be a quaternary ammonium compound of Formula (4A):

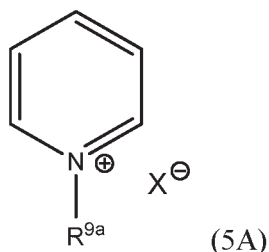


wherein R^{1a}, R^{2a}, and R^{3a} are independently C₁ to C₂₀ alkyl, R^{4a} is methyl or benzyl, and X⁻ is a halide or methosulfate.

- 10 Suitable alkyl, hydroxyalkyl, alkylaryl, arylalkyl or aryl amine quaternary salts include those alkylaryl, arylalkyl and aryl amine quaternary salts of the formula [N⁺R^{5a}R^{6a}R^{7a}R^{8a}][X⁻] wherein R^{5a}, R^{6a}, R^{7a}, and R^{8a} contain one to 18 carbon atoms, and X is Cl, Br or I. For the quaternary salts, R^{5a}, R^{6a}, R^{7a}, and R^{8a} can each be independently alkyl (e.g., C₁-C₁₈ alkyl), hydroxyalkyl (e.g., C₁-C₁₈ hydroxyalkyl), and arylalkyl (e.g.,
- 15 benzyl). The mono or polycyclic aromatic amine salt with an alkyl or alkylaryl halide include salts of the formula [N⁺R^{5a}R^{6a}R^{7a}R^{8a}][X⁻] wherein R^{5a}, R^{6a}, R^{7a}, and R^{8a} contain one to 18 carbon atoms and at least one aryl group, and X is Cl, Br or I.

- Suitable quaternary ammonium salts include, but are not limited to, a tetramethyl ammonium salt, a tetraethyl ammonium salt, a tetrapropyl ammonium salt, a tetrabutyl
- 20 ammonium salt, a tetrahexyl ammonium salt, a tetraoctyl ammonium salt, a benzyltrimethyl ammonium salt, a benzyltriethyl ammonium salt, a phenyltrimethyl ammonium salt, a phenyltriethyl ammonium salt, a cetyl benzyldimethyl ammonium salt, a hexadecyl trimethyl ammonium salt, a dimethyl alkyl benzyl quaternary ammonium salt, a monomethyl dialkyl benzyl quaternary ammonium salt, or a trialkyl benzyl quaternary
- 25 ammonium salt, wherein the alkyl group has about 6 to about 24 carbon atoms, about 10 and about 18 carbon atoms, or about 12 to about 16 carbon atoms. The quaternary ammonium salt can be a benzyl trialkyl quaternary ammonium salt, a benzyl triethanolamine quaternary ammonium salt, or a benzyl dimethylaminoethanolamine quaternary ammonium salt.

The one or more additional corrosion inhibitors can be a pyridinium salt such as those represented by Formula (5A):



wherein R^{9a} is an alkyl group, an aryl group, or an arylalkyl group, wherein said alkyl groups have from 1 to about 18 carbon atoms and X⁻ is a halide such as chloride, bromide, or iodide. Among these compounds are alkyl pyridinium salts and alkyl pyridinium benzyl quats. Exemplary compounds include methyl pyridinium chloride, ethyl pyridinium chloride, propyl pyridinium chloride, butyl pyridinium chloride, octyl pyridinium chloride, decyl pyridinium chloride, lauryl pyridinium chloride, cetyl pyridinium chloride, benzyl pyridinium chloride and an alkyl benzyl pyridinium chloride, preferably wherein the alkyl is a C₁-C₆ hydrocarbyl group. Preferably, the pyridinium compound includes benzyl pyridinium chloride.

The one or more additional corrosion inhibitors can be a phosphate ester, monomeric or oligomeric fatty acid, alkoxyated amine, or mixture thereof.

The one or more additional corrosion inhibitors can be a phosphate ester. Suitable mono-, di- and tri-alkyl as well as alkylaryl phosphate esters and phosphate esters of mono, di, and triethanolamine typically contain between from 1 to about 18 carbon atoms. Preferred mono-, di- and trialkyl phosphate esters, alkylaryl or arylalkyl phosphate esters are those prepared by reacting a C₃-C₁₈ aliphatic alcohol with phosphorous pentoxide. The phosphate intermediate interchanges its ester groups with triethylphosphate producing a broader distribution of alkyl phosphate esters.

Alternatively, the phosphate ester can be made by admixing with an alkyl diester, a mixture of low molecular weight alkyl alcohols or diols. The low molecular weight alkyl alcohols or diols preferably include C₆ to C₁₀ alcohols or diols. Further, phosphate esters of polyols and their salts containing one or more 2-hydroxyethyl groups, and hydroxylamine phosphate esters obtained by reacting polyphosphoric acid or phosphorus pentoxide with hydroxylamines such as diethanolamine or triethanolamine are preferred.

The one or more additional corrosion inhibitors can be a monomeric or oligomeric fatty acid. Preferred monomeric or oligomeric fatty acids are C₁₄-C₂₂ saturated and unsaturated fatty acids as well as dimer, trimer and oligomer products obtained by polymerizing one or more of such fatty acids.

5 The one or more additional corrosion inhibitors can be an alkoxyated amine. The alkoxyated amine can be an ethoxyated alkyl amine. The alkoxyated amine can be ethoxyated tallow amine.

In some embodiments, the additional corrosion inhibitor in the corrosion control composition is tall oil diethylenetriamine imidazoline, 1-(2-hydroxyethyl)-2-coconut oil-2-
10 imidazoline, 1-benzyl-1-(2-hydroxyethyl)-2-coconut oil-2-imidazolinium chloride, benzyl-dimethyl-dodecyl-ammonium chloride, N-coco alkyl 1,3, propylenediamine acetate, morpholine, morpholine derivative, didecyl-dimethyl-ammonium chloride, 1-benzyl-1-(2-hydroxyethyl)-2-tall oil-2-imidazolinium chloride, and N-benzyl-alkylpyridinium chloride. tall oil fatty acid, trimeric C₁₈ unsaturated fatty acid, dimeric C₁₈ unsaturated fatty acid,
15 alkylpyridine, N-benzyl-alkylpyridinium chloride, quinoline, quinoline quaternary compound with benzyl chloride, or mixture thereof.

Dispersant

In some embodiments, the corrosion control compositions disclosed herein can further comprise a dispersant. A dispersant keeps particulate matter present in the water of
20 a water system dispersed, so that it does not agglomerate. The composition can comprise from about 0.1 to 10 wt-%, from about 0.5 to 5 wt-%, or from about 0.5 to 4 wt-% of a dispersant, based on total weight of the composition.

A dispersant may be an acrylic acid polymer, maleic acid polymer, copolymer of acrylic acid with sulfonated monomers, alkyl esters thereof, or combination thereof. These
25 polymers may include terpolymers of acrylic acid, acrylamide and sulfonated monomers. These polymers may also include quad-polymers consisting of acrylic acid and three other monomers.

Suitable dispersants include, but are not limited to, aliphatic phosphonic acids with 2-50 carbons, such as hydroxyethyl diphosphonic acid, and aminoalkyl phosphonic acids,
30 e.g. polyaminomethylene phosphonates with 2-10 N atoms e.g. each bearing at least one methylene phosphonic acid group; examples of the latter are ethylenediamine tetra(methylene phosphonate), diethylenetriamine penta(methylene phosphonate), and the

triamine- and tetramine-polymethylene phosphonates with 2-4 methylene groups between each N atom, at least 2 of the numbers of methylene groups in each phosphonate being different. Other suitable dispersion agents include lignin, or derivatives of lignin such as lignosulfonate and naphthalene sulfonic acid and derivatives.

5 In some embodiments, the dispersant in the corrosion control compositions disclosed herein is a reaction product of tall oil fatty acids with diethylenetriamine and acrylic acid (1:1:1), reaction product of fatty acids or tall-oil with triethylenetetramine or tetraethylenepentamine, reaction product of diethylenetriamine and naphthenic acid.

10 The corrosion control composition can further comprise an organic sulfur compound, such as a mercaptoalkyl alcohol, mercaptoacetic acid, thioglycolic acid, 3,3'-dithiodipropionic acid, sodium thiosulfate, thiourea, L-cysteine, tert-butyl mercaptan, sodium thiosulfate, ammonium thiosulfate, sodium thiocyanate, ammonium thiocyanate, sodium metabisulfite, or a combination thereof. Preferably, the mercaptoalkyl alcohol comprises 2-mercaptoethanol. Such compounds are used as synergists in the composition.

15 In some embodiments, the organic sulfur compound in the corrosion control composition is 2-mercaptoethanol, sodium thiosulfate, thioglycolic acid, or a mixture thereof.

20 The organic sulfur compound can constitute from about 0.5 wt-% to about 15 wt-% of the composition, based on total weight of the composition, preferably from about 1 wt-% to about 10 wt-% and more preferably from about 1 wt-% to about 5 wt-%. The organic sulfur compound can constitute about 1 wt-%, about 2 wt-%, about 3 wt-%, about 4 wt-%, about 5 wt-%, about 6 wt-%, about 7 wt-%, about 8 wt-%, about 9 wt-%, about 10 wt-%, about 11 wt-%, about 12 wt-%, about 13 wt-%, about 14 wt-%, or about 15 wt-% of the composition.

25 The corrosion control composition can further comprise a de-emulsifier. Preferably, the demulsifier comprises an oxyalkylate polymer, such as a polyalkylene glycol. The de-emulsifier can constitute from about 0.1 wt-% to about 10 wt-%, from about 0.5 wt-% to about 5 wt.%, or from about 0.5 wt-% to about 4 wt-% of the composition, based on total weight of the composition. The de-emulsifier can constitute about 0.5 wt-%,
30 about 1 wt-%, about 1.5 wt-%, about 2 wt-%, about 2.5 wt-%, about 3 wt-%, about 3.5 wt-%, about 4 wt-%, about 4.5 wt-%, or about 5 wt-% of the composition.

The corrosion control composition can further comprise an asphaltene inhibitor. The composition can comprise from about 0.1 wt-% to about 10 wt-%, from about 0.1 wt-% to about 5 wt-%, or from about 0.5 wt-% to about 4 wt-% of an asphaltene inhibitor, based on total weight of the composition. Suitable asphaltene inhibitors include, but are not limited to, aliphatic sulfonic acids; alkyl aryl sulfonic acids; aryl sulfonates; lignosulfonates; alkylphenol/aldehyde resins and similar sulfonated resins; polyolefin esters; polyolefin imides; polyolefin esters with alkyl, alkylphenyl or alkylpyridyl functional groups; polyolefin amides; polyolefin amides with alkyl, alkylphenyl or alkylpyridyl functional groups; polyolefin imides with alkyl, alkylphenyl or alkylpyridyl functional groups; alkenyl/vinyl pyrrolidone copolymers; graft polymers of polyolefins with maleic anhydride or vinyl imidazole; hyperbranched polyester amides; polyalkoxylated asphaltenes, amphoteric fatty acids, salts of alkyl succinates, sorbitan monooleate, and polyisobutylene succinic anhydride.

The corrosion control composition can further comprise a paraffin inhibitor. The composition can comprise from about 0.1 wt-% to about 10 wt-%, from about 0.1 wt-% to about 5 wt-%, or from about 0.5 wt-% to about 4 wt-% of a paraffin inhibitor, based on total weight of the composition. Suitable paraffin inhibitors include, but are not limited to, paraffin crystal modifiers, and dispersant/crystal modifier combinations. Suitable paraffin crystal modifiers include, but are not limited to, alkyl acrylate copolymers, alkyl acrylate vinylpyridine copolymers, ethylene vinyl acetate copolymers, maleic anhydride ester copolymers, branched polyethylenes, naphthalene, anthracene, microcrystalline wax and/or asphaltenes. Suitable paraffin dispersants include, but are not limited to, dodecyl benzene sulfonate, oxyalkylated alkylphenols, and oxyalkylated alkylphenolic resins.

The corrosion control composition can further comprise a scale inhibitor. The composition can comprise from about 0.1 wt-% to about 20 wt-%, from about 0.5 wt-% to about 10 wt-%, or from about 1 wt-% to about 10 wt-% of a scale inhibitor, based on total weight of the composition. Suitable scale inhibitors include, but are not limited to, phosphates, phosphate esters, phosphoric acids, phosphonates, phosphonic acids, polyacrylamides, salts of acrylamidomethyl propane sulfonate/acrylic acid copolymer (AMPS/AA), phosphinated maleic copolymer (PHOS/MA), mono-, bis- and oligomeric phosphinosuccinic acid (PSO) derivatives, polycarboxylic acid, hydrophobically modified

polycarboxylic acid, and salts of a polymaleic acid/acrylic acid/acrylamidomethyl propane sulfonate terpolymer (PMA/AA/AMPS).

The corrosion control composition can further comprise an emulsifier. The composition can comprise from about 0.1 wt-% to about 10 wt-%, from about 0.5 wt-% to about 5 wt-%, or from about 0.5 wt-% to about 4 wt-% of an emulsifier, based on total weight of the composition. Suitable emulsifiers include, but are not limited to, salts of carboxylic acids, products of acylation reactions between carboxylic acids or carboxylic anhydrides and amines, and alkyl, acyl and amide derivatives of saccharides (alkyl-saccharide emulsifiers).

The corrosion control composition can further comprise a water clarifier. The composition can comprise from about 0.1 wt-% to about 10 wt-%, from about 0.5 wt-% to about 5 wt-%, or from about 0.5 wt-% to about 4 wt-% of a water clarifier, based on total weight of the composition. Suitable water clarifiers include, but are not limited to, inorganic metal salts such as alum, aluminum chloride, and aluminum chlorohydrate, or organic polymers such as acrylic acid-based polymers, acrylamide-based polymers, polymerized amines, alkanolamines, thiocarbamates, and cationic polymers such as diallyldimethylammonium chloride (DADMAC).

The corrosion control composition can further comprise an emulsion breaker. The composition can comprise from about 0.1 wt-% to about 10 wt-%, from about 0.5 wt-% to about 5 wt-%, or from about 0.5 wt-% to about 4 wt-% of an emulsion breaker, based on total weight of the composition. Suitable emulsion breakers include, but are not limited to, dodecylbenzylsulfonic acid (DDBSA), the sodium salt of xylenesulfonic acid (NAXSA), epoxylated and propoxylated compounds, and resins, such as phenolic and epoxide resins.

The corrosion control composition can further comprise a hydrogen sulfide scavenger. The composition can comprise from about 1 wt-% to about 50 wt-%, from about 1 wt-% to about 40 wt-%, from about 1 wt-% to about 30 wt-%, from about 0.1 wt-% to about 10 wt-%, from about 0.5 wt-% to about 5 wt-%, or from about 0.5 wt-% to about 4 wt-% of a hydrogen sulfide scavenger, based on total weight of the composition. Suitable additional hydrogen sulfide scavengers include, but are not limited to, oxidants (e.g., inorganic peroxides such as sodium peroxide or chlorine dioxide); aldehydes (e.g., of 1-10 carbons such as formaldehyde, glyoxal, glutaraldehyde, acrolein, or methacrolein; triazines (e.g., monoethanolamine triazine, monomethylamine triazine, and triazines from multiple

amines or mixtures thereof); condensation products of secondary or tertiary amines and aldehydes, and condensation products of alkyl alcohols and aldehydes.

The corrosion control composition can further comprise a gas hydrate inhibitor. The composition can comprise from about 0.1 wt-% to about 25 wt-%, from about 0.5 wt-% to about 20 wt-%, from about 1 wt-% to about 10 wt-%, from about 0.1 wt-% to about 10 wt-%, from about 0.5 wt-% to about 5 wt-%, or from about 0.5 wt-% to about 4 wt-% of a gas hydrate inhibitor, based on total weight of the composition. Suitable gas hydrate inhibitors include, but are not limited to, thermodynamic hydrate inhibitors (THI), kinetic hydrate inhibitors (KHI), and anti-agglomerates (AA). Suitable thermodynamic hydrate inhibitors include, but are not limited to, sodium chloride, potassium chloride, calcium chloride, magnesium chloride, sodium bromide, formate brines (e.g. potassium formate), polyols (such as glucose, sucrose, fructose, maltose, lactose, gluconate, monoethylene glycol, diethylene glycol, triethylene glycol, mono-propylene glycol, dipropylene glycol, tripropylene glycols, tetrapropylene glycol, monobutylene glycol, dibutylene glycol, tributylene glycol, glycerol, diglycerol, triglycerol, and sugar alcohols (e.g. sorbitol, mannitol)), methanol, propanol, ethanol, glycol ethers (such as diethyleneglycol monomethylether, ethyleneglycol monobutylether), and alkyl or cyclic esters of alcohols (such as ethyl lactate, butyl lactate, methylethyl benzoate).

The corrosion control composition can further comprise a kinetic hydrate inhibitor. The composition can comprise from about 0.1 wt-% to about 25 wt-%, from about 0.5 wt-% to about 20 wt-%, from about 1 wt-% to about 10 wt-%, from about 0.1 wt-% to about 10 wt-%, from about 0.5 wt-% to about 5 wt-%, or from about 0.5 wt-% to about 4 wt-% of a kinetic hydrate inhibitor, based on total weight of the composition. Suitable kinetic hydrate inhibitors and anti-agglomerates include, but are not limited to, polymers and copolymers, polysaccharides (such as hydroxyethylcellulose (HEC), carboxymethylcellulose (CMC), starch, starch derivatives, and xanthan), lactams (such as polyvinylcaprolactam, polyvinyl lactam), pyrrolidones (such as polyvinyl pyrrolidone of various molecular weights), fatty acid salts, ethoxylated alcohols, propoxylated alcohols, sorbitan esters, ethoxylated sorbitan esters, polyglycerol esters of fatty acids, alkyl glucosides, alkyl polyglucosides, alkyl sulfates, alkyl sulfonates, alkyl ester sulfonates, alkyl aromatic sulfonates, alkyl betaine, alkyl amido betaines, hydrocarbon based

dispersants (such as lignosulfonates, iminodisuccinates, polyaspartates), amino acids, and proteins.

The corrosion control composition can further comprise a pH modifier. The composition can comprise from about 0.1 wt-% to about 20 wt-%, from about 0.5 wt-% to about 10 wt-%, or from about 0.5 wt-% to about 5 wt-% of a pH modifier, based on total weight of the composition. Suitable pH modifiers include, but are not limited to, alkali hydroxides, alkali carbonates, alkali bicarbonates, alkaline earth metal hydroxides, alkaline earth metal carbonates, alkaline earth metal bicarbonates and mixtures or combinations thereof. Exemplary pH modifiers include sodium hydroxide, potassium hydroxide, calcium hydroxide, calcium oxide, sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, magnesium oxide, and magnesium hydroxide.

The corrosion control composition can further comprise a surfactant. The composition can comprise from about 0.1 wt-% to about 10 wt-%, from about 0.5 wt-% to about 5 wt-%, or from about 0.5 wt-% to about 4 wt-% of a surfactant, based on total weight of the composition. A suitable surfactant can be a nonionic, semi-nonionic, cationic, anionic, amphoteric, zwitterionic, Gemini, di-cationic, di-anionic surfactant, or mixtures thereof. Anionic surfactants include alkyl aryl sulfonates, olefin sulfonates, paraffin sulfonates, alcohol sulfates, alcohol ether sulfates, alkyl carboxylates and alkyl ether carboxylates, and alkyl and ethoxylated alkyl phosphate esters, and mono and dialkyl sulfosuccinates and sulfosuccinamates. Nonionic surfactants include alcohol alkoxyates, alkylphenol alkoxyates, block copolymers of ethylene, block copolymers of ethylene and propylene, propylene and butylene oxides, alkyl dimethyl amine oxides, alkyl-bis(2-hydroxyethyl) amine oxides, alkyl amidopropyl dimethyl amine oxides, alkylamidopropyl-bis(2-hydroxyethyl) amine oxides, alkyl polyglucosides, polyalkoxylated glycerides, sorbitan esters and polyalkoxylated sorbitan esters, and alkoyl polyethylene glycol esters and diesters. Also included are betaines and sultanes, amphoteric surfactants such as alkyl amphoacetates and amphodiacetates, alkyl amphopropionates and amphodipropionates, and alkyliminodipropionate.

In some embodiments, the surfactant is phosphate esters of ethoxylated C10-C16 alcohols, ethoxylated C11-C14 iso or C13 rich phosphates, ethoxylated nonylphenol, ethoxylated branched nonylphenol, or mixture thereof.

The corrosion control composition can further comprise other additional corrosion control composition agents that provide a functional and/or beneficial property. For example, additional corrosion control composition agent can be a sequestrant, solubilizer, lubricant, buffer, cleaning agent, rinse aid, preservative, binder, thickener or other viscosity modifier, processing aid, water-conditioning agent, foam inhibitor or foam generator, threshold agent or system, aesthetic enhancing agent (e.g., dye, odorant, perfume), or other agent suitable for formulation with the corrosion inhibitor composition, and mixtures thereof. Additional agents vary according to the specific corrosion control composition being manufactured and its intended use as one skilled in the art will appreciate.

Alternatively, the corrosion control composition does not contain or is free of any of the additional corrosion control composition agents.

Additionally, the corrosion control composition can be formulated into exemplary compositions comprising the following components as shown in following **Table 1**. These formulations include the ranges of the components listed and can optionally include additional agents. The values in the **Table 1** below are weight percentages.

Table 1. Exemplary Corrosion Control Compositions

Component	1	2	3	4	5	6	7	8	9	10	11	12
Di-cationic or di-anionic compounds	0.1-20	0.1-20	0.1-20	0.1-20	0.1-20	0.1-20	10-20	10-20	10-20	10-20	10-20	0.1-20
Carrier	5-40	-	5-50	-	5-50	5-50	5-40	-	5-50	-	-	10-20
additional corrosion inhibitor	0.1-20	0.1-20	-	-	-	-	0.1-20	0.1-20	-	-	-	0.1-20
Organic sulfur compound	0.1-5	0.1-5	0.1-5	0.1-5	-	-	0.1-5	0.1-5	0.1-5	-	-	0.1-5
Scale inhibitor	1-10	1-10	1-10	1-10	1-10	-	1-10	1-10	1-10	1-10	-	1-10
surfactant	-	-	-	-	-	-	-	-	-	-	-	0.1-25
Biocide	0.5-5	0.5-5	0.5-5	0.5-5	0.5-5	0.5-5	0.5-5	0.5-5	0.5-5	0.5-5	0.5-5	

Water	0.00	0-40	0-10	0-60	0-15	0-25	0.00	0-40	0-10	0-65	0-75	
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Component	13	14	15	16	17	18	19	20	21	22	23	24
Di-cationic or di-anionic compounds	0.1-20	0.1-20	0.1-20	0.1-20	0.1-20	0.1-20	10-20	10-20	10-20	10-20	10-20	10-20
carrier	-	10-20	-	10-35	10-35	-	10-15	-	-	10-35	10-35	-
Additional corrosion inhibitor	0.1-20	0.1-20	0.1-20	0.1-20	0.1-20	0.1-20	0.1-20	0.1-20	0.1-20	0.1-20	0.1-20	0.1-20
Organic sulfur compound	0.1-5	-	-	-	-	-	0.1-5	-	-	-	-	-
Scale inhibitor	1-10	1-10	-	-	1-10	-	1-10	1-10	-	-	-	1-10
surfactant	0.1-25	0.1-25	0.1-25	-	-	-	0.1-25	0.1-25	0.1-25	-	0.1-25	-
Biocide	-	-	-	-	-	0.5-5	0.5-5	0.5-5	0.5-5	0.5-5	-	-
Water	0-20	0-5	0-35	0-25	0-15	0-55	0.00	0-20	0-30	0-20	0.00	0-50

Water System

The corrosion control composition or its use solution is applied to a water system to prevent corrosion on surfaces in the water system or onto surfaces within the water system. In some embodiments, the water system in the disclosed methods herein is an industrial water system. In other embodiments, the water system can be, but is not limited to, a cooling water system, including an open recirculating system, closed and once-through cooling water system, boilers and boiler water system, petroleum well system, downhole formation, geothermal well, and other water system in oil and gas field applications, a mineral washing system, flotation and benefaction system, paper mill digester, washer, bleach plant, stock chest, white water system, paper machine surface, black liquor

evaporator in the pulp industry, gas scrubber and air washer, continuous casting processes in the metallurgical industry, air conditioning and refrigeration system, industrial and petroleum process water, indirect contact cooling and heating water, water reclamation system, water purification system, membrane filtration water system, food processing stream (meat, vegetable, sugar beets, sugar cane, grain, poultry, fruit and soybean), waste treatment system, clarifier, liquid-solid application, municipal sewage treatment, municipal water system, potable water system, aquifer, water tank, sprinkler system, or water heater.

The water system can be those used in oil and gas operations. The water system can comprise water, oil, and solid. In some embodiments, the water system comprises mostly oil or hydrocarbons. For example, the water systems include oil or gasoline in tanks or pipelines. In some embodiments, the water system is one used in oil and gas operations.

In some embodiments, the water system is a cooling water system, including open recirculating, closed and once-through cooling water system, paper machine surface, food processing stream, waste treatment system, or potable water system.

Use of the methods or compositions disclosed

In some embodiments, for the methods disclosed herein, providing a corrosion control composition into a water system means that the corrosion control composition, one or more di-cationic or di-anionic compounds, or a use solution thereof is added into a fluid comprising water or onto a surface of a water system. In other embodiments, providing a corrosion control composition into a water system means adding the corrosion control composition or the di-cationic or di-anionic compounds onto the surface or into the water of the water system. In some other embodiments, providing a corrosion control composition into a water system means adding the corrosion control composition, di-cationic or di-anionic compounds, or use solution thereof to a fluid or gas that in turn contacts the surfaces of the water system. The corrosion control composition, di-cationic or di-anionic compounds, or use solution thereof may be added continuously, or intermittently when more compounds or compositions may be needed.

A use solution of a corrosion control composition or of one or more di-cationic or di-anionic compounds as used herein refers to a diluted solution for the composition or compounds by a diluent. A diluent as used herein refers to water, the water of a water system, or one of the carriers or solvents defined herein. The corrosion control

composition or the compounds can be diluted by a factor of 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11-1,000,000, or any value there between to generate a use solution and then provide the use solution to a water system or onto a surface. In this disclosure, when a composition or di-cationic or di-anionic compounds are applied, either the composition/compounds or use
5 solution thereof is applied.

In some embodiments, the corrosion control composition or the di-cationic or di-anionic compounds disclosed herein may be added to the water of the water system, so the concentration of the composition or compounds in the treated water system is in an concentration of from about 1 ppm to about 1000 ppm. In other embodiments, the amount
10 of the corrosion control composition or the di-cationic or di-anionic compounds in the water of the water system may range from about 5 ppm to about 100 ppm, about 5 ppm to about 50 ppm, about 5 ppm to about 40 ppm, about 5 ppm to about 30 ppm, about 10 ppm to about 60 ppm, about 10 ppm to about 50 ppm, about 10 ppm to about 40 ppm, about 10 ppm to about 30 ppm, about 20 ppm to about 60 ppm, about 20 ppm to about 50 ppm,
15 about 20 ppm to about 40 ppm, or about 20 ppm to about 30 ppm. In some embodiments, the corrosion control composition or the di-cationic or di-anionic compounds may be added to the water to an amount ranging from about 100 ppm to about 1000 ppm, about 125 ppm to about 1000 ppm, about 250 ppm to about 1000 ppm, or about 500 ppm to about 1000 ppm.

20 The corrosion control composition or the di-cationic or di-anionic compounds can be used for corrosion control in oil and gas applications such as by treating a gas or liquid stream with an effective amount of the compound or composition as described herein. The compounds and compositions can be used in any industry where it is desirable to prevent corrosion at a surface.

25 The corrosion control composition or the di-cationic or di-anionic compounds can be used in a condensate/oil systems/gas system, or any combination thereof. For example, the corrosion control composition or the di-cationic or di-anionic compounds can be used in corrosion control on heat exchanger surfaces. The corrosion control composition or the di-cationic or di-anionic compounds can be applied to a gas or liquid produced, or used in
30 the production, transportation, storage, and/or separation of crude oil or natural gas. The corrosion control composition or the di-cationic or di-anionic compounds can be applied to a gas stream used or produced in a coal-fired process, such as a coal-fired power plant.

The corrosion control composition or the di-cationic or di-anionic compounds can be applied to a gas or liquid produced or used in a waste-water process, a farm, a slaughter house, a land-fill, a municipality waste-water plant, a coking coal process, or a biofuel process.

5 A fluid to which the corrosion control composition or the di-cationic or di-anionic compounds can be introduced can be an aqueous medium. The aqueous medium can comprise water, gas, and optionally liquid hydrocarbon.

10 A fluid to which the corrosion control composition or the di-cationic or di-anionic compounds can be introduced can be a liquid hydrocarbon. The liquid hydrocarbon can be any type of liquid hydrocarbon including, but not limited to, crude oil, heavy oil, processed residual oil, bituminous oil, coker oils, coker gas oils, fluid catalytic cracker feeds, gas oil, naphtha, fluid catalytic cracking slurry, diesel fuel, fuel oil, jet fuel, gasoline, and kerosene. The fluid or gas can be a refined hydrocarbon product.

15 A fluid or gas treated with the corrosion control composition or the di-cationic or di-anionic compounds can be at any selected temperature, such as ambient temperature or an elevated temperature. The fluid (e.g., liquid hydrocarbon) or gas can be at a temperature of from about 40°C to about 250°C. The fluid or gas can be at a temperature of from about -50°C to about 300°C, from about 0°C to about 200°C, from about 10°C to about 100°C, or from about 20°C to about 90°C. The fluid or gas can be at a temperature
20 of about 22°C, about 23°C, about 24°C, about 25°C, about 26°C, about 27°C, about 28°C, about 29°C, about 30°C, about 31°C, about 32°C, about 33°C, about 34°C, about 35°C, about 36°C, about 37°C, about 38°C, about 39°C, or about 40°C. The fluid or gas can be at a temperature of about 85°C, about 86°C, about 87°C, about 88°C, about 89°C, about 90°C, about 91°C, about 92°C, about 93°C, about 94°C, about 95°C, about 96°C, about
25 97°C, about 98°C, about 99°C, or about 100°C.

 The corrosion control composition or the di-cationic or di-anionic compounds can be added to a fluid (or water system) at various levels of water cut. For example, the water cut can be from 0% to 100% volume/volume (v/v), from 1% to 80% v/v, or from 1% to 60% v/v. The fluid can be an aqueous medium that contains various levels of salinity. The
30 fluid can have a salinity of 0% to 25%, about 1% to 24%, or about 10% to 25% weight/weight (w/w) total dissolved solids (TDS).

The fluid or gas of a water system or the water of a water system, in which the corrosion control composition or the di-cationic or di-anionic compounds are introduced, can be contained in and/or exposed to many types of apparatuses. For example, the fluid or gas can be contained in an apparatus that transports fluid or gas from one point to
5 another, such as an oil and/or gas pipeline. The apparatus can be part of an oil and/or gas refinery, such as a pipeline, a separation vessel, a dehydration unit, or a gas line. The fluid can be contained in and/or exposed to an apparatus used in oil extraction and/or production, such as a wellhead. The apparatus can be part of a coal-fired power plant. The apparatus can be a scrubber (e.g., a wet flue gas desulfurizer, a spray dry absorber, a dry
10 sorbent injector, a spray tower, a contact or bubble tower, or the like). The apparatus can be a cargo vessel, a storage vessel, a holding tank, or a pipeline connecting the tanks, vessels, or processing units.

The corrosion control composition or the di-cationic or di-anionic compounds can be introduced into a fluid or gas of the water system by any appropriate method for
15 ensuring dispersal through the fluid or gas. For examples, the corrosion control composition or the di-cationic or di-anionic compounds can be added to the hydrocarbon fluid before the hydrocarbon fluid contacts the surface.

The corrosion control composition or the di-cationic or di-anionic compounds can be added at a point in a flow line upstream from the point at which corrosion control is
20 desired. The corrosion control composition or the di-cationic or di-anionic compounds can be injected using mechanical equipment such as chemical injection pumps, piping tees, injection fittings, atomizers, quills, and the like.

The corrosion control composition or the di-cationic or di-anionic compounds can be pumped into an oil and/or gas pipeline using an umbilical line. A capillary injection
25 system can be used to deliver the corrosion control composition or the di-cationic or di-anionic compounds to a selected fluid.

A fluid to which the corrosion control composition or the di-cationic or di-anionic compounds can be introduced can be an aqueous medium. The aqueous medium can
comprise water, gas, and optionally liquid hydrocarbon. A fluid to which the corrosion
30 control composition or the di-cationic or di-anionic compounds can be introduced can be a liquid hydrocarbon.

The corrosion control composition or the di-cationic or di-anionic compounds can be introduced into a liquid and a mixture of several liquids, a liquid and gas, liquid, solid, and gas. The corrosion control composition or the di-cationic or di-anionic compounds can be injected into a gas stream as an aqueous or non-aqueous solution, mixture, or slurry.

5 The fluid or gas can be passed through an absorption tower comprising the corrosion control composition or the di-cationic or di-anionic compounds.

10 The corrosion control composition or the di-cationic or di-anionic compounds can be applied to a fluid or gas to provide any selected concentration. In practice, the corrosion control composition or the di-cationic or di-anionic compounds are typically added to a flow line to provide an effective treating dose of the corrosion control composition or the di-cationic or di-anionic compounds from about 0.01 ppm to about 5,000 ppm. The corrosion control composition or the di-cationic or di-anionic compounds can be applied to a fluid or gas to provide an active concentration of about 1 parts per million (ppm) to about 1,000,000 ppm, about 1 parts per million (ppm) to about 100,000 ppm, or about 10 ppm to about 75,000 ppm. The polymer salts/compositions can be applied to a fluid to provide an actives concentration of about 100 ppm to about 10,000 ppm, about 200 ppm to about 8,000 ppm, or about 500 ppm to about 6,000 ppm. The actives concentration means the concentration of corrosion control composition or the di-cationic or di-anionic compounds.

20 The corrosion control composition or the di-cationic or di-anionic compounds can be applied to a fluid or gas to provide an active concentration of about 0.1 ppm, about 0.5 ppm, about 1 ppm, about 2 ppm, about 5 ppm, about 10 ppm, about 20 ppm, about 100 ppm, about 200 ppm, about 500 ppm, or about 1,000 ppm in the treated fluid or gas, e.g., the treated water system. The corrosion control composition or the di-cationic or di-anionic compounds can be applied to a fluid or gas or water system to provide an actives concentration of about 0.125 ppm, about 0.25 ppm, about 0.625 ppm, about 1 ppm, about 1.25 ppm, about 2.5 ppm, about 5 ppm, about 10 ppm, or about 20 ppm in the treated fluid, gas, or water system. Each water system can have its own dose level requirements, and the effective dose level of the corrosion control composition or the di-cationic or di-anionic compounds to sufficiently reduce the rate of microbial or biofilm growth can vary with the water system in which it is used.

30 The corrosion control composition or the di-cationic or di-anionic compounds can be applied continuously, in batch, or a combination thereof. The corrosion control

composition or the di-cationic or di-anionic compounds dosing can be continuous. The corrosion control composition or the di-cationic or di-anionic compounds dosing can be intermittent (e.g., batch treatment) or can be continuous/maintained and/or intermittent.

5 Dosage rates for continuous treatments typically range from about 10 ppm to about 500 ppm, or about 10 ppm to about 200 ppm. Dosage rates for batch treatments typically range from about 10 ppm to about 400,000 ppm, or about 10 ppm to about 20,000 ppm. The corrosion control composition or the di-cationic or di-anionic compounds can be applied as a pill to a pipeline, providing a high dose (e.g., 20,000 ppm) of the composition.

10 The flow rate of a flow line in which the corrosion control composition or the di-cationic or di-anionic compounds is used can be between about 0.1 feet per second and about 1,000 feet per second, or between about 0.1 feet per second and about 50 feet per second. The corrosion control composition or the di-cationic or di-anionic compounds can also be formulated with water to facilitate addition to the flow line.

15 A surface of a water system can be any surface that can make contact to the water or vapor of the water of the water system in any way. The surface can be a part of a wellbore or equipment used in the production, transportation, storage, and/or separation of a fluid such as crude oil or natural gas.

20 More specifically, the surface can be a part of equipment used a coal-fired process, a waste-water process, a farm, a slaughter house, a land-fill, a municipality waste-water plant, a coking coal process, or a biofuel process. Preferably, the surface can be a part of equipment used in the production of crude oil or natural gas.

The equipment can comprise a pipeline, a storage vessel, downhole injection tubing, a flow line, or an injection line.

25 The corrosion control composition or the di-cationic or di-anionic compounds are useful for prevention corrosion of containers, processing facilities, or equipment in the food service or food processing industries. The corrosion control composition or the di-cationic or di-anionic compounds have particular value for use on food packaging materials and equipment, and especially for cold or hot aseptic packaging. Examples of process facilities in which the corrosion control composition or the di-cationic or di-anionic compounds can be employed include a milk line dairy, a continuous brewing system, food
30 processing lines such as pumpable food systems and beverage lines, ware wash machines, low temperature ware wash machines, dishware, bottle washers, bottle chillers, warmers,

third sink washers, processing equipment such as tanks, vats, lines, pumps and hoses (e.g., dairy processing equipment for processing milk, cheese, ice cream and other dairy products), and transportation vehicles. The corrosion control composition or the di-cationic or di-anionic compounds can be used to inhibit corrosion in tanks, lines, pumps, and other equipment used for the manufacture and storage of soft drink materials, and also used in the bottling or containers for the beverages.

The corrosion control composition or the di-cationic or di-anionic compounds can also be used on or in other industrial equipment and in other industrial process streams such as heaters, cooling towers, boilers, retort waters, rinse waters, aseptic packaging wash waters, and the like. The corrosion control composition or the di-cationic or di-anionic compounds can be used to treat surfaces in recreational waters such as in pools, spas, recreational flumes and water slides, fountains, and the like.

The corrosion control composition or the di-cationic or di-anionic compounds can be used to treat metal surfaces contacted with cleaners in surfaces found in janitorial and/or housekeeping applications, food processing equipment and/or plant applications, and in laundry applications. For example, washers, such as tunnel washers for washing textiles, can be treated according to methods disclosed herein.

The corrosion control composition or the di-cationic or di-anionic compounds can be used or applied in combination with low temperature dish and/or warewash sanitizing final rinse, toilet bowl cleaners, and laundry bleaches. The corrosion control composition or the di-cationic or di-anionic compounds can be used to treat metal surfaces, such as ware, cleaned and/or sanitized with corrosive sources.

The corrosion control composition or the di-cationic or di-anionic compounds can be dispensed in any suitable method generally known by one skilled in the art. For example, a spray-type dispenser can be used. A spray-type dispenser functions by impinging a water spray upon an exposed surface of a composition to dissolve a portion of the composition, and then immediately directing the concentrate solution including the composition out of the dispenser to a storage reservoir or directly to a point of use.

The corrosion control composition or the di-cationic or di-anionic compounds can be dispensed by immersing either intermittently or continuously in the water, fluid, or gas of the water system. The corrosion control composition or the di-cationic or di-anionic compounds can then dissolve, for example, at a controlled or predetermined rate. The rate

can be effective to maintain a concentration of the dissolved compounds or compositions that are effective for use according to the methods disclosed herein.

The corrosion control composition disclosed herein can comprise from about 10 wt-% to about 90 wt-% of the carrier, biocide, additional corrosion inhibitor, additional corrosion control composition agent, or a combination thereof and from about 10 wt-% to about 90 wt-% of one or more di-cationic or di-anionic compounds, from about 20 wt-% to about 80 wt-% of the carrier, biocide, additional corrosion inhibitor, additional corrosion control composition agent, or a combination thereof and from about 20 wt-% to about 80 wt-% of one or more di-cationic or di-anionic compounds; from about 30 wt-% to about 70 wt-% of the carrier, biocide, additional corrosion inhibitor, additional corrosion control composition agent, or a combination thereof and from about 30 wt-% to about 70 wt-% of the one or more di-cationic or di-anionic compounds, or from about 40 wt-% to about 60 wt-% of the carrier, biocide, additional corrosion inhibitor, additional corrosion control composition agent, or a combination thereof and from about 40 to about 60 wt.% of the one or more di-cationic or di-anionic compounds.

As used herein, the term "substantially free", "free" or "free of" refers to compositions completely lacking the component or having such a small amount of the component that the component does not affect the performance of the composition. The component may be present as an impurity or as a contaminant and shall be less than 0.5 wt-%. In another embodiment, the amount of the component is less than 0.1 wt-% and in yet another embodiment, the amount of component is less than 0.01 wt-%.

The term "weight percent", "wt-%", "percent by weight", "% by weight", and variations thereof, as used herein, refer to the concentration of a substance as the weight of that substance divided by the total weight of the composition and multiplied by 100. It is understood that, as used here, "percent", "%", and the like are intended to be synonymous with "weight percent", "wt-%", etc.

EXAMPLES

Embodiments of the present invention are further defined in the following non-limiting Examples. It should be understood that these Examples, while indicating certain embodiments of the invention, are given by way of illustration only. From the above discussion and these Examples, one skilled in the art can ascertain the essential

characteristics of this invention, and without departing from the spirit and scope thereof, can make various changes and modifications of the embodiments of the invention to adapt it to various usages and conditions. Thus, various modifications of the embodiments of the invention, in addition to those shown and described herein, will be apparent to those skilled in the art from the foregoing description. Such modifications are also intended to fall within the scope of the appended claims.

EXAMPLE 1

General Scheme to Synthesize Exemplary Di-cationic Compounds Containing Two Quaternary Groups:

Exemplary di-cationic compounds containing two quaternary groups as disclosed herein were synthesized, by aza Michael addition reaction between a primary amine (1 mole) and α,β -unsaturated carbonyl compound containing at least one quaternary group (at least 2 moles). The generic synthesis reaction scheme for preparation of disclosed di-cationic surfactants is shown in **FIG. 2**.

In **FIG. 2**, R^{11} is R^1 or $R^1-Z-(CH_2)_m$; R^1 is an unsubstituted or substituted, linear or branched C_1 - C_{30} alkyl, cyclic alkyl, alkenyl, or alkynyl group; Z is NH or O; R^2 is H, CH_3 , or an unsubstituted, linear or branched C_2 - C_{10} alkyl, alkenyl, or alkynyl group; m is an integer of 1 to 4; and n is an integer of 1-20.

The reaction shown in **FIG. 2** can be carried out in water at 80°C. The progression of this reaction is monitored by ESI-MS and/or NMR spectroscopy for consumption of the monomer. The reaction is typically stopped at time when a yield of about 98% for the diquat product is obtained. The synthesized compounds in the following Examples were made according to this scheme, except the reactants were different in each of the Examples as set forth in further detailed in each Example.

EXAMPLE 2

Synthesis of 3,3'-((3,3'-(octylazanediyl))bis(propanoyl))bis(azanediy))bis(N,N,N-trimethylpropan-1-aminium) chloride (I)

In this Example, (3-acrylamidopropyl) trimethylammonium chloride (APTAC, 75%, 30 grams, 0.10 mol) was charged into a 250-mL three-necked round bottom flask (RBF) equipped with an overhead stirrer, temperature probe, and condenser.

Benzyltrimethylammonium hydroxide (0.9 grams, 10%, 0.0005 mol) and water (41 g) were added into the flask. Octylamine (7 grams, 99%, 0.053 mol) was then added portion wise to the well-stirred reaction mixture. The resulting suspension was stirred at 80°C overnight. As the reaction proceeded to completion, the suspension turned into a clear yellowish solution. The resulting (~37 wt%) aqueous solution of the diquat compound, 3,3'-((3,3'-(octylazanediyl)bis(propanoyl))bis(azanediyl))bis(N,N,N-trimethylpropan-1-aminium) chloride (referred as compound **I**), was stored in the container. Mass spectrometry (+ESI-MS) confirmed synthesis of the di-cationic compound **I**: calc. $[M-2Cl]^{2+}$ 235.73, found 235.7241; calc. $[M-Cl]^+$ 506.42, found 506.4182.

10

EXAMPLE 3

Synthesis of 3,3'-((3,3'-(dodecylazanediyl)bis(propanoyl))bis(azanediyl))bis(N,N,N-trimethylpropan-1-aminium) chloride (II)

In this Example, (3-acrylamidopropyl) trimethylammonium chloride (APTAC, 75%, 30 grams, 0.10 mol) was charged into a 250-mL three-necked RBF equipped with an overhead stirrer, temperature probe, and condenser. Benzyltrimethylammonium hydroxide (0.9 grams, 10%, 0.0005 mol) and water (63 g) were added into the flask. Dodecylamine (10 grams, 98%, 0.053 mol) was then added portion wise to the well-stirred reaction mixture. The resulting suspension was stirred at 80°C overnight. As the reaction proceeded to completion, the suspension turned into a clear yellowish solution. The resulting (~31 wt%) aqueous solution of the diquat compound, 3,3'-((3,3'-(dodecylazanediyl)bis(propanoyl))bis(azanediyl))bis(N,N,N-trimethylpropan-1-aminium) chloride (referred as compound **II**) was used as is. Mass spectrometry (+ESI-MS) confirmed synthesis of the diquat compound (**II**): calc. $[M-2Cl]^{2+}$ 263.76, found 263.7554; calc. $[M-Cl]^+$ 562.48, found 562.4806.

25

EXAMPLE 4

Synthesis of 3,3'-((3,3'-(hexadecylazanediyl)bis(propanoyl))bis(azanediyl))bis(N,N,N-trimethylpropan-1-aminium) chloride (III)

In this Example, (3-acrylamidopropyl) trimethylammonium chloride (APTAC, 75%, 41 grams, 0.149 mol) was charged into a 250-mL three-necked RBF equipped with an overhead stirrer, temperature probe, and condenser. Benzyltrimethylammonium

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hydroxide (0.9 grams, 10%, 0.0005 mol) and water (100 g) were added into the flask. Hexadecylamine (20 grams, 90%, 0.0745 mol) was then added portion wise to the well-stirred reaction mixture. The resulting suspension was stirred at 80°C overnight. As the reaction proceeded to completion, the suspension turned into a clear yellowish solution.

- 5 The resulting (~30 wt%) aqueous solution of the diquat compound, 3,3'-((3,3'-(hexadecylazanediyl)bis(propanoyl))bis(azanediyl))bis(N,N,N-trimethylpropan-1-aminium) chloride (referred as compound **III**), was used as is. Mass spectrometry (+ESI/MS) confirmed synthesis of the diquat compound (**III**): calc. $[M-2Cl]^{2+}$ 291.79, found 291.7870; calc. $[M-Cl]^+$ 618.54, found 618.5439.

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EXAMPLE 5

Synthesis of 3,3'-((3,3'-(octylazanediyl)bis(propanoyl))bis(azanediyl))bis(N,N,N-trimethylpropan-1-aminium) chloride (IV)

- In this Example, (3-acrylamidopropyl) trimethylammonium chloride (APTAC, 15 75%, 40 grams, 0.145 mol) was charged into a 250-mL three-necked RBF equipped with an overhead stirrer, temperature probe, and condenser. Benzyltrimethylammonium hydroxide (0.9 grams, 10%, 0.0005 mol) and water (100 g) were added into the flask. Octadecylamine (20 grams, 98%, 0.072 mol) was then added portion wise to the well-stirred reaction mixture. The resulting suspension was stirred at 80°C overnight. As the 20 reaction proceeded to completion, the suspension turned into a clear yellowish solution. The resulting (~31 wt%) aqueous solution of the diquat compound, 3,3'-((3,3'-(octylazanediyl)bis(propanoyl))bis(azanediyl))bis(N,N,N-trimethylpropan-1-aminium) chloride (referred as compound **IV**), was used as is. Mass spectrometry (+ESI-MS) confirmed synthesis of the diquat compound **IV**: calc. $[M-2Cl]^{2+}$ 305.80, found 305.8014; 25 calc. $[M-Cl]^+$ 646.58, found 648.5791.

EXAMPLE 6

Synthesis of 3,3'-((3,3'-(octadec-9-en-1-ylazanediyl) bis(propanoyl)) bis(azanediyl)) bis(N,N,N-trimethylpropan-1-aminium) chloride (V)

- 30 In this Example, (3-acrylamidopropyl) trimethylammonium chloride (APTAC, 75%, 30 grams, 0.109 mol) was charged into a 250-mL three-necked RBF equipped with an overhead stirrer, temperature probe, and condenser. Benzyltrimethylammonium

hydroxide (0.25 grams, 10%, 0.0001 mol) and water (70 g) were added into the flask. Oleylamine (15 grams, 95%, 0.053 mol) was then added portion wise to the well-stirred reaction mixture. The resulting suspension was stirred at 80°C overnight. As the reaction proceeded to completion, the suspension turned into a clear yellowish solution. The resulting (~32 wt%) aqueous solution of the diquat compound, 3,3'-((3,3'-(octadec-9-en-1-ylazanediyl) bis(propanoyl)) bis(azanediyl)) bis(N,N,N-trimethylpropan-1-aminium) chloride (referred as **V**), was used as is. Mass spectrometry (+ESI-MS) confirmed synthesis of the diquat compound: calc. $[M-2Cl]^{2+}$ 304.80, found 304.7949; calc. $[M-Cl]^+$ 644.56, found 644.5596.

EXMAPLE 7

Synthesis of 3,3'-((3,3'-((3-(octadec-9-en-1-ylamino)propyl)azanediyl)bis(propanoyl))bis (azanediyl)) bis(N,N,N-trimethylpropan-1-aminium) chloride (**VI**)

In this Example, (3-acrylamidopropyl) trimethylammonium chloride (APTAC, 75%, 42 grams, 0.152 mol) was charged into a 250-mL three-necked RBF equipped with an overhead stirrer, temperature probe, and condenser. Benzyltrimethylammonium hydroxide (0.25 grams, 10%, 0.0001 mol) and water (130 g) were added into the flask. N-oleylpropanediamine (25 grams, 99%, 0.076 mol) was then added portion wise to the well-stirred reaction mixture. The resulting suspension was stirred at 80°C overnight. As the reaction proceeded to completion, the suspension turned into a clear yellowish solution. The resulting (~28 wt%) aqueous solution of the diquat compound, 3,3'-((3,3'-((3-(octadec-9-en-1-ylamino)propyl)azanediyl)bis(propanoyl))bis (azanediyl)) bis(N,N,N-trimethylpropan-1-aminium) chloride (referred as **VI**), was used as is. Mass spectrometry (+ESI/MS) confirmed synthesis of the diquat compound **VI**: calc. $[M-2Cl]^{2+}$ 333.32, found 333.3238; calc. $[M-Cl]^+$ 701.62, found 701.6173.

EXAMPLE 8

Surface Tension Measurements

Surface tension measurements were conducted on a Tracker tensiometer (Teclis Instruments) at room temperature. Various solutions with different concentrations of the exemplary di-cationic compounds were prepared, and surface tension measurements were

conducted. The surface tension as a function of concentration of the exemplary di-cationic compounds were measured and are listed in **Table 2**.

Table 2. Surface tension measurements of the exemplary diquat compounds (I-VI)

Concentration (%)	Surface Tension (dynes/cm)					
	I	II	III	IV	V	VI
0.010	49.19	53.35	70.43	68.98	69.3	61.78
0.025	44.36	46.29	53.79	53.29	54.24	57.85
0.050	35.86	43.64	48.49	50.25	43.95	46.67
0.100	31.85	42.20	46.07	50.57	39.81	45.32
0.500	25.1	36.36	45.61	47.13	40.84	44.81

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EXAMPLE 9

Corrosion Control Efficacy of Some Exemplary Di-cationic Compounds

In this Example, some exemplary di-cationic compounds were tested for their efficacy to prevent corrosion. The tested samples were made according to the reaction presented in Example 1 and listed in the following **Table 3**. The precursor primary amine for each compound is listed and the other reactant to produce the listed samples is (3-acrylamidopropyl) trimethylammonium chloride.

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Table 3. List of the exemplary compounds for corrosion control test.

Sample ID:	Chemistry AMINE (R-NH ₂)
1	HEXADECYLAMINE
2	OCTADECYLAMINE
3	OLEYLAMINE
4	N-OLEYLPROPANEDIAMINE
5	OCTYLAMINE
6	DODECYLAMINE
7	CORSAMINE DT
8	CORSAMINE TRT

The efficacy for corrosion control is usually measured by corrosion bubble cell tests. The bubble test simulates low flow areas where little or no mixing of water and oil

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occurs. The test was conducted in fluids containing 80% brine (3% sodium chloride) and 20% hydrocarbon (75% LVT-200 and 25% xylene). The fluids were placed into kettles and purged with carbon dioxide. The brine was placed into kettles and purged with carbon dioxide. The brine was continually purged with carbon dioxide to saturate the brine prior to starting the test. After the test began, the test cell was blanketed with carbon dioxide one hour prior to electrode insertion and through the duration of the test to maintain saturation. The kettles were stirred at 150 revolutions per minute (rpm) for the duration of the test to maintain thermal equilibrium at 80°C. The corrosion rate was measured by Linear Polarization Resistance (LPR) techniques. The working electrode used was 1018 carbon steel. The counter and reference electrodes were both Hastelloy. The electrodes were all cleaned and polished prior to testing. Data were collected for three hours before 20 ppm of each of the compositions (containing 2 ppm of each of various di-cationic compounds or salts thereof or the control C₁₂-C₁₈ alkyl dimethyl benzyl ammonium chloride and 1% 2-mercaptoethanol (2ME) as synergist in an organic solvent) was dosed into its respective cell. Data were collected overnight.

The control compounds for this Example are commonly used benzyl ammonium chloride quaternary chemistry and imidazoline chemistry, respectively.

The results of the bubble test are shown in **FIG. 3** and **Table 3**, wherein ppm is parts per million, CI is corrosion inhibitor, and mpy is mils per year. 0.2 ppm of 2-mercaptoethanol (2ME) were present with each tested di-cationic compound or control. **FIG. 3** shows the corrosion rate in mils per year during the bubble test period (18 hour). For the blank sample, no 2-mercaptoethanol (2ME) was added.

Table 3. Corrosion rate at 15th Hour after Di-cationic compound or control compound addition in bubble test results

Di-cationic Salt or Control Cationic Compound	Dosage of Cationic Polymer Salt or Compound (ppm)	Inhibited Corrosion Rate 15 h After Di-cationic Salt or Control Addition (mpy)	% Protection
Blank	0	500	-92
C ₁₂ -C ₁₈ alkyl dimethyl benzyl ammonium	2	339	32

chloride (Control 1)			
TOFA:DETA imidazoline salted with acetic acid (Control 2)	2	432	14
1	2	235	53
2	2	264	47
3	2	239	52
4	2	232	54
5	2	206	59
6	2	258	48
7	2	318	36
8	2	220	88

The inventions being thus described, it will be obvious that the same may be varied in many ways. Such variations are not to be regarded as a departure from the spirit and scope of the disclosures and all such modifications are intended to be included within the scope of the following claims.

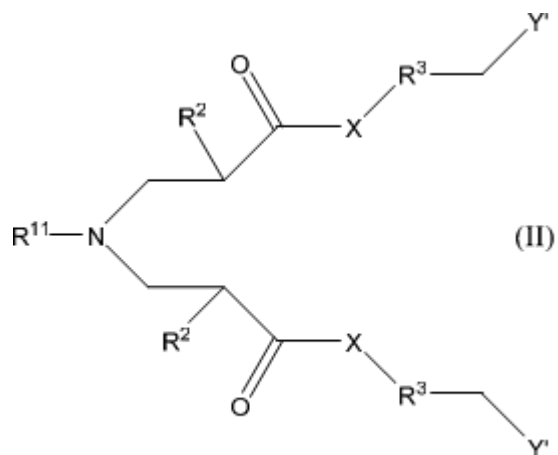
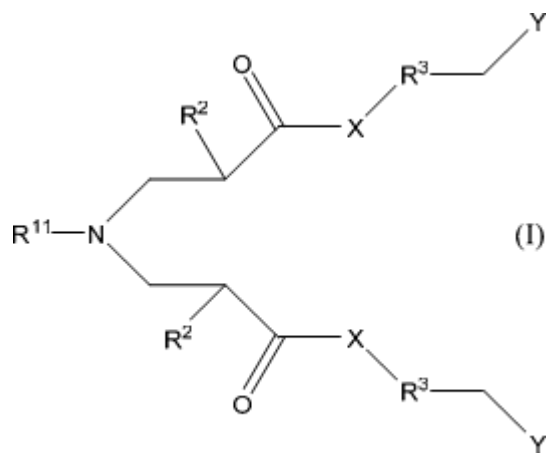
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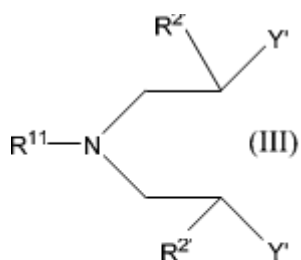
The above specification provides a description of the novel compounds, their synthesis and use, and the compositions, products, or articles that comprise the disclosed compounds. Since many embodiments can be made without departing from the spirit and scope of the disclosure, the invention resides in the claims.

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What is claimed is:

1. A method of inhibiting corrosion at a surface in a water system comprising:
providing a corrosion control composition or a use solution of the corrosion control
composition into a water system to generate a treated water system or onto to a
surface of the water system,
wherein the corrosion control composition comprises one or more compounds according to
one of Formula I, Formula II, Formula III and one or more additional corrosion
control composition agents,





wherein:

X is NH or O;

R^{11} is R^1 or $R^1-Z-(CH_2)_m$;

R^1 is an unsubstituted or substituted, linear or branched C_5 - C_{30} alkyl, cyclic alkyl, alkenyl, or alkynyl group;

Z is NH or O;

R^2 is H, CH_3 , or an unsubstituted, linear or branched C_2 - C_{10} alkyl, alkenyl, or alkynyl group;

m is an integer of 1 to 4;

R^3 is absent or an unsubstituted, linear C_1 - C_{30} alkylene group;

Y is $-NR^4R^5R^{6(+)}$;

Y' is $-SO_3H$, $-PO_3H$, $-OSO_3H$, $-OPO_3H$, or a salt thereof; and

R^4 , R^5 , and R^6 are independently a C_1 - C_{10} alkyl group;

$R^{2'}$ is H, CH_3 , or an unsubstituted or substituted, linear or branched C_1 - C_{10} alkyl, alkenyl, alkynyl group, $-COOH$, $-CH_2COOH$, Y', or $-(CH_2)_m-Y'$ and

wherein the corrosion control composition mitigates corrosion on the surface in the water system.

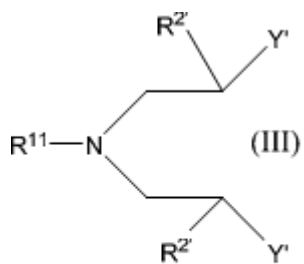
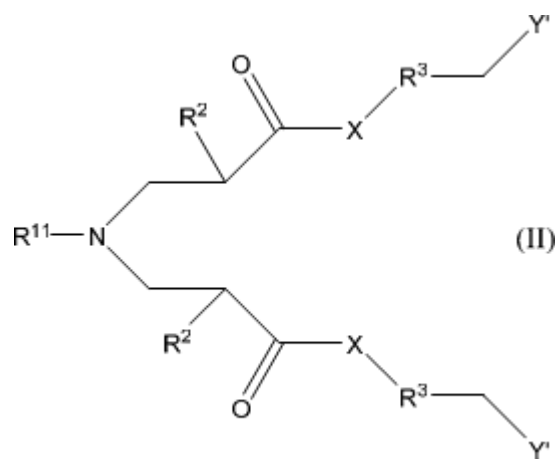
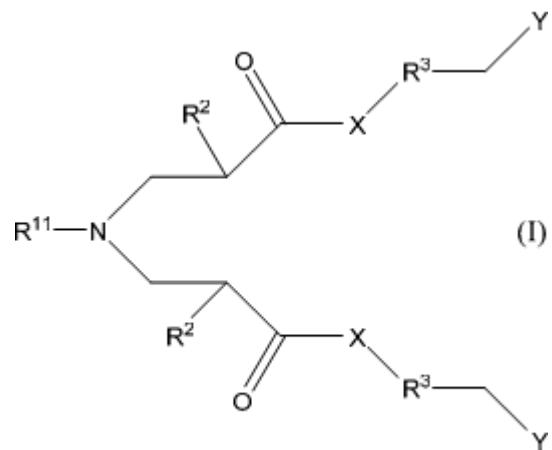
2. The method according to claim 1, wherein the corrosion control composition comprises one or more compounds according to Formula I, wherein Y is $-NR^4R^5R^{6(+)}$, $N(CH_3)_3^+$, or $N(CH_3)_2R_6^+$, and wherein R^6 is a C_2 - C_{12} alkyl, aryl, or is $-CH_2-C_6H_5$.
3. The method according to any one of claims 1-2, wherein the corrosion control

composition comprises one or more compounds according to Formula I or Formula II, wherein R³ is CH₂, CH₂CH₂, or C(CH₃)₂, or an unsubstituted and linear C₂-C₁₀ alkylene group.

4. The method according to any one of claims 1-3, wherein R¹¹ is a C₆-C₂₀ alkenyl group with at least one *trans* or *cis* double bond.
5. The method according to any one of claims 1-4, wherein the corrosion control composition agent is water, an organic solvent, a surfactant, one or more additional corrosion inhibitors, a scale inhibitor, gas hydrate inhibitor, pH modifier, an emulsion breaker, reverse emulsion breaker, a fouling control agent, coagulant/flocculant agent, an emulsifier, a water clarifier, a dispersant, antioxidant, polymer degradation prevention agent, permeability modifier, foaming agent, antifoaming agent, emulsifying agent, scavenger agent for CO₂, and/or O₂, gelling agent, lubricant, friction reducing agent, salt, or any mixture thereof.
6. The method according to any one of claims 1-5, wherein the corrosion control composition agent is a biocide, wherein the biocide is chlorine, hypochlorite, ClO₂, bromine, ozone, hydrogen peroxide, peracetic acid, peroxydisulfate, peroxydicarboxylic acid composition, glutaraldehyde, dibromonitripropionamide, isothiazolone, terbutylazine, polymeric biguanide, methylene bithiocyanate, tetrakis hydroxymethyl phosphonium sulphate, or any combination thereof.
7. The method according to any one of claims 1-5, wherein the corrosion control composition agent is an acid and wherein the corrosion control composition comprises from about 1 wt-% to about 20 wt-% of the acid, wherein the acid is hydrochloric acid, hydrofluoric acid, citric acid, formic acid, acetic acid, or a mixture thereof.
8. The method according to any one of claims 1-7, wherein the corrosion control

composition is a liquid, gel, or a mixture comprising liquid/gel and solid, and wherein the corrosion control composition or a use solution thereof has a pH of from about 1 to about 11.

9. The method according to any one of claims 1-8, wherein the corrosion control composition comprises from about 10 wt-% to about 80 wt-% of the compound and has a concentration of from about 1 ppm to about 1000 ppm in the treated water system.
10. The method according to any one of claims 1-9, wherein the water system is a cooling water system, boiler water system, water system in oil and gas operations, in a petroleum well, downhole formation, geothermal well, mineral washing, flotation and benefaction, papermaking, gas scrubber, air washer, continuous casting processes in the metallurgical industry, air conditioning and refrigeration, water reclamation, water purification, membrane filtration, food processing, clarifiers, municipal sewage treatment, municipal water treatment, or potable water system, and wherein the water system comprises fresh water, recycled water, salt water, surface water, produced water, oil, hydrocarbon, solid, or mixture thereof.
11. A corrosion control composition comprising one or more compounds according to one of Formula **I**, Formula **II**, and Formula **III** and one or more additional corrosion control composition agents,



wherein:

X is NH or O;

R¹¹ is R¹ or R¹-Z-(CH₂)_m;

R¹ is an unsubstituted or substituted, linear or branched C₅-C₃₀ alkyl, cyclic alkyl,

alkenyl, or alkynyl group;
 Z is NH or O;
 R^2 is H, CH₃, or an unsubstituted, linear or branched C₂-C₁₀ alkyl, alkenyl, or alkynyl group;
 m is an integer of 1 to 4;
 R^3 is absent or an unsubstituted, linear C₁-C₃₀ alkylene group;
 Y is -NR⁴R⁵R⁶⁽⁺⁾;
 Y' is -SO₃H, -PO₃H, -OSO₃H, -OPO₃H, or a salt thereof;
 R^4 , R^5 , and R^6 are independently a C₁-C₁₀ alkyl group;
 $R^{2'}$ is H, CH₃, or an unsubstituted or substituted, linear or branched C₁-C₁₀ alkyl, alkenyl, alkynyl group, -COOH, -CH₂COOH, Y', or -(CH₂)_m-Y', and
 wherein the corrosion control composition mitigates corrosion on the surface in the water system.

**MOLECULES HAVING ONE HYDROPHOBIC GROUP AND TWO
IDENTICAL HYDROPHILIC IONIC GROUPS AND COMPOSITIONS
THEREOF**

ABSTRACT OF THE DISCLOSURE

A novel class of compounds is described here. The disclosed novel compounds have one hydrophilic group and two identical hydrophilic ionic groups. The two hydrophilic groups of the disclosed compounds contain or end with a cationic or anionic charged group. A method to synthesize the disclosed novel compounds is also described. The disclosed novel compounds herein can be used as surfactants in an article, product, or composition, or for some other purposes. Also disclosed herein are the corrosion control compositions comprising di-cationic or di-anionic compounds and methods of using thereof in a corrosion control composition to reduce corrosion of a surface in a water system. The disclosed methods or compositions are found to be more effective than those methods or compositions including commonly used single quaternary compounds for mitigating corrosion for a metal surface in water systems.

[Figure 1A]