

DETERGENT COMPOSITIONS WITH ENHANCED ANTI-SCALING EFFICACY

TECHNICAL FIELD

[0001] The disclosure relates generally to detergent compositions and methods of using the compositions. The compositions containing scale-inhibiting organic phosphonates, additional scale inhibitor comprising at least one polycarboxylate, polycarboxylic acid, or salt thereof, and an alkalinity source provide effective cleaning and enhanced antiscaling performance compared to traditional detergent compositions.

BACKGROUND

[0002] The development of more highly alkaline detergent compositions while also improving antiscaling performance remains as an unmet commercial need. Highly alkaline and concentrated detergents that are used with water having various hardness levels can have deleterious effects in many systems. For example, when hard water alone, or in conjunction with detergent compositions, contacts a surface, it can cause precipitation of hard water scale on the contacted surface. Scaling is the precipitation of a salt from a solution that is supersaturated with respect to the salt. In general, hard water refers to water having a total level of calcium and magnesium ions in excess of about 100 ppm expressed in units of ppm calcium carbonate.

[0003] Hard water is known to reduce the efficacy of conventional alkaline detergents. Detergents include chelating agents or sequestrants that are intended to be mixed with hard water in an amount sufficient to handle the hardness and also prevent scaling. However, often water hardness exceeds the chelating capacity of the composition. As a result, free calcium ions may be available to cause precipitation, or to attack active components of the composition causing other deleterious effects, such as poor cleaning effectiveness or lime scale build up. Therefore, the improvement in antiscaling performance remains a critical need.

[0004] Scaling causes significant interruptions in cleaning. In particular in areas having high water hardness scaling issues can present extreme challenges. For example, descaling steps, such as treatment with acid washes, may be required on occasion. The reduction of descaling frequency will save labor time and costs, freight and energy.

[0005] It is therefore an object of this disclosure to provide detergent compositions that provide desirable cleaning and improved antiscaling performance.

[0006] It is a further object of the disclosure to provide detergent compositions that can result in scale accumulation occurring more slowly and therefore requiring less frequent (or eliminated the need) descaling intervention.

[0007] It is another object of this disclosure to formulate detergent compositions that provide improved customer acceptance through use.

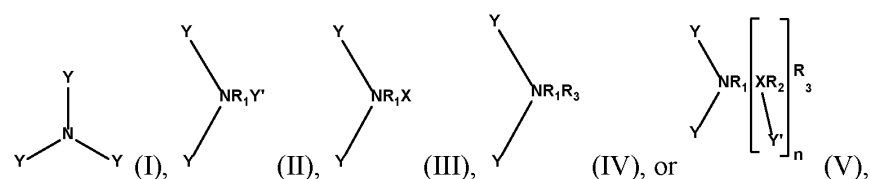
[0008] Other objects, embodiments and advantages of this disclosure will be apparent to one skilled in the art in view of the following disclosure, the drawings, and the appended claims.

BRIEF SUMMARY

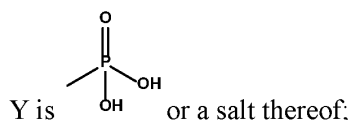
[0009] The following objects, features, advantages, aspects, and/or embodiments, are not exhaustive and do not limit the overall disclosure. No single embodiment need provide each and every object, feature, or advantage. Any of the objects, features, advantages, aspects, and/or embodiments disclosed herein can be integrated with one another, either in full or in part.

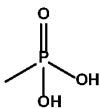
[0010] It is a primary object, feature, and/or advantage of the present disclosure to improve on or overcome the deficiencies in the art and commercial products, including by providing enhanced detergency and antiscaling performance compared to alkaline detergent compositions containing traditional chelants and builders.

[0011] According to some aspects of the present disclosure, detergent compositions comprise: a scale-inhibiting organic phosphonate having one of the following structures:



wherein:



Y' is absent,  or a salt thereof;

X is N, O, or OH;

R₁ and R₂ are independently a linear or branched C1-C10 alkyl group;

R₃ is -N(Y)₂; and

n is 1-20;

an additional scale inhibitor comprising at least one polycarboxylate, polycarboxylic acid, or salt thereof; an alkalinity source comprising an alkali metal hydroxide; and water.

[0012] According to additional aspects of the present disclosure, methods of using a detergent composition comprise: providing a detergent composition as described herein; contacting the detergent composition with water to form a use solution; and contacting the use solution to a surface in need of cleaning and antiscaling.

[0013] These and/or other objects, features, advantages, aspects, and/or embodiments will become apparent to those skilled in the art after reviewing the following brief and detailed descriptions of the drawings. Furthermore, the present disclosure encompasses aspects and/or embodiments not expressly disclosed but which can be understood from a reading of the present disclosure, including at least: (a) combinations of disclosed aspects and/or embodiments and/or (b) reasonable modifications not shown or described.

[0014] While multiple embodiments are disclosed, still other embodiments will become apparent to those skilled in the art from the following detailed description, which shows and describes illustrative embodiments. Accordingly, the drawings and detailed description are to be regarded as illustrative in nature and not restrictive.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015] **Figure 1** shows a graph depicting % inhibition of scaling with the evaluated detergent compositions as described herein and in Example 1.

[0016] **Figures 2A-2C** shows photographs of glasses treated with a detergent composition as described in Example 2.

[0017] Various embodiments of the present disclosure 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 disclosure.

Figures represented herein are not limitations to the various embodiments according to the disclosure and are presented for exemplary illustration of the invention. An artisan of ordinary skill in the art need not view, within isolated figure(s), the near infinite number of distinct permutations of features described in the following detailed description to facilitate an understanding of the present invention.

DETAILED DESCRIPTION

[0018] The present disclosure is not to be limited to that described herein, which can vary and are understood by skilled artisans. No features shown or described are essential to permit basic operation of the present disclosure unless otherwise indicated. It has been surprisingly found that the described detergent compositions have enhanced and synergistic antiscaling performance compared to traditional chelants and threshold inhibitors used in detergent compositions.

[0019] It is further to be understood that all terminology used herein is for the purpose of describing particular 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.

[0020] Numeric ranges recited within the specification are inclusive of the numbers defining the range and include each integer within the defined range. Throughout this disclosure, various aspects of this disclosure are presented in a range format. It should be understood that 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 disclosure. Accordingly, the description of a range should be considered to have specifically disclosed all the possible sub-ranges, fractions, and individual numerical values within that range. For example, description of a range such as from 1 to 6 should be considered to have specifically disclosed sub-ranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 6, from 3 to 6 etc., as well as individual numbers within that range, for example, 1, 2, 3, 4, 5, and 6, and decimals and fractions, for example, 1.2, 3.8, $1\frac{1}{2}$, and $4\frac{3}{4}$. This applies regardless of the breadth of the range.

[0021] As used herein, the term “and/or”, e.g., “X and/or Y” shall be understood to mean either “X and Y” or “X or Y” and shall be taken to provide explicit support for both meanings or for either meaning, e.g. A and/or B includes the options i) A, ii) B or iii) A and B.

[0022] It is to be appreciated that certain features that are, for clarity, described herein in the context of separate embodiments, may also be provided in combination in a single embodiment. Conversely, various features that are, for brevity, described in the context of a single embodiment, may also be provided separately or in any sub-combination.

[0023] The methods and compositions of the present disclosure may comprise, consist essentially of, or consist of the components and ingredients of the present disclosure as well as other ingredients described herein. As used herein, “consisting essentially of” means that the methods, systems, apparatuses 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, systems, apparatuses, and compositions.

[0024] Unless defined otherwise, all technical and scientific terms used above have the same meaning as commonly understood by one of ordinary skill in the art to which embodiments of the present disclosure pertain.

[0025] The terms “invention” or “present invention” are not intended to refer to any single embodiment of the particular invention but encompass all possible embodiments as described in the specification and the claims.

[0026] The term “about,” as used herein, refers to variation in the numerical quantity that can occur, for example, through typical measuring techniques and equipment, with respect to any quantifiable variable, including, but not limited to, mass, volume, time, temperature, pH, and the like. Further, given solid and liquid handling procedures used in the real world, there is certain inadvertent error and variation that is likely 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 these variations. Whether or not modified by the term “about,” the claims include equivalents to the quantities.

[0027] The term “actives” or “percent actives” or “percent by weight actives” or “actives concentration” are used interchangeably herein and refers to the concentration of those ingredients involved in cleaning expressed as a percentage minus inert ingredients such as

water or salts. It is also sometimes indicated by a percentage in parentheses, for example, “chemical (10%).”

[0028] 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).

[0029] 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, alkoxycarbonyloxy, aryloxy, aryloxy carbonyloxy, carboxylate, alkylcarbonyl, arylcarbonyl, alkoxycarbonyl, 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.

[0030] 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.

[0031] The term “configured” describes structure capable of performing a task or adopting a particular configuration. The term “configured” can be used interchangeably with other similar phrases, such as constructed, arranged, adapted, manufactured, and the like.

[0032] Terms characterizing sequential order, a position, and/or an orientation are not limiting and are only referenced according to the views presented.

[0033] As used herein, the term “exemplary” refers to an example, an instance, or an illustration, and does not indicate a most preferred embodiment unless otherwise stated.

[0034] As used herein, the phrase “food processing surface” refers to a surface of a tool, a machine, equipment, a structure, a building, or the like that is employed as part of a food processing, preparation, or storage activity. Examples of food processing surfaces include surfaces of food processing or preparation equipment (e.g., slicing, canning, or transport equipment, including flumes), of food processing wares (e.g., utensils, dishware, wash ware, and bar glasses), and of floors, walls, or fixtures of structures in which food processing occurs. Food processing surfaces are found and employed in food anti-spoilage air circulation systems, aseptic packaging sanitizing, food refrigeration and cooler cleaners and sanitizers, ware washing sanitizing, blancher cleaning and sanitizing, food packaging materials, cutting board additives, third-sink sanitizing, beverage chillers and warmers, meat chilling or scalding waters, autodish sanitizers, sanitizing gels, cooling towers, food processing antimicrobial garment sprays, and non-to-low-aqueous food preparation lubricants, oils, and rinse additives.

[0035] As used herein, the term “free” 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 about 0.1 wt-% and in yet another embodiment, the amount of component is less than about 0.01 wt-%, or 0 wt-%.

[0036] The term “generally” encompasses both “about” and “substantially.”

[0037] The term “hard surface” refers to a solid, substantially non-flexible surface such as a counter top, tile, floor, wall, panel, window, plumbing fixture, kitchen and bathroom furniture, appliance, engine, circuit board, dish, mirror, window, monitor, touch screen, and thermostat. Hard surfaces are not limited by the material; for example, a hard surface can be glass, metal, tile, vinyl, linoleum, composite, wood, plastic, etc. Hard surfaces may include for example, health care surfaces and food processing surfaces.

[0038] As used herein, the term “instrument” refers to the various medical or dental instruments or devices that can benefit from cleaning with a composition as described herein. As used herein, the phrases “medical instrument,” “dental instrument,” “medical device,” “dental device,” “medical equipment,” or “dental equipment” refer to instruments, devices, tools, appliances, apparatus, and equipment used in medicine or dentistry. Such instruments, devices, and equipment can be cold sterilized, soaked or washed and then heat sterilized, or otherwise benefit from cleaning in a composition of the present disclosure. These various instruments, devices and equipment include, but are not limited to: diagnostic instruments, trays, pans, holders, racks, forceps, scissors, shears, saws (e.g. bone saws and their blades), hemostats, knives, chisels, rongeurs, files, nippers, drills, drill bits, rasps, burs, spreaders, breakers, elevators, clamps, needle holders, carriers, clips, hooks, gouges, curettes, retractors, straightener, punches, extractors, scoops, keratomes, spatulas, expressers, trocars, dilators, cages, glassware, tubing, catheters, cannulas, plugs, stents, scopes (e.g., endoscopes, stethoscopes, and arthroscopes) and related equipment, and the like, or combinations thereof.

[0039] As used herein the term "polymer" refers to a molecular complex comprised of a more than ten monomeric units and generally includes, but is not limited to, homopolymers, copolymers, such as for example, block, graft, random and alternating copolymers, terpolymers, and higher "x"mers, further including their analogs, derivatives, combinations, and blends thereof. Furthermore, unless otherwise specifically limited, the term "polymer" shall include all possible isomeric configurations of the molecule, including, but are not limited to isotactic, syndiotactic and random symmetries, and combinations thereof. Furthermore, unless otherwise specifically limited, the term "polymer" shall include all possible geometrical configurations of the molecule.

[0040] As used herein, the term “soil” or “stain” refers to any soil, including, but not limited to, non-polar oily and/or hydrophobic substances which may or may not contain particulate matter such as industrial soils, mineral clays, sand, natural mineral matter, carbon black, graphite, kaolin, environmental dust, and/or food based soils such as blood, proteinaceous soils, starchy soils, fatty soils, cellulosic soils, etc.

[0041] The “scope” of the present disclosure is defined by the appended claims, along with the full scope of equivalents to which such claims are entitled. The scope of the disclosure is further qualified as including any possible modification to any of the aspects and/or

embodiments disclosed herein which would result in other embodiments, combinations, subcombinations, or the like that would be obvious to those skilled in the art.

[0042] The term “substantially” refers to a great or significant extent. “Substantially” can thus refer to a plurality, majority, and/or a supermajority of said quantifiable variable, given proper context.

[0043] The term "surfactant" or "surface active agent" refers to an organic chemical that when added to a liquid changes the properties of that liquid at a surface.

[0044] As used herein, the term “ware” refers to items such as eating and cooking utensils, dishes, and other hard surfaces such as showers, sinks, toilets, bathtubs, countertops, windows, mirrors, transportation vehicles, and floors. As used herein, the term “warewashing” refers to washing, cleaning, or rinsing ware. Ware also refers to items made of plastic. Types of plastics that can be cleaned with the compositions include but are not limited to, those that include polypropylene polymers (PP), polycarbonate polymers (PC), melamine formaldehyde resins or melamine resin (melamine), acrylonitrile-butadiene-styrene polymers (ABS), and polysulfone polymers (PS). Other exemplary plastics that can be cleaned using the compounds and compositions of the disclosure include polyethylene terephthalate (PET) polystyrene polyamide.

[0045] 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.

[0046] DETERGENT COMPOSITIONS

[0047] According to embodiments, the detergent compositions include an organic phosphonate, an additional scale inhibitor that is a polycarboxylate, polycarboxylic acid, or salt thereof, alkalinity source, and water. The detergent compositions can include additional functional ingredients and can be provided as concentrate or use compositions. Exemplary compositions are shown in Tables 1A (solid) and 1B (liquid) in weight percentage. While the components may have a percent actives of 100%, it is noted that Tables 1A-1B do not recite the percent actives of the components, but rather, recites the total weight percentage of the raw materials (*i.e.* active concentration plus inert ingredients).

[0048] TABLE 1A

Material	First Exemplary Range wt.-%	Second Exemplary Range wt.-%	Third Exemplary Range wt.-%
Organic Phosphonate	1-30	1-20	1-10
At least one polycarboxylate, polycarboxylic acid, or salt thereof	0-20	1-10	1-8
Alkalinity source	10-90	10-80	20-80
Water	1-30	5-30	10-30
Additional Functional Ingredients	0-30	0-25	0-20

[0049] TABLE 1B

Material	First Exemplary Range wt.-%	Second Exemplary Range wt.-%	Third Exemplary Range wt.-%
Organic Phosphonate	1-30	1-20	1-10
At least one polycarboxylate, polycarboxylic acid, or salt thereof	0-20	1-10	1-8
Alkalinity source	5-80	10-70	10-60
Water	30-90	40-90	50-90
Additional Functional Ingredients	0-30	0-25	0-20

Solid Compositions

[0050] The detergent compositions are preferably solid compositions. A solid detergent composition encompasses a variety of forms including, for example, solids, pellets, blocks, tablets, and powders. By way of example, pellets can have diameters of between about 1 mm and about 10 mm, tablets can have diameters of between about 1 mm and about 10 mm or between about 1 cm and about 10 cm, and blocks can have diameters of at least about 10 cm. It should be understood that the term "solid" refers to the state of the composition under the expected conditions of storage and use of the solid cleaning composition. In general, it is expected that the detergent composition will remain a solid when provided at a temperature of up to about 100°F or lower than about 120°F.

[0051] In certain embodiments, the solid cleaning composition is provided in the form of a unit dose. A unit dose refers to a solid cleaning composition unit sized so that the entire unit is used during a single cycle, for example, a single washing cycle of a warewash machine. When the solid cleaning composition is provided as a unit dose, it can have a mass of about 1 g to about 50 g. In other embodiments, the composition can be a solid, a pellet, or a tablet having a size of about 50 g to 250 g, of about 100 g or greater, or about 40 g to about 11,000 g.

[0052] In other embodiments, the solid cleaning composition is provided in the form of a multiple-use solid, such as, a block or a plurality of pellets, and can be repeatedly used to generate aqueous cleaning compositions for multiple washing cycles. In certain embodiments, the solid cleaning composition is provided as a solid having a mass of about 5 g to about 10 kg. In certain embodiments, a multiple-use form of the solid cleaning composition has a mass of about 1 to about 10 kg. In further embodiments, a multiple-use form of the solid cleaning composition has a mass of about 5 kg to about 8 kg. In other embodiments, a multiple-use form of the solid cleaning composition has a mass of about 5 g to about 1 kg, or about 5 g and to about 500 g.

[0053] In embodiments the solids is a cast, pressed, or extruded solid. The components can be mixed and extruded or cast to form a solid such as pellets, powders or blocks. Heat can be applied from an external source to facilitate processing of the mixture.

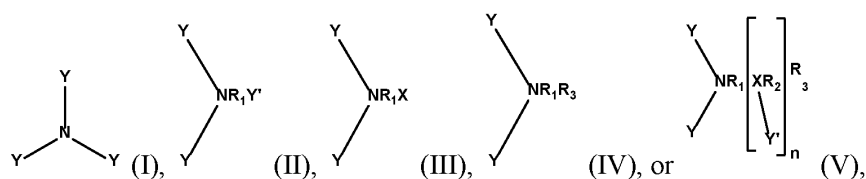
Liquid Compositions

[0054] The detergent compositions can also include liquid compositions. Any form of a liquid composition can be provided, including concentrate compositions.

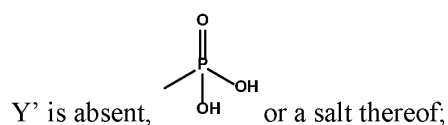
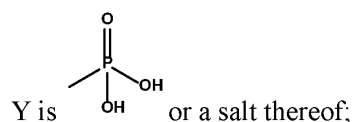
Organic Phosphonate

[0055] The detergent compositions comprise an organic phosphonate. Organic phosphonates are organic derivatives of phosphonic acid, HP(O)(OH)_2 . The organic phosphonates preferably contain a single C-N bond adjacent (vicinal) to the C-P bond, unlike conventional organic phosphonate scale inhibitors, such as 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP) or 2-Phosphonobutane-1,2,4-tricarboxylic acid (PBTC).

[0056] Organic phosphonates have one of the following general structures:



wherein:



X is N, O, or OH;

R_1 and R_2 are independently a linear or branched C1-C10 alkyl group;

R_3 is $-\text{N(Y)}_2$; and

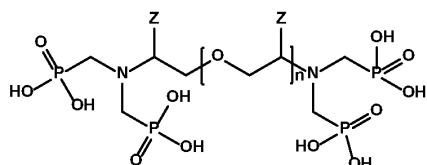
n is 1-20.

[0057] In the structures I-V the salt form of Y or Y' is preferably a suitable cation, such as sodium or potassium.

[0058] The described organic phosphonates are particularly suitable for use in antiscaling in ware washing applications, including detergent applications.

[0059] A preferred class of organic phosphonates include polyether phosphonic acids, including polyamino polyether methylene phosphonic acid and polyamino polyether

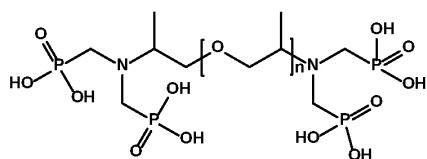
methylene phosphonates such as the those having the following structure:



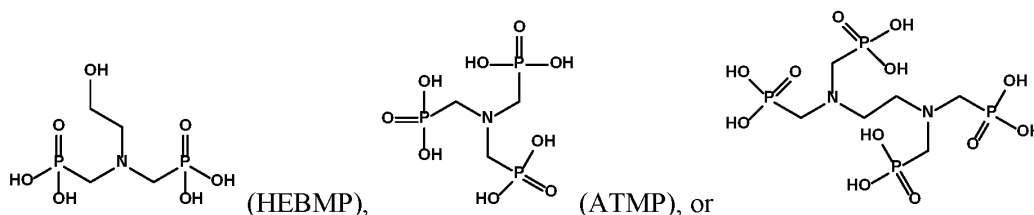
wherein Z is independently H or CH₃, and

wherein n is 2-12. In a preferred embodiment the organic phosphonate is PAPEMP

((HO)₂P(O)CH₂)₂NCH(CH₃)CH₂(OCH₂CH(CH₃)₂N(CH₂)₆N(CH₂P(O)(OH)₂)₂) having the structure:



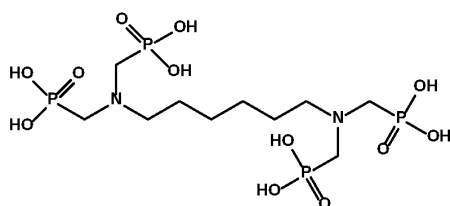
[0060] Additional exemplary organic phosphonates include the structures:



(EDTMP).

[0061] Still further exemplary organic phosphonates include HMDTMP

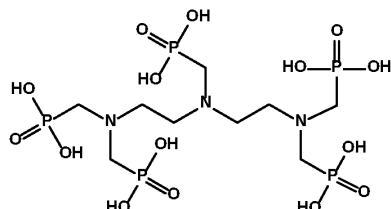
((HO)₂P(O)CH₂)₂N(CH₂)₆N(CH₂2P(O)(OH)₂)₂) having the structure:



, and the like.

[0062] Still further exemplary organic phosphonates include DTMPA

((HO)₂P(O)CH₂N[CH₂CH₂N(CH₂P(O)(OH)₂)₂]₂) having the structure:



[0063] A further preferred class of organic phosphonates include alkylene oxide phosphonates. Any combination of the foregoing scale inhibitors may be used and salts of any of these compounds can be used as well, such as ammonium salts. In some embodiments, the foregoing scale inhibitors can further be combined with conventional phosphonates. Examples of phosphonates include, but are not limited to: phosphinosuccinic acid oligomer (PSO) described in U.S. Patent No. 8,871,699, 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC), 1-hydroxyethane-1, 1-diphosphonic acid, HEDP, aminotri(methylenephosphonic acid); 2-hydroxyethyliminobis(methylenephosphonic acid), diethylenetriaminepenta(methylenephosphonic acid), diethylenetriaminepenta(methylenephosphonate), sodium salt (DTPMP), hexamethylenediamine(tetramethylenephosphonate), potassium salt bis(hexamethylene)triamine(pentamethylenephosphonic acid); and phosphorus acid.

[0064] In some embodiments, the organic phosphonate is included in the solid detergent composition at an amount of at least about 1 wt-% to about 30 wt-%, about 1 wt-% to about 25 wt-%, about 1 wt-% to about 20 wt-%, about 1 wt-% to about 15 wt-%, about 1 wt-% to about 10 wt-%, or about 1 wt-% to about 8 wt-%. In addition, without being limited according to the disclosure, all ranges recited are inclusive of the numbers defining the range and include each integer within the defined range.

[0065] In some embodiments, the organic phosphonate is included in the liquid detergent composition at an amount of at least about 1 wt-% to about 30 wt-%, about 1 wt-% to about 25 wt-%, about 1 wt-% to about 20 wt-%, about 1 wt-% to about 15 wt-%, about 1 wt-% to about 10 wt-%, or about 1 wt-% to about 8 wt-%. In addition, without being limited according to the disclosure, all ranges recited are inclusive of the numbers defining the range and include each integer within the defined range.

[0066] As described herein the organic phosphonate according to the formulae and various structures disclosed herein is a phosphonate or a salt thereof, including a cation. In preferred embodiments the organic phosphonate does not include any betaine or polybetaine structures, such that there is a charge separated, neutral molecule.

[0067] In some embodiments the organic phosphonate does not include ATMP (aminotris(methylenephosphonic acid) with chemical formula $N(CH_2PO_3H_2)_3$). In still further embodiments, the organic phosphonate does not include PBTC (2-Phosphonobutane-1,2,4-tricarboxylic acid).

Additional Scale Inhibitor

[0068] The detergent compositions comprises at least one additional scale inhibitor comprising a polycarboxylate, polycarboxylic acid, or salt thereof. Beneficially the combination of the organic phosphonate and the polycarboxylate, polycarboxylic acid, or salt thereof provides synergistic improvement in antiscaling over conventional antiscaling or threshold inhibitors used for antiscaling and hard water treatment in detergent compositions.

[0069] Exemplary polycarboxylates that can be used as scale inhibitors include, but are not limited to: those having pendant carboxylate ($-\text{CO}_2^-$) groups such as polyacrylic acid, maleic acid, maleic/olefin copolymer, sulfonated copolymer or terpolymer, acrylic/maleic copolymer, polymethacrylic acid, acrylic acid-methacrylic acid copolymers, hydrolyzed polyacrylamide, hydrolyzed polymethacrylamide, hydrolyzed polyamide-methacrylamide copolymers, hydrolyzed polyacrylonitrile, hydrolyzed polymethacrylonitrile, and hydrolyzed acrylonitrile-methacrylonitrile copolymers.

[0070] Examples of suitable additional polymers include polyacrylic acid, polymethacrylic acid, polymaleic acid homopolymers, copolymers of acrylic methacrylic or maleic acids (and combinations thereof).

[0071] A preferred group of polycarboxylates include polycarboxylic acid polymers (e.g. Acusol polymers), including polyacrylic acid homopolymers and polymaleic acid homopolymers, and polymers modified by a fatty acid end group. Exemplary polyacrylic acid homopolymers include those with a molecular weight between about 500-100,000 g/mol, or between about 1,000-50,000 g/mol, or between about 1,000-25,000 g/mol.

[0072] A variety of such polycarboxylate homopolymers, copolymers and terpolymers are known and described in patent and other literature, and are available commercially. Exemplary polycarboxylates that may be utilized include for example: homopolymers, copolymers and terpolymers of polyacrylates; polymethacrylates; polymaleates. Examples of suitable polymers include acrylic acid homopolymers, maleic acid homopolymers, methacrylic acid homopolymers, acrylic/maleic copolymers, maleic acid copolymers, acrylic/ methacrylic copolymers, maleic acid terpolymers, hydrophobically modified acrylic acid copolymers and terpolymers, hydrophobically modified maleic acid copolymers and terpolymers, hydrophobically modified methacrylic acid copolymers and terpolymers. Suitable polymers preferably have a molecular weight between about 500 to about 50,000

g/mol, more preferably between about 500 and about 25,000 g/mol and particularly between about 500 and about 10,000 g/mol.

[0073] Further suitable polycarboxylic acids are acyclic, alicyclic, heterocyclic and aromatic carboxylic acids, in which case they contain at least two carboxyl groups which are in each case separated from one another by, preferably, no more than two carbon atoms.

Polycarboxylates which comprise two carboxyl groups include, for example, water-soluble salts of, malonic acid, (ethyl enedioxy) diacetic acid, maleic acid, diglycolic acid, tartaric acid, tartronic acid and fumaric acid. Polycarboxylates which contain three carboxyl groups include, for example, water-soluble citrate. Correspondingly, a suitable hydroxycarboxylic acid is, for example, citric acid. Another suitable polycarboxylic acid is the homopolymer of acrylic acid. Polycarboxylates can further be end capped with sulfonates.

[0074] In some embodiments the detergent composition include more than one additional scale inhibitor comprising a polycarboxylate, polycarboxylic acid, or salt thereof. In some embodiments the detergent composition includes two additional scale inhibitor comprising a polycarboxylate, polycarboxylic acid, or salt thereof. In further preferred embodiments the detergent composition includes a polyacrylic acid and a polymaleic acid.

[0075] In some embodiments, the additional scale inhibitor(s) is included in the solid detergent composition at an amount of at least about 0 wt-% to about 20 wt-%, about 1 wt-% to about 20 wt-%, about 1 wt-% to about 15 wt-%, about 1 wt-% to about 10 wt-%, about 1 wt-% to about 8 wt-%, or about 2 wt-% to about 8 wt-%. In addition, without being limited according to the disclosure, all ranges recited are inclusive of the numbers defining the range and include each integer within the defined range.

[0076] In some embodiments, the additional scale inhibitor(s) is included in the solid detergent composition at an amount of at least about 0 wt-% to about 20 wt-%, about 1 wt-% to about 20 wt-%, about 1 wt-% to about 15 wt-%, about 1 wt-% to about 10 wt-%, about 1 wt-% to about 8 wt-%, or about 1 wt-% to about 6 wt-%. In addition, without being limited according to the disclosure, all ranges recited are inclusive of the numbers defining the range and include each integer within the defined range.

[0077] In embodiments the detergent compositions do not include carboxylic acid terpolymers.

Alkalinity Source

[0078] The detergent composition comprises one or more alkalinity sources. The source of alkalinity can be any source of alkalinity that is compatible with the other components of the detergent composition. In embodiments, the alkalinity source comprises an alkali metal hydroxide. Preferred sources of alkalinity include alkali metal hydroxides, including sodium hydroxide, potassium hydroxide, and lithium hydroxide or mixtures thereof, and most preferred is sodium hydroxide and/or potassium hydroxide.

[0079] Additional alkalinity sources that can be combined with the alkali metal hydroxide include alkali metal carbonates, alkali metal silicates, alkali metal salts, phosphates, amines, and mixtures thereof. In some embodiments, the alkali metal hydroxide alkalinity source is combined with a secondary source of alkalinity comprising an alkali metal carbonate.

[0080] In some embodiments, the alkalinity source is included in the solid detergent composition at an amount of at least about 10 wt-% to about 90 wt-%, or about 10 wt-% to about 80 wt-%, about 20 wt-% to about 80 wt-%, about 30 wt-% to about 80 wt-%, about 40 wt-% to about 80 wt-%, or about 50 wt-% to about 80 wt-%. In some embodiments for solid compositions the total amount of alkalinity source to (alkalinity source plus water) is about 60-80% (*e.g.* alkalinity / (water + alkalinity)) and the solid maintains stability. In addition, without being limited according to the disclosure, all ranges recited are inclusive of the numbers defining the range and include each integer within the defined range.

[0081] In some embodiments, the alkalinity source is included in the liquid detergent composition at an amount of at least about 5 wt-% to about 80 wt-%, about 10 wt-% to about 70 wt-%, about 10 wt-% to about 60 wt-%, about 10 wt-% to about 50 wt-%, or about 10 wt-% to about 40 wt-%. In addition, without being limited according to the disclosure, all ranges recited are inclusive of the numbers defining the range and include each integer within the defined range.

Water

[0082] The detergent compositions may comprise water in amounts that vary depending upon techniques for processing the solid composition. Water provides a medium which dissolves, suspends, or carries the other components of the composition. Water can also function to deliver and wet the composition on an object.

[0083] In some embodiments, water makes up a remainder portion of the detergent compositions and may be the balance of the detergent composition apart from the scale-

inhibiting organic phosphonate, additional scale inhibitor, source of alkalinity and any additional functional ingredients. The water amount and type will depend upon the nature of the composition as a whole, the environmental storage, and method of application including concentration composition, form of the composition, and intended method of deliver, among other factors. Notably the carrier should be chosen and used at a concentration which does not inhibit the efficacy of the functional components in the composition of the invention for the intended use, e.g., bleaching, sanitizing, cleaning.

[0084] In certain embodiments, the solid detergent composition includes about 1 wt-% to about 30 wt-% water, about 5 wt-% to about 30 wt-% water, or about 10 wt-% to about 30 wt-% water. It is to be understood that all values and ranges between these values and ranges are encompassed by the present invention.

[0085] In certain embodiments, the liquid detergent composition includes about 30 wt-% to about 90 wt-% water, about 40 wt-% to about 90 wt-% water, or about 50 wt-% to about 90 wt-% water. It is to be understood that all values and ranges between these values and ranges are encompassed by the present invention.

Additional Functional Ingredients

[0086] The components of the detergent compositions can further be combined with various functional components suitable for uses disclosed herein. In some embodiments, the detergent compositions including the scale-inhibiting organic phosphonate, additional scale inhibitor comprising at least one polycarboxylate, polycarboxylic acid, or salt thereof, and an alkalinity source make up a large amount, or even substantially all of the total weight of the compositions. In other embodiments, the detergent compositions including the scale-inhibiting organic phosphonate, additional scale inhibitor comprising at least one polycarboxylate, polycarboxylic acid, or salt thereof, an alkalinity source, and/or at least one additional functional ingredient make up a large amount, or even substantially all of the total weight of the compositions. For example, in some embodiments few or no additional functional ingredients are disposed therein.

[0087] In other embodiments, additional functional ingredients may be included in the detergent compositions. The functional ingredients provide desired properties and functionalities to the compositions. For the purpose of this application, the term "functional ingredient" includes a material that when dispersed or dissolved in a use and/or concentrate solution, such as an aqueous solution, provides a beneficial property in a particular use.

Some particular examples of functional materials are discussed in more detail below, although the particular materials discussed are given by way of example only, and that a broad variety of other functional ingredients may be used. For example, many of the functional materials discussed below relate to materials used in cleaning. However, other embodiments may include functional ingredients for use in other applications.

[0088] In some embodiments, the detergent compositions may include optical brighteners, defoaming agents, anti-redeposition agents, bleaching agents, solubility modifiers, dispersants, metal protecting agents, stabilizing agents, hardening agents, fillers, preservatives, corrosion inhibitors, builders/sequestrants/chelating agents, enzymes, aesthetic enhancing agents including fragrances and/or dyes, additional rheology and/or solubility modifiers or thickeners, hydrotropes or couplers, buffers, solvents, additional cleaning agents, including surfactants, and the like.

[0089] In some embodiments, additional cleaning agents may be included in the detergent composition. In some embodiments the detergent composition and the additional cleaning agent does not include an alkanolamines, including ethanolamine, and/or taurine. In further embodiments the detergent composition does not include polyethylene glycols. In further embodiments the detergent composition and the additional cleaning agent does not include surfactants or does not include alcohol alkoxylates, including alcohol ethoxylates, alcohol ethoxylate polyoxyethylene ethers.

[0090] According to embodiments of the disclosure, the various additional functional ingredients may be provided in a composition in the amount from about 0 wt-% and about 30 wt-%, from about 0 wt-% and about 25 wt-%, from about 0 wt-% and about 20 wt-%, from about 0.01 wt-% and about 30 wt-%, from about 0.1 wt-% and about 30 wt-%, from about 1 wt-% and about 30 wt-%, from about 1 wt-% and about 25 wt-%, from about 1 wt-% and about 20 wt-%, or from about 1 wt-% and about 15 wt-%. In addition, without being limited according to the disclosure, all ranges recited are inclusive of the numbers defining the range and include each integer within the defined range.

Detergent Builders

[0091] The components of the detergent compositions can further be combined with a non-phosphonate builder. Although various components may include trace amounts of phosphorous, carboxylates such as citrate, tartrate or gluconate are also suitable. Useful aminocarboxylic acid materials containing little or no NTA include, but are not limited to: N-

hydroxyethylaminodiacetic acid, ethylenediaminetetraacetic acid (EDTA), hydroxyethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, N-hydroxyethyl-ethylenediaminetriacetic acid (HEDTA), diethylenetriaminepentaacetic acid (DTPA), hydroxyethylethylenediaminetriacetic acid and methylglycinediacetic acid (MGDA), glutamic acid-diacetic acid (GLDA), iminodisuccinic acid (IDA), hydroxyiminodisuccinic acid, ethylenediaminedisuccinic acid (EDDS), aspartic acid-diacetic acid, and salts thereof. Particularly preferred building agents are MGDA and GLDA and salts thereof and/or other similar acids having an amino group with a carboxylic acid substituent.

[0092] The components of the detergent compositions can further be combined with an additional phosphonate builder, including conventional organic phosphonate scale inhibitors, such as 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP) or 2-Phosphonobutane-1,2,4-tricarboxylic acid (PBTC).

[0093] In an aspect, exemplary building agents are selected from the group consisting of ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, hydroxyethylethylenediaminetriacetic acid and methylglycinediacetic acid, glutamic acid-diacetic acid, iminodisuccinic acid, hydroxyiminodisuccinic acid, ethylenediaminedisuccinic acid, aspartic acid-diacetic acid, and salts thereof. Particularly preferred building agents are methylglycinediacetic acid and salts thereof.

[0094] According to embodiments of the disclosure, the additional builder may be provided in a composition in the amount from about 0 wt-% and about 30 wt-%, from about 0 wt-% and about 25 wt-%, from about 0 wt-% and about 20 wt-%, from about 0.01 wt-% and about 30 wt-%, from about 0.1 wt-% and about 30 wt-%, from about 1 wt-% and about 30 wt-%, from about 1 wt-% and about 25 wt-%, from about 1 wt-% and about 20 wt-%, or from about 1 wt-% and about 15 wt-%. In addition, without being limited according to the disclosure, all ranges recited are inclusive of the numbers defining the range and include each integer within the defined range.

[0095] METHODS OF USE

[0096] Methods of using the detergent compositions are particularly suitable for consumer or institutional ware washing. The methods can include first contacting the detergent composition with water to form a use solution of the detergent composition, which could be provided as a liquid concentrate or a solid composition. Beneficially the concentrate or a use solution of the composition provide cleaning efficacy and antiscaling efficacy to various

surfaces in need of cleaning. These methods overcome limitations of detergent compositions that provide insufficient anti-scaling, including common scaling challenges in various applications where hard water sources are used in the cleaning and/or rinsing process.

[0097] The detergent compositions are particularly suitable for use in alkaline detergent applications where the prevention of hard water scale accumulation on surfaces is desired. In addition, the methods are well suited for controlling water hardness buildup on a plurality of surfaces. The methods prevent moderate to heavy accumulation of hardness on treated substrate surfaces which beneficially improving the aesthetic appearance of the surface. In certain embodiments, surfaces in need of hard water scale accumulation prevention, include for example, plastics, metal and/or glass surfaces.

[0098] The detergent compositions are particularly suitable for treating ware surfaces, such as utensils, instruments, and the like, as well as various appliance surfaces such as kitchen or food processing surfaces. Each of these ware and appliance surfaces can be made of various materials. Beneficially the methods provide effective cleaning (*i.e.* detergency) and descaling. In an embodiment the use of the detergent containing the scale-inhibiting organic phosphonate reduces the need for supplemental descaling steps as the compositions provide effective antiscaling. As a result, the methods of use reduce the need for acid rinse steps and/or deliming steps (*i.e.* separate cleaning cycle using strong acids to clean a machine) to remove the films or residues on treated surfaces that accumulate over time. These benefits are achieved while providing at least substantially similar or improved cleaning and antiscaling.

[0099] In an embodiment, the methods of using the detergent compositions significantly reduce the need to use a descaling step in the dish machine. In embodiments, use of the multipurpose liquid rinse aid compositions provide rinsing efficacy that further prevents the need for machine descaling for at least about 1,000 hours of machine operation, at least about 1,100 hours of machine operation, at least about 1,200 hours of machine operation, at least about 1,300 hours of machine operation, or at least about 1,400 hours of machine operation.

[0100] In further embodiments, the methods of using the detergent compositions significantly reduce the need to use a descaling step in the rinsing cylinder. In embodiments, use of the detergent compositions provide antiscaling efficacy that further prevents the need for descaling the rinsing cylinder for at least about 4 months, at least about 5 months, or at least about 6 months.

[0101] Without being limited to a particular mechanism of action, the organic phosphonates that are alkylene oxide phosphonates add hydrophilicity with the ethylene oxide groups and have high solubility and calcium tolerance, providing benefits in hard water conditions where scaling is deleterious to various surfaces and appliances. Moreover, a synergistic combination of antiscaling is achieved by combining the organic phosphonate with the polycarboxylate polymers that provide further physical separation or dispersion effects.

[0102] Exemplary disclosure of warewashing applications is set forth in U.S. Patent Nos. 8,758,520, 9,139,800, and 10,905,305. The method may be carried out in any consumer or institutional dish machine, including for example those described in U.S. Patent No. 8,092,613, which is incorporated herein by reference in its entirety, including all figures and drawings. Some non-limiting examples of dish machines include door machines or hood machines, conveyor machines, undercounter machines, glasswashers, flight machines, pot and pan machines, utensil washers, and consumer dish machines. The dish machines may be either single tank or multi-tank machines.

[0103] A door dish machine, also called a hood dish machine, refers to a commercial dish machine wherein the soiled dishes are placed on a rack and the rack is then moved into the dish machine. Door dish machines clean one or two racks at a time. In such machines, the rack is stationary and the wash and rinse arms move. A door machine includes two sets arms, a set of wash arms and a rinse arm, or a set of rinse arms. Door machines may be a high temperature or low temperature machine. In a high temperature machine the dishes are sanitized by hot water. In a low temperature machine the dishes are sanitized by the chemical sanitizer. The door machine may either be a recirculation machine or a dump and fill machine. In a recirculation machine, the detergent solution is reused, or "recirculated" between wash cycles. The concentration of the detergent solution is adjusted between wash cycles so that an adequate concentration is maintained. In a dump and fill machine, the wash solution is not reused between wash cycles. New detergent solution is added before the next wash cycle.

[0104] In addition to the cleaning of ware, the detergent compositions are suitable for cleaning various additional surfaces to provide cleaning and descaling. The ability to treat other surfaces, such as appliances and surfaces, that in contact with hard water and therefore prone to scaling provides a benefit to the detergent compositions.

[0105] In embodiments of using the detergent compositions, the composition is contacted with an aqueous source, preferably water, or may be mixed with an aqueous source, preferably water, prior to or at the point of use. This step provides a use solution from the detergent compositions.

[0106] In some embodiments for use of the compositions in a ware washing process, the composition can be housed within a dispenser to provide the use dilution into a warewashing machine (or other point of use). In an embodiment, a dispenser may be employed to spray water (*e.g.* in a spray pattern from a nozzle) to form a use solution. For example, water may be sprayed toward an apparatus or other holding reservoir with the solid composition, wherein the water reacts to form the diluted use solution. In an aspect, the use solution may be dispensed into a wash solution of a ware wash machine.

[0107] The compositions or use solutions thereof can contact the surface or article by numerous methods for applying a composition, such as spraying the composition, immersing the object in the composition, or a combination thereof. A concentrate or use concentration of a composition can be applied to or brought into contact with an article by any conventional method or apparatus for applying a cleaning composition to an object. For example, the object can be wiped with, sprayed with, and/or immersed in the composition, or a use solution made from the composition. The composition can be sprayed, or wiped onto a surface; the composition can be caused to flow over the surface, or the surface can be dipped into the composition. Contacting can be manual or by machine. Preferred embodiments contact a use solution of the solid composition in a warewash machine.

[0108] In embodiments, a use solution of the detergent compositions has a pH from about 11-13, from about 11.5-13, or from about 11-12, or from about 11.5-12. In some embodiments the use solution has a pH of at least about 11, or at least about 11.5.

[0109] The methods of using the detergent composition beneficially reduce the formation, precipitation and/or deposition of scaling, including hard water scale, such as calcium carbonate, on hard surfaces contacted by the detergent compositions. In an embodiment, the detergent compositions are employed for the prevention of formation, precipitation and/or deposition of hard water scale on hard surfaces and articles such as glasses, plates, silverware, etc. The detergent compositions beneficially provide such prevention of formation, precipitation and/or deposition of hard water scale despite the high alkalinity of the detergent composition use solutions in the presence of hard water. The detergent

compositions are effective at preventing hard water scale accumulation and/or preventing the redeposition of soils in warewashing applications using a variety of water sources, including hard water. In addition, the detergent compositions are suitable for use at temperature ranges typically used in industrial warewashing applications, including for example from about 150° F to about 165°F during washing steps and from about 170°F to about 185°F during rinsing steps.

[0110] In embodiments, the use solution of the detergent compositions applied to surfaces in need of treatment can include at least about 5 ppm to about 1,500 ppm, about 5 ppm to about 1,000 ppm, about 10 ppm to about 1,000 ppm, or about 20 ppm to about 1,000 ppm of antiscaling components, including the scale-inhibiting organic phosphonate and the additional scale inhibitor.

[0111] Exemplary articles for treatment with the compositions disclosed herein are in the warewashing industry, including ware, such as metal ware, plastics, dishware, cups, glasses, flatware, and cookware. For the purposes of this invention, the terms "dish" and "ware" are used in the broadest sense to refer to various types of articles used in the preparation, serving, consumption, and disposal of food stuffs including pots, pans, trays, pitchers, bowls, plates, saucers, cups, glasses, forks, knives, spoons, spatulas, and other glass, metal, ceramic, plastic composite articles commonly available in the institutional or household kitchen or dining room. In general, these types of articles can be referred to as food or beverage contacting articles because they have surfaces which are provided for contacting food and/or beverage.

[0112] EXAMPLES

[0113] Embodiments of the present disclosure are further defined in the following non-limiting Examples. It should be understood that these Examples, while indicating certain embodiments of the disclosure, 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 disclosure, and without departing from the spirit and scope thereof, can make various changes and modifications of the embodiments of the disclosure to adapt it to various usages and conditions. Thus, various modifications of the embodiments of the disclosure, 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

[0114] Calcium carbonate will precipitate from water containing calcium hardness and alkalinity when these ions exceed the normal solubility limit of the calcium carbonate. As the pH of the water increases, the driving force for calcium carbonate precipitation increases. A water that is stable at pH 8.0 can instantaneously precipitate calcium carbonate when the pH is increased to 9.0. Antiscaling efficacy of liquid rinse aid compositions shown in Table 3 were evaluated. The efficiency of scale removal was evaluated according to % inhibition using an alkaline detergent composition and comparing the scale inhibitor packages comparing a single scale inhibitor (phosphonate / polycarboxylate) compared to combinations thereof.

[0115] After the equal volumes of the preheated (60°C) hardness and alkalinity solution are mixed, the test solution is stored for 48 hours at 60°C. At the end of the incubation time, soluble calcium is measured using the calcium titration and percent inhibition is calculated from the titration volumes as a measure of the effectiveness of an inhibitor.

[0116] Test Methodology:

[0117] All flasks were rinsed with dilute HCL (3:1 distilled deionized water - concentrated HCl) and thoroughly rinsed with deionized water prior to use. Any flasks with remaining discoloration, excessive scratches or particle adherence not removed by the acid should be discarded.

[0118] Solutions to be Heated:

[0119] Alkalinity Solution: Add 96 grams, minus inhibitor volume, of distilled deionized water to a cleaned 250 mL Erlenmeyer flask. Add inhibitor volume (1 mL = 1 mg/L), cap or stopper the flask and place in an oven or water bath controlled at 60°C.

[0120] Calcium Solution: Add 95 grams of distilled deionized water to a 250 mL Erlenmeyer flask followed by 5 mL of Calcium Stock solution. Cap or stopper the flask and place in an oven or water bath controlled at 60°C.

[0121] Allow all flasks to equilibrate to 60°C (water bath - approximately 20 minutes; oven - approximately 1 hour, 15 minutes).

[0122] Test Solution Preparation:

[0123] Alkalinity Addition: Add 4 mL of the Alkalinity Stock solution to the alkalinity flask after removing it from the constant temperature source.

[0124] Solution Mixing: Add the alkalinity and calcium solutions to a 500 mL Erlenmeyer flask by simultaneously pouring both solutions from a funnel. Record the pH and place the capped or stoppered flask back in the constant 60°C temperature source for 5 hours.

[0125] After the 5 hour equilibration period, remove flasks from bath or oven. Immediately record final pH. Examine flask appearance and note what type of scale may have formed.

Typical observations would include:

[0126] -Adherent scale on sides of flasks.

[0127] -Scale particles settled to bottom of flask.

[0128] -Fluffy, non-adherent scale particles.

[0129] -Colloidal scale indicated by blue cast of solution.

[0130] Titration: Filter at least 10 g of the test solution through a 0.2 µm membrane filter.

Dilute 10 g of the filtered sample to 50 mL total volume with distilled deionized water.

Titrate the sample using Calgon Field Test No. 35-182-G for Determination of Calcium or

Calgon Field Test No. 35-183-H for Total Hardness Determination. Prepare a calcium

reference by diluting 10 mL of the Calcium Stock Solution to 500 mL with distilled

deionized water. Analyze for calcium as described in prior steps.

[0131] Calculate % inhibition from the following equation:

$$\% \text{ Inhibition} = \frac{V_E - V_o}{V_T - V_o} \times 100$$

$$\{ V_T - V_o \}$$

Where: V_E = titrant volume (mL) required for treated test sample

V_o = titrant volume (mL) required for untreated (blank) test sample

V_T = titrant volume (mL) required for calcium reference sample

[0132] The % inhibition of calcium carbonate scale was assessed for single components as

shown in Table 2, and for combinations of the scale-inhibiting organic phosphonate

(PAPEMP) with polycarboxylic acid (PAA / PMA).

[0133] TABLE 2

<i>Single Component</i>	<i>VE, drops</i>	<i>%Inhibition</i>
10 ppm PAPEMP	4	0.0%
20 ppm PAPEMP	11	14.6%
40 ppm PAPEMP	13	18.8%
20 ppm PAA	8	8.3%

40 ppm PAA	8	8.3%
20 ppm PMA	14	20.8%
40 ppm PMA	15	22.9%
20 ppm MGDA	4	0.0%
40 ppm MGDA	5	2.1%

[0134] TABLE 3

Combinations	VE, drops	%Inhibition
20 ppm PAPEMP + 20 ppm PAA	15	22.9%
20 ppm PAPEMP + 20 ppm PMA	15	22.9%
20 ppm PAPEMP + 20 ppm MGDA	12	16.7%
10 ppm PAPEMP + 20 ppm PMA	7	6.3%
20 ppm PAPEMP + 20 ppm PAA+ 20 ppm PMA	17	27.1%
5 ppm PBTC + 35 ppm PAA	4	0.0%
15 ppm PAPEMP + 38 ppm PAA +56 ppm MGDA	18	29.2%

[0135] The results are shown in FIG. 1 and Tables 2-3. The results show that 20 ppm PAPEMP + 20 ppm PAA/PMA provides at least substantially similar antiscaling efficacy as 40 ppm PAPEMP alone. Similarly, 20 ppm PAPEMP out performs 40 ppm PAA. The PMA, PAPEMP and PAA all reach maximum efficacy along at about 20 ppm, however the combination of the components can be enhanced with the about 1:1 (or 1:1:1) combining of components.

EXAMPLE 2

[0136] Antiscaling efficacy of detergent compositions were evaluated using glasses in a commercial dish machine. The efficiency of scale removal was evaluated according to % inhibition comparing scale inhibitor packages comparing a single scale inhibitor (phosphonate / chelant / polycarboxylate) compared to combinations thereof.

[0137] Before experimentation the dish machine was prepared as follows: Turn on the dish machine, fill water, after the water temperature as desired, add delimer (Strip Away or Lime A Way 0.5-1L, wash 3 cycles). Then turn off the dish machine, drain all the water in the

washing tank, and check whether the scale is completely removed. Rinse the dish machine with tap water (rinse out residual acid and foam). Prepare compositions (detergent and rinse aid) to be used in experiment.

[0138] Turn on the dish machine, fill water, and keep the overflow pipe open for about 2 min (drain the water in the rinsing cylinder). After 2 min, plug the overflow pipe tightly, adjust the chemical concentration, and start to fill water. After the dish machine is settled, wash 2-3 cycles, test water hardness, concentration and volume of chemicals.

[0139] Experiment Methodology: Seven glass and ten stainless steel coupons were arranged in a dish machine (coupons are weighted and tied around the rack). Seven glasses are placed in the rack, from corner to corner in the dish machine for 100 cycles. When 100 cycles were finish, they were removed the rack from dish machine.

[0140] For water hardness: take 5ml water from washing tank into 5ml tube, add moderate amounts of indicator (Eriochrome Black T), the solution color changes to pink after the indicator dissolves completely, drop 0.02N EDTA until the solution color becomes blue, indicating that the titration end point is reached. The number of drops divided by 2 is the water hardness (gpg).

[0141] The detergents evaluated are shown in Table 4 compared to a basement or benchmark formulation that provides PBTC and PAA/PMA (without any PAPEMP).

[0142] TABLE 4

Component	Formula (wt-%)		
	Benchmark	Formula 1	Formula 2
Sodium hydroxide	60-70	60-70	60-70
PAPEMP	0	3-5	3-5
PAA	7-8	6-7	4-5
PMA	0	0	4-5
MGDA	0	10-11	0
PBTC	1-2	0	0
Water	Remainder	Remainder	Remainder

[0143] TABLE 5

	Detergent, drops	Rinse Aid, ml/rack	Water hardness, GPG	
Start	7	1	20	
End	9	1	25	
#	Before, g	After, g	Weight Gain, g	Scale Rate g/m ²
5520	22.1691	22.1691	0.0000	0
5254	22.1289	22.1329	0.0040	2.531646
5034	21.6699	21.6703	0.0004	0.253165
5559	21.3184	21.3182	-0.0002	-0.12658
5031	21.9605	21.9607	0.0002	0.126582
5508	22.019	22.0199	0.0009	0.56962
5020	22.2379	22.2379	0.0000	0
5022	20.6902	20.6901	-0.0001	-0.06329
5029	21.1925	21.1926	0.0001	0.063291
5149	22.5653	22.5655	0.0002	0.126582
				0.419304

[0144] The results in Table 5 showing scale rate, which is the Weight gain / Exposure area of coupon (*i.e.* scale accumulation). The results are also shown in FIG. 2A-2C, where FIG. 2A shows glasses after 100 cycle with a baseline formulation, FIG. 2B shows glasses after 100 cycle with Formula 1 with a significant decrease in scale accumulation compared to benchmark, and FIG. 2C shows glasses after 100 cycle with Formula 2 with a significant decrease in scale accumulation compared to benchmark.

[0145] The results also included assessment of scale inhibition rate on the steel coupons. This was calculated by comparing percent inhibition to sodium hydroxide alone in a dish machine without scale inhibitors (9 drops 250 ppm NaOH). Results is shown in Table 6.

[0146] TABLE 6

	NaOH	Benchmark	Formula 1	Formula 2
Scale accumulation, g/m ²	7.19156	0.79905	0.18196	0.13449
Inhibition Rate	0%	89%	97%	98%

[0147] It is to be understood that while the invention has been described in conjunction with the detailed description thereof, the foregoing description is intended to illustrate, and not limit the scope of the invention, which is defined by the scope of the appended claims. Other embodiments, advantages, and modifications are within the scope of the following claims. Any reference to accompanying drawings which form a part hereof, are shown, by way of illustration only. It is understood that other embodiments may be utilized and structural changes may be made without departing from the scope of the present disclosure. All publications discussed and/or referenced herein are incorporated herein in their entirety.

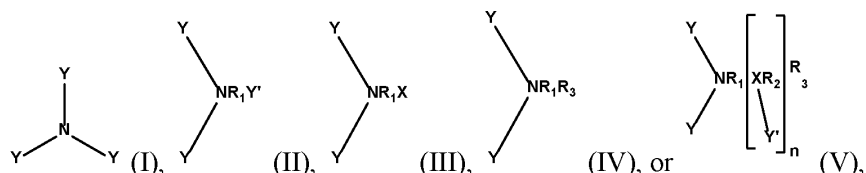
[0148] The features disclosed in the foregoing description, or the following claims, or the accompanying drawings, expressed in their specific forms or in terms of a means for performing the disclosed function, or a method or process for attaining the disclosed result, as appropriate, may, separately, or in any combination of such features, be utilized for realizing the invention in diverse forms thereof.

CLAIMS

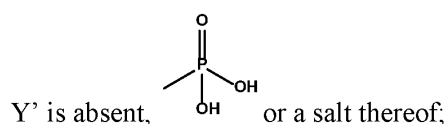
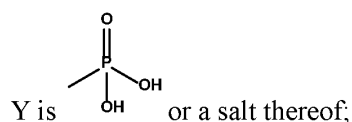
What is claimed is:

1. A detergent composition comprising:

a scale-inhibiting organic phosphonate having one of the following structures:



wherein:



X is N, O, or OH;

R₁ and R₂ are independently a linear or branched C1-C10 alkyl group;

R₃ is -N(Y)₂; and

n is 1-20;

an additional scale inhibitor comprising at least one polycarboxylate, polycarboxylic acid, or salt thereof;

an alkalinity source comprising an alkali metal hydroxide; and

water.

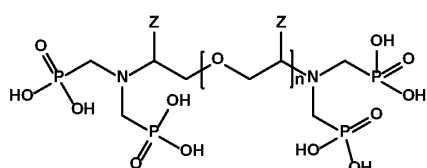
2. The composition of claim 1, wherein a solid composition comprises from about 1 wt-% to about 30 wt-% of the scale-inhibiting organic phosphonate, from about 0 wt-% to about 20 wt-% of the additional scale inhibitor comprising at least one polycarboxylate, polycarboxylic acid or salt thereof, from about 10 wt-% to about 90 wt-% of the alkalinity source, and from about 1 wt-% to about 30 wt-% of the water, and wherein a liquid composition comprises from about 1 wt-% to about 30 wt-% of the scale-inhibiting organic phosphonate, from about 0 wt-% to about 20 wt-% of the additional scale inhibitor

comprising at least one polycarboxylate, polycarboxylic acid or salt thereof comprises, from about 5 wt-% to about 80 wt-% of the alkalinity source, and from about 30 wt-% to about 90 wt-% of the water.

3. The composition of claim 1, wherein the scale-inhibiting organic phosphonate comprises from about 1 wt-% to about 10 wt-% of the composition, wherein the additional scale inhibitor comprising at least one polycarboxylate, polycarboxylic acid or salt thereof comprises from about 1 wt-% to about 10 wt-% of the composition, and the alkalinity source comprises from about 15 wt-% to about 90 wt-% of the composition.

4. The composition of any one of claims 1-3, wherein the salt of Y or Y' is a cation, preferably sodium or potassium.

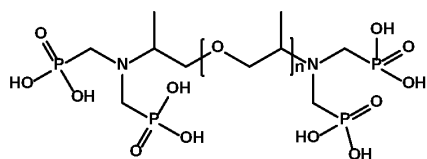
5. The composition of any one of claims 1-4, wherein the organic phosphonate has the structure:



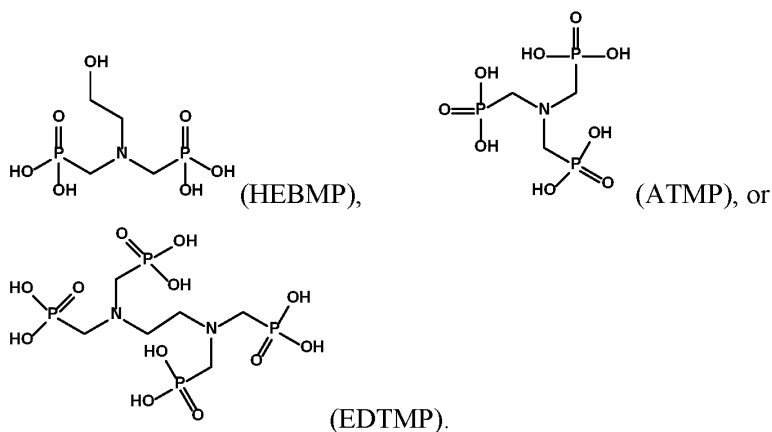
, wherein Z is independently H or CH₃, and wherein n is

2-12.

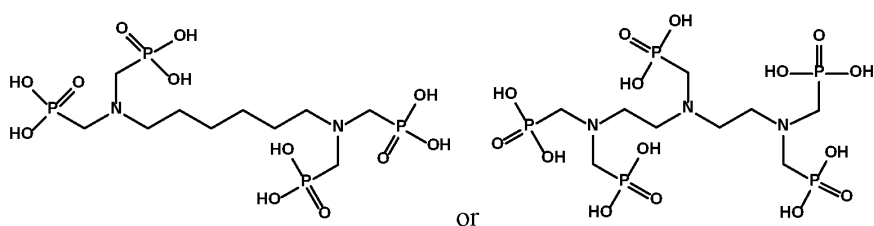
6. The composition of claim 5, wherein the organic phosphonate has the structure:



7. The composition of any one of claims 1-4, wherein the organic phosphonate has one of the following structures:



8. The composition of any one of claims 1-4, wherein the organic phosphonate has one of the following structures:



9. The composition of any one of claims 1-8, wherein the polycarboxylate, polycarboxylic acid, or salt thereof comprise a homopolymer, copolymer or terpolymer of a polyacrylate, polymethacrylate, and/or polymaleate.
10. The composition of claim 9, wherein the polycarboxylate, polycarboxylic acid, or salt thereof is a polyacrylic acid polymer and/or a polyacrylic/polymaleic acid polymer.
11. The composition of any one of claims 1-10, wherein the alkalinity source further comprises a secondary source of alkalinity comprising an alkali metal carbonate.
12. The composition of any one of claims 1-11, further comprising at least one additional

functional ingredient comprising a builder and/or enzyme.

13. The composition of any one of claims 1-12, wherein the composition is liquid or a pressed or cast solid.

14. A method of using a detergent composition comprising:
providing a detergent composition according to any of claims 1-13;
contacting the detergent composition with water to form a use solution;
contacting the use solution to a surface in need of cleaning and antiscaling.

15. The method of claim 14, wherein the use solution has a pH from of at least about 11, or at least about 11.5.

16. The method of any one of claims 14-15, wherein the use solution is dispensed into a wash solution of a ware wash machine.

17. The method of claim 16, wherein the ware wash machine is an institutional dish machine, a clean in place dish machine, or a consumer dish machine.

18. The method of any one of claims 14-17, wherein the surface is an article comprising ware.

19. The method of any one of claims 14-18, wherein the surface is a hard surface comprising metal, glass, or plastic.

20. The method of any one of claims 14-19, wherein the use solution has a concentration from about 5 ppm to about 1,500 ppm, about 10 ppm to about 1,000 ppm, or about 20 ppm to about 1,000 ppm of the scale-inhibiting organic phosphonate and the additional scale inhibitor.