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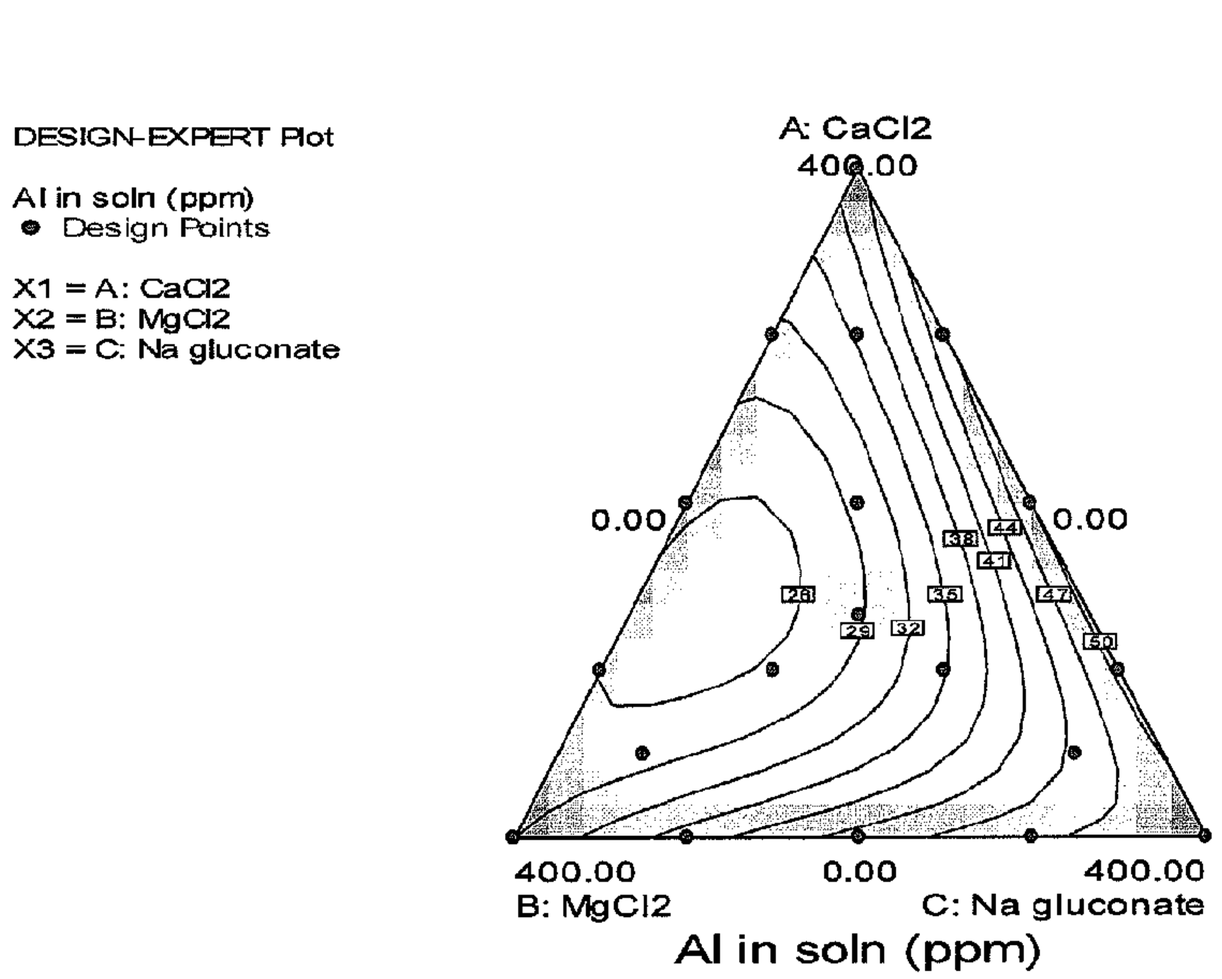
(54) **Titre : COMPOSITIONS COMPRENANT DES IONS DE DURETE ET DU GLUCONATE, ET PROCEDE LES EMPLOYANT POUR LIMITER LA CORROSION ET LE MORDANCAGE**
(54) **Title: COMPOSITIONS INCLUDING HARDNESS IONS AND GLUCONATE AND METHODS EMPLOYING THEM TO REDUCE CORROSION AND ETCH**



(57) **Abrégé/Abstract:**
The present invention relates to compositions including a water soluble magnesium salt, water soluble calcium salt, and gluconate, which have a beneficial effect on corrosion during cleaning. The present compositions can reduce corrosion of glass, aluminum, or steel. The present invention also relates to methods employing these compositions.

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(54) **Title:** COMPOSITIONS INCLUDING HARDNESS IONS AND GLUCONATE AND METHODS EMPLOYING THEM TO REDUCE CORROSION AND ETCH

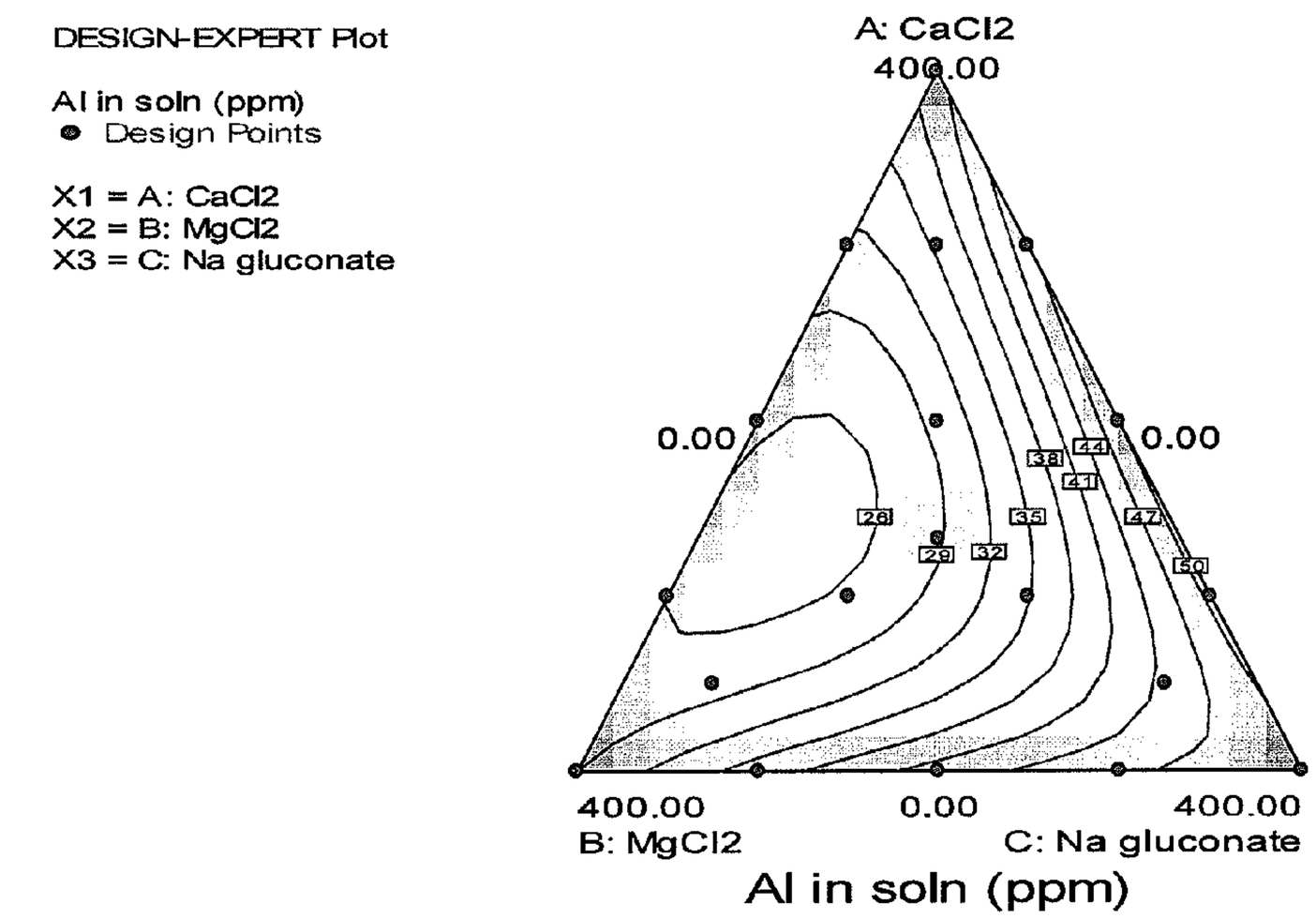

Figure 1

(57) **Abstract:** The present invention relates to compositions including a water soluble magnesium salt, water soluble calcium salt, and gluconate, which have a beneficial effect on corrosion during cleaning. The present compositions can reduce corrosion of glass, aluminum, or steel. The present invention also relates to methods employing these compositions.

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COMPOSITIONS INCLUDING HARDNESS IONS AND GLUCONATE AND METHODS EMPLOYING THEM TO REDUCE CORROSION AND ETCH

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Field of the Invention

The present invention relates to compositions including a water soluble magnesium salt, water soluble calcium salt, and gluconate, which have a beneficial effect on corrosion during cleaning. The present compositions can reduce corrosion of glass, aluminum, or steel. The present invention also relates to methods employing these compositions.

Background of the Invention

Hard water can cause stains on articles as a result of a visible film depositing onto the surface of the articles. The film may be caused by calcium present in hard water precipitating and depositing onto the surface. To prevent such precipitation, cleaning compositions can include a chelating agent.

In some circumstances, precipitation of calcium salts can be beneficial. Etching or corrosion of glass or aluminum is a common problem in warewashing and surface cleaning. Glassware that is repetitively washed in automatic dishwashing machines has a tendency to develop an etching problem as evidenced by a surface cloudiness that is irreversible. The cloudiness can manifest itself as an iridescent film that displays rainbow hues in light reflected from the glass surface. The glass becomes progressively more opaque with repeated washings. It is believed that the glassware corrosion problem relates to two separate phenomena; the first is corrosion or etching due to the leaching out of minerals from the glass composition itself together with hydrolysis of the silicate network, and the second is chelation of ions contained in the glass by the detergent's builder.

Common corrosion inhibitors work by causing controlled precipitation of calcium salts, which can reduce such etching or corrosion. Calcium gluconate is one such corrosion inhibitor. However, calcium gluconate can produce undesirable scale or deposits on the object to be cleaned.

It is counterintuitive to include a second hardness ion (e.g., magnesium ion) with calcium gluconate to achieve a corrosion inhibitor which does not cause scaling as an undesirable side-effect.

Summary of the Invention

Unexpectedly, the present inventors have developed compositions that synergistically reduce corrosion of glass and aluminum. The synergistic compositions include defined ratios of water soluble calcium salt, water soluble magnesium salt, and gluconate that do not leave visible scale on surfaces. Synergy was determined from the data obtained from designed experiments and an analysis specifically focused on finding synergy. Ratios of ingredients that achieve synergy include:

Water soluble calcium salt to water soluble magnesium salt	1-2:1-2	1-1.50:1-1.50	1-1.25:1-1.25	1:1
Water soluble magnesium salt to gluconate	1:1 or greater	1.25:1 or greater	1.5:1 or greater	2:1 or greater
Water soluble calcium salt to gluconate	1-19:1-13	1-15:1-8	3-10:1-5	3-8:2-4

Combinations of these ratios of ingredients also result in synergy. An illustrative combination of ratios is a composition that includes a weight ratio of 1-2:2-1 for water soluble calcium salt to water soluble magnesium salt; weight ratio of 1:1 or greater of water soluble magnesium salt to gluconate; and a weight ratio of 1-19:1-13 for water soluble calcium salt to gluconate. The present invention includes corrosion inhibitor compositions including water soluble calcium salt, water soluble magnesium salt, and gluconate; cleaning compositions including the corrosion inhibitor; and methods of cleaning and reducing corrosion.

In an embodiment, the present invention relates to a corrosion inhibiting composition. The corrosion inhibitor can include water soluble calcium salt, water soluble magnesium salt, and gluconate. The composition can include about 1 to about 98 wt-% water soluble calcium salt and water soluble magnesium salt and about 1 to about 60 wt-% gluconate. In the composition, the weight ratio of water soluble magnesium salt to water soluble calcium salt can be about 1-2:1-2; the

weight ratio of water soluble magnesium salt to gluconate can be greater than 1:1; and the weight ratio of water soluble calcium salt to gluconate can be about 1-19:1:13.

In an embodiment, the present invention relates to a cleaning composition including the present corrosion inhibitor. The cleaning composition can be a detergent for warewashing or automatic dishwashing. This detergent can include source of alkalinity and about 0.01 to about 20 wt-% of the present corrosion inhibitor. The cleaning composition can be a hard surface cleaner. This hard surface cleaner can include source of alkalinity and about 0.01 to about 20 wt-% of the present corrosion inhibitor.

In an embodiment, the present invention relates to a method employing the present corrosion inhibitor or the present cleaning composition. The method can include providing the present corrosion inhibitor or the present cleaning composition. The method can include preparing an aqueous use composition of the present corrosion inhibitor or the present cleaning composition. The method includes contacting an object, such as ware or a hard surface, in need of cleaning with the aqueous use composition.

Brief Description of the Figures

Figure 1 shows data from Example 1 in the form of a ternary graph illustrating the reduced corrosion of the aluminum as a function of the concentrations of magnesium chloride, calcium chloride, and sodium gluconate. The synergistic interaction of select ratios of these three components gave reduced aluminum dissolved from aluminum test coupons without the formation of visible scale on the aluminum surface.

Detailed Description of the Invention

Definitions

As used herein, the term "water soluble" refers to a compound that can be dissolved in water at a concentration of more than 1 wt-%.

As used herein, the terms "sparingly soluble" or "sparingly water soluble" refer to a compound that can be dissolved in water only to a concentration of 0.1 to 1.0 wt-%.

As used herein, the term "water insoluble" refers to a compound that can be dissolved in water only to a concentration of less than 0.1 wt-%.

As used herein, the terms "chelating agent" and "sequestrant" refer to a compound that forms a complex (soluble or not) with water hardness ions (from the wash water, soil and substrates being washed) in a specific molar ratio. Chelating agents that can form a water soluble complex include sodium tripolyphosphate, EDTA, DTPA, NTA, citrate, and the like. Sequestrants that can form an insoluble complex include sodium triphosphate, zeolite A, and the like. As used herein, the terms "chelating agent" and "sequestrant" are synonymous.

As used herein, the term "threshold agent" refers to a compound that inhibits crystallization of water hardness ions from solution, but that need not form a specific complex with the water hardness ion. This distinguishes a threshold agent from a chelating agent or sequestrant. Threshold agents include a polyacrylate, a polymethacrylate, an olefin/maleic copolymer, and the like.

As used herein, the term "antiredeposition agent" refers to a compound that helps keep suspended in water instead of redepositing onto the object being cleaned.

As used herein, the term "phosphate-free" refers to a composition, mixture, or ingredient that does not contain a phosphate or phosphate-containing compound or to which a phosphate or phosphate-containing compound has not been added. Should a phosphate or phosphate-containing compound be present through contamination of a phosphate-free composition, mixture, or ingredients, the amount of phosphate shall be less than 0.5 wt %. In an embodiment, the amount of phosphate is less then 0.1 wt-%. In an embodiment, the amount of phosphate is less than 0.01 wt %.

As used herein, the term "phosphorus-free" refers to a composition, mixture, or ingredient that does not contain phosphorus or a phosphorus-containing compound or to which phosphorus or a phosphorus-containing compound has not been added. Should phosphorus or a phosphorus-containing compound be present through contamination of a phosphorus-free composition, mixture, or ingredients,

the amount of phosphorus shall be less than 0.5 wt %. In an embodiment, the amount of phosphorus is less than 0.1 wt-%. In an embodiment, the amount of phosphorus is less than 0.01 wt %.

"Cleaning" means to perform or aid in soil removal, bleaching, microbial population reduction, or combination thereof.

As used herein, the term "ware" includes items such as eating and cooking utensils. As used herein, the term "warewashing" refers to washing, cleaning, or rinsing ware.

As used herein, the term "hard surface" includes showers, sinks, toilets, bathtubs, countertops, windows, mirrors, transportation vehicles, floors, and the like.

As used herein, the phrase "health care surface" refers to a surface of an instrument, a device, a cart, a cage, furniture, a structure, a building, or the like that is employed as part of a health care activity. Examples of health care surfaces include surfaces of medical or dental instruments, of medical or dental devices, of electronic apparatus employed for monitoring patient health, and of floors, walls, or fixtures of structures in which health care occurs. Health care surfaces are found in hospital, surgical, infirmity, birthing, mortuary, and clinical diagnosis rooms. These surfaces can be those typified as "hard surfaces" (such as walls, floors, bed-pans, etc.,), or fabric surfaces, e.g., knit, woven, and non-woven surfaces (such as surgical garments, draperies, bed linens, bandages, etc.,), or patient-care equipment (such as respirators, diagnostic equipment, shunts, body scopes, wheel chairs, beds, etc.,), or surgical and diagnostic equipment. Health care surfaces include articles and surfaces employed in animal health care.

As used herein, the term "instrument" refers to the various medical or dental instruments or devices that can benefit from cleaning with a stabilized composition according to the present invention.

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 invention. 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, burrs, spreaders, breakers, elevators, clamps, needle holders, carriers, clips, hooks, gouges, curettes, retractors, straightener, punches, extractors, scoops, keratomes, spatulas, expressors, trocars, dilators, cages, glassware, tubing, catheters, cannulas, plugs, stents, scopes (e.g., endoscopes, stethoscopes, and arthoscopes) and related equipment, and the like, or combinations thereof.

As used herein, a solid cleaning composition refers to a cleaning composition in the form of a solid such as a powder, a flake, a granule, a pellet, a tablet, a lozenge, a puck, a briquette, a brick, a solid block, a unit dose, or another solid form known to those of skill in the art. The term "solid" refers to the state of the detergent composition under the expected conditions of storage and use of the solid detergent composition. In general, it is expected that the detergent composition will remain in solid form when exposed to temperatures of up to about 100 °F and greater than about 120 °F.

By the term "solid" as used to describe the processed composition, it is meant that the hardened composition will not flow perceptibly and will substantially retain its shape under moderate stress or pressure or mere gravity, as for example, the shape of a mold when removed from the mold, the shape of an article as formed upon extrusion from an extruder, and the like. The degree of hardness of the solid cast composition can range from that of a fused solid block which is relatively dense and hard, for example, like concrete, to a consistency characterized as being malleable and sponge-like, similar to caulking material.

As used herein, the term "organic component used in cell culture media" refers to sugars (e.g., glucose or dextrose), amino acids, vitamins, cofactors, pyruvate, organic buffers, fatty acids, and nucleosides that are employed in cell culture media to nourish cells and provide them energy for growth. The ATCC (American Type Culture Collection) catalog lists cell culture media including Dulbecco's Modified Eagle's Medium (DMEM), variants of DMEM (e.g., ES-DMEM, DMEM: F12 medium), Eagle's Minimum Essential Medium (EMEM), F-12K Medium, Hybri-Care Medium, Iscove's Modified Dulbecco's Medium

(IMDM), Leibovitz's L-15 Medium, McCoy's 5A Medium, RPMI-1640 Medium and provides lists of ingredients and the amounts of ingredients in these media. These media are standards whose contents are known. In an embodiment, the present composition if substantially free of any organic component of cell culture media. In an embodiment, the present composition is free of any organic component of cell culture media.

As used herein, weight percent (wt-%), percent by weight, % by weight, and the like are synonyms that 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.

As used herein, the term "about" modifying the quantity of an ingredient in the compositions of the invention or employed in the methods of the invention 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 inadvertent error in these procedures; through differences in the manufacture, source, or purity of the ingredients employed to make the compositions or carry out the methods; and the like. Whether or not modified by the term "about", the claims include equivalents to the quantities.

Calcium Magnesium Gluconate Composition

The present inventors have unexpectedly discovered that compositions including water soluble magnesium salt, water soluble calcium salt, and gluconate reduce corrosion during cleaning of, for example, articles of glass, porcelain, ceramic, aluminum, or steel with alkaline cleaners. The compositions even synergistically reduced corrosion of aluminum. The synergistic compositions include defined ratios of water soluble calcium salt, water soluble magnesium salt, and gluconate. Ratios of ingredients that achieve synergy are shown in Table A.

Table A - Synergistic Weight Ratios

Water soluble calcium salt to water soluble magnesium salt	1-2:1-2	1-1.50:1-1.50	1-1.25:1-1.25	1:1
Water soluble magnesium salt to gluconate	1:1 or greater	1.25:1 or greater	1.5:1 or greater	2:1 or greater
Water soluble calcium salt to gluconate	1-19:1-13	1-15:1-8	3-10:1-5	3-8:2-4
Water soluble calcium salt to gluconate	4-7:1-3	5-6:1-2	5.2-5.8:1.2-1.8	11:3

By "or greater" is meant that the number presented first in the ratio can increase. For example, 1:1 or greater includes 2:1, 3:1, 1.1:1, 1.2:1, and so on. The present invention also includes the amounts and ranges stated in the tables modified by the word "about".

Various combinations of water soluble magnesium salt, water soluble calcium salt, and water soluble gluconate salt were evaluated as protectants for aluminum as described in Example 1 with results reported as the ppm of aluminum dissolved in solution from an aluminum test coupon. The data clearly shows synergistic ratios of the three components which was synergistic, using as the definition of synergy a performance better than any individual component, and which also protected the aluminum better than any binary combination of components, including the calcium gluconate system known to be a corrosion inhibiter. Further, no scaling was observed for the synergistic areas which corresponded to the ratios in Table A.

Compositions of the invention can include amounts of water soluble magnesium salt, water soluble calcium salt, and gluconate shown in Table B.

Table B – Concentrate Corrosion Inhibitor Composition by Wt-%

Water soluble magnesium salt	5-98	10-95	25-95	30-75
Water soluble calcium salt	1-94	2-85	1-65	15-50
Gluconate	1-60	2-50	1-35	1-25

The amounts of each ingredient can be selected to achieve the ratios listed in Table A. For example, a composition that includes 10 wt-% gluconate can include 20 wt-% water soluble magnesium salt and 20 wt-% water soluble calcium salt, which provides a weight ratio of water soluble calcium salt to water soluble magnesium salt of 1:1, a weight ratio of water soluble magnesium salt to gluconate of 2:1, and a weight ratio of water soluble calcium salt to gluconate of 2:1. Each of these values is listed in or falls within a range listed in Table A. For example, a synergistic combination of the three components can include 15-50% water soluble calcium salt, 30-75% water soluble magnesium salt, and 1-25% gluconate at the appropriate ratios.

The present corrosion inhibitor can include only water soluble calcium salt, water soluble magnesium salt, and gluconate in the amounts and ratios listed in Tables A and B. Alternatively, the present corrosion inhibitor can be part of a composition that also includes additional ingredient(s), in which case the amounts of ingredients selected from Table B need not add up to 100 wt-%, the remainder can be any additional ingredient(s). The present invention also includes the amounts and ranges stated in the tables modified by the word "about".

The present invention relates to a cleaning composition including the present corrosion inhibitor composition and to methods employing the cleaning composition. This composition can include surfactant, alkalinity source, and sufficient water soluble magnesium salt, water soluble calcium salt, and water soluble gluconate salt to provide corrosion/etch resistance without scale formation in the use solution. The present cleaning composition can include surfactant, alkalinity source and the present corrosion inhibitor in amounts shown in Table C.

Table C – Concentrate Cleaning Composition by Wt-%

Surfactant	0.1-20	1-15	2-10	3-8
Alkalinity Source	0.1-70	1-50	2-40	5-30
Corrosion Inhibitor	0.01-20	0.1-15	0.2-10	0.3-8

The present cleaning composition can also include additional ingredients, in which case the amounts of ingredients selected from Table C need not add up to 100 wt-%, the remainder can be any additional ingredient(s). The corrosion inhibitor can be used in any application where it is desirable to reduce surface corrosion, such as in a detergent composition. The present invention also includes the amounts and ranges stated in the tables modified by the word "about".

In an embodiment, the present invention relates to a composition and it's use for corrosion and/or etch control which is substantially free of (or even free of) common detergent components. In an embodiment, the present corrosion inhibitor provided substantially free of (or even free of) surfactant, alkalinity source, or builder. This composition can include sufficient water soluble magnesium salt, water soluble calcium salt, and water soluble gluconate salt to provide corrosion/etch resistance without scale formation in the use solution. Such a corrosion inhibitor composition can be employed alone or, at the locus of use, the corrosion inhibitor or use composition of the corrosion inhibitor can be employed or combined with a separate cleaning composition known to those skilled in the art.

In certain embodiments, the present composition consists essentially of water soluble magnesium salt, water soluble calcium salt, and gluconate. As used herein, the phrases "consisting essentially of" or "consists essentially of" refer to a composition including the listed ingredients (e.g., water soluble magnesium salt, water soluble calcium salt, and gluconate) but lacking an effective amount of any cleaning component commonly used in cleaning compositions.

In an embodiment, the present composition is free of cleaning components commonly used in cleaning compositions. As used herein, the phrase "free of cleaning components commonly used in cleaning compositions" refers to a composition, mixture, or ingredient that does not contain a cleaning component commonly used in cleaning compositions or to which a cleaning component commonly used in a cleaning composition has not been added. Should a cleaning component commonly used in cleaning compositions be present through contamination of a composition free of cleaning components commonly used in cleaning, the amount of cleaning component commonly used in cleaning compositions shall be less than 0.5 wt %. In an embodiment, the amount of cleaning

component commonly used in cleaning compositions is less then 0.1 wt-%. In an embodiment, the amount of cleaning component commonly used in cleaning compositions is less than 0.01 wt %.

As used herein, "cleaning component commonly used in cleaning compositions" refers to: source of alkalinity, organic surfactant or cleaning agent (e.g., surfactant or surfactant system, e.g., anionic, nonionic, cationic, and zwitterionic surfactant), pH modifier (e.g., organic or inorganic source of alkalinity or a pH buffering agent), builder (e.g., inorganic builder such as silicate, carbonate, sulfate, salt or acid form thereof), processing aid, active oxygen compound, glass or metal corrosion inhibitor, activator, rinse aid functional material, bleaching agent, defoaming agent, anti-redeposition agent, stabilizing agent, enzyme, chelating agent or sequestrant (e.g., phosphonate, phosphate, aminocarboxylate, polycarboxylate, and the like), detersive polymer, softener, source of acidity, solubility modifier, bleaching agent or additional bleaching agent, effervescent agent, and activator for the source of alkalinity.

The water soluble magnesium salt, water soluble calcium salt, and water soluble gluconate salt are sufficiently water-soluble so that when the composition is combined with a diluent, such as water, the compounds dissolve. In this context, sufficiently water-soluble means that the salts dissolve at a relatively quick rate in water. In an embodiment, the solubility of the water soluble magnesium salt, water soluble calcium salt, and water soluble gluconate salt is at least about 0.5 wt-% in water at about 20 °C and atmospheric pressure. In an embodiment, the water soluble magnesium salt, water soluble calcium salt, and water soluble gluconate salt remain soluble in solution. In an embodiment, the water soluble magnesium salt, water soluble calcium salt, and water soluble gluconate salt remain dispersed in solution. In an embodiment, once solubilized, the water soluble magnesium salt, water soluble calcium salt, and water soluble gluconate salt interact to form a salt having limited water solubility (e.g., even water insoluble). In this context, the phrase "limited water solubility" means that the salt has a tendency to precipitate from the solution. In an embodiment, a salt having limited water solubility has a solubility of less than about 0.5 wt-% in water at about 20°C and atmospheric pressure.

The water-insoluble salt may be formed *in-situ* when the diluent is added to the present composition or may be added to a liquid as a premade complex. Forming the water insoluble salt *in situ* can result in its more homogeneous dispersion in solution. Forming the water insoluble salt as a premade complex can allow use of lower concentrations while achieving the same level of effectiveness as forming the corrosion inhibitor *in situ*.

Theories of Operation

Although not limiting to the present invention, it is believed that, in certain embodiments, a salt formed from the hardness ions (e.g., magnesium and calcium) and the gluconate forms a microscopic protective film on the surface of articles exposed to the present composition. The protective film can be transparent or not visible to the unaided eye. Such as film can function as a protective layer to slow or prevent other components that may be present in solution from attacking and corroding the surface of the article. Thus, the film functions as a sacrificial layer and allows other components such as alkalinity sources, builders, or sequestrants, to attack and remove portions of the film, rather than attack the surface of the article. A relatively thin film that may be easily removed from the surface during subsequent cleaning so that a new film may be deposited on the surface to provide a new protective layer. Thus, it does not permanently build up on the surface and form an iridescent film or surface cloudiness. As a result, the precipitate film is available to protect the surface but can be removed and regenerated.

Although not limiting to the present invention, it is believed that, in certain embodiments, the corrosion inhibitor protects the surface by replacing ions extracted from the surface by an alkalinity source or builder in solution and/or by annealing the surface to remove surface hydroxyl groups. The protective film can degrade during subsequent wash cycles and can be continually regenerated as a result of precipitation of the salt

Although not limiting to the present invention, it is believed that, in certain embodiments, the rate of deposition of the salt is largely dependent on the ratio of total cations to anions and also the ratio of magnesium ion to calcium ion provided in the present composition. It is believed that these ratios may be manipulated such

that the film deposited onto the surface is thick enough to protect against etching but is thin enough that it is relatively transparent and/or and substantially invisible to the naked eye such as by an individual casually inspecting the glass in normal use situations (e.g., at a dinner table). In selecting the ratio of cations to anions, numerous factors can be considered, including, but not limited to: the hardness level of the water, the cation source, the anion source, and the material of the surface to be protected.

Although not limiting to the present invention, it is believed that, in certain embodiments, it is believed that magnesium ions moderate the precipitation/film formation of calcium gluconate such that the protection layer does not build-up to the extent to which it is visible to the unaided eye, i.e. does not build-up as scale.

Water Soluble Magnesium Salts

Suitable water soluble magnesium compounds include those selected from the group consisting of magnesium acetate, magnesium benzoate, magnesium bromide, magnesium bromate, magnesium chlorate, magnesium chloride, magnesium chromate, magnesium citrate, magnesium formate, magnesium hexafluorosilicate, magnesium iodate, magnesium iodide, magnesium lactate, magnesium molybdate, magnesium nitrate, magnesium perchlorate, magnesium phosphinate, magnesium salicylate, magnesium sulfate, magnesium sulfite, magnesium thiosulfate, a hydrate thereof, and a mixture thereof. These salts can be provided as hydrated salts or anhydrous salts.

Water soluble magnesium compounds approved as GRAS for direct food contact include magnesium chloride and magnesium sulfate.

Water Soluble Calcium Salts

Suitable water soluble calcium salts include those selected from the group consisting of calcium acetate, calcium benzoate, calcium bromate, calcium bromide, calcium chlorate, calcium chloride, calcium chromate, calcium dihydrogen phosphate, calcium dithionate, calcium formate, calcium gluconate, calcium glycerophosphate, calcium hydrogen sulfide, calcium iodide, calcium lactate, calcium metasilicate, calcium nitrate, calcium nitrite, calcium pantothenate, calcium

perchlorate, calcium permanganate, calcium phosphate, calcium phosphinate, calcium salicylate, calcium succinate, a hydrate thereof, and a mixture thereof. These salts can be provided as hydrated compounds or anhydrous compounds.

Gluconate

Gluconate is the salt of gluconic acid. Water soluble gluconate salts, e.g., sodium gluconate are commercially available. Additional commercially available forms of gluconate include potassium gluconate, lithium gluconate, and magnesium gluconate.

Water

Water can be hard water, city water, well water, water supplied by a municipal water system, water supplied by a private water system, treated water, or water directly from the system or well. In general, hard water refers to water having a level of calcium and magnesium ions in excess of about 100 ppm. Often, the molar ratio of calcium to magnesium in hard water is about 2:1 or about 3:1. Although most locations have hard water, water hardness tends to vary from one location to another. Water can be potable water as obtained from a municipal or private water system, e.g., a public water supply or a well.

Embodiments of the Present Compositions

The present calcium magnesium gluconate composition can be provided in any of a variety of embodiments of compositions. For example, the calcium magnesium gluconate composition can be a component of a cleaning composition. Such a cleaning composition can include calcium magnesium gluconate composition, surfactant, and alkalinity source.

In an embodiment, the present composition is substantially free of zinc. In general, the present composition can be characterized as substantially free of zinc if the corrosion inhibitor contains no intentionally added zinc. For example, the present composition may be characterized as substantially free of zinc if it contains no zinc, or if zinc is present, the amount of zinc is less than about 0.01 wt-%. Zinc

can unnecessarily consume certain builders or chelating agents, which is a reason to exclude it.

In an embodiment, the present composition does not include phosphorus or nitrilotriacetic acid (NTA) containing compounds. Phosphorus-free refers to a composition, mixture, or ingredients to which phosphorus-containing compounds are not added. Should phosphorus-containing compounds be present, the level of phosphorus-containing compounds in the resulting composition should be less than about 1 wt-%, less than about 0.5 wt-%, less than about 0.1 wt-%, or less than about 0.01 wt-%. NTA-free refers to a composition, mixture, or ingredients to which NTA-containing compounds are not added. Should NTA-containing compounds be present, the level of NTA in the resulting composition should be less than about 1 wt-%, less than about 0.5 wt-%, less than about 0.1 wt-%, or less than about 0.01 wt-%. When the detergent composition is NTA-free, the detergent composition is also compatible with chlorine, which functions as an anti-redeposition and stain-removal agent.

In an embodiment, the present composition includes a source of hardness ions (e.g., magnesium and calcium ions) and a gluconate that are characterized by the United States Food and Drug Administration as direct or indirect food additives.

Warewashing Composition

The present calcium magnesium gluconate composition can be employed as a component of a warewashing composition. Warewashing can etch wares made of, for example, aluminum, glass, ceramic, or porcelain. Table D describes ingredients for suitable warewashing compositions. The present invention also includes the amounts and ranges stated in the tables modified by the word "about".

Table D - Warewashing Compositions

Ingredient	Warewashing Composition 1 (wt-%)	Warewashing Composition 2 (wt-%)
Calcium Magnesium Gluconate Composition	0.01-20	0.1-10
alkaline source	5-60	10-50
surfactant	0.05-20	0.5-15
builder	1-60	3-50
water	0.1-60	
Optional Ingredients:		
bleaching agent	0.1-60	1-20
filler	1-20	3-15
defoaming agent	0.01-3	0.1-2
anti-deposition agent	0.5-10	1-5
stabilizing agent	0.5-15	2-10
dispersant	0.5-15	2-9
enzyme	0.5-10	1-5

The present composition can be a warewashing composition. The warewashing detergent composition includes a cleaning agent, an alkaline source, and a corrosion inhibitor. The cleaning agent comprises a detersive amount of a surfactant. The alkaline source is provided in an amount effect to provide a use composition having a pH of at least about 8 when measured at a concentration of about 0.5 wt. %. The corrosion inhibitor can be provided in an amount sufficient for reducing corrosion of glass, porcelain, ceramic, or aluminum when the warewashing detergent composition is combined with water of dilution at a dilution ratio of dilution water to detergent composition of at least about 20:1. A method for using a warewashing detergent composition is provided according to the invention. The method includes steps of diluting the warewashing detergent composition with water of dilution at a ratio of water dilution to warewashing detergent composition of at

least about 20:1, and washing glass with the use composition in an automatic dishwashing machine.

The warewashing composition, can be available for cleaning in environments other than inside an automatic dishwashing or warewashing machine. For example, the composition can be used as a pot and pan cleaner for cleaning glass, dishes, etc. in a sink. The warewashing composition includes an effective amount of a corrosion inhibitor to provide a use composition exhibiting resistance to glass corrosion. The phrase "effective amount" in reference to the corrosion inhibitor refers to an amount sufficient to provide a use composition exhibiting reduced glass corrosion compared with a composition that is identical except that it does not contain a sufficient amount of the corrosion inhibitor to reduce corrosion of glass after multiple washings.

The warewashing composition prior to dilution to provide the use composition can be referred to as the warewashing composition concentrate or more simply as the concentrate. The concentrate can be provided in various forms including as a liquid or as a solid. Pastes and gels can be considered types of liquid. Powders, agglomerates, pellets, tablets, and blocks can be considered types of solid.

Hard Surface Cleaner

The present calcium magnesium gluconate composition can be employed as a component of a hard surface cleaning composition. Hard surface cleaners can etch objects made of, for example, aluminum or glass. Table E describes ingredients for suitable hard surface cleaners. The present invention also includes the amounts and ranges stated in the tables modified by the word “about”.

Table E - Hard Surface Cleaning Compositions

Ingredient	Hard Surface Cleaner 1 (wt-%)	Hard Surface Cleaner 2 (wt-%)	Hard Surface Cleaner 3 (wt-%)
Calcium Magnesium Gluconate Composition	0.01-20	0.1-10	0.2-8
nonionic surfactant	0.01-20	0.1-15	0.5-8
Optional Ingredients:			
anionic surfactant	0-20	0.1-15	0.5-8
amphoteric surfactant	0-10	0.1-8	0.5-5
non-phosphorus containing builder	0.01-30	0.1-25	1-15
anti-redeposition agent	0-10	0.1-8	0.3-5
alkalinity source	0.1-30	0.5-25	1-15
thickener	0-5	0.1-4	0.5-3
organic solvent	0-20	0.1-15	0.5-10
antimicrobial agent	0-20	0.01-15	0.03-10
solidification agent	5-90	10-80	20-60
water	balance	balance	balance

Table E, continued - Hard Surface Cleaning Compositions

Ingredient	Hard Surface Cleaner 4 (wt-%)	Hard Surface Cleaner 5 (wt-%)	Hard Surface Cleaner 6 (wt-%)
Calcium Magnesium Gluconate Composition	0.3-6	0.4-5	0.5-4
nonionic surfactant	0.01-20	0.1-15	0.5-8
Optional Ingredients:			
anionic surfactant	0-20	0.1-15	0.5-8
amphoteric surfactant	0-10	0.1-8	0.5-5
non-P containing builder	0.01-30	0.1-25	1-15
anti-redeposition agent	0-10	0.1-8	0.3-5
alkalinity source	0.1-30	0.5-25	1-15
thickener	0-5	0.1-4	0.5-3
organic solvent	0-20	0.1-15	0.5-10
antimicrobial agent	0-20	0.01-15	0.03-10
water	balance	balance	balance

A hard surface cleaner can be configured to be diluted with water to provide a use composition that can be used to clean hard surfaces. Examples of hard surfaces include, but are not limited to: architectural surfaces such as walls, showers, floors, sinks, mirrors, windows, and countertops; transportation vehicles such as cars, trucks, buses, trains, and planes; surgical or dental instruments; food processing equipment; and washing equipment such as dishwashers or laundry machines.

Solid Cleaning Compositions

The present calcium magnesium gluconate composition can be employed as a component of a solid cleaning composition. Solid cleaning composition can etch objects made of, for example, aluminum, glass, ceramic, or porcelain. Table F describes ingredients for solid cleaning compositions. The present invention also includes the amounts and ranges stated in the tables modified by the word "about".

Table F - Solid Cleaning Compositions

Ingredient	Solid Cleaning Composition 1 (wt-%)	Solid Cleaning Composition 2 (wt-%)
Calcium Magnesium Gluconate Composition	0.01-20	0.1-10
Surfactant	0.1-40	1-20
alkaline source	10-80	15-70
solidifying agent	0.1-80	1-60
water	0-50	0.1-30
binding agent	0.1-80	1 - 60

Additional Ingredients

Solid cleaning compositions made according to the invention may further include additional functional materials or additives that provide a beneficial property, for example, to the composition in solid form or when dispersed or dissolved in an aqueous solution, e.g., for a particular use. Examples of conventional additives include one or more of each of polymer, surfactant, secondary hardening agent, solubility modifier, detergent filler, defoamer, anti-redeposition agent, antimicrobial, aesthetic enhancing agent (i.e., dye, odorant, perfume), optical brightener, bleaching agent or additional bleaching agent, enzyme, effervescent agent, activator for the source of alkalinity, and mixtures thereof.

Builder

In an embodiment, the present composition includes a builder that is incapable of chelating a significant amount of or any of the magnesium. Zeolite 3A is an example of this type of builder. A purpose of such builder can be to increase the molar ratio of Mg/Ca in the use solution. This can reduce the amount of magnesium compound used as an ingredient in the solid composition.

Organic Surfactants or Cleaning Agents

The composition can include at least one cleaning agent which can be a surfactant or surfactant system. A variety of surfactants can be used in a cleaning composition, including anionic, nonionic, cationic, and zwitterionic surfactants, which are commercially available from a number of sources. Suitable surfactants include nonionic surfactants. Suitable nonionic surfactants include low foaming non-ionic surfactants. For a discussion of surfactants, see Kirk-Othmer, Encyclopedia of Chemical Technology, Third Edition, volume 8, pages 900-912.

Nonionic surfactants are useful in the present solid compositions, include those having a polyalkylene oxide polymer as a portion of the surfactant molecule. Such nonionic surfactants include, for example, chlorine-, benzyl-, methyl-, ethyl-, propyl-, butyl- and other like alkyl-capped polyethylene and/or polypropylene glycol ethers of fatty alcohols; polyalkylene oxide free nonionics such as alkyl polyglycosides; sorbitan and sucrose esters and their ethoxylates; alkoxylated ethylene diamine; carboxylic acid esters such as glycerol esters, polyoxyethylene esters, ethoxylated and glycol esters of fatty acids, and the like; carboxylic amides such as diethanolamine condensates, monoalkanolamine condensates, polyoxyethylene fatty acid amides, and the like; and ethoxylated amines and ether amines commercially available from Tomah Corporation and other like nonionic compounds. Silicone surfactants such as the ABIL B8852 (Goldschmidt) can also be used.

Additional suitable nonionic surfactants having a polyalkylene oxide polymer portion include nonionic surfactants of C6-C24 alcohol ethoxylates (e.g., C6-C14 alcohol ethoxylates) having 1 to about 20 ethylene oxide groups (e.g., about 9 to about 20 ethylene oxide groups); C6-C24 alkylphenol ethoxylates (e.g., C8-C10 alkylphenol ethoxylates) having 1 to about 100 ethylene oxide groups (e.g., about 12 to about 20 ethylene oxide groups); C6-C24 alkylpolyglycosides (e.g., C6-C20 alkylpolyglycosides) having 1 to about 20 glycoside groups (e.g., about 9 to about 20 glycoside groups); C6-C24 fatty acid ester ethoxylates, propoxylates or glycerides; and C4-C24 mono or dialkanolamides.

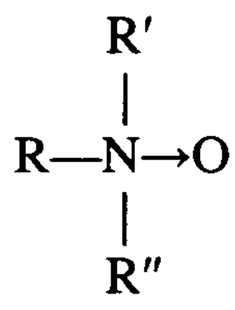
Specific alcohol alkoxylates include alcohol ethoxylate propoxylates, alcohol propoxylates, alcohol propoxylate ethoxylate propoxylates, alcohol ethoxylate

butoxylates, and the like; nonylphenol ethoxylate, polyoxyethylene glycol ethers and the like; and polyalkylene oxide block copolymers including an ethylene oxide/propylene oxide block copolymer such as those commercially available under the trademark PLURONIC (BASF-Wyandotte), and the like.

Suitable nonionic surfactants include low foaming nonionic surfactants. Examples of suitable low foaming nonionic surfactants include secondary ethoxylates, such as those sold under the trade name TERGITOL™, such as TERGITOL™ 15-S-7 (Union Carbide), Tergitol 15-S-3, Tergitol 15-S-9 and the like. Other suitable classes of low foaming nonionic surfactant include alkyl or benzyl-capped polyoxyalkylene derivatives and polyoxyethylene/polyoxypropylene copolymers.

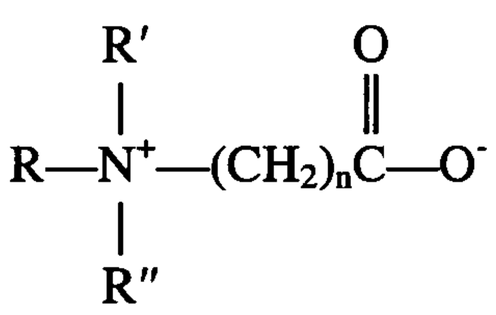
A useful nonionic surfactant for use as a defoamer is nonylphenol having an average of 12 moles of ethylene oxide condensed thereon, it being end capped with a hydrophobic portion comprising an average of 30 moles of propylene oxide. Silicon-containing defoamers are also well-known and can be employed in the compositions and methods of the present invention.

Suitable amphoteric surfactants include amine oxide compounds having the formula:



where R, R′, R″, and R‴ are each a C_1-C_{24} alkyl, aryl or aralkyl group that can optionally contain one or more P, O, S or N heteroatoms.

Another class of suitable amphoteric surfactants includes betaine compounds having the formula:



where R, R′, R″ and R‴ are each a C_1-C_{24} alkyl, aryl or aralkyl group that can optionally contain one or more P, O, S or N heteroatoms, and n is about 1 to about 10.

Suitable surfactants include food grade surfactants, linear alkylbenzene sulfonic acids and their salts, and ethylene oxide/propylene oxide derivatives sold under the Pluronic™ trade name. Suitable surfactants include those that are compatible as an indirect or direct food additive or substance; especially those described in the Code of Federal Regulations (CFR), Title 21 -Food and Drugs, parts 170 to 186.

Anionic surfactants suitable for the present cleaning compositions, include, for example, carboxylates such as alkylcarboxylates (carboxylic acid salts) and polyalkoxycarboxylates, alcohol ethoxylate carboxylates, nonylphenol ethoxylate carboxylates, and the like; sulfonates such as alkylsulfonates, alkylbenzenesulfonates, alkylarylsulfonates, sulfonated fatty acid esters, and the like; sulfates such as sulfated alcohols, sulfated alcohol ethoxylates, sulfated alkylphenols, alkylsulfates, sulfosuccinates, alkylether sulfates, and the like; and phosphate esters such as alkylphosphate esters, and the like. Suitable anionics include sodium alkylarylsulfonate, alpha-olefin sulfonate, and fatty alcohol sulfates. Examples of suitable anionic surfactants include sodium dodecylbenzene sulfonic acid, potassium laureth-7 sulfate, and sodium tetradecenyl sulfonate.

The surfactant can be present at amounts listed in the tables or about 0.01 to about 20 wt-% or about 0.1 to about 10 wt-%, about 0.2 to about 5 wt-%.

pH Modifier

The pH modifier can be an organic or inorganic source of alkalinity or a pH buffering agent. Nonlimiting examples include the alkali metal hydroxides, alkali metal carbonates, alkanolamines, salts of weak organic acids, etc. Suitable pH modifiers include sodium hydroxide, lithium hydroxide, potassium hydroxide, sodium carbonate, lithium carbonate, potassium carbonate, the corresponding bicarbonate or sesquicarbonate salts, and mixtures thereof. Suitable pH modifiers include acetate, formate, and the like. Suitable pH modifiers have no or only weak calcium sequestration capability at the pH of the use solution.

The pH modifier can be present at amounts listed in the tables or about 1 to about 70 wt-% or about 2 to about 50 wt-%, about 3 to about 30 wt-%.

Processing Aid

Processing aids are materials which enhance the production process for the detergent composition. They can serve as drying agents, modify the rate of solidification, alter the transfer of water of hydration in the formula, or even act as the solidifying matrix itself. Processing aids can have some overlap with other functionalities in the formula. Nonlimiting examples include silica, alkali metal silicates, urea, polyethylene glycols, solid surfactants, sodium carbonate, potassium chloride, sodium sulfate, sodium hydroxide, water, etc. Which processing aid(s) is suitable would of course vary with the manufacturing procedure and specific detergent composition.

The processing aid can be present at amounts of about 1 to about 70 wt-%, about 2 to about 50 wt-%, about 3 to about 30 wt-%.

Active Oxygen Compounds

The active oxygen compound acts to provide a source of active oxygen, but can also act to form at least a portion of the solidification agent. The active oxygen compound can be inorganic or organic, and can be a mixture thereof. Some examples of active oxygen compound include peroxygen compounds, and peroxygen compound adducts that are suitable for use in forming the binding agent.

Many active oxygen compounds are peroxygen compounds. Any peroxygen compound generally known and that can function, for example, as part of the binding agent can be used. Examples of suitable peroxygen compounds include inorganic and organic peroxygen compounds, or mixtures thereof.

The active oxygen compound can be in the present solid composition at amounts of about 1 to about 80 wt-%, about 5 to about 50 wt-%, or about 10 wt-% to about 40 wt-%.

<u>Inorganic Active Oxygen Compound</u>

Examples of inorganic active oxygen compounds include the following types of compounds or sources of these compounds, or alkali metal salts including these types of compounds, or forming an adduct therewith:

hydrogen peroxide;

group 1 (IA) active oxygen compounds, for example lithium peroxide, sodium peroxide, and the like;

group 2 (IIA) active oxygen compounds, for example magnesium peroxide, calcium peroxide, strontium peroxide, barium peroxide, and the like;

group 12 (IIB) active oxygen compounds, for example zinc peroxide, and the like;

group 13 (IIIA) active oxygen compounds, for example boron compounds, such as perborates, for example sodium perborate hexahydrate of the formula $Na_2[Br_2(O_2)_2(OH)_4] \cdot 6H_2O$ (also called sodium perborate tetrahydrate and formerly written as $NaBO_3 \cdot 4H_2O$); sodium peroxyborate tetrahydrate of the formula $Na_2Br_2(O_2)_2[(OH)_4] \cdot 4H_2O$ (also called sodium perborate trihydrate, and formerly written as $NaBO_3 \cdot 3H_2O$); sodium peroxyborate of the formula $Na_2[B_2(O_2)_2(OH)_4]$ (also called sodium perborate monohydrate and formerly written as $NaBO_3 \cdot H_2O$); and the like; e.g., perborate;

group 14 (IVA) active oxygen compounds, for example persilicates and peroxycarbonates, which are also called percarbonates, such as persilicates or peroxycarbonates of alkali metals; and the like; e.g., percarbonate, e.g., persilicate;

group 15 (VA) active oxygen compounds, for example peroxynitrous acid and its salts; peroxyphosphoric acids and their salts, for example, perphosphates; and the like; e.g., perphosphate;

group 16 (VIA) active oxygen compounds, for example peroxysulfuric acids and their salts, such as peroxymonosulfuric and peroxydisulfuric acids, and their salts, such as persulfates, for example, sodium persulfate; and the like; e.g., persulfate;

group VIIa active oxygen compounds such as sodium periodate, potassium perchlorate and the like.

Other active inorganic oxygen compounds can include transition metal peroxides; and other such peroxygen compounds, and mixtures thereof.

In certain embodiments, the compositions and methods of the present invention employ certain of the inorganic active oxygen compounds listed above. Suitable inorganic active oxygen compounds include hydrogen peroxide, hydrogen peroxide adduct, group IIIA active oxygen compounds, group VIA active oxygen

compound, group VA active oxygen compound, group VIIA active oxygen compound, or mixtures thereof. Examples of such inorganic active oxygen compounds include percarbonate, perborate, persulfate, perphosphate, persilicate, or mixtures thereof. Hydrogen peroxide presents an example of an inorganic active oxygen compound. Hydrogen peroxide can be formulated as a mixture of hydrogen peroxide and water, e.g., as liquid hydrogen peroxide in an aqueous solution. The mixture of solution can include about 5 to about 40 wt-% hydrogen peroxide or 5 to 50 wt-% hydrogen peroxide.

In an embodiment, the inorganic active oxygen compounds include hydrogen peroxide adduct. For example, the inorganic active oxygen compounds can include hydrogen peroxide, hydrogen peroxide adduct, or mixtures thereof. Any of a variety of hydrogen peroxide adducts are suitable for use in the present compositions and methods. For example, suitable hydrogen peroxide adducts include percarbonate salt, urea peroxide, peracetyl borate, an adduct of H_2O_2 and polyvinyl pyrrolidone, sodium percarbonate, potassium percarbonate, mixtures thereof, or the like. Suitable hydrogen peroxide adducts include percarbonate salt, urea peroxide, peracetyl borate, an adduct of H_2O_2 and polyvinyl pyrrolidone, or mixtures thereof. Suitable hydrogen peroxide adducts include sodium percarbonate, potassium percarbonate, or mixtures thereof, e.g., sodium percarbonate.

Organic Active Oxygen Compound

Any of a variety of organic active oxygen compounds can be employed in the compositions and methods of the present invention. For example, the organic s active oxygen compound can be a peroxycarboxylic acid, such as a mono- or di-peroxycarboxylic acid, an alkali metal salt including these types of compounds, or an adduct of such a compound. Suitable peroxycarboxylic acids include C_1-C_{24} peroxycarboxylic acid, salt of C_1-C_{24} peroxycarboxylic acid, ester of C_1-C_{24} peroxycarboxylic acid, diperoxycarboxylic acid, salt of diperoxycarboxylic acid, ester of diperoxycarboxylic acid, or mixtures thereof.

Suitable peroxycarboxylic acids include C_1-C_{10} aliphatic peroxycarboxylic acid, salt of C_1-C_{10} aliphatic peroxycarboxylic acid, ester of C_1-C_{10} aliphatic peroxycarboxylic acid, or mixtures thereof; e.g., salt of or adduct of peroxyacetic

acid; e.g., peroxyacetyl borate. Suitable diperoxycarboxylic acids include C_4-C_{10} aliphatic diperoxycarboxylic acid, salt of C_4-C_{10} aliphatic diperoxycarboxylic acid, or ester of C_4-C_{10} aliphatic diperoxycarboxylic acid, or mixtures thereof; e.g., a sodium salt of perglutaric acid, of persuccinic acid, of peradipic acid, or mixtures thereof.

Organic active oxygen compounds include other acids including an organic moiety. Suitable organic active oxygen compounds include perphosphonic acids, perphosphonic acid salts, perphosphonic acid esters, or mixtures or combinations thereof.

Active Oxygen Compound Adducts

Active oxygen compound adducts include any generally known and that can function, for example, as a source of active oxygen and as part of the solidified composition. Hydrogen peroxide adducts, or peroxyhydrates, are suitable. Some examples of source of alkalinity adducts include the following: alkali metal percarbonates, for example sodium percarbonate (sodium carbonate peroxyhydrate), potassium percarbonate, rubidium percarbonate, cesium percarbonate, and the like; ammonium carbonate peroxyhydrate, and the like; urea peroxyhydrate, peroxyacetyl borate; an adduct of H_2O_2 polyvinyl pyrrolidone, and the like, and mixtures of any of the above.

Antimicrobials

Antimicrobial agents are chemical compositions that can be used in a solid functional material that alone, or in combination with other components, act to reduce or prevent microbial contamination and deterioration of commercial products material systems, surfaces, etc. In some aspects, these materials fall in specific classes including phenolics, halogen compounds, quaternary ammonium compounds, metal derivatives, amines, alkanol amines, nitro derivatives, analides, organosulfur and sulfur-nitrogen compounds and miscellaneous compounds.

It should also be understood that the source of alkalinity used in the formation of compositions embodying the invention also act as antimicrobial agents, and can even provide sanitizing activity. In fact, in some embodiments, the ability

of the source of alkalinity to act as an antimicrobial agent reduces the need for secondary antimicrobial agents within the composition. For example, percarbonate compositions have been demonstrated to provide excellent antimicrobial action. Nonetheless, some embodiments incorporate additional antimicrobial agents.

The given antimicrobial agent, depending on chemical composition and concentration, may simply limit further proliferation of numbers of the microbe or may destroy all or a portion of the microbial population. The terms "microbes" and "microorganisms" typically refer primarily to bacteria, virus, yeast, spores, and fungus microorganisms. In use, the antimicrobial agents are typically formed into a solid functional material that when diluted and dispensed, optionally, for example, using an aqueous stream forms an aqueous disinfectant or sanitizer composition that can be contacted with a variety of surfaces resulting in prevention of growth or the killing of a portion of the microbial population. A three log reduction of the microbial population results in a sanitizer composition. The antimicrobial agent can be encapsulated, for example, to improve its stability.

Common antimicrobial agents include phenolic antimicrobials such as pentachlorophenol, orthophenylphenol, a chloro-p-benzylphenol, p-chloro-m-xylenol. Halogen containing antibacterial agents include sodium trichloroisocyanurate, sodium dichloro isocyanate (anhydrous or dihydrate), iodine-poly(vinylpyrolidinone) complexes, bromine compounds such as 2-bromo-2-nitropropane-1,3-diol, and quaternary antimicrobial agents such as benzalkonium chloride, and didecyldimethyl ammonium chloride. Other antimicrobial compositions such as hexahydro-1,3,5-tris(2-hydroxyethyl)-*s*-triazine, dithiocarbamates such as sodium dimethyldithiocarbamate, and a variety of other materials are known in the art for their anti-microbial properties. In some embodiments, an antimicrobial component, such as TAED can be included in the range of 0.001 to 75 wt-% of the composition, about 0.01 to 20 wt-%, or about 0.05 to about 10 wt-%.

If present in compositions, the additional antimicrobial agent can be those listed in a table or about 0.01 to about 30 wt-% of the composition, 0.05 to about 10 wt-%, or about 0.1 to about 5 wt-%. In a use solution the additional antimicrobial

agent can be about 0.001 to about 5 wt-% of the composition, about 0.01 to about 2 wt-%, or about 0.05 to about 0.5 wt-%.

Activators

In some embodiments, the antimicrobial activity or bleaching activity of the composition can be enhanced by the addition of a material which, when the composition is placed in use, reacts with the active oxygen to form an activated component. For example, in some embodiments, a peracid or a peracid salt is formed. For example, in some embodiments, tetraacetylethylene diamine can be included within the composition to react with the active oxygen and form a peracid or a peracid salt that acts as an antimicrobial agent. Other examples of active oxygen activators include transition metals and their compounds, compounds that contain a carboxylic, nitrile, or ester moiety, or other such compounds known in the art. In an embodiment, the activator includes tetraacetylethylene diamine; transition metal; compound that includes carboxylic, nitrile, amine, or ester moiety; or mixtures thereof.

In some embodiments, an activator component can include in the range of 0.001 to 75 wt-%, about 0.01 to about 20 wt-%, or about 0.05 to about 10 wt-% of the composition.

In an embodiment, the activator for the source of alkalinity combines with the active oxygen to form an antimicrobial agent.

The solid composition typically remains stable even in the presence of activator of the source of alkalinity. In many compositions it would be expected to react with and destabilize or change the form of the source of alkalinity. In contrast, in an embodiment of the present invention, the composition remains solid; it does not swell, crack, or enlarge as it would if the source of alkalinity were reacting with the activator.

In an embodiment, the composition includes a solid block, and an activator material for the active oxygen is coupled to the solid block. The activator can be coupled to the solid block by any of a variety of methods for coupling one solid cleaning composition to another. For example, the activator can be in the form of a solid that is bound, affixed, glued or otherwise adhered to the solid block.

Alternatively, the solid activator can be formed around and encasing the block. By way of further example, the solid activator can be coupled to the solid block by the container or package for the cleaning composition, such as by a plastic or shrink wrap or film.

Additional Bleaching Agents

Additional bleaching agents for use in inventive formulations for lightening or whitening a substrate, include bleaching compounds capable of liberating an active halogen species, such as Cl_2, Br_2, 1_2, ClO_2, BrO_2, $1O_2$, $-OCl^{"}$, $-OBr^{"}$ and/or, $-01^{"}$, under conditions typically encountered during the cleansing process. Suitable bleaching agents for use in the present cleaning compositions include, for example, chlorine-containing compounds such as a chlorite, a hypochlorite, chloramine. Suitable halogen-releasing compounds include the alkali metal dichloroisocyanurates, chlorinated trisodium phosphate, the alkali metal hypochlorites, alkali metal chlorites, monochloramine and dichloramine, and the like, and mixtures thereof. Encapsulated chlorine sources may also be used to enhance the stability of the chlorine source in the composition (see, for example, U.S. Patent Nos. 4,618,914 and 4,830,773. A bleaching agent may also be an additional peroxygen or active oxygen source such as hydrogen peroxide, perborates, for example sodium perborate mono and tetrahydrate, sodium carbonate peroxyhydrate, phosphate peroxyhydrates, and potassium permonosulfate, with and without activators such as tetraacetylethylene diamine, and the like, as discussed above.

A cleaning composition may include a minor but effective additional amount of a bleaching agent above that already available from the stabilized source of alkalinity, e.g., about 0.1-10 wt-% or about 1-6 wt-%. The present solid compositions can include bleaching agent in an amount those listed in a table or about 0.1 to about 60 wt-%, about 1 to about 20 wt-%, about 3 to about 8 wt-%, or about 3 to about 6 wt-%.

Hardening Agents

The detergent compositions may also include a hardening agent in addition to, or in the form of, the builder. A hardening agent is a compound or system of compounds, organic or inorganic, which significantly contributes to the uniform solidification of the composition. The hardening agents should be compatible with the cleaning agent and other active ingredients of the composition and should be capable of providing an effective amount of hardness and/or aqueous solubility to the processed detergent composition. The hardening agents should also be capable of forming a homogeneous matrix with the cleaning agent and other ingredients when mixed and solidified to provide a uniform dissolution of the cleaning agent from the detergent composition during use.

The amount of hardening agent included in the detergent composition will vary according to factors including, but not limited to: the type of detergent composition being prepared, the ingredients of the detergent composition, the intended use of the detergent composition, the quantity of dispensing solution applied to the detergent composition over time during use, the temperature of the dispensing solution, the hardness of the dispensing solution, the physical size of the detergent composition, the concentration of the other ingredients, and the concentration of the cleaning agent in the composition. The amount of the hardening agent included in the solid detergent composition should be effective to combine with the cleaning agent and other ingredients of the composition to form a homogeneous mixture under continuous mixing conditions and a temperature at or below the melting temperature of the hardening agent.

The hardening agent may also form a matrix with the cleaning agent and other ingredients which will harden to a solid form under ambient temperatures of about 30° C to about 50° C, particularly about 35° C to about 45° C, after mixing ceases and the mixture is dispensed from the mixing system, within about 1 minute to about 3 hours, particularly about 2 minutes to about 2 hours, and particularly about 5 minutes to about 1 hour. A minimal amount of heat from an external source may be applied to the mixture to facilitate processing of the mixture. The amount of the hardening agent included in the detergent composition should be effective to provide a desired hardness and desired rate of controlled solubility of the processed

composition when placed in an aqueous medium to achieve a desired rate of dispensing the cleaning agent from the solidified composition during use.

The hardening agent may be an organic or an inorganic hardening agent. A particular organic hardening agent is a polyethylene glycol (PEG) compound. The solidification rate of detergent compositions comprising a polyethylene glycol hardening agent will vary, at least in part, according to the amount and the molecular weight of the polyethylene glycol added to the composition. Examples of suitable polyethylene glycols include, but are not limited to: solid polyethylene glycols of the general formula $H(OCH_2CH_2)_nOH$, where n is greater than 15, more particularly about 30 to about 1700. Typically, the polyethylene glycol is a solid in the form of a free-flowing powder or flakes, having a molecular weight of about 1,000 to about 100,000, particularly having a molecular weight of at least about 1,450 to about 20,000, more particularly between about 1,450 to about 8,000. The polyethylene glycol is present at a concentration of from about 1% to about 75% by weight and particularly about 3% to about 15% by weight. Suitable polyethylene glycol compounds include, but are not limited to: PEG 4000, PEG 1450, and PEG 8000 among others, with PEG 4000 and PEG 8000 being most preferred. An example of a commercially available solid polyethylene glycol includes, but is not limited to: CARBOWAX™, available from Union Carbide Corporation, Houston, TX.

Particular inorganic hardening agents are hydratable inorganic salts, including, but not limited to: sulfates, acetates, and bicarbonates. In an exemplary embodiment, the inorganic hardening agents are present at concentrations of up to about 50% by weight, particularly about 5% to about 25% by weight, and more particularly about 5% to about 15% by weight.

Urea particles may also be employed as hardeners in the detergent compositions. The solidification rate of the compositions will vary, at least in part, to factors including, but not limited to: the amount, the particle size, and the shape of the urea added to the detergent composition. For example, a particulate form of urea may be combined with a cleaning agent and other ingredients, as well as a minor but effective amount of water. The amount and particle size of the urea is effective to combine with the cleaning agent and other ingredients to form a homogeneous mixture without the application of heat from an external source to

melt the urea and other ingredients to a molten stage. The amount of urea included in the solid detergent composition should be effective to provide a desired hardness and desired rate of solubility of the composition when placed in an aqueous medium to achieve a desired rate of dispensing the cleaning agent from the solidified composition during use. In an exemplary embodiment, the detergent composition includes between about 5% to about 90% by weight urea, particularly between about 8% and about 40% by weight urea, and more particularly between about 10% and about 30% by weight urea.

The urea may be in the form of prilled beads or powder. Prilled urea is generally available from commercial sources as a mixture of particle sizes ranging from about 8-15 U.S. mesh, as for example, from Arcadian Sohio Company, Nitrogen Chemicals Division. A prilled form of urea is milled to reduce the particle size to about 50 U.S. mesh to about 125 U.S. mesh, particularly about 75-100 U.S. mesh, particularly using a wet mill such as a single or twin-screw extruder, a Teledyne mixer, a Ross emulsifier, and the like.

Secondary Hardening Agents/Solubility Modifiers.

The present compositions may include a minor but effective amount of a secondary hardening agent, as for example, an amide such stearic monoethanolamide or lauric diethanolamide, or an alkylamide, and the like; a solid polyethylene glycol, or a solid EO/PO block copolymer, and the like; starches that have been made water-soluble through an acid or alkaline treatment process; various inorganics that impart solidifying properties to a heated composition upon cooling, and the like. Such compounds may also vary the solubility of the composition in an aqueous medium during use such that the cleaning agent and/or other active ingredients may be dispensed from the solid composition over an extended period of time. The composition may include a secondary hardening agent in an amount those listed in a table or about 5 to about 20 wt-% or about 10 to about 15 wt-%.

Detergent Fillers

A cleaning composition may include an effective amount of one or more of a detergent filler which does not perform as a cleaning agent per se, but cooperates

with the cleaning agent to enhance the overall processability of the composition. Examples of fillers suitable for use in the present cleaning compositions include sodium sulfate, sodium chloride, starch, sugars, C_1-C_{10} alkylene glycols such as propylene glycol, and the like. A filler such as a sugar (e.g. sucrose) can aid dissolution of a solid composition by acting as a disintegrant. A detergent filler can be included in an amount listed in a table or up to about 50 wt-%, of about 1 to about 20 wt-%, about 3 to about 15 wt-%, about 1 to about 30 wt-%, or about 1.5 to about 25 wt-%.

Defoaming Agents

An effective amount of a defoaming agent for reducing the stability of foam may also be included in the present cleaning compositions. The cleaning composition can include about 0.0001-5 wt-% of a defoaming agent, e.g., about 0.01-3 wt-%. The defoaming agent can be provided in an amount of about 0.0001% to about 10 wt-%, about 0.001% to about 5 wt-%, or about 0.01% to about 1.0 wt-%.

Examples of defoaming agents suitable for use in the present compositions include silicone compounds such as silica dispersed in polydimethylsiloxane, EO/PO block copolymers, alcohol alkoxylates, fatty amides, hydrocarbon waxes, fatty acids, fatty esters, fatty alcohols, fatty acid soaps, ethoxylates, mineral oils, polyethylene glycol esters, alkyl phosphate esters such as monostearyl phosphate, and the like. A discussion of defoaming agents may be found, for example, in U.S. Patent No. 3,048,548 to Martin et al., U.S. Patent No. 3,334,147 to Brunelle et al., and U.S. Patent No. 3,442,242 to Rue et al.

Anti-redeposition Agents

A cleaning composition may also include an anti-redeposition agent capable of facilitating sustained suspension of soils in a cleaning solution and preventing the removed soils from being redeposited onto the substrate being cleaned. Examples of suitable anti-redeposition agents include fatty acid amides, fluorocarbon surfactants, complex phosphate esters, styrene maleic anhydride copolymers, and cellulosic derivatives such as hydroxyethyl cellulose, hydroxypropyl cellulose, and the like. A

cleaning composition may include about 0.5 to about 10 wt-%, e.g., about 1 to about 5 wt-%, of an anti-redeposition agent.

Optical Brighteners

Optical brightener is also referred to as fluorescent whitening agents or fluorescent brightening agents provide optical compensation for the yellow cast in fabric substrates. With optical brighteners yellowing is replaced by light emitted from optical brighteners present in the area commensurate in scope with yellow color. The violet to blue light supplied by the optical brighteners combines with other light reflected from the location to provide a substantially complete or enhanced bright white appearance. This additional light is produced by the brightener through fluorescence. Optical brighteners absorb light in the ultraviolet range 275 through 400 nm. and emit light in the ultraviolet blue spectrum 400-500 nm.

Fluorescent compounds belonging to the optical brightener family are typically aromatic or aromatic heterocyclic materials often containing condensed ring system. An important feature of these compounds is the presence of an uninterrupted chain of conjugated double bonds associated with an aromatic ring. The number of such conjugated double bonds is dependent on substituents as well as the planarity of the fluorescent part of the molecule. Most brightener compounds are derivatives of stilbene or 4,4'-diamino stilbene, biphenyl, five membered heterocycles (triazoles, oxazoles, imidazoles, etc.) or six membered heterocycles (cumarins, naphthalamides, triazines, etc.). The choice of optical brighteners for use in detergent compositions will depend upon a number of factors, such as the type of detergent, the nature of other components present in the detergent composition, the temperature of the wash water, the degree of agitation, and the ratio of the material washed to the tub size. The brightener selection is also dependent upon the type of material to be cleaned, e.g., cottons, synthetics, etc. Since most laundry detergent products are used to clean a variety of fabrics, the detergent compositions should contain a mixture of brighteners which are effective for a variety of fabrics. It is of course necessary that the individual components of such a brightener mixture be compatible.

Optical brighteners useful in the present invention are commercially available and will be appreciated by those skilled in the art. Commercial optical brighteners which may be useful in the present invention can be classified into subgroups, which include, but are not necessarily limited to, derivatives of stilbene, pyrazoline, coumarin, carboxylic acid, methinecyanines, dibenzothiophene-5,5-dioxide, azoles, 5- and 6-membered-ring heterocycles and other miscellaneous agents. Examples of these types of brighteners are disclosed in 'The Production and Application of Fluorescent Brightening Agents", M. Zahradnik, Published by John Wiley & Sons, New York (1982).

Stilbene derivatives which may be useful in the present invention include, but are not necessarily limited to, derivatives of bis(triazinyl)amino-stilbene; bisacylamino derivatives of stilbene; triazole derivatives of stilbene; oxadiazole derivatives of stilbene; oxazole derivatives of stilbene; and styryl derivatives of stilbene.

For laundry cleaning or sanitizing compositions, suitable optical brighteners include stilbene derivatives, which can be employed at concentrations of up to 1 wt-%.

Stabilizing Agents

The solid detergent composition may also include a stabilizing agent. Examples of suitable stabilizing agents include, but are not limited to: borate, calcium/magnesium ions, propylene glycol, and mixtures thereof. The composition need not include a stabilizing agent, but when the composition includes a stabilizing agent, it can be included in an amount that provides the desired level of stability of the composition. Suitable ranges of the stabilizing agent include those listed in a table or up to about 20 wt-%, about 0.5 to about 15 wt-%, or about 2 to about 10 wt-%.

Dispersants

The solid detergent composition may also include a dispersant. Examples of suitable dispersants that can be used in the solid detergent composition include, but

are not limited to: maleic acid/olefin copolymers, polyacrylic acid, and mixtures thereof. The composition need not include a dispersant, but when a dispersant is included it can be included in an amount that provides the desired dispersant properties. Suitable ranges of the dispersant in the composition can be those listed in a table or up to about 20 wt-%, about 0.5 to about 15 wt-%, or about 2 to about 9 wt-%.

Enzymes

Enzymes that can be included in the solid detergent composition include those enzymes that aid in the removal of starch and/or protein stains. Suitable types of enzymes include, but are not limited to: proteases, alpha-amylases, and mixtures thereof. Suitable proteases that can be used include, but are not limited to: those derived from *Bacillus licheniformix*, *Bacillus lenus*, *Bacillus alcalophilus*, and *Bacillus amyloliquefacins*. Suitable alpha-amylases include *Bacillus subtilis*, *Bacillus amyloliquefaciens*, and *Bacillus licheniformis*. The composition need not include an enzyme, but when the composition includes an enzyme, it can be included in an amount that provides the desired enzymatic activity when the solid detergent composition is provided as a use composition. Suitable ranges of the enzyme in the composition include those listed in a table or up to about 15 wt-%, about 0.5 to about 10 wt-%, or about 1 to about 5 wt-%.

Thickeners

The solid detergent compositions can include a rheology modifier or a thickener. The rheology modifier may provide the following functions: increasing the viscosity of the compositions; increasing the particle size of liquid use solutions when dispensed through a spray nozzle; providing the use solutions with vertical cling to surfaces; providing particle suspension within the use solutions; or reducing the evaporation rate of the use solutions.

The rheology modifier may provide a use composition that is pseudo plastic, in other words the use composition or material when left undisturbed (in a shear mode), retains a high viscosity. However, when sheared, the viscosity of the material is substantially but reversibly reduced. After the shear action is removed,

the viscosity returns. These properties permit the application of the material through a spray head. When sprayed through a nozzle, the material undergoes shear as it is drawn up a feed tube into a spray head under the influence of pressure and is sheared by the action of a pump in a pump action sprayer. In either case, the viscosity can drop to a point such that substantial quantities of the material can be applied using the spray devices used to apply the material to a soiled surface. However, once the material comes to rest on a soiled surface, the materials can regain high viscosity to ensure that the material remains in place on the soil. In an embodiment, the material can be applied to a surface resulting in a substantial coating of the material that provides the cleaning components in sufficient concentration to result in lifting and removal of the hardened or baked-on soil. While in contact with the soil on vertical or inclined surfaces, the thickeners in conjunction with the other components of the cleaner minimize dripping, sagging, slumping or other movement of the material under the effects of gravity. The material should be formulated such that the viscosity of the material is adequate to maintain contact substantial quantities of the film of the material with the soil for at least a minute, five minutes or more.

Examples of suitable thickeners or rheology modifiers are polymeric thickeners including, but not limited to: polymers or natural polymers or gums derived from plant or animal sources. Such materials may be polysaccharides such as large polysaccharide molecules having substantial thickening capacity.
Thickeners or rheology modifiers also include clays.

A substantially soluble polymeric thickener can be used to provide increased viscosity or increased conductivity to the use compositions. Examples of polymeric thickeners for the aqueous compositions of the invention include, but are not limited to: carboxylated vinyl polymers such as polyacrylic acids and sodium salts thereof, ethoxylated cellulose, polyacrylamide thickeners, cross-linked, xanthan compositions, sodium alginate and algin products, hydroxypropyl cellulose, hydroxyethyl cellulose, and other similar aqueous thickeners that have some substantial proportion of water solubility. Examples of suitable commercially available thickeners include, but are not limited to: Acusol™, available from Rohm & Haas Company, Philadelphia, PA; and Carbopol™, available from B. F. Goodrich, Charlotte, NC.

Examples of suitable polymeric thickeners include, but not limited to: polysaccharides. An example of a suitable commercially available polysaccharide includes, but is not limited to, Diutan™, available from Kelco Division of Merck, San Diego, CA. Thickeners for use in the solid detergent compositions further include polyvinyl alcohol thickeners, such as, fully hydrolyzed (greater than 98.5 mol acetate replaced with the -OH function).

An example of a suitable polysaccharide includes, but is not limited to, xanthans. Such xanthan polymers are suitable due to their high water solubility, and great thickening power. Xanthan is an extracellular polysaccharide of Xanthomonas campestras. Xanthan may be made by fermentation based on corn sugar or other corn sweetener by-products. Xanthan includes a poly beta-(l-4)-D-Glucopyranosyl backbone chain, similar to that found in cellulose. Aqueous dispersions of xanthan gum and its derivatives exhibit novel and remarkable rheological properties. Low concentrations of the gum have relatively high viscosities which permit it to be used economically. Xanthan gum solutions exhibit high pseudo plasticity, i.e. over a wide range of concentrations, rapid shear thinning occurs that is generally understood to be instantaneously reversible. Non-sheared materials have viscosities that appear to be independent of the pH and independent of temperature over wide ranges. Suitable xanthan materials include crosslinked xanthan materials. Xanthan polymers can be crosslinked with a variety of known covalent reacting crosslinking agents reactive with the hydroxyl functionality of large polysaccharide molecules and can also be crosslinked using divalent, trivalent or polyvalent metal ions. Such crosslinked xanthan gels are disclosed in U.S. Patent No. 4,782,901. Suitable crosslinking agents for xanthan materials include, but are not limited to: metal cations such as Al+3, Fe+3, Sb+3, Zr+4 and other transition metals. Examples of suitable commercially available xanthans include, but are not limited to: KELTROL®, KELZAN® AR, KELZAN® D35, KELZAN® S, KELZAN® XZ, available from Kelco Division of Merck, San Diego, CA. Known organic crosslinking agents can also be used. A suitable crosslinked xanthan is KELZAN® AR, which provides a pseudo plastic use solution that can produce large particle size mist or aerosol when sprayed.

The thickener can be in the present composition at amounts listed in a table or about 0.05 to about 10 wt-%, about 0.1 to about 8 wt-%, or about 0.2 wt-% to about 6 wt-%.

Dyes/Odorants

Various dyes, odorants including perfumes, and other aesthetic enhancing agents may also be included in the composition. Dyes may be included to alter the appearance of the composition, as for example, Direct Blue 86 (Miles), Fastusol Blue (Mobay Chemical Corp.), Acid Orange 7 (American Cyanamid), Basic Violet 10 (Sandoz), Acid Yellow 23 (GAF), Acid Yellow 17 (Sigma Chemical), Sap Green (Keyston Analine and Chemical), Metanil Yellow (Keystone Analine and Chemical), Acid Blue 9 (Hilton Davis), Sandolan Blue/Acid Blue 182 (Sandoz), Hisol Fast Red (Capitol Color and Chemical), Fluorescein™ (Capitol Color and Chemical), Acid Green 25 (Ciba-Geigy), and the like.

Fragrances or perfumes that may be included in the compositions include, for example, terpenoids such as citronellol, aldehydes such as amyl cinnamaldehyde, a jasmine such as CIS-jasmine or jasmal, vanillin, and the like.

The dye or odorant can be in the present solid composition at amounts of about 0.005 to about 5 wt-%, about 0.01 to about 3 wt-%, or about 0.2 wt-% to about 3 wt-%.

Use Compositions

The present calcium magnesium gluconate composition or a composition containing the calcium magnesium gluconate composition can be provided in the form of a concentrate or a use solution. In general, a concentrate refers to a composition that is intended to be diluted with water to provide a use solution that contacts an object to provide the desired cleaning, rising, or the like. A use solution may be prepared from the concentrate by diluting the concentrate with water at a dilution ratio that provides a use solution having desired detersive properties. In an exemplary embodiment, the concentrate may be diluted at a weight ratio of diluent to concentrate of at least about 1:1 or about 1:1 to about 2000:1.

The concentrate may be diluted with water at the location of use to provide the use solution. When the detergent composition is used in an automatic warewashing or dishwashing machine, it is expected that that the location of use will be inside the automatic warewashing machine. For example, when the detergent composition is used in a residential warewashing machine, the composition may be placed in the detergent compartment of the warewashing machine. Depending on the machine, the detergent may be provided in a unit dose form or in a multi-use form. In larger warewashing machines, a large quantity of detergent composition may be provided in a compartment that allows for the release of a single dose amount of the detergent composition for each wash cycle. Such a compartment may be provided as part of the warewashing machine or as a separate structure connected to the warewashing machine. For example, a block of the detergent composition may be provided in a hopper and introduced into the warewashing machine when water is sprayed against the surface of the block to provide a liquid concentrate.

The detergent composition may also be dispensed from a spray-type dispenser. Briefly, a spray-type dispenser functions by impinging a water spray upon an exposed surface of the detergent composition to dissolve a portion of the detergent composition, and then immediately directing the use solution out of the dispenser to a storage reservoir or directly to a point of use. When used, the product may be removed from the packaging (e.g. film) and inserted into the dispenser. The spray of water may be made by a nozzle in a shape that conforms to the shape of the solid detergent composition. The dispenser enclosure may also closely fit the shape of the detergent composition to prevent introducing and dispensing an incorrect detergent composition.

Embodiments of Solids

The present invention also relates to solid cleaning compositions including the calcium magnesium gluconate composition. For example, the present invention includes a cast solid block of the calcium magnesium gluconate composition and other components as desired. By way of further example, the present invention includes a pressed solid block or puck including calcium magnesium gluconate composition.

According to the present invention, a solid cleaning composition of a calcium magnesium gluconate composition can be prepared by a method including: providing a powder or crystalline form of calcium magnesium gluconate composition; melting the powder or crystalline form of the calcium magnesium gluconate composition; transferring the molten calcium magnesium gluconate composition into a mold; and cooling the molten composition to solidify it.

According to the present invention, a solid cleaning composition of a calcium magnesium gluconate composition can be prepared by a method including: providing a powder or crystalline form of a calcium magnesium gluconate composition; gently pressing the calcium magnesium gluconate to form a solid (e.g., block or puck).

A solid cleaning or rinsing composition as used in the present disclosure encompasses a variety of forms including, for example, solids, pellets, blocks, and tablets, but not powders. It should be understood that the term "solid" refers to the state of the detergent 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 greater than 120 °F.

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 washing cycle. 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.

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 detergent 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 10 kg. In certain embodiments, a multiple-use form of the solid cleaning composition has a mass of about 1 to 10 kg. In further embodiments, a multiple-use form of the solid cleaning composition has a mass of

about 5 g to about 8 kg. In other embodiments, a multiple-use form of the solid cleaning composition has a mass of about 5 kg to about 1 kg, or about 5 g and to 500 g.

Packaging System

In some embodiments, the solid composition can be packaged. The packaging receptacle or container may be rigid or flexible, and composed of any material suitable for containing the compositions produced according to the invention, as for example glass, metal, plastic film or sheet, cardboard, cardboard composites, paper, and the like.

Advantageously, since the composition is processed at or near ambient temperatures, the temperature of the processed mixture is low enough so that the mixture may be formed directly in the container or other packaging system without structurally damaging the material. As a result, a wider variety of materials may be used to manufacture the container than those used for compositions that processed and dispensed under molten conditions.

Suitable packaging used to contain the compositions is manufactured from a flexible, easy opening film material.

Dispensing of the Processed Compositions

The solid cleaning composition according to the present invention can be dispensed in any suitable method generally known. The cleaning or rinsing composition can be dispensed from a spray-type dispenser such as that disclosed in U.S. Patent Nos. 4,826,661, 4,690,305, 4,687,121, 4,426,362 and in U.S. Patent Nos. Re 32,763 and 32,818. Briefly, a spray-type dispenser functions by impinging a water spray upon an exposed surface of the solid 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. When used, the product is removed from the package (e.g.) film and is inserted into the dispenser. The spray of water can be made by a nozzle in a shape that conforms to the solid shape. The dispenser enclosure can also closely fit the detergent shape in a

dispensing system that prevents the introduction and dispensing of an incorrect detergent. The aqueous concentrate is generally directed to a use locus.

In an embodiment, the present composition can be dispensed by immersing either intermittently or continuously in water. The composition can then dissolve, for example, at a controlled or predetermined rate. The rate can be effective to maintain a concentration of dissolved cleaning agent that is effective for cleaning.

In an embodiment, the present composition can be dispensed by scraping solid from the solid composition and contacting the scrapings with water. The scrapings can be added to water to provide a concentration of dissolved cleaning agent that is effective for cleaning.

Methods Employing the Present Compositions

In an embodiment, the present invention includes methods employing the present calcium magnesium gluconate composition or a composition including the calcium magnesium gluconate composition. For example, in an embodiment, the present invention includes a method of reducing corrosion of a surface of a material exposed to alkalinity. The method includes contacting the surface with a liquid containing the calcium magnesium gluconate composition or a composition including the calcium magnesium gluconate composition. The liquid can include dissolved or dispersed composition. The method can also include providing the calcium magnesium gluconate composition or a composition including the gluconate; and dissolving the composition in a liquid diluent (e.g., water). The method can apply the liquid to any of a variety of surfaces or objects including surfaces or objects including or made of glass, ceramic, porcelain, or aluminum.

The present composition may be applied in any situation where it is desired to prevent surface corrosion or etching. The present composition may be employed in a commercial warewashing detergent composition to protect articles from corrosion or etching in automatic dishwashing or warewashing machines during cleaning, in the cleaning of transportation vehicles, or in the cleaning of bottles. Applications in which the present composition may be used include: warewashing, rinse aids, vehicle cleaning and care applications, hard surface cleaning and destaining, kitchen and bath cleaning and destaining, cleaning-in-place operations in

food and beverage production facilities, food processing equipment, general purpose cleaning and destaining, bottlewashing, and industrial or household cleaners.

Clean in Place

Other hard surface cleaning applications for the corrosion inhibitor compositions of the invention (or cleaning compositions including them) include clean-in-place systems (CIP), clean-out-of-place systems (COP), washer-decontaminators, sterilizers, textile laundry machines, ultra and nano-filtration systems and indoor air filters. COP systems can include readily accessible systems including wash tanks, soaking vessels, mop buckets, holding tanks, scrub sinks, vehicle parts washers, non-continuous batch washers and systems, and the like.

The cleaning of the in-place system or other surface (i.e., removal of unwanted offal therein) can be accomplished with a formulated detergent including the corrosion inhibitor compositions of the invention which is introduced with heated water. CIP typically employ flow rates on the order of about 40 to about 600 liters per minute, temperatures from ambient up to about 70°C, and contact times of at least about 10 seconds, for example, about 30 to about 120 seconds.

A method of cleaning substantially fixed in-place process facilities includes the following steps. The use solution of the invention is introduced into the process facilities at a temperature in the range of about 4 °C to 60 °C. After introduction of the use solution, the solution is held in a container or circulated throughout the system for a time sufficient to clean the process facilities (i.e., to remove undesirable soil). After the surfaces have been cleaned by means of the present composition, the use solution is drained. Upon completion of the cleaning step, the system optionally may be rinsed with other materials such as potable water. The composition can be circulated through the process facilities for 10 minutes or less.

Embodiments of Ratios

In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-2:1-2 and the weight ratio of water soluble magnesium salt to gluconate is 1:1 or greater. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-2:1-2 and the weight ratio

of water soluble magnesium salt to gluconate is 1.25:1 or greater. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-2:1-2 and the weight ratio of water soluble magnesium salt to gluconate is 1.5:1 or greater. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-2:1-2 and the weight ratio of water soluble magnesium salt to gluconate is 2:1 or greater.

In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.50:1-1.50 and the weight ratio of water soluble magnesium salt to gluconate is 1:1 or greater. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.50:1-1.50 and the weight ratio of water soluble magnesium salt to gluconate is 1.25:1 or greater. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.50:1-1.50 and the weight ratio of water soluble magnesium salt to gluconate is 1.5:1 or greater. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.50:1-1.50 and the weight ratio of water soluble magnesium salt to gluconate is 2:1 or greater.

In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.25:1-1.25 and the weight ratio of water soluble magnesium salt to gluconate is 1:1 or greater. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.25:1-1.25 and the weight ratio of water soluble magnesium salt to gluconate is 1.25:1 or greater. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.25:1-1.25 and the weight ratio of water soluble magnesium salt to gluconate is 1.5:1 or greater. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.25:1-1.25 and the weight ratio of water soluble magnesium salt to gluconate is 2:1 or greater.

In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1:1 and the weight ratio of water soluble magnesium salt to gluconate is 1:1 or greater. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1:1 and the weight ratio of water soluble magnesium salt to gluconate is 1.25:1 or greater. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1:1 and

the weight ratio of water soluble magnesium salt to gluconate is 1.5:1 or greater. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1:1 and the weight ratio of water soluble magnesium salt to gluconate is 2:1 or greater.

In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-2:1-2 and the weight ratio of water soluble calcium salt to gluconate is 1-19:1-13. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-2:1-2 and the weight ratio of water soluble calcium salt to gluconate is 1-15:1-8. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-2:1-2 and the weight ratio of water soluble calcium salt to gluconate is 3-10:1-5. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-2:1-2 and the weight ratio of water soluble calcium salt to gluconate is 3-8:2-4.

In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.50:1-1.50 and the weight ratio of water soluble calcium salt to gluconate is 1-19:1-13. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.50:1-1.50 and the weight ratio of water soluble calcium salt to gluconate is 1-15:1-8. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.50:1-1.50 and the weight ratio of water soluble calcium salt to gluconate is 3-10:1-5. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.50:1-1.50 and the weight ratio of water soluble calcium salt to gluconate is 3-8:2-4.

In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.25:1-1.25 and the weight ratio of water soluble calcium salt to gluconate is 1-19:1-13. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.25:1-1.25 and the weight ratio of water soluble calcium salt to gluconate is 1-15:1-8. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.25:1-1.25 and the weight ratio of water soluble calcium salt to gluconate is 3-10:1-5. In an embodiment, the weight ratio of water soluble calcium salt to water soluble

magnesium salt is 1-1.25:1-1.25 and the weight ratio of water soluble calcium salt to gluconate is 3-8:2-4.

In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1:1 and the weight ratio of water soluble calcium salt to gluconate is 1-19:1-13. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1:1 and the weight ratio of water soluble calcium salt to gluconate is 1-15:1-8. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1:1 and the weight ratio of water soluble calcium salt to gluconate is 3-10:1-5. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1:1 and the weight ratio of water soluble calcium salt to gluconate is 3-8:2-4.

In an embodiment, the weight ratio of water soluble magnesium salt to gluconate is 1:1 or greater and the weight ratio of water soluble calcium salt to gluconate is 1-19:1-13. In an embodiment, the weight ratio of water soluble magnesium salt to gluconate is 1:1 or greater and the weight ratio of water soluble calcium salt to gluconate is 1-15:1-8. In an embodiment, the weight ratio of water soluble magnesium salt to gluconate is 1:1 or greater and the weight ratio of water soluble calcium salt to gluconate is 3-10:1-5. In an embodiment, the weight ratio of water soluble magnesium salt to gluconate is 1:1 or greater and the weight ratio of water soluble calcium salt to gluconate is 3-8:2-4.

In an embodiment, the weight ratio of water soluble magnesium salt to gluconate is 1.25:1 or greater and the weight ratio of water soluble calcium salt to gluconate is 1-19:1-13. In an embodiment, the weight ratio of water soluble magnesium salt to gluconate is 1.25:1 or greater and the weight ratio of water soluble calcium salt to gluconate is 1-15:1-8. In an embodiment, the weight ratio of water soluble magnesium salt to gluconate is 1.25:1 or greater and the weight ratio of water soluble calcium salt to gluconate is 3-10:1-5. In an embodiment, the weight ratio of water soluble magnesium salt to gluconate is 1.25:1 or greater and the weight ratio of water soluble calcium salt to gluconate is 3-8:2-4.

In an embodiment, the weight ratio of water soluble magnesium salt to gluconate is 1.5:1 or greater and the weight ratio of water soluble calcium salt to gluconate is 1-19:1-13. In an embodiment, the weight ratio of water soluble

magnesium salt to gluconate is 1.5:1 or greater and the weight ratio of water soluble calcium salt to gluconate is 1-15:1-8. In an embodiment, the weight ratio of water soluble magnesium salt to gluconate is 1.5:1 or greater and the weight ratio of water soluble calcium salt to gluconate is 3-10:1-5. In an embodiment, the weight ratio of water soluble magnesium salt to gluconate is 1.5:1 or greater and the weight ratio of water soluble calcium salt to gluconate is 3-8:2-4.

In an embodiment, the weight ratio of water soluble magnesium salt to gluconate is 2:1 or greater and the weight ratio of water soluble calcium salt to gluconate is 1-19:1-13. In an embodiment, the weight ratio of water soluble magnesium salt to gluconate is 2:1 or greater and the weight ratio of water soluble calcium salt to gluconate is 1-15:1-8.

In an embodiment, the weight ratio of water soluble magnesium salt to gluconate is 2:1 or greater and the weight ratio of water soluble calcium salt to gluconate is 3-10:1-5. In an embodiment, the weight ratio of water soluble magnesium salt to gluconate is 2:1 or greater and the weight ratio of water soluble calcium salt to gluconate is 3-8:2-4.

In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-2:1-2, the weight ratio of water soluble magnesium salt to gluconate is 1:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 1-19:1-13. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-2:1-2, the weight ratio of water soluble magnesium salt to gluconate is 1:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 1-15:1-8. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-2:1-2, the weight ratio of water soluble magnesium salt to gluconate is 1:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 3-10:1-5. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-2:1-2, the weight ratio of water soluble magnesium salt to gluconate is 1:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 3-8:2-4.

In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-2:1-2, the weight ratio of water soluble magnesium salt to gluconate is 1.25:1 or greater, and the weight ratio of water soluble calcium salt to

gluconate is 1-19:1-13. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-2:1-2, the weight ratio of water soluble magnesium salt to gluconate is 1.25:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 1-15:1-8. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-2:1-2, the weight ratio of water soluble magnesium salt to gluconate is 1.25:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 3-10:1-5. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-2:1-2, the weight ratio of water soluble magnesium salt to gluconate is 1.25:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 3-8:2-4.

In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-2:1-2, the weight ratio of water soluble magnesium salt to gluconate is 1.5:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 1-19:1-13. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-2:1-2, the weight ratio of water soluble magnesium salt to gluconate is 1.5:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 1-15:1-8. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-2:1-2, the weight ratio of water soluble magnesium salt to gluconate is 1.5:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 3-10:1-5. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-2:1-2, the weight ratio of water soluble magnesium salt to gluconate is 1.5:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 3-8:2-4.

In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-2:1-2, the weight ratio of water soluble magnesium salt to gluconate is 2:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 1-19:1-13. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-2:1-2, the weight ratio of water soluble magnesium salt to gluconate is 2:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 1-15:1-8. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-2:1-2, the weight ratio of

water soluble magnesium salt to gluconate is 2:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 3-10:1-5. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-2:1-2, the weight ratio of water soluble magnesium salt to gluconate is 2:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 3-8:2-4.

In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.50:1-1.50, the weight ratio of water soluble magnesium salt to gluconate is 1:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 1-19:1-13. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.50:1-1.50, the weight ratio of water soluble magnesium salt to gluconate is 1:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 1-15:1-8. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.50:1-1.50, the weight ratio of water soluble magnesium salt to gluconate is 1:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 3-10:1-5. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.50:1-1.50, the weight ratio of water soluble magnesium salt to gluconate is 1:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 3-8:2-4.

In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.50:1-1.50, the weight ratio of water soluble magnesium salt to gluconate is 1.25:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 1-19:1-13. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.50:1-1.50, the weight ratio of water soluble magnesium salt to gluconate is 1.25:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 1-15:1-8. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.50:1-1.50, the weight ratio of water soluble magnesium salt to gluconate is 1.25:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 3-10:1-5. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.50:1-1.50, the weight ratio of water

soluble magnesium salt to gluconate is 1.25:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 3-8:2-4.

In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.50:1-1.50, the weight ratio of water soluble magnesium salt to gluconate is 1.5:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 1-19:1-13. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.50:1-1.50, the weight ratio of water soluble magnesium salt to gluconate is 1.5:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 1-15:1-8. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.50:1-1.50, the weight ratio of water soluble magnesium salt to gluconate is 1.5:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 3-10:1-5. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.50:1-1.50, the weight ratio of water soluble magnesium salt to gluconate is 1.5:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 3-8:2-4.

In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.50:1-1.50, the weight ratio of water soluble magnesium salt to gluconate is 2:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 1-19:1-13. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.50:1-1.50, the weight ratio of water soluble magnesium salt to gluconate is 2:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 1-15:1-8. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.50:1-1.50, the weight ratio of water soluble magnesium salt to gluconate is 2:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 3-10:1-5. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.50:1-1.50, the weight ratio of water soluble magnesium salt to gluconate is 2:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 3-8:2-4.

In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.25:1-1.25, the weight ratio of water soluble

magnesium salt to gluconate is 1:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 1-19:1-13. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.25:1-1.25, the weight ratio of water soluble magnesium salt to gluconate is 1:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 1-15:1-8. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.25:1-1.25, the weight ratio of water soluble magnesium salt to gluconate is 1:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 3-10:1-5. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.25:1-12.5, the weight ratio of water soluble magnesium salt to gluconate is 1:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 3-8:2-4.

In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.25:1-1.25, the weight ratio of water soluble magnesium salt to gluconate is 1.25:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 1-19:1-13. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.25:1-1.25, the weight ratio of water soluble magnesium salt to gluconate is 1.25:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 1-15:1-8. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.25:1-1.25, the weight ratio of water soluble magnesium salt to gluconate is 1.25:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 3-10:1-5. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.25:1-1.25, the weight ratio of water soluble magnesium salt to gluconate is 1.25:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 3-8:2-4.

In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.25:1-1.25, the weight ratio of water soluble magnesium salt to gluconate is 1.5:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 1-19:1-13. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.25:1-1.25, the weight ratio of water soluble magnesium salt to gluconate is 1.5:1 or greater, and the weight

ratio of water soluble calcium salt to gluconate is 1-15:1-8. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.25:1-1.25, the weight ratio of water soluble magnesium salt to gluconate is 1.5:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 3-10:1-5. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.25:1-1.25, the weight ratio of water soluble magnesium salt to gluconate is 1.5:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 3-8:2-4.

In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.25:1-1.25, the weight ratio of water soluble magnesium salt to gluconate is 2:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 1-19:1-13. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.25:1-1.25, the weight ratio of water soluble magnesium salt to gluconate is 2:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 1-15:1-8. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.25:1-1.25, the weight ratio of water soluble magnesium salt to gluconate is 2:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 3-10:1-5. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.25:1-1.25, the weight ratio of water soluble magnesium salt to gluconate is 2:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 3-8:2-4.

In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1:1, the weight ratio of water soluble magnesium salt to gluconate is 1:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 1-19:1-13. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1:1, the weight ratio of water soluble magnesium salt to gluconate is 1:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 1-15:1-8. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1:1, the weight ratio of water soluble magnesium salt to gluconate is 1:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 3-10:1-5. In an embodiment, the weight ratio of

water soluble calcium salt to water soluble magnesium salt is 1:1, the weight ratio of water soluble magnesium salt to gluconate is 1:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 3-8:2-4.

In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1:1, the weight ratio of water soluble magnesium salt to gluconate is 1.25:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 1-19:1-13. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1:1, the weight ratio of water soluble magnesium salt to gluconate is 1.25:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 1-15:1-8. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1:1, the weight ratio of water soluble magnesium salt to gluconate is 1.25:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 3-10:1-5. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 11:1, the weight ratio of water soluble magnesium salt to gluconate is 1.25:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 3-8:2-4.

In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1:1, the weight ratio of water soluble magnesium salt to gluconate is 1.5:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 1-19:1-13. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1:1, the weight ratio of water soluble magnesium salt to gluconate is 1.5:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 1-15:1-8. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1:1, the weight ratio of water soluble magnesium salt to gluconate is 1.5:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 3-10:1-5. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1:1, the weight ratio of water soluble magnesium salt to gluconate is 1.5:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 3-8:2-4.

In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1:1, the weight ratio of water soluble magnesium salt to gluconate is 2:1 or greater, and the weight ratio of water soluble calcium salt to

gluconate is 1-19:1-13. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1:1, the weight ratio of water soluble magnesium salt to gluconate is 2:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 1-15:1-8. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1:1, the weight ratio of water soluble magnesium salt to gluconate is 2:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 3-10:1-5. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1:1, the weight ratio of water soluble magnesium salt to gluconate is 2:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 3-8:2-4.

In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-2:1-2 and the weight ratio of water soluble calcium salt to gluconate is 4-7:1-3. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-2:1-2 and the weight ratio of water soluble calcium salt to gluconate is 5-6:1-2. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-2:1-2 and the weight ratio of water soluble calcium salt to gluconate is 5.2-5.8:1.2-1.8. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-2:1-2 and the weight ratio of water soluble calcium salt to gluconate is 11:3.

In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.50:1-1.50 and the weight ratio of water soluble calcium salt to gluconate is 4-7:1-3. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.50:1-1.50 and the weight ratio of water soluble calcium salt to gluconate is 5-6:1-2. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.50:1-1.50 and the weight ratio of water soluble calcium salt to gluconate is 5.2-5.8:1.2-1.8. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.50:1-1.50 and the weight ratio of water soluble calcium salt to gluconate is 11:3.

In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.25:1-1.25 and the weight ratio of water soluble calcium salt to gluconate is 4-7:1-3. In an embodiment, the weight ratio of water

soluble calcium salt to water soluble magnesium salt is 1-1.25:1-1.25 and the weight ratio of water soluble calcium salt to gluconate is 5-6:1-2. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.25:1-1.25 and the weight ratio of water soluble calcium salt to gluconate is 5.2-5.8:1.2-1.8. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.25:1-1.25 and the weight ratio of water soluble calcium salt to gluconate is 11:3.

In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1:1 and the weight ratio of water soluble calcium salt to gluconate is 4-7:1-3. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1:1 and the weight ratio of water soluble calcium salt to gluconate is 5-6:1-2. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1:1 and the weight ratio of water soluble calcium salt to gluconate is 5.2-5.8:1.2-1.8. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1:1 and the weight ratio of water soluble calcium salt to gluconate is 11:3.

In an embodiment, the weight ratio of water soluble magnesium salt to gluconate is 1:1 or greater and the weight ratio of water soluble calcium salt to gluconate is 4-7:1-3. In an embodiment, the weight ratio of water soluble magnesium salt to gluconate is 1:1 or greater and the weight ratio of water soluble calcium salt to gluconate is 5-6:1-2. In an embodiment, the weight ratio of water soluble magnesium salt to gluconate is 1:1 or greater and the weight ratio of water soluble calcium salt to gluconate is 5.2-5.8:1.2-1.8. In an embodiment, the weight ratio of water soluble magnesium salt to gluconate is 1:1 or greater and the weight ratio of water soluble calcium salt to gluconate is 11:3.

In an embodiment, the weight ratio of water soluble magnesium salt to gluconate is 1.25:1 or greater and the weight ratio of water soluble calcium salt to gluconate is 4-7:1-3. In an embodiment, the weight ratio of water soluble magnesium salt to gluconate is 1.25:1 or greater and the weight ratio of water soluble calcium salt to gluconate is 5-6:1-2. In an embodiment, the weight ratio of water soluble magnesium salt to gluconate is 1.25:1 or greater and the weight ratio of water soluble calcium salt to gluconate is 5.2-5.8:1.2-1.8. In an embodiment, the

weight ratio of water soluble magnesium salt to gluconate is 1.25:1 or greater and the weight ratio of water soluble calcium salt to gluconate is 11:3.

In an embodiment, the weight ratio of water soluble magnesium salt to gluconate is 1.5:1 or greater and the weight ratio of water soluble calcium salt to gluconate is 4-7:1-3. In an embodiment, the weight ratio of water soluble magnesium salt to gluconate is 1.5:1 or greater and the weight ratio of water soluble calcium salt to gluconate is 5-6:1-2. In an embodiment, the weight ratio of water soluble magnesium salt to gluconate is 1.5:1 or greater and the weight ratio of water soluble calcium salt to gluconate is 5.2-5.8:1.2-1.8. In an embodiment, the weight ratio of water soluble magnesium salt to gluconate is 1.5:1 or greater and the weight ratio of water soluble calcium salt to gluconate is 11:3.

In an embodiment, the weight ratio of water soluble magnesium salt to gluconate is 2:1 or greater and the weight ratio of water soluble calcium salt to gluconate is 4-7:1-3. In an embodiment, the weight ratio of water soluble magnesium salt to gluconate is 2:1 or greater and the weight ratio of water soluble calcium salt to gluconate is 5-6:1-2.

In an embodiment, the weight ratio of water soluble magnesium salt to gluconate is 2:1 or greater and the weight ratio of water soluble calcium salt to gluconate is 5.2-5.8:1.2-1.8. In an embodiment, the weight ratio of water soluble magnesium salt to gluconate is 2:1 or greater and the weight ratio of water soluble calcium salt to gluconate is 11:3.

In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-2:1-2, the weight ratio of water soluble magnesium salt to gluconate is 1:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 4-7:1-3. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-2:1-2, the weight ratio of water soluble magnesium salt to gluconate is 1:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 5-6:1-2. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-2:1-2, the weight ratio of water soluble magnesium salt to gluconate is 1:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 5.2-5.8:1.2-1.8. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-2:1-

2, the weight ratio of water soluble magnesium salt to gluconate is 1:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 11:3.

In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-2:1-2, the weight ratio of water soluble magnesium salt to gluconate is 1.25:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 4-7:1-3. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-2:1-2, the weight ratio of water soluble magnesium salt to gluconate is 1.25:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 5-6:1-2. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-2:1-2, the weight ratio of water soluble magnesium salt to gluconate is 1.25:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 5.2-5.8:1.2-1.8. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-2:1-2, the weight ratio of water soluble magnesium salt to gluconate is 1.25:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 11:3.

In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-2:1-2, the weight ratio of water soluble magnesium salt to gluconate is 1.5:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 4-7:1-3. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-2:1-2, the weight ratio of water soluble magnesium salt to gluconate is 1.5:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 5-6:1-2. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-2:1-2, the weight ratio of water soluble magnesium salt to gluconate is 1.5:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 5.2-5.8:1.2-1.8. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-2:1-2, the weight ratio of water soluble magnesium salt to gluconate is 1.5:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 11:3.

In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-2:1-2, the weight ratio of water soluble magnesium salt to gluconate is 2:1 or greater, and the weight ratio of water soluble calcium salt to

gluconate is 4-7:1-3. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-2:1-2, the weight ratio of water soluble magnesium salt to gluconate is 2:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 5-6:1-2. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-2:1-2, the weight ratio of water soluble magnesium salt to gluconate is 2:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 5.2-5.8:1.2-1.8. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-2:1-2, the weight ratio of water soluble magnesium salt to gluconate is 2:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 11:3.

In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.50:1-1.50, the weight ratio of water soluble magnesium salt to gluconate is 1:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 4-7:1-3. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.50:1-1.50, the weight ratio of water soluble magnesium salt to gluconate is 1:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 5-6:1-2. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.50:1-1.50, the weight ratio of water soluble magnesium salt to gluconate is 1:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 5.2-5.8:1.2-1.8. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.50:1-1.50, the weight ratio of water soluble magnesium salt to gluconate is 1:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 11:3.

In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.50:1-1.50, the weight ratio of water soluble magnesium salt to gluconate is 1.25:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 4-7:1-3. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.50:1-1.50, the weight ratio of water soluble magnesium salt to gluconate is 1.25:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 5-6:1-2. In an embodiment, the weight ratio of water soluble calcium salt to water soluble

magnesium salt is 1-1.50:1-1.50, the weight ratio of water soluble magnesium salt to gluconate is 1.25:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 5.2-5.8:1.2-1.8. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.50:1-1.50, the weight ratio of water soluble magnesium salt to gluconate is 1.25:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 11:3.

In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.50:1-1.50, the weight ratio of water soluble magnesium salt to gluconate is 1.5:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 4-7:1-3. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.50:1-1.50, the weight ratio of water soluble magnesium salt to gluconate is 1.5:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 5-6:1-2. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.50:1-1.50, the weight ratio of water soluble magnesium salt to gluconate is 1.5:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 5.2-5.8:1.2-1.8. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.50:1-1.50, the weight ratio of water soluble magnesium salt to gluconate is 1.5:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 11:3.

In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.50:1-1.50, the weight ratio of water soluble magnesium salt to gluconate is 2:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 4-7:1-3. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.50:1-1.50, the weight ratio of water soluble magnesium salt to gluconate is 2:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 5-6:1-2. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.50:1-1.50, the weight ratio of water soluble magnesium salt to gluconate is 2:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 5.2-5.8:1.2-1.8. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.50:1-1.50, the weight ratio of water soluble

magnesium salt to gluconate is 2:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 11:3.

In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.25:1-1.25, the weight ratio of water soluble magnesium salt to gluconate is 1:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 4-7:1-3. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.25:1-1.25, the weight ratio of water soluble magnesium salt to gluconate is 1:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 5-6:1-2. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.25:1-1.25, the weight ratio of water soluble magnesium salt to gluconate is 1:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 5.2-5.8:1.2-1.8. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.25:1-12.5, the weight ratio of water soluble magnesium salt to gluconate is 1:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 11:3.

In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.25:1-1.25, the weight ratio of water soluble magnesium salt to gluconate is 1.25:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 4-7:1-3. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.25:1-1.25, the weight ratio of water soluble magnesium salt to gluconate is 1.25:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 5-6:1-2. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.25:1-1.25, the weight ratio of water soluble magnesium salt to gluconate is 1.25:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 5.2-5.8:1.2-1.8. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.25:1-1.25, the weight ratio of water soluble magnesium salt to gluconate is 1.25:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 11:3.

In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.25:1-1.25, the weight ratio of water soluble

magnesium salt to gluconate is 1.5:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 4-7:1-3. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.25:1-1.25, the weight ratio of water soluble magnesium salt to gluconate is 1.5:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 5-6:1-2. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.25:1-1.25, the weight ratio of water soluble magnesium salt to gluconate is 1.5:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 5.2-5.8:1.2-1.8. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.25:1-1.25, the weight ratio of water soluble magnesium salt to gluconate is 1.5:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 11:3.

In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.25:1-1.25, the weight ratio of water soluble magnesium salt to gluconate is 2:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 4-7:1-3. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.25:1-1.25, the weight ratio of water soluble magnesium salt to gluconate is 2:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 5-6:1-2. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.25:1-1.25, the weight ratio of water soluble magnesium salt to gluconate is 2:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 5.2-5.8:1.2-1.8. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1-1.25:1-1.25, the weight ratio of water soluble magnesium salt to gluconate is 2:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 11:3.

In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1:1, the weight ratio of water soluble magnesium salt to gluconate is 1:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 4-7:1-3. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1:1, the weight ratio of water soluble magnesium salt to gluconate is 1:1 or greater, and the weight ratio of water soluble

calcium salt to gluconate is 5-6:1-2. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1:1, the weight ratio of water soluble magnesium salt to gluconate is 1:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 5.2-5.8:1.2-1.8. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1:1, the weight ratio of water soluble magnesium salt to gluconate is 1:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 11:3.

In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1:1, the weight ratio of water soluble magnesium salt to gluconate is 1.25:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 4-7:1-3. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1:1, the weight ratio of water soluble magnesium salt to gluconate is 1.25:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 5-6:1-2. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1:1, the weight ratio of water soluble magnesium salt to gluconate is 1.25:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 5.2-5.8:1.2-1.8. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 11:1, the weight ratio of water soluble magnesium salt to gluconate is 1.25:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 11:3.

In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1:1, the weight ratio of water soluble magnesium salt to gluconate is 1.5:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 4-7:1-3. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1:1, the weight ratio of water soluble magnesium salt to gluconate is 1.5:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 5-6:1-2. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1:1, the weight ratio of water soluble magnesium salt to gluconate is 1.5:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 5.2-5.8:1.2-1.8. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1:1, the weight

ratio of water soluble magnesium salt to gluconate is 1.5:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 11:3.

In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1:1, the weight ratio of water soluble magnesium salt to gluconate is 2:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 4-7:1-3. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1:1, the weight ratio of water soluble magnesium salt to gluconate is 2:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 5-6:1-2. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1:1, the weight ratio of water soluble magnesium salt to gluconate is 2:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 5.2-5.8:1.2-1.8. In an embodiment, the weight ratio of water soluble calcium salt to water soluble magnesium salt is 1:1, the weight ratio of water soluble magnesium salt to gluconate is 2:1 or greater, and the weight ratio of water soluble calcium salt to gluconate is 11:3.

The present corrosion inhibitor can include 1 wt-% gluconate and also include amounts of water soluble magnesium salt and water soluble calcium salt to provide an embodiment of these ratios. The present corrosion inhibitor can include 2wt-% gluconate and also include amounts of water soluble magnesium salt and water soluble calcium salt to provide an embodiment of these ratios. The present corrosion inhibitor can include 3wt-% gluconate and also include amounts of water soluble magnesium salt and water soluble calcium salt to provide an embodiment of these ratios. The present corrosion inhibitor can include 4wt-% gluconate and also include amounts of water soluble magnesium salt and water soluble calcium salt to provide an embodiment of these ratios. The present corrosion inhibitor can include 5 wt-% gluconate and also include amounts of water soluble magnesium salt and water soluble calcium salt to provide an embodiment of these ratios. The present corrosion inhibitor can include 6 wt-% gluconate and also include amounts of water soluble magnesium salt and water soluble calcium salt to provide an embodiment of these ratios. The present corrosion inhibitor can include 7 wt-% gluconate and also include amounts of water soluble magnesium salt and water soluble calcium salt to provide an embodiment of these ratios. The present corrosion inhibitor can include

8 wt-% gluconate and also include amounts of water soluble magnesium salt and water soluble calcium salt to provide an embodiment of these ratios. The present corrosion inhibitor can include 9 wt-% gluconate and also include amounts of water soluble magnesium salt and water soluble calcium salt to provide an embodiment of these ratios.

The present corrosion inhibitor can include 10 wt-% gluconate and also include amounts of water soluble magnesium salt and water soluble calcium salt to provide an embodiment of these ratios. The present corrosion inhibitor can include 11 wt-% gluconate and also include amounts of water soluble magnesium salt and water soluble calcium salt to provide an embodiment of these ratios. The present corrosion inhibitor can include 12 wt-% gluconate and also include amounts of water soluble magnesium salt and water soluble calcium salt to provide an embodiment of these ratios. The present corrosion inhibitor can include 13 wt-% gluconate and also include amounts of water soluble magnesium salt and water soluble calcium salt to provide an embodiment of these ratios. The present corrosion inhibitor can include 14 wt-% gluconate and also include amounts of water soluble magnesium salt and water soluble calcium salt to provide an embodiment of these ratios. The present corrosion inhibitor can include 15 wt-% gluconate and also include amounts of water soluble magnesium salt and water soluble calcium salt to provide an embodiment of these ratios. The present corrosion inhibitor can include 16 wt-% gluconate and also include amounts of water soluble magnesium salt and water soluble calcium salt to provide an embodiment of these ratios. The present corrosion inhibitor can include 17 wt-% gluconate and also include amounts of water soluble magnesium salt and water soluble calcium salt to provide an embodiment of these ratios. The present corrosion inhibitor can include 18 wt-% gluconate and also include amounts of water soluble magnesium salt and water soluble calcium salt to provide an embodiment of these ratios. The present corrosion inhibitor can include 19 wt-% gluconate and also include amounts of water soluble magnesium salt and water soluble calcium salt to provide an embodiment of these ratios.

The present corrosion inhibitor can include 20 wt-% gluconate and also include amounts of water soluble magnesium salt and water soluble calcium salt to

provide an embodiment of these ratios. The present corrosion inhibitor can include 21 wt-% gluconate and also include amounts of water soluble magnesium salt and water soluble calcium salt to provide an embodiment of these ratios. The present corrosion inhibitor can include 22 wt-% gluconate and also include amounts of water soluble magnesium salt and water soluble calcium salt to provide an embodiment of these ratios. The present corrosion inhibitor can include 23 wt-% gluconate and also include amounts of water soluble magnesium salt and water soluble calcium salt to provide an embodiment of these ratios. The present corrosion inhibitor can include 24 wt-% gluconate and also include amounts of water soluble magnesium salt and water soluble calcium salt to provide an embodiment of these ratios. The present corrosion inhibitor can include 25 wt-% gluconate and also include amounts of water soluble magnesium salt and water soluble calcium salt to provide an embodiment of these ratios.

The present invention may be better understood with reference to the following examples. These examples are intended to be representative of specific embodiments of the invention, and are not intended as limiting the scope of the invention.

EXAMPLES

Example 1 -- Magnesium Salt, Calcium Salt and Gluconate Synergistically Reduced Corrosion of Aluminum

Compositions of hardness ions (e.g., calcium and magnesium ions) and gluconate synergistically reduced corrosion of aluminum.

Materials and Methods

Coupons of aluminum 6061(1" x 3"x 1/16") were immersed in a series of compositions having a total of about 400 ppm of magnesium chloride, calcium chloride, and sodium gluconate. Table 1, below, shows the actual amounts of magnesium chloride, calcium chloride and gluconate in each composition. The compositions also included about 400 ppm of a 50/50 blend of sodium carbonate/sodium hydroxide to provide alkalinity as a source of corrosion. The

compositions were prepared by mixing the components of the compositions together and stirring until a homogeneous mixture was formed.

The compositions were incubated for 24 hours at 160 °F. The amount of aluminum dissolved into solution from the aluminum coupons by the alkalinity was determined. The amount of aluminum present in solution reflected the rate of aluminum corrosion and etching.

Results

Table 1 shows the component compositions and amount of aluminum removed from the aluminum coupons.

Table 1

Composition	$MgCl_2$ (ppm)	$CaCl_2$ (ppm)	Sodium Gluconate (ppm)	Aluminum Dissolved Into Solution (ppm)
1	0	400	0	38.2
2	100	300	0	30.4
3	200	200	0	62.1
4	300	100	0	26.5
5	400	0	0	29.9
6	300	0	100	31.5
7	200	0	200	41.2
8	100	0	300	53.9
9	0	0	400	50.6
10	0	100	300	48.3
11	0	200	200	49.5
12	0	300	100	52.3
13	100	200	100	31
14	200	100	100	27.6
15	100	100	200	37.5
16	50	300	50	33.3
17	300	50	50	30.3
18	50	50	300	36
19	133	133	132	27.2

Figure 1 shows a ternary graph illustrating the reduced corrosion of aluminum as a function of the concentrations of magnesium, calcium, and gluconate. This ternary graph was produced by entering the data in Table 1 into a statistics program, Design Expert, version 6.0.11, available from Stat-Ease, Minneapolis, MN. The program analyzed the raw data to find a trend and developed the following equation, Equation 1:

Al in soln (ppm) = 0.099653 * CaCl2 + 0.072577 * MgCl2 + 0.12246 * Na gluconate - 1.96236E-004 * CaCl2 * MgCl2 + 1.35722E-004 * CaCl2 * Na gluconate + 7.92997E-005 * MgCl2 * Na gluconate - 4.61845E-006 * CaCl2 * MgCl2 * Na gluconate

Equation 1 was then plotted to create the ternary graph depicted in Figure 1.

Discussion

Figure 1 shows that water soluble magnesium salt, water soluble calcium salt, and gluconate reduced aluminum corrosion at selected synergistic ratios and beyond. Synergistic ratios include:

	Synergistic Weight Ratios			
Water soluble calcium salt to water soluble magnesium salt	1-2:1-2	1-1.50:1-1.50	1-1.25:1-1.25	1:1
Water soluble magnesium salt to gluconate	1:1 or greater	1.25:1 or greater	1.5:1 or greater	2:1 or greater
Water soluble calcium salt to gluconate	1-19:1-13	1-15:1-8	3-10:1-5	3-8:2-4

Example 2 -- Magnesium Salt, Calcium Salt and Gluconate Reduced Corrosion of Aluminum and Galvanized Steel Better Than Other Corrosion Inhibitors

Corrosion inhibitors containing hardness ions (e.g., Ca^{2+} and Mg^{2+}) and gluconate were compared to conventional corrosion inhibitors and found to provide superior protection of two soft metals, aluminum and galvanized steel.

Materials and Methods

Coupons were cut from aluminum (1100 grade) and from galvanized steel to a size of 1"x3". The coupons were cleaned, weighed, and contacted with an alkaline cleaning composition by immersion or foaming. The aluminum coupons were immersed for 8 hours, the galvanized steel coupons for 24 hours. In a first foaming method, the coupons were suspended above a foaming alkaline cleaning composition, the composition was foamed, and the coupons remained in the foam for 8 hours (Glewwe foaming test). In a second foaming method, the coupons were suspended in a foaming station. The coupons were subjected to repeated cycles of contacting with a foaming alkaline cleaning composition, rinsing, and drying over 24 hours. After contacting with the cleaning composition, the coupons are cleaned and weighed again.

The alkaline cleaning compositions were:

wt-%

Ingredient	A	B
Alkali Metal Hydroxide	16	11
Builder	4.1	5
Surfactant	6	25
Water	67	32
Chlorine Source	0.1	0.1
Corrosion Inhibitor	v	v
Use Dilution	2.5	1.4

The corrosion inhibitors tested were: 500 ppm amine borate corrosion inhibitor; 500 ppm amine borate plus 500 ppm ester of oxid petro; 700 ppm Crodasinic™ O; 175 ppm potassium silicate plus 1400 ppm boric acid; 425 ppm Berol™ 425; 900 ppm sodium nitrate; 400 ppm PEG-600 Diacid; 2000 ppm PEG-600; calcium magnesium gluconate composition #1 (inverted, 133 ppm, 229 ppm, 57 ppm); calcium magnesium gluconate composition #2 (344 ppm, 80 ppm, 57 ppm); calcium chloride, magnesium chloride, silicate (186 ppm, 80 ppm, 200 ppm); Acusol, sodium sulfite, sodium gluconate (325 ppm, 1130 ppm, 2828 ppm); calcium

chloride, magnesium chloride, aminopropylsilanetriol (186 ppm, 80 ppm, 200 ppm); 200 ppm aminopropylsilanetriol (APST); aminopropylsilanetriol pretreatment; and mineral oil pretreatment.

Results

The amount of corrosion in mil per year is reported in the graphs below. These graphs show that the calcium magnesium gluconate composition #1 (inverted, 133 ppm, 229 ppm, 57 ppm) was superior to the other corrosion inhibitors.

Table 2 – Immersion Test Aluminum Corrosion Using Composition A and Various Corrosion Inhibitors

Corrosion Inhibitor	Corrosion (MPY)
None	1366.44
Amine Borate with Oil	519.04
Amine Borate	572.16
Crodasinic O	609.69
Potassium Silicate + Boric Acid	221.87
Sodium Nitrite	799.86
PEG 600	611.34
$MgCl_2$ $CaCl_2$ Silicate	426.36
$MgCl_2$ $CaCl_2$ Gluconate	586.23
$MgCl_2$ $CaCl_2$ APST	345.86
Berol 275	657.23
Pretreat with APST	635.68
Pretreat with WM Oil	750.03
PEG 600 Diacid	644.05
APST	556.69
Acusol, Sulfite, Gluconate	734.06
Inverted $MgCl_2$ $CaCl_2$ Gluconate	180

Table 3 – Immersion Test Aluminum Corrosion Using Compositions A and B Including Selected Corrosion Inhibitors

	Corrosion (MPY)	
Corrosion Inhibitor	A	B
None	1366.44	702.98
Amine Borate with Oil	519.04	604.1
Amine Borate	572.16	599.04
Crodasinic O	609.69	402.91
Potassium Silicate + Boric Acid	221.87	123.10
Na Nitrite	799.86	418.38
PEG 600	611.34	455.40
$MgCl_2$ $CaCl_2$ Silicate	426.3	103.90
$MgCl_2$ $CaCl_2$ Gluconate	586.23	128.05
$MgCl_2$ $CaCl_2$ APST	345.86	86.84
APST	556.69	295.40
Acusol, Sulfite, Gluconate	734.00	435.62

Table 4 – Glewwe Foam Test Aluminum Corrosion Using Composition A and Various Corrosion Inhibitors

Corrosion Inhibitor	Corrosion (MPY)
None	392.86
Amine Borate with Oil	371.85
Amine Borate	572.41
Crodasinic O	552.26
Potassium Silicate + Boric Acid	133.25
Sodium Nitrite	336.98
PEG 600	831.55
$MgCl_2$, $CaCl_2$ Silicate	61.49
$MgCl_2$ $CaCl_2$ Gluconate	101.17
$MgCl_2$ $CaCl_2$ APST	43.23
Berol 275	194.99
PEG Diacid	240.88
APST	243.29
Acusol, Sulfite, Gluconate	125.77
Inverted $MgCl_2$ $CaCl_2$ Gluconate	89

Table 5 – Glewwe Foam Test Aluminum Corrosion Using Compositions A and B Including Selected Corrosion Inhibitors

	Corrosion (MPY)	
Corrosion Inhibitor	A	B
None	392.86	286.21
Amine Borate with Oil	371.85	372.61
Amine Borate	572.41	158.98
Crodasinic O	552.26	240.63
Potassium Silicate + Boric Acid	133.25	28.78
Na Nitrite	339.9	267.89
PEG 600	831.55	218.82
$MgCl_2$, $CaCl_2$, Silicate	61.49	115.40
$MgCl_2$, $CaCl_2$, Gluconate	101.17	127.03
$MgCl_2$, $CaCl_2$, APST	43.23	117.27
APST	243.29	197.27
Acusol, Sulfite, Gluconate	125.77	281.96

Table 6 –Foam Station Test Aluminum Corrosion Using Compositions A and B Including Selected Corrosion Inhibitors

	Corrosion (MPY)	
Corrosion Inhibitor	A	B
None	23.58	30.55
Mg/Ca/Gluconate	10.57	19.44
Mg/Ca/Si	11.03	10.1
Ksil/Boric Acid	0.85	0.3
Mg/Ca/APST	8.24	12.17

Table 7 – Immersion Test Steel Corrosion Using Composition A and Various Corrosion Inhibitors

Corrosion Inhibitor	Corrosion (MPY)
Control	0.96
$CaCl_2$ $MgCl_2$ Na Gluconate	1.33
$CaCl_2$ $MgCl_2$ Silicate	1.21
Potassium Silicate + Boric Acid	4.15
PEG-600	0.97
$CaCl_2$ $MgCl_2$ APST	0.92
Na Nitrite	0.93
Amine Borate with Oil	1.34
Amine Borate	0.92
Crodasinic O	0.93
Berol 725	0.96
APST	1.14
Acusol, sulfite, gluconate	2.66
PEG-600 Diacid	0.43
Inverted $CaCl_2$ $MgCl_2$ Na Gluconate	2.3

Table 8 – Immersion Test Steel Corrosion Using Composition B and Various Corrosion Inhibitors

Corrosion Inhibitor	Corrosion (MPY)
Control	0.99
$CaCl_2$ $MgCl_2$ Na Gluconate	3.19
$CaCl_2$ $MgCl_2$ Silicate	0.59
Potassium Silicate + Boric Acid	3.96
PEG-600	0.92
$CaCl_2$ $MgCl_2$ APST	1.04
Na Nitrite	0.78
Amine Borate with Oil	2.98
Amine Borate	1.85
Crodasinic O	1.02
Berol 725	0.78
APST	1.19
Acusol, sulfite, gluconate	5.88

Table 9 –Foam Station Test Aluminum Corrosion Using Compositions A and B Including Selected Corrosion Inhibitors

	Corrosion (MPY)	
Corrosion Inhibitor	A	B
Control	3.5	7.50
$MgCl_2$ $CaCl_2$ Gluconate	2.58	7.89
$MgCl_2$ $CaCl_2$ Silicate	2.56	7.03
Potassium Silicate + Boric Acid	2.2	5.41
$CaCl_2$ $MgCl_2$ APST	2.03	8.73
PEG 600	3.46	

It should be noted that, as used in this specification and the appended claims, the singular forms "a," "an," "and," "the" include plural referents unless the content clearly dictates otherwise. Thus, for example, reference to a composition containing "a compound" includes a mixture of two or more compounds. It should also be

noted that the term "or" is generally employed in its sense including "and/or" unless the content clearly dictates otherwise.

It should also be noted that, as used in this specification and the appended claims, the term "configured" describes a system, apparatus, or other structure that is constructed or configured to perform a particular task or adopt a particular configuration. The term "configured" can be used interchangeably with other similar phrases such as arranged and configured, constructed and arranged, adapted and configured, adapted, constructed, manufactured and arranged, and the like.

All publications and patent applications in this specification are indicative of the level of ordinary skill in the art to which this invention pertains.

The invention has been described with reference to various specific and preferred embodiments and techniques. The scope of the claims should not be limited by the preferred embodiments set forth in the examples, but should be given the broadest interpretation consistent with the description as a whole.

WE CLAIM:

1. A corrosion inhibiting composition consisting essentially of :

about 2 to about 85 wt-% water soluble calcium salt;

about 10 to about 95 wt-% water soluble magnesium salt; and

about 2 to about 50 wt-% gluconate;

wherein the weight ratio of water soluble magnesium salt to water soluble calcium salt is about 1-2:1-2; the weight ratio of water soluble magnesium salt to gluconate is greater than 1:1; and the weight ratio of water soluble calcium salt to gluconate is about 1-19:1-13.

2. The composition of claim 1, wherein the weight ratio of water soluble magnesium salt to water soluble calcium salt is about 1-1.5:1-1.5; the weight ratio of water soluble magnesium salt to gluconate is greater than 1.25:1; and the weight ratio of water soluble calcium salt to gluconate is about 1-15:1-8.

3. The composition of claim 1, wherein the weight ratio of water soluble magnesium salt to water soluble calcium salt is about 1-1.25:1-1.25; the weight ratio of water soluble magnesium salt to gluconate is greater than 1.5:1; and the weight ratio of water soluble calcium salt to gluconate is about 3-10:1-5.

4. The composition of claim 1, wherein the weight ratio of water soluble magnesium salt to water soluble calcium salt is about 1:1; the weight ratio of water soluble magnesium salt to gluconate is greater than 2: 1; and the weight ratio of water soluble calcium salt to gluconate is about 3-8:2-4.

5. The composition of claim 1, wherein the gluconate is selected from the group consisting of sodium gluconate, lithium gluconate, potassium gluconate or a mixture thereof.

6. The composition of claim 1, wherein the water soluble magnesium salt is selected from the group consisting ofmagnesium acetate, magnesium benzoate, magnesium bromide, magnesium bromate, magnesium chlorate, magnesium chloride, magnesium chromate, magnesium citrate, magnesium formate, magnesium hexafluorosilicate, magnesium iodate, magnesium iodide, magnesium lactate, magnesium molybdate, magnesium nitrate, magnesium perchlorate, magnesium phosphinate, magnesium salicylate, magnesium sulfate, magnesium sulfite, magnesium thiosulfate, a hydrate thereof, and a mixture thereof.

7. The composition of claim 1, wherein the water soluble calcium salt is selected from the group consisting of calcium acetate, calcium benzoate, calcium bromate, calcium bromide, calcium chlorate, calcium chloride, calcium chromate, calcium dihydrogen phosphate, calcium dithionate, calcium formate, calcium gluconate, calcium glycerophosphate, calcium hydrogen sulfide, calcium iodide, calcium lactate, calcium metasilicate, calcium nitrate, calcium nitrite, calcium pantothenate, calcium perchlorate, calcium permanganate, calcium phosphate, calcium phosphinate, calcium salicylate, calcium succinate, a hydrate thereof, and a mixture thereof.

8. The composition of claim 1, comprising less than 0.5 wt-% zinc-containing compounds.

9. The composition of claim 1, comprising less than 0.5 wt-% aluminum-containing compounds.

10. The composition of claim 1, comprising less than 0.5 wt-% phosphorous-containing compounds.

11. A detergent for warewashing or automatic dishwashing, the detergent comprising:

about 0.1 to about 70 wt-% of a source of alkalinity;

about 0.01 to about 20 wt-% corrosion inhibitor; the corrosion inhibitor consisting essentially of:

about 2 to about 85 wt-% water soluble calcium salt;

about 10 to about 95 wt-% water soluble magnesium salt;

about 2 to about 50 wt-% gluconate; and

about 0.1 to about 20 wt-% of surfactant

wherein the weight ratio of water soluble magnesium salt to water soluble calcium salt is about 1-2:1-2; the weight ratio of water soluble magnesium salt to gluconate is greater than 1:1; and the weight ratio of water soluble calcium salt to gluconate is about 1-19:1-13, and the detergent comprises less than 0.5 wt-% phosphorous-containing compounds.

12. The detergent of claim 11, comprising about 0.1 to about 10 wt-% corrosion inhibitor.

13. The detergent of claim 11, wherein the weight ratio of water soluble magnesium salt to water soluble calcium salt is about 1-1.5:1-1.5; the weight ratio of water soluble magnesium salt to gluconate is greater than 1.25:1; and the weight ratio of water soluble calcium salt to gluconate is about 1-15:1-8.

14. The detergent of claim 11, wherein the weight ratio of water soluble magnesium salt to water soluble calcium salt is about 1-1.25:1-1.25; the weight ratio of water soluble magnesium salt to gluconate is greater than 1.5:1; and the weight ratio of water soluble calcium salt to gluconate is about 3-10:1-5.

15. The detergent of claim 11, wherein the weight ratio of water soluble magnesium salt to water soluble calcium salt is about 1:1; the weight ratio of water soluble magnesium salt to gluconate is greater than 2: 1; and the weight ratio of water soluble calcium salt to gluconate is about 3-8:2-4.

16. The detergent of claim 11, wherein the gluconate is selected from the group consisting of sodium gluconate, lithium gluconate, potassium gluconate or a mixture thereof.

17. The detergent of claim 11, wherein the water soluble magnesium salt is selected from the group consisting of: magnesium acetate, magnesium benzoate, magnesium bromide, magnesium bromate, magnesium chlorate, magnesium chloride, magnesium chromate, magnesium citrate, magnesium formate, magnesium hexafluorosilicate, magnesium iodate, magnesium iodide, magnesium lactate, magnesium molybdate, magnesium nitrate, magnesium perchlorate, magnesium phosphinate, magnesium salicylate, magnesium sulfate, magnesium sulfite, magnesium thiosulfate, a hydrate thereof, and a mixture thereof.

18. The detergent of claim 11, wherein the water soluble calcium salt is selected from the group consisting of calcium acetate, calcium benzoate, calcium bromate, calcium bromide, calcium chlorate, calcium chloride, calcium chromate, calcium dihydrogen phosphate, calcium dithionate, calcium formate, calcium gluconate, calcium glycerophosphate, calcium hydrogen sulfide, calcium iodide, calcium lactate, calcium metasilicate, calcium nitrate, calcium nitrite, calcium pantothenate, calcium perchlorate, calcium permanganate, calcium phosphate, calcium phosphinate, calcium salicylate, calcium succinate, a hydrate thereof, and a mixture thereof.

19. The detergent of claim 11, comprising less than 0.5 wt-% zinc-containing compounds.

20. The detergent of claim 11, comprising less than 0.5 wt-% aluminum-containing compounds.

21. A hard surface cleaner comprising about 0.01 to about 50 wt-% surfactant and about 0.01 to about 20 wt-% corrosion inhibitor; the corrosion inhibitor consisting essentially of:

about 2 to about 85 wt-% water soluble calcium salt;

about 10 to about 95 wt-% water soluble magnesium salt; and

about 2 to about 50 wt-% gluconate;

wherein the weight ratio of water soluble magnesium salt to water soluble calcium salt is about 1-2:1-2; the weight ratio of water soluble magnesium salt to gluconate is greater than 1:1; and the weight ratio of water soluble calcium salt to gluconate is about 1-19:1-13, and the cleaner comprises less than 0.5 wt-% phosphorous containing compounds.

22. The cleaner of claim 21, comprising about 0.1 to about 10 wt-% corrosion inhibitor.

23. The cleaner of claim 21, further comprising an alkalinity source.

24. The cleaner of claim 21, wherein the weight ratio of water soluble magnesium salt to water soluble calcium salt is about 1-1.5: 1-1.5; the weight ratio of water soluble magnesium salt to gluconate is greater than 1.25: 1; and the weight ratio of water soluble calcium salt to gluconate is about 1-15:1-8.

25. The cleaner of claim 21, wherein the weight ratio of water soluble magnesium salt to water soluble calcium salt is about 1-1.25: 1-1.25; the weight ratio of water soluble magnesium salt to gluconate is greater than 1.5:1; and the weight ratio of water soluble calcium salt to gluconate is about 3-10:1-5.

26. The cleaner of claim 21, wherein the weight ratio of water soluble magnesium salt to water soluble calcium salt is about 1:1; the weight ratio of water soluble magnesium salt to gluconate is greater than 2: 1; and the weight ratio of water soluble calcium salt to gluconate is about 3-8:2-4.

27. The cleaner of claim 21, wherein the gluconate is selected from the group consisting of sodium gluconate, lithium gluconate, potassium gluconate or a mixture thereof.

28. The cleaner of claim 21, wherein the water soluble magnesium salt is selected from the group consisting of magnesium acetate, magnesium benzoate, magnesium bromide, magnesium bromate, magnesium chlorate, magnesium chloride, magnesium chromate, magnesium citrate, magnesium formate, magnesium hexafluorosilicate, magnesium iodate, magnesium iodide, magnesium lactate, magnesium molybdate, magnesium nitrate, magnesium perchlorate, magnesium phosphinate, magnesium salicylate, magnesium sulfate, magnesium sulfite, magnesium thiosulfate, a hydrate thereof, and a mixture thereof.

29. The cleaner of claim 21, wherein the water soluble calcium salt is selected from the group consisting of calcium acetate, calcium benzoate, calcium bromate, calcium bromide, calcium chlorate, calcium chloride, calcium chromate, calcium dihydrogen phosphate, calcium dithionate, calcium formate, calcium gluconate, calcium glycerophosphate, calcium hydrogen sulfide, calcium iodide, calcium lactate, calcium metasilicate, calcium nitrate, calcium nitrite, calcium pantothenate, calcium perchlorate, calcium permanganate, calcium phosphate, calcium phosphinate, calcium salicylate, calcium succinate, a hydrate thereof, and a mixture thereof.

30. The cleaner of claim 21, comprising less than 0.5 wt-% zinc-containing compounds.

31. The cleaner of claim 21, comprising less than 0.5 wt-% aluminum-containing compounds.

32. A method of inhibiting corrosion during cleaning, the method comprising:

providing a corrosion inhibitor consisting essentially of:

about 2 to about 85 wt-% water soluble calcium salt;

about 10 to about 95 wt-% water soluble magnesium salt; and

about 2 to about 50 wt-% gluconate;

wherein the weight ratio of water soluble magnesium salt to water soluble calcium salt is about 1-2:1-2; the weight ratio of water soluble magnesium salt to gluconate is greater than 1:1; and the weight ratio of water soluble calcium salt to gluconate is about 1-19:1-13;

preparing an aqueous use composition of the corrosion inhibitor; and

contacting an object in need of cleaning with the aqueous use composition.

33. A method of washing ware, the method comprising:

providing a detergent for warewashing or automatic dishwashing, the detergent comprising:

about 0.1 to about 70 wt-% of a source of alkalinity;

about 0.01 to about 20 wt-% corrosion inhibitor; the corrosion inhibitor consisting essentially of:

about 2 to about 85 wt-% water soluble calcium salt;

about 10 to about 95 wt-% water soluble magnesium salt;

about 2 to about 50 wt-% gluconate; and

about 0.1 to about 20 wt% of surfactant

wherein the weight ratio of water soluble magnesium salt to water soluble calcium salt is about 1-2:1-2; the weight ratio of water soluble magnesium salt to gluconate is greater than 1:1; and the weight ratio of water soluble calcium salt to gluconate is about 1-19:1-13, and the detergent comprises less than 0.5 wt-% phosphorous-containing compounds;

preparing an aqueous use composition of the detergent for warewashing or automatic dishwashing; and

contacting the ware with the aqueous use composition.

34. A method of cleaning a hard surface, the method comprising:

providing a hard surface cleaner comprising about 0.01 to about 50 wt-% surfactant and about 0.01 to about 20 wt-% corrosion inhibitor; the corrosion inhibitor consisting essentially of:

about 2 to about 85 wt-% water soluble calcium salt;

about 10 to about 95 wt-% water soluble magnesium salt; and

about 2 to about 50 wt-% gluconate;

wherein the weight ratio of water soluble magnesium salt to water soluble calcium salt is about 1-2:1-2; the weight ratio of water soluble magnesium salt to gluconate is greater than 1:1; and the weight ratio of water soluble calcium salt to gluconate is about 1-19:1-13, and the cleaner comprises less than 0.5 wt-% phosphorous-containing compounds;

preparing an aqueous use composition of the hard surface cleaner; and

contacting the hard surface with the aqueous use composition.

35. A method of corrosion control in a food or beverage processing facility, the method comprising:

providing an alkaline cleaner or a corrosion control composition comprising:

about 0.1 to about 70 wt-% of a source of alkalinity;

about 0.01 to about 99 wt-% corrosion inhibitor; the corrosion inhibitor comprising:

about 2 to about 85 wt-% water soluble calcium salt;

about 10 to about 95 wt-% water soluble magnesium salt; and

about 2 to about 50 wt-% gluconate;

wherein the weight ratio of water soluble magnesium salt to water soluble calcium salt is about 1-2:1-2; the weight ratio of water soluble magnesium salt to gluconate is greater than 1:1; and the weight ratio of water soluble calcium salt to gluconate is about 1-19:1-13;

preparing an aqueous use composition of the alkaline cleaner or corrosion control inhibitor;

introducing the aqueous use composition into the process facilities at a temperature in the range of about 4 °C to 60°C;

holding the aqueous use composition in a container or circulating the aqueous use composition throughout the system for a time sufficient to clean; and

draining the aqueous use composition from the container or system.

36. The cleaner of claim 21, comprising about 0.05 wt. % to about 15 wt. % surfactant.

37. The cleaner of claim 21, wherein the surfactant is selected from the group consisting of anionic surfactant, nonionic surfactant, cationic surfactant, zwitterionic surfactant, and a mixture thereof.

38. The detergent of claim 11, wherein the alkaline source is selected from thegroup consisting of alkali metal carbonate, alkali metal hydroxide, and mixture thereof.

39. The detergent of claim 11, wherein the alkaline source is selected from the group consisting of sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, sodium sesquicarbonate, potassium sesquicarbonate, and mixture thereof.

40. The detergent of claim 11, wherein the alkaline source is selected from the group consisting of sodium hydroxide, potassium hydroxide, and mixture thereof.

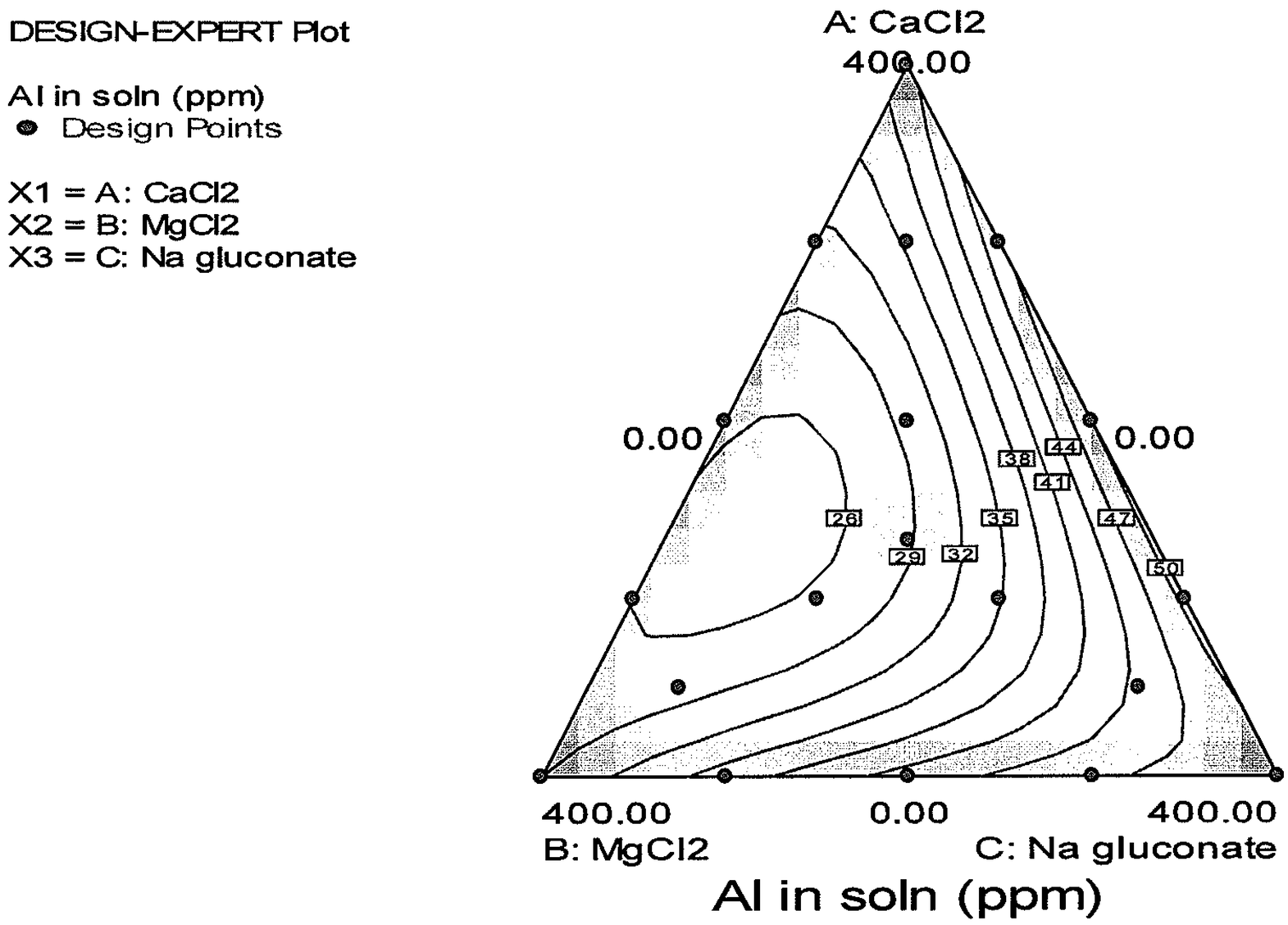

DESIGN-EXPERT Plot
Al in soln (ppm)
Design Points
X1 = A: CaCl2
X2 = B: MgCl2
X3 = C: Na gluconate
A: CaCl2
400.00
0.00
0.00
26
29
32
35
38
41
44
47
50
400.00
0.00
400.00
B: MgCl2
C: Na gluconate
Al in soln (ppm)

Figure 1

DESIGN-EXPERT Plot

Al in soln (ppm)
● Design Points

X1 = A: CaCl2
X2 = B: MgCl2
X3 = C: Na gluconate