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(54) **Title:** COMPOSITION FOR IN SITU MANUFACTURE OF INSOLUBLE HYDROXIDE WHEN CLEANING HARD SURFACES AND FOR USE IN AUTOMATIC WAREWASHING MACHINES, AND METHODS FOR MANUFACTURING AND USING

(57) **Abstract:** A composition useful in hard surface treatment and particularly useful in automatic warewashing is provided according to the invention. The composition may comprise a pretreatment composition, a detersive composition, a rinse agent composition or a combination thereof. The composition includes water-soluble cation and a source of alkalinity. The anionic alkaline source is selected from at least one of hydroxide anion or carbonate anion or a combination thereof. The cation is selected from magnesium, titanium, and aluminum, or combinations thereof. The source of alkalinity is provided in an amount effective to provide a use composition having a pH of greater than about 7. The cation is present in sufficient amount to form an in situ conversion agent. A conversion agent is a water-insoluble hydroxide precipitate that causes calcium in hard water to precipitate as aragonite thereby softening the water. The insoluble hydroxide reduces the contact angle of water on hard surfaces such as wares thus reducing water spotting. Methods for using and manufacturing such compositions are provided.

COMPOSITION FOR *IN SITU* MANUFACTURE OF INSOLUBLE HYDROXIDE WHEN CLEANING HARD SURFACES AND FOR USE IN AUTOMATIC WAREWASHING MACHINES, AND METHODS FOR MANUFACTURING AND USING

This application is being filed on 02 May 2008, as a PCT International Patent application in the name of Ecolab Inc., a U.S. national corporation, applicant for the designation of all countries except the US, and Kim R. Smith, Keith E. Olson, Lee J. Monsrud, Kristen A. Mills, and Michael Rischmiller, all citizens of the U.S., applicants for the designation of the US only, and claims priority to U.S. Provisional Patent Application Serial No. 60/927,575, filed May 4, 2007.

Field of the Invention

The invention relates to compositions useful in automatic warewashing, methods and articles of manufacture comprising *in situ* generation of a magnesium hydroxide in a detergent or rinse agent composition to impart surface modifying benefits for all types of hard surfaces.

The use of the composition of the invention allows for the creation of water-insoluble hydroxide *in situ* providing benefits that include at least one of the following improved surface properties: wetting and sheeting, uniform drying, anti-spotting, anti-staining, anti-filming, and self cleaning relative to dishware surfaces unmodified with such systems. *In situ* generation of water-insoluble hydroxide overcomes the many drawbacks associated with incorporating preexisting magnesium hydroxide or nanoparticles into a product. Compositions of the invention are useful in automatic dishwashing machines including commercial and/or domestic dishwashing machines. Compositions of the invention are also

useful in hard surface cleaning such as shower stalls and automotive cleaning to name a couple.

Background of the Invention

Hard surfaces that are washed but not dried often suffer from spotting. In particular, glassware, dishes, and cutlery washed in an automatic dishwasher may develop hard water spots. Such hard water spots are undesirable because they have an undesirable appearance causing the clean objects to appear dirty. To overcome this problem, rinse aids are often used to minimize or hopefully eliminate such spotting.

Some commercially available rinse aids include nanoparticles. Adding nanoparticles to rinse aids provide desirable results in improving sheeting, thus reducing hard water spots. However, incorporating nanoparticles into rinse aids has its drawbacks. While the benefits of including nanoparticles are impressive, the drawbacks may outweigh the advantages. Incorporating nanoparticles into a detergent or rinse aid is expensive. Nanoparticles may be purchased commercially from vendors, but in the detergent and rinse aid market, it is often a prohibitively expensive ingredient. While nanoparticles are sold commercially, their availability is largely limited because many vendors do not sell them nor do many manufacturers manufacture them. Additionally, nanoparticles can be difficult and dangerous to handle. They pose a potential hazard to workers who risk aspirating the minute particles into their respiratory system resulting in serious health problems. Another drawback is that the nanoparticles often clump or agglomerate thus reducing or eliminating their effectiveness. Agglomeration results in particles that are not present in the form of discrete particles, but instead predominantly assume the form

of agglomerates due to consolidation of the primary particles. Such agglomerates may reach diameters of several thousand nanometers, such that the desired characteristics associated with the nanoscale nature of the particles cannot be achieved. If agglomeration occurs, an expensive, dangerous to handle ingredient loses its ability to improve sheeting and reduce hard water spots.

Alternatively, one may add magnesium hydroxide to a detergent to attempt to control hard water scale through the precipitation of calcium carbonate in a nonscaling crystalline form believed to be aragonite. However, the commercially available forms of magnesium hydroxide are a very fine powder, an aqueous slurry, or very large granules; all of which present problems in bulk handling in a plant. It is apparent that there is a continuing need to improve the various properties of all dishware surfaces in automatic dishwashers, including but not limited to glass, plastics, mirrors, metals, and ceramic surfaces. Such improvement would result in dishware surfaces having one or more of the following highly desirable modified surface properties such as improved wetting and sheeting, uniform drying, anti-spotting, anti-staining, anti-filming, and durability. Desirably, such improvement would provide the benefits of including nanoparticles or magnesium hydroxide into the composition yet would exclude all of the drawbacks associated with inclusion of such ingredients in the composition.

Summary of the Invention

A warewashing composition is provided according to the invention. A composition useful in automatic warewashing is provided comprising a substantially sequestrant-free water-soluble source of at least one cation selected from

magnesium, titanium, or aluminum, and a source of alkalinity selected from at least one hydroxide anion such that the cation and anion react causing *in situ* formation of a water-insoluble hydroxide thereby causing calcium in hard water to precipitate in a non-hard water scaling form believed to be aragonite. Without being bound by theory, it is believed that water-insoluble hydroxide precipitate that forms are particles. In an embodiment of the invention, these particles are nanoparticles. In the environment of an automatic warewashing machine due to agitation, the precipitate/particles actually are nanoparticles having an average particulate size of less than about 500 nanometers. However, we have found that even when the particles exceed 500 nanometers, they are effective in reducing water spotting and the like.

The aragonite crystals are exceedingly fragile crystals that do not readily adhere to hard surfaces. This is compared to calcite crystals that are very sturdy cubic formations and readily adhere and bind to hard surfaces. Without being bound by theory, it is believed that forcing calcium to precipitate as aragonite minimizes the likelihood that calcium carbonate crystals will grow in the hard water scaling form of calcite. While we are uncertain whether or not the aragonite acts as a coating on the wares thus providing dishware surfaces having one or more of the following highly desirable modified surface properties such as improved wetting and sheeting, uniform drying, anti-spotting, anti-staining, anti-filming, and durability or simply is a form of calcium carbonate crystals with adhesion to the ware surfaces is unimportant. From an appearance standpoint an important improvement is reducing the untoward appearance of water spots and lime scale formation over prolonged use. In short, it is believed that the composition of the invention provides *in situ*

production of water-insoluble hydroxide particles that in turn cause aragonite crystal formation thus providing a composition with all of the benefits of including nanoparticles or magnesium hydroxide yet obviating the need to purchase or handle fine powders, large granules, or aqueous slurries of these ingredients.

In order to produce the insoluble hydroxide precipitate *in situ*, a sufficient amount of the water-soluble cation must be present. The water-soluble cation is available to react with the hydroxide anion present in the alkaline source thus forming a water-insoluble hydroxide. The water-insoluble hydroxide is generated *in situ* and may be in the form of nanoparticulates and is a conversion agent thus causing aragonite crystal formation and prohibiting calcium carbonate crystal formation. The overall result is fewer water spots on treated wares or surfaces, softened water and no calcite formation otherwise referred to as lime scale.

One may practice the invention in any order or simultaneously. That is, the alkaline hydroxide source may be introduced to the wares followed by the cation or the two may be introduced simultaneously. In one aspect of the invention, the water-soluble cation source and the water-soluble hydroxide anion source are incorporated into a detergent or a rinsing composition. The water-soluble cation reacts with the alkaline hydroxide source to form a water-insoluble hydroxide. It is undetermined whether the hydroxide precipitate acts to coat the wares or merely acts to prevent calcite from forming and coating the wares. The overall result is that the hydroxide precipitate acts to improve the wetting characteristics of the ware surfaces resulting in reduced water spots. One feature of the invention is that the particles or the water-insoluble hydroxide precipitate is formed in situ as compared to adding the hydroxide precipitate to a concentrated composition or to a use composition.

A method for using the composition is provided according to the invention. The method can include steps of diluting a composition with water at a dilution ratio of water to concentrate (whether the concentrate is a detergent composition or a rinse agent composition) of at least about 20:1, and washing ware with the use composition in an automatic dishwashing machine. The method can include steps of diluting a concentrate composition with water to achieve a use composition having at least about 500 to 5000 ppm total detergent, and treating ware with the use composition in an automatic dishwashing machine. The term "ware" includes items such as eating and cooking utensils. As used herein, the term "warewashing" refers to washing, cleaning, or rinsing ware.

A method for using a composition is provided according to the invention. The method can include steps of diluting a concentrated composition with water at a dilution ratio of water to concentrated composition of at least about 20:1 and washing or rinsing a hard surface with the use composition. The method can include steps of diluting a concentrate composition with water to achieve a use composition having at least about 500 to 20000 ppm total detergent, and washing or rinsing a hard surface with the use composition. Exemplary "hard surfaces" that can be washed or rinsed using a composition of the invention include showers, sinks, toilets, bathtubs, countertops, windows, mirrors, transportation vehicles, floors, and the like.

An advantage of the invention is that it is substantially free of hard water ion chelating agents or sequestrants otherwise necessary in such warewashing or hard-surface cleaning compositions. Chelating agents or sequestrants are expensive ingredients that are largely biologically unfriendly components. It is an advantage

of the present invention that the benefits of reduced water spotting and the like are observed even without the incorporation of chelants or sequestrants. Such chelants or sequestrants are commonly referred to as "builders" in the art.

Detailed Description of the Invention

The invention provides a composition for protecting articles such as glassware from water spots in an automatic dishwashing or warewashing machine during automatic dishwashing or warewashing or during hard surface treatment. The invention provides improved washed dishware surfaces having one or more of the following highly desirable modified surface properties such as improved wetting and sheeting, uniform drying, anti-spotting, anti-staining, anti-filming, and durability.

According to the invention, a water-soluble source of at least one cation is selected from magnesium, aluminum, or titanium. In a preferred embodiment, the composition is substantially builder or sequestrant free.

The term "builder" as used herein refers to components of the composition that bind with ions that cause hard water. One skilled in the art will recognize that hardness in water usually consists of calcium (Ca^{2+}), magnesium (Mg^{2+}) ions and possibly other dissolved compounds such as bicarbonates and sulfates. Although water hardness usually only measures the total concentrations of calcium and magnesium (the two most prevalent, divalent metal ions), iron, aluminum, and manganese may also be present at elevated ppm levels in some geographical locations. In the case of automatic warewashing machines, the ions causing hard water may be present from the incoming wash water, the soil, or from the substrates

being washed. "Builders" as used herein bind with water hardness ions in a specific molar ratio to form water-soluble or insoluble compounds. Some examples of builders that form insoluble compounds include sodium triphosphate (STP) and zeolite A. Some examples of builders forming soluble compounds include sodium tripolyphosphate (STPP), ethylenediaminetetraacetic acid (EDTA), diethylene triamine pentaacetic acid (DTPA), nitrilotriacetate (NTA), and citrate to name a few.

As used herein, the terms "chelating agent" and "sequestrant" do not include compounds that soften water by precipitating water hardness ions as the scale-forming calcium or magnesium salts of bicarbonate, carbonate, hydroxide, or silicate anion, i.e. precipitating water hardness ions as water hardness scale. Some materials that aren't chelating agents or sequestrants can also reduce water hardness by precipitating water hardness ions as the scale-forming calcium or magnesium salts of bicarbonate, carbonate, hydroxide, or silicate anion. Such formation of hard water scale is undesirable and leads to hard water spotting during the warewashing process.

As used herein, the term "free of chelating agent" or "substantially sequestrant free" refers to a composition, mixture, or ingredients that does not contain a chelating agent or sequestrant or to which a chelating agent or sequestrant has not been added. Should a chelating agent or sequestrant be present through contamination of a composition, mixture, or ingredient that is free of chelating agent, the amount of a chelating agent or sequestrant shall be less than 5.0 wt-%. In an embodiment, such an amount of a chelating agent or sequestrant shall be less than 2.0 wt-%. In an embodiment, such an amount of a chelating agent or sequestrant is

less then 0.5 wt-%. In an embodiment, such an amount of a chelating agent or sequestrant is less than 0. 1 wt-%.

As used herein, the term "lacking an effective amount of builder" refers to a composition, mixture, or ingredients that contains too little chelating agent, builder, threshold agent or sequestrant to measurably affect the hardness of water.

The term "builder-free" as used herein refers to a composition that is substantially free of those compounds that chelate or sequester calcium or form insoluble compounds when binding with any of the cations of the invention. The cations useful in the composition of the invention include magnesium, calcium, molybdenum, titanium, iron, and zinc.

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

The term "water-insoluble" as used herein 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 "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 "conversion agent" refers to a species that causes solubilized calcium in water to precipitate from solution as calcium carbonate in a form that is believed to be the thermodynamically unfavorable crystal form aragonite rather than as the thermodynamically favorable crystal form calcite. Aragonite is a fragile crystal which doesn't bind well to surfaces and doesn't form hard water scale while calcite is a more robust crystal which binds tightly to surfaces, forming a hard water scale that's not seen with aragonite.

The term, "threshold agent" as used herein 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 terms "residue" or "coating" include substantially covering a surface, or portion thereof, as well as only partially covering a surface, such as those residues or coatings that after drying leave gaps in coverage on a surface. When it is said that the particles leave a residue or coating as described herein, it is understood that the residues or coatings need not cover the entire surface. For instance, the particles or coatings are considered applied to a surface even if they modify a portion of the surface.

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 ingredients 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 ingredients that do 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 %.

The term "functional material" or "functional additives" refers to an active compound or material that affords desirable properties to the solid or dissolved composition. For example, the functional material can afford desirable properties to the solid composition such as enhancing solidification characteristics or dilution rate. The functional material can also, when dissolved or dispersed in an aqueous phase, provide a beneficial property to the aqueous material when used. Examples of optional functional materials include surfactant, cleaning agent, softening agent, buffer, anti-corrosion agent, bleach activators secondary hardening agent or solubility modifier, detergent filler, defoamer, anti-redeposition agent, antimicrobials, rinse aid compositions, a threshold agent or system, aesthetic enhancing agent (i.e., dye, perfume), lubricant compositions, additional bleaching agents, functional salts, hardening agents, solubility modifiers, enzymes, other such additives or functional ingredients, and the like, and mixtures thereof. Functional materials added to a composition will vary according to the type of composition being manufactured, and the intended end use of the composition.

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

The term "solid" also is used to describe the processed composition, it is meant that the hardened composition 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 that 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, 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. The term about also encompasses amounts that differ due to different equilibrium conditions for a composition resulting from a particular initial mixture. Whether or not modified by the term "about", the claims include equivalents to the quantities.

The term *"in situ"* as used herein refers to creation of an element, or in the case of the invention, creation of a water-insoluble hydroxide precipitate either upon formation of a use composition, or upon delivery of the use composition to the treatment surface, or when forming the concentrate composition of the invention. *"In situ"* formation does not include compositions or concentrates wherein the water-insoluble hydroxide is in existence before creation of the concentrate. That is, *"in situ"* would not include concentrate compositions or use compositions in which water-insoluble magnesium hydroxide is added as a pre-existing ingredient.

Cation Source

The composition of the invention includes a source of a water-soluble cation selected from at least one water-soluble cation of magnesium, aluminum, or titanium. The cationic source also refers to the possibility that any combination of cations is provided. The cation is provided in sufficient amount to react with the source of alkalinity to form a cation hydroxide compound that causes calcium carbonate to precipitate as aragonite instead of calcite. One method of providing sufficient cation is to leave a residue on the wares. The amount of cation provided in the composition is preferably sufficient to react with the anionic source of alkalinity as hydroxide anion to form a conversion agent.

Preferably, the water-soluble source of the cations provided in the composition of the invention are comprised of water-soluble salts of magnesium, titanium, iron, and aluminum. The composition of the cations is important, as the cations should be soluble in water, particularly during the particular phase of the ware washing in which they are employed. Once contacted with the anions from the alkaline source, the cations form an insoluble hydroxide precipitate.

The cationic source preferably remains in solution until the anionic alkaline source contacts the cations. In an alternate embodiment, the insoluble hydroxide precipitate may form before contacting the wares. This will occur when the cationic source and the alkaline anions come into contact in the event of a pretreatment step or in the detergent concentrate itself.

It should be understood that magnesium cation, titanium cation, aluminum cation, and zinc cation can be considered a source of magnesium cation, titanium cation, aluminum cation, and zinc cation. The source of cation can be provided as organic salts, inorganic salts, and mixtures thereof. Exemplary sources of magnesium cation include magnesium salts such as magnesium acetate, magnesium chloride, magnesium sulfate, and mixtures thereof. An exemplary source of titanium cation ion includes titanium chloride. Exemplary sources of aluminum cation include aluminum sulfate, aluminum chloride and mixtures thereof. In addition, the source of cation can be selected as those components that are characterized by the United States Food and Drug Administration as direct or indirect food additives. Because the warewashing detergent composition will be used to wash articles that contact food, it may be desirable to select the source of cation as components that are characterized by the United States Food and Drug

Administration as direct or indirect food additives. By way of theory, it is believed that the source of cation that deposit onto the surfaces of articles that are being washed. In addition, it is believed that the alkaline source of anions causes the cations to precipitate. The precipitate remains on the article to improve wetting, sheeting, uniform drying, anti-spotting, anti-staining, anti-filming, and reduces the untoward appearance of water spots

It is expected that the cationic source will form a water insoluble conversion agent when contacted with the anionic alkaline source. Without being bound by theory it is believed that the water insoluble hydroxide, also referred to as a conversion agent may also be referred to herein as particles. As a result, the conversion agent causes calcium carbonate present in the water to precipitate as non-scaling aragonite instead of calcite. If the particles deposit on the surface of the wares it can be substantially invisible to the human eye. It should be understood that the phrase "substantially invisible to the human eye" refers to the lack of visible filming by the particles. Visible filming refers to a cloudy appearance that may begin with an iridescent film that displays rainbow hues in light reflected from the glass. It is expected that the precipitate that forms on the glass provides a film on the glass that is both substantially invisible to the human eye and that provides a functional layer. By functional layer it is meant that particles provide modified surface properties on the wares such as improved wetting and sheeting, uniform drying, anti-spotting, anti-staining, anti-filming, and durability.

Anionic Source of Alkalinity

A source of alkalinity is provided in the composition of the invention as a hydroxide anion.

As used herein, the term "alkaline" refers to those compositions having a pH above 7, preferably a pH of above about 8, and more preferably a pH above about 9.

The alkaline source of the anions has a pH high enough to cause the cations present to form an oxide precipitate whether the cations are present in the automatic warewashing machine, in the feedwater or precursor to the detersive cycle, or in the wash water, or in the rinse water. Such a pH is above about 7, preferably above about 8, and more preferably above about 9. One skilled in the art will recognize that the amount of anions necessary will in part depend upon the pH of the alkaline source.

According to the invention, an alkaline source is a hydroxide anion such that the cation and anion react to form a water-insoluble conversion agent. The anionic alkaline source of the invention preferably has a pKa of greater than about 8, more preferably the alkaline source of the invention comprises a pKa of greater than about 9, and most preferably the alkaline source of the invention comprises a pKa of greater than about 10. Additional alkaline agents such as, for example, alkali metal carbonates, alkanolamines, alkali metal silicates and the like may also be present in the composition for other purposes than forming a water-insoluble conversion agent.

As previously mentioned with respect to the detersive agents, the alkaline component(s) of the invention are best selected from those components characterized by the United States Food and Drug Administration as direct or indirect food additives. When the composition of the invention is used to wash articles that contact food, it is desirable to select the source of alkalinity as components that are characterized by the United States Food and Drug Administration as direct or indirect food additives.

The alkaline source of the composition may be organic or inorganic. Examples of organic bases useful in the present invention include but are not limited to triethanolamine, dodecyldi (hydroxyethyl)amine, diethanolamine, tributylamine, ethoxylated tetradecylamine or mixtures thereof. Examples of inorganic bases useful in the composition of the present invention include but are not limited to sodium hydroxide, potassium hydroxide, lithium hydroxide, cesium hydroxide, sodium carbonate, potassium carbonate, lithium carbonate, sodium silicate, potassium silicate, lithium silicate, or mixtures thereof. One skilled in the art will also recognize inorganic and organic bases may be combined to form the alkaline source of the anion of the invention.

It is hypothesized that the water-insoluble hydroxide precipitate that is formed is in part on the surface of the wares. The hydroxide precipitate is preferably a fine precipitate that is undetected by the naked eye. Such particles have novel and useful properties due to the small dimensions of the particulates. As previously mentioned, in an embodiment the particles are nanoparticles. The term nanoparticles as used herein are particles with diameters of about 500 nm or less. Particle size distributions of the nanoparticles in the present invention may fall anywhere within the range from about 1 nm, or less, to less than about 500 nm, alternatively from about 1 nm to less than about 100 nm, and alternatively from about 1 nm to less than about 50 nm. Alternatively, nanoparticles can also include crystalline or amorphous particles with a particle size from about 1, or less, to about 100 nanometers, alternatively from about 1 to about 50 nanometers. In another embodiment, the particles may be a combination of nanoparticles and particles larger than 500 nm. In yet another embodiment of the invention, substantially all of

the particles are greater than 500 nm. The in situ created insoluble oxide precipitate can include particles ranging from 1 nm up to about 5,000 nm. The benefits of the invention are experienced regardless of the resultant particle size.

One theory is that use of the composition of the invention would serve to create the insoluble hydroxide precipitate to create a layer on glassware in particular to help inhibit the etched appearance commonly found when glass is repeatedly washed in an automatic dishwasher. Without being bound by theory, it is likely that the insoluble hydroxide particulates, also referred to herein as the *in situ* created particles, create a sacrificial layer on the glassware prohibiting or reducing leaching of the silicon in the glass. Practicing the invention could therefore prolong the clarity of glass routinely washed in automatic dishwashing machines.

Yet another theory is one advanced previously. That theory relies upon the nature of the crystals of the precipitate. In a preferred embodiment of the invention, the insoluble oxide precipitate serves to cause calcium carbonate in the water to crystallize as non-scale forming aragonite crystals rather than as the scale-forming calcite. Aragonite crystals are fragile as compared to the sturdier carbonate crystals. Formation of aragonite crystals prohibits or greatly diminishes the formation of calcite scale thereby eliminating the chance that calcium carbonate crystals can deposit upon the wares. It is a widely held belief that calcium carbonate as its calcite crystalline form is a major source of lime scale deposits on wares and a source of the hazy appearance of wares.

The composition of the invention can be referred to as a cleaning composition, a rinse composition, or a pre-treat composition and is desirably used in automatic warewashing machines but can be available for cleaning in environments

other than inside an automatic dishwashing or warewashing machine. It should be understood that the term "warewashing" refers to and is meant to include both warewashing and dishwashing. Furthermore, the warewashing composition can refer to a concentrate and to a use composition. In general, a concentrate is the composition that is diluted with water to provide the use composition that contacts the ware surfaces to provide the desired effect, such as, cleaning.

One skilled in the art will appreciate that the composition of the invention may be provided in different embodiments. In a first embodiment, the source of water-soluble cation may be provided in a stand-alone detergent that may be provided in solid or liquid form. The alkaline anion component may then also be provided in a stand-alone format and may be provided in solid or liquid form. In this embodiment, either component may be used as the first treatment. Alternatively, the stand-alone components of this embodiment may simultaneously treat the wares by themselves or as part of a detergent.

In a second embodiment the water-soluble cation component and the alkaline source of anion component are provided together as a pre-treatment or a precursor to a detersive agent. The composition of the invention may be provided along with the detersive agents but the combination of the invention may be provided such that when diluted with water the components are dispersed together. That is, the components of the invention are more readily diluted with water than the detersive agents allowing the components of the invention to contact the wares before the detersive agents.

In a third embodiment the water-soluble cation component and the alkaline source of anion component are provided together as part of a detergent or as a rinse agent.

The composition according to the invention may include an effective amount of one or more non-conversion agent forming alkaline sources to maintain the composition at an alkaline pH. The alkaline source may also enhance cleaning of a substrate and improve soil removal performance of the composition. In general, an effective amount of one or more alkaline sources should be considered as an amount that provides a use composition having a pH of at least about 8. When the use composition has a pH of between about 8 and about 10 it can be considered mildly alkaline, and when it has a pH of between 10 and 11 it can be considered alkaline, and when the pH is greater than about 12 the use composition can be considered caustic. In general, it is desirable to provide the use composition as an alkaline cleaning composition or caustic cleaning composition because of improved cleaning performance.

In general, it is expected that the concentrate of the invention will include the anionic alkaline source in an amount of at least about 5 wt.%, at least about 10 wt.%, or at least about 15 wt.%. In order to provide sufficient room for other components in the concentrate, the anionic alkaline source can be provided in the concentrate in an amount of less than about 60 wt.%. In addition, the anionic alkaline source can be provided at a level of less than about 30 wt.% and less than about 20 wt%.

The composition that contacts the articles to be washed in an automatic dishwashing process can be referred to as the use composition. The use composition can be provided as a detersive agent at a solids concentration that provides a desired

level of detersive properties. The solids concentration refers to the concentration of the non-water components in the use composition. 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 and as a solid. In a preferred embodiment the composition of the invention is provided in solid form. It should be understood that pastes and gels can be considered a type of liquid. In addition, it should be understood that powders, agglomerates, pellets, tablets, and blocks are types of a solid.

It is expected that the composition of the invention will be used by diluting the concentrate with water at the site or location of use to provide the use composition. In many cases when using the composition of the invention in an automatic dishwashing or warewashing machine, it is expected that the site or location of use will be inside the automatic dishwashing or warewashing machine. Although the location of use will generally be at or inside an automatic dishwashing machine, whether or not the cation source and alkaline anion source of the invention are combined will depend upon the particular embodiment of the invention used. That is, if the components of the invention are stand-alone components, then the composition is used in a residential or home-style dishwashing machine, it is expected that the alkaline source may be placed in the detergent compartment along with the cation source. Alternatively, both may be placed in the rinse aid compartment of the dishwashing machine. Often these detergent compartments and rinse aid compartments are located in the door of the dishwashing machine on top of machine or in close proximity to the machine. The cation and alkaline source may

be provided in the form that allows for introduction of a single dose of the composition into the appropriate compartment. In general, single dose refers to the amount of the cation or source of alkalinity that is desired for a single warewashing application. In many commercial dishwashing or warewashing machines, and even for certain residential dishwashing machines, it is expected that a large quantity of concentrate can be provided in a compartment that allows for the release of a single dose amount of the composition for each warewashing or dishwashing cycle. Such a compartment may be provided as part of the warewashing or dishwashing machine or it may be provided as a separate structure connected to the warewashing or dishwashing machine by a hose for delivery of liquid thereto. For example, a block of the concentrate can be provided in a hopper, and water can be sprayed against the surface of the block to provide a liquid concentrate that can be introduced into the dishwashing machine. The hopper can be a part of the dishwashing machine or it can be provided separate from the dishwashing machine.

The use composition of the invention can have a solids content that is sufficient to provide the desired level of cleaning while avoiding wasting the use composition by using too much. In general, it is expected that the use composition will have a solids content of at least about 0.05 wt.%, and can have a solids content of between about 0.05 wt.% and about 0.75 wt.%. The use composition can be prepared from the concentrate by diluting with water at a dilution ratio that provides convenient use of the concentrate and provides the formation of a use composition having desired detersive properties. It is expected that the concentrate can be diluted at a ratio of water to concentrate of at least about 20:1, and can be at between about

20:1 and about 200:1, and can be between about 20:1 and about 2000:1 to provide a use composition having desired properties.

The warewashing composition can be provided in the form of a solid. Exemplary solid dishwashing compositions and methods of manufacturing such solid compositions are disclosed in U.S. Patent Nos. 6,410,495 to Lentsch et al., 6,369,021 to Man et al., 6,258,765 to Wei et al, 6,177,392 to Lentsch et al., 6,164,296 to Lentsch et al., 6,156,715 to Lentsch et al., and 6,150,324 to Lentsch et al. The compositions and methods of manufacturing of each of these patents are incorporated herein by reference for all purposes.

Cleaning Agent

The composition of the invention can optionally include at least one cleaning agent comprising a surfactant or surfactant system. A variety of surfactants can be used in a warewashing composition, such as additional nonionic, anionic, cationic, and zwitterionic surfactants. It should be understood that surfactants are an optional component of the warewashing composition and can be excluded from the concentrate. The warewashing detergent composition, when provided as a concentrate, can include the cleaning agent in a range of between about 0.5 wt.% and about 20 wt.%, between about 0.5 wt.% and about 15 wt.%, between about 1.5 wt.% and about 15 wt.%, between about 1 wt.% and about 10 wt.%, and between about 2 wt.% and about 5 wt.%. Additional exemplary ranges of surfactant in a concentrate include about 0.5 wt.% to about 5 wt.%, and about 1 wt.% to about 3 wt.%.

Exemplary surfactants that can be used are commercially available from a number of sources. For a discussion of surfactants, see Kirk-Othmer, Encyclopedia

of Chemical Technology, Third Edition, volume 8, pages 900-912 incorporated herein for all purposes. When the composition of the invention includes a cleaning agent, the cleaning agent can be provided in an amount effective to provide a desired level of cleaning.

Anionic surfactants useful in the composition of the invention (whether it is a detersive composition, or a pretreatment composition, or a rinse agent composition) includes, 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. Exemplary anionic surfactants include sodium alkylarylsulfonate, alpha-olefinsulfonate, and fatty alcohol sulfates.

Nonionic surfactants useful in the composition of the invention include, for example, 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 glycol ethers of fatty alcohols; polyalkylene oxide free nonionics such as alkyl polyglycosides; sorbitan and sucrose esters and their ethoxylates; alkoxylated ethylene diamine; alcohol alkoxylates such as alcohol ethoxylate propoxylates, alcohol propoxylates, alcohol propoxylate ethoxylate propoxylates, alcohol ethoxylate butoxylates, and the like; nonylphenol ethoxylate, polyoxyethylene

glycol ethers and the like; 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 polyalkylene oxide block copolymers including an ethylene oxide/propylene oxide block copolymer such as those commercially available under the trademarks PLURONIC® and PLURONIC® R Series (BASF-Wyandotte), and the like; and other like nonionic compounds. Silicone surfactants such as the ABIL® B8852 can also be used.

Cationic surfactants that can be used in the warewashing detergent composition or rinse agent composition include amines such as primary, secondary and tertiary monoamines with C_{18} alkyl or alkenyl chains, ethoxylated alkylamines, alkoxylates of ethylenediamine, imidazoles such as a 1-(2-hydroxyethyl)-2-imidazoline, a 2-alkyl-1-(2-hydroxyethyl)-2-imidazoline, and the like; and quaternary ammonium salts, as for example, alkylquaternary ammonium chloride surfactants such as n-alkyl(C_{12}-C_{18})dimethylbenzyl ammonium chloride, n-tetradecyldimethylbenzylammonium chloride monohydrate, a naphthylene-substituted quaternary ammonium chloride such as dimethyl-1-naphthylmethylammonium chloride, and the like. Useful cationic surfactants also include cationic polymers such as diallyldimethylammonium chloride (DADMAC), vinylbenzyldimethylammonium chloride, and the like. The cationic surfactant can be used to provide antimicrobial properties.

Zwitterionic surfactants that can be used in the pretreatment composition or detersive (warewashing) composition or rinse agent composition include betaines,

imidazolines, and propinates. When the composition is intended for use as a warewashing composition in an automatic dishwashing or warewashing machine, the surfactants selected, if any surfactant is used, can be those that provide an acceptable level of foaming when used inside a dishwashing or warewashing machine. It should be understood that warewashing compositions for use in automatic dishwashing or warewashing machines are generally considered to be low-foaming compositions.

The surfactant can be selected to provide low foaming properties. One would understand that low foaming surfactants that provide the desired level of detersive activity are advantageous in an environment such as a dishwashing machine where the presence of large amounts of foaming can be problematic. In addition to selecting low foaming surfactants, one would understand that defoaming agents could be utilized to reduce the generation of foam. Accordingly, surfactants that are considered low foaming surfactants as well as other surfactants can be used in the warewashing composition and the level of foaming can be controlled by the addition of a defoaming agent.

Other Additives

The composition of the invention can include other additives, including conventional additives such as bleaching agents, hardening agents or solubility modifiers, defoamers, anti-redeposition agents, threshold agents, stabilizers, dispersants, enzymes, aesthetic enhancing agents (i.e., dye, perfume), and the like. Adjuvants and other additive ingredients will vary according to the type of composition being manufactured. It should be understood that these additives are optional and need not be included in the cleaning composition. When they are

included, they can be included in an amount that provides for the effectiveness of the particular type of component.

The composition of the invention generally does not include any chelating/sequestering agents such as an aminocarboxylic acid, a condensed phosphate, a phosphonate, or the like.

Bleaching agents for use in a cleaning compositions for lightening or whitening a substrate, include bleaching compounds capable of liberating an active halogen species, such as Cl_2, Br_2, $-OCl^-$ and/or $-OBr^-$, 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 chlorine, a hypochlorite, and chloramine. Exemplary halogen-releasing compounds include the alkali metal dichloroisocyanurates, chlorinated trisodium phosphate, the alkali metal hypochlorites, monochloramine and dichloramine, and the like. 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, the disclosure of which is incorporated by reference herein for all purposes). A bleaching agent may also be a peroxygen or active oxygen source such as hydrogen peroxide, perborates, sodium carbonate peroxyhydrate, phosphate peroxyhydrates, potassium permonosulfate, and sodium perborate mono and tetrahydrate, with and without activators such as tetraacetylethylene diamine, and the like. The composition can include an effective amount of a bleaching agent. When the concentrate includes a bleaching agent, it can be included in an amount of about 0.1 wt.% to about 60 wt.%, about 1 wt.% to about 20 wt.%, about 3 wt.% to about 8 wt.%, and about 3 wt.% to about 6 wt.%.

The composition can include an effective amount of detergent fillers, which does not perform as a cleaning agent per se, but cooperates with the cleaning agent to enhance the overall cleaning capacity of the composition. Examples of detergent 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. When the concentrate includes a detergent filler, it can be included an amount of about 1 wt.% to about 20 wt.% and between about 3 wt.% to about 15 wt.%.

A defoaming agent for reducing the stability of foam may also be included in the composition to reduce foaming. When the concentrate includes a defoaming agent, the defoaming agent can be provided in an amount of between about 0.01 wt.% and about 3 wt.%.

Examples of defoaming agents that can be used in the composition includes ethylene oxide/propylene block copolymers such as those available under the name Pluronic N3, silicone compounds such as silica dispersed in polydimethylsiloxane, polydimethylsiloxane, and functionalized polydimethylsiloxane such as those available under the name Abil B9952, 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., the disclosures of which are incorporated by reference herein for all purposes.

The composition can include an anti-redeposition agent for 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. When the concentrate includes an anti-redeposition agent, the anti-redeposition agent can be included in an amount of between about 0.5 wt.% to about 10 wt.%, and between about 1 wt.% and about 5 wt.%.

Stabilizing agents that can be used include primary aliphatic amines, betaines, borate, calcium ions, sodium citrate, citric acid, sodium formate, glycerine, maleonic acid, organic diacids, polyols, propylene glycol, and mixtures thereof. The concentrate need not include a stabilizing agent, but when the concentrate includes a stabilizing agent, it can be included in an amount that provides the desired level of stability of the concentrate. Exemplary ranges of the stabilizing agent include about 0 to about 20 wt.%, about 0.5 wt.% to about 15 wt.%, and about 2 wt.% to about 10 wt.%.

Dispersants that can be used in the composition include maleic acid/olefin copolymers, polyacrylic acid, and its copolymers, and mixtures thereof. The concentrate need not include a dispersant, but when a dispersant is included it can be included in an amount that provides the desired dispersant properties. Exemplary ranges of the dispersant in the concentrate can be between about 0 and about 20 wt.%, between about 0.5 wt.% and about 15 wt.%, and between about 2 wt.% and about 9 wt.%.

Enzymes that can be included in the composition include those enzymes that aid in the removal of starch and/or protein stains. Exemplary types of enzymes include proteases, alpha-amylases, and mixtures thereof. Exemplary proteases that can be used include those derived from Bacillus licheniformix, Bacillus lenus, Bacillus alcalophilus, and Bacillus amyloliquefacins. Exemplary alpha-amylases include Bacillus subtilis, Bacillus amyloliquefaceins and Bacillus licheniformis. The concentrate need not include an enzyme. When the concentrate includes an enzyme, it can be included in an amount that provides the desired enzymatic activity when the warewashing composition is provided as a use composition. Exemplary ranges of the enzyme in the concentrate include between about 0 and about 15 wt.%, between about 0.5 wt.% and about 10 wt.%, and between about 1 wt.% and about 5 wt.%.

The concentrate can include water. In general, it is expected that water may be present as a processing aid and may be removed or become water of hydration. It is expected that water may be present in both the liquid concentrate and in the solid concentrate. In the case of the liquid concentrate, it is expected that water will be present in a range of between about 5 wt.% and about 60 wt.%, between about 10 wt.% and about 35 wt.%, and between about 15 wt.% and about 25 wt.%. In the case of a solid concentrate, it is expected that the water will be present in ranges of between about 0 wt.% and about 10 wt.%, about 0.1 wt.% and about 10 wt.%, about 1 wt.% and about 5 wt.%, and about 2 wt.% and about 3 wt.%. It should be additionally appreciated that the water may be provided as deionized water or as softened water.

Various dyes, odorants including perfumes, and other aesthetic enhancing agents can 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 (Keystone 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 C1S-jasmine or jasmal, vanillin, and the like.

The components used to form the concentrate can include an aqueous medium such as water as an aid in processing. It is expected that the aqueous medium will help provide the components with a desired viscosity for processing. In addition, it is expected that the aqueous medium may help in the solidification process when is desired to form the concentrate as a solid. When the concentrate is provided as a solid, it can be provided in the form of a block or pellet. It is expected that blocks will have a size of at least about 5 grams, and can include a size of greater than about 50 grams. It is expected that the concentrate will include water in an amount of between about 1 wt.% and about 50 wt.%, and between about 2 wt.% and about 40 wt.%.

When the components that are processed to form the concentrate are processed into a block, it is expected that the components can be processed by

extrusion techniques or casting techniques. In general, when the components are processed by extrusion techniques, it is believed that the composition can include a relatively smaller amount of water as an aid for processing compared with the casting techniques. In general, when preparing the solid by extrusion, it is expected that the composition can contain between about 2 wt.% and about 10 wt.% water. When preparing the solid by casting, it is expected that the amount of water can be provided in an amount of between about 20 wt.% and about 40 wt.%. A solid that is easily removed from a mold or extruder or removed with minimal damage is preferred.

Forming The Concentrate

As previously mentioned, the cationic source may be formed separate of the anionic source or the cationic source and the anionic source may be formed together with each of these instances alone or as part of a pretreatment composition, a detergent or rinsing composition or any combination thereof. The following may refer to either the formation of the cationic source, the anionic source or a combination of both. It is noted that it may be desirable for the cationic source and the anionic source to contact the wares simultaneously either during a pretreatment, during the wash cycle of an automatic warewashing machine, or during a rinse cycle to create a conversion agent and to reduce and hopefully eliminate the formation of calcite crystal formation in the wash cycle. It might also be desirable that the cationic source and the anionic source are able to react to form the conversion agent *in situ*. Therefore, it might also be desirable that if the cationic source and the anionic source are formed into a single concentrate that either the cation or the anionic alkaline source is encapsulated or otherwise treated to delay reaction until

delivery to the water. Such encapsulation may be achieved through the use of water soluble polymers or similar methods. However, it is not believed that such encapsulation is necessary. The components can be mixed and extruded agglomerated, pressed or cast to form a solid such as particles, pellets or blocks. Heat can be applied from an external source to facilitate processing of the mixture.

A mixing system provides for continuous mixing of the ingredients at high shear to form a substantially homogeneous liquid or semi-solid mixture in which the ingredients are distributed throughout its mass. The mixing system includes means for mixing the ingredients to provide shear effective for maintaining the mixture at a flowable consistency, with a viscosity during processing of about 1,000-1,000,000 cP, preferably about 50,000-200,000 cP. The mixing system can be a continuous flow mixer or a single or twin screw extruder apparatus.

The mixture can be processed at a temperature to maintain the physical and chemical stability of the ingredients, such as at ambient temperatures of about 20-80°C, and about 25-55°C. Although limited external heat may be applied to the mixture, the temperature achieved by the mixture may become elevated during processing due to friction, variances in ambient conditions, and/or by an exothermic reaction between ingredients. Optionally, the temperature of the mixture may be increased, for example, at the inlets or outlets of the mixing system.

An ingredient may be in the form of a liquid or a solid such as a dry particulate, and may be added to the mixture separately or as part of a premix with another ingredient, as for example, the cleaning agent, the aqueous medium, and additional ingredients such as a second cleaning agent, a detergent adjuvant or other

additive, a secondary hardening agent, and the like. One or more premixes may be added to the mixture.

The ingredients are mixed to form a substantially homogeneous consistency wherein the ingredients are distributed substantially evenly throughout the mass. The mixture can be discharged from the mixing system through a die or other shaping means. The profiled extrudate can be divided into useful sizes with a controlled mass. The extruded solid can be packaged in film. The temperature of the mixture when discharged from the mixing system can be sufficiently low to enable the mixture to be cast or extruded directly into a packaging system without first cooling the mixture. The time between extrusion discharge and packaging can be adjusted to allow the hardening of the detergent block for better handling during further processing and packaging. The mixture at the point of discharge can be about 20-90°C, and about 25-55°C. The composition can be allowed to harden to a solid form that may range from a low density, sponge-like, malleable, caulky consistency to a high density, fused solid, concrete-like block.

Optionally, heating and cooling devices may be mounted adjacent to mixing apparatus to apply or remove heat in order to obtain a desired temperature profile in the mixer. For example, an external source of heat may be applied to one or more barrel sections of the mixer, such as the ingredient inlet section, the final outlet section, and the like, to increase fluidity of the mixture during processing. Preferably, the temperature of the mixture during processing, including at the discharge port, is maintained preferably at about 20-90°C.

When processing of the ingredients is completed, the mixture may be discharged from the mixer through a discharge die. The composition eventually

hardens due to the chemical reaction of the ingredients forming a hydrate binder. The solidification process may last from a few minutes to about six hours, depending, for example, on the size of the cast or extruded composition, the ingredients of the composition, the temperature of the composition, and other like factors. Preferably, the cast or extruded composition "sets up" or begins to hardens to a solid form within about 1 minute to about 3 hours, preferably about 1 minute to about 2 hours, preferably about 1 minute to about 20 minutes.

The concentrate can be provided in the form of a liquid. Various liquid forms include gels and pastes. Of course, when the concentrate is provided in the form of a liquid, it is not necessary to harden the composition to form a solid. In fact, it is expected that the amount of water in the composition will be sufficient to preclude solidification. In addition, dispersants and other components can be incorporated into the concentrate in order to maintain a desired distribution of components.

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 cast or extruded directly into 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. Preferred packaging used to contain the compositions is

manufactured from a flexible, easy opening film material. Use instructions and/or safety precautions may be attached to or printed directly on the packaging material for the safety of the user.

The packaging material can be provided as a water-soluble packaging material such as a water-soluble packaging film. Exemplary water-soluble packaging films are disclosed in U.S. Patent Nos. 6,503,879; 6,228,825; 6,303,553; 6,475,977; and 6,632,785, the disclosures of which are incorporated herein by reference for all purposes. An exemplary water-soluble polymer that can provide a packaging material that can be used to package the concentrate includes polyvinyl alcohol. The packaged concentrate can be provided as unit dose packages or multiple dose packages. In the case of unit dose packages, it is expected that a single packaged unit will be placed in a dishwashing machine, such as the detergent compartment of the dishwashing machine, and will be used up during a single wash cycle. In the case of a multiple dose package, it is expected that the unit will be placed in a hopper and a stream of water will degrade a surface of the concentrate to provide a liquid concentrate that will be introduced into the dishwashing machine.

Suitable water-soluble polymers that may be used in the invention are described in Davidson and Sittig, *Water Soluble* Resins, Van Nostrand Reinhold Company, New York (1968), herein incorporated by reference for all purposes. The water-soluble polymer should have proper characteristics such as strength and pliability in order to permit machine handling. Preferred water soluble polymers include polyvinyl alcohol, cellulose ethers, polyethylene oxide, starch, polyvinylpyrrolidone, polyacrylamide, polyvinyl methyl ether-maleic anhydride, polymaleic anhydride, styrene maleic anhydride, hydroxyethylcellulose,

methylcellulose, polyethylene glycols, carboxymethylcellulose, polyacrylic acid salts, alginates, acrylamide copolymers, guar gum, casein, ethylene-maleic anhydride resin series, polyethyleneimine, ethyl hydroxyethylcellulose, ethyl methylcellulose, hydroxyethyl methylcellulose. Lower molecular weight water soluble, polyvinyl alcohol film-forming polymers are generally, preferred. Polyvinyl alcohols that can be used include those having a weight average molecular weight of between about 1,000 and about 300,000, and between about 2,000 and about 150,000, and between about 3,000 and about 100,000.

The composition made according to the present invention may 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, the disclosures of which are incorporated by reference herein for all purposes. 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 comprising the composition out of the dispenser to a storage reservoir or directly to a point of use. When used, the product can be 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 detergent 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.

While the invention is described in the context of a warewashing composition for washing articles in an automatic dishwashing machine, it should be understood that the warewashing composition can be used for washing non-ware

items. That is, the composition can be referred to as a cleaning composition and can be used to clean various items and, in particular, any items that may suffer from water spotting. Examples of other uses of the composition of the invention include but are not limited to automotive washes, window washes, shower stall cleaners, to name a few. It should be understood that certain components that may be included in a warewashing composition because it is intended to be used in an automatic dishwashing machine can be excluded from a cleaning composition that is not intended to be used in an automatic dishwashing machine, and vice versa. For example, surfactants that have a tendency to create quite a bit of foaming may be used in a cleaning composition that is not intended to be used in an automatic dishwashing machine.

The warewashing composition can be provided in several forms including solids and liquids. When provided in the form of a solid, the warewashing composition can be provided in the form of powder, granules, pellets, tablets, blocks, cast solids, and extruded solids. By way of example, pellets can have sizes of between about 1 mm and about 10 mm diameter, tablets can have sizes of between about 1 mm and about 10 mm diameter, tablets can have sizes of between about 1 cm and about 10 cm diameter, and blocks can have sizes of at least about 10 cm diameter. When provided in the form of a liquid, the warewashing composition can be provided as a gel or a paste. Exemplary ranges for components of the warewashing composition when provided as a gel or a paste are shown in Table 1. Exemplary ranges for components of the warewashing composition when provided as a solid are shown in Table 2.

Table 1 - Gel or Paste Warewashing Composition (wt.%)

Component	First Exemplary Range	Second Exemplary Range	Third Exemplary Range
Water	5-60	10-35	15-25
Cationic Source	1-60	5-40	10-30
Alkaline Source	1-60	5-40	10-30
Non-Conversion Agent Forming Alkaline Source	0-50	0.5-30	2-20
Stabilizer	0-20	0.5-15	2-10
Dispersant	0-20	0.5-15	2-9
Enzyme	0-15	0.5-10	1-5
Corrosion Inhibitor	0-15	1-10	2-5
Surfactant	0-15	1-10	2-5
Fragrance	0-10	0.01-5	0.1-2
Dye	0-1	0.001-0.5	0.01-0.25

Table 2 - Solid Warewashing Composition (wt.%)

Component	First Exemplary Range	Second Exemplary Range	Third Exemplary Range
Water	0-30	1-15	2-8
Cationic Source	1-60	5-40	10-30
Bleach	0-55	15-45	25-35
Alkaline Anionic Source	1-60	0.5-30	2-20
Non-Conversion Agent-Forming Alkaline Source	0-50	0.5-30	2-20
Dispersant	0-10	0.001-5	0.01-1
Enzyme	0-15	1-10	2-5
Corrosion Inhibitor	0-15	1-10	2-5
Surfactant	0-15	1-10	2-5
Fragrance	0-10	0.01-5	0.1-2
Dye	0-1	0.001-0.5	0.01-0.25

The various forms of the warewashing composition concentrate can be provided in a water soluble packaging film. That is, solids and liquids can be packaged in the water soluble films. Exemplary solids that can be packaged in a

water soluble film include powders, pellets, tablets, and blocks. Exemplary liquids that can be packaged in the water soluble film include gels and pastes.

Table 3: Exemplary Rinse Agent Compositions

COMPONENT	Composition 1, Wt.%	Composition 2, Wt.%
Cationic Source		
Alkaline Anionic Source		
Sheeting agent	1-90	3-50
Humectant	0-90	3-50
Water	0-90	3-50
Solidification agent	0-90	20-50
Defoamer	0-10	0.1-5
Chelating agent/threshold inhibitor	0-30	0.1-20
pH buffers	To desired pH	To desired pH
Glass corrosion inhibitors	0-20	0.1-10

The rinse agent composition may contain the cationic source in an amount sufficient to provide a desired molar equivalent of cation to anion in the use composition. Exemplary cationic and alkaline anionic sources include those discussed above in the warewashing detergent composition section.

It is believed that the rinse agent composition can be used in a high solids containing water environment (in excess of about 200 ppm) in order to reduce the appearance of a visible film caused by the level of dissolved solids present in the water. The applications where the presence of a visible film after washing a substrate is a particular problem include the restaurant or warewashing industry, the car wash industry, and the general cleaning of hard surfaces. Exemplary articles in the warewashing industry that can be treated with a rinse agent include, but are not limited to: dishware, cups, glasses, flatware, and cookware. For the purposes of this

invention, the terms "dish" and "ware" are used in the broadest sense to refer to various types of articles used in the preparation, serving, consumption, and disposal of food stuffs including, but not limited to: pots, pans, trays, pitchers, bowls, plates, saucers, cups, glasses, forks, knives, spoons, spatulas, and other glass, metal, ceramic, plastic composite articles commonly available in the institutional or household kitchen or dining room. In general, these types of articles can be referred to as food or beverage contacting articles because they have surfaces that are provided for contacting food and/or beverage. In the car wash industry, filming on the surface of a washed motor vehicle is undesirable. Accordingly, the rinse agent is particularly useful for the glass and painted surfaces of a motor vehicle. Accordingly, the rinse agent can be used to reduce the occurrence of visible filming on hard surfaces caused by high solids containing water. Exemplary hard surfaces include, but are not limited to: glass, vehicle exteriors, ware, counter tops, light fixtures, windows, mirrors, plastics, clear coats, painted surfaces including painted metal and painted wood, and treated surfaces including treated metal and treated wood.

As an example, when the rinse agent composition is used in warewashing applications, the rinse agent composition should provide effective sheeting action and low foaming properties. In car washing applications, it is desirable for the rinse agent to provide effective sheeting action. Generally, rinse agents used for rinsing motor vehicles can tolerate a higher level of foaming than rinse agents used in warewashing machines.

The above specification provides a basis for broadly understanding the invention. The following examples and test data provide an understanding of certain

specific embodiments of the invention. The examples are not meant to limit the scope of the invention that has been set forth in the foregoing description. Variations within the concepts of the invention are apparent to those skilled in the art.

EXAMPLES

The following examples were conducted to compare the contact angle of water based on warewashing compositions of the invention as compared to pre-existing particle or nanoparticle-containing compositions. The following procedure was followed to prepare ceramic tiles for the examples:

1. Gloves were worn during washing the tiles to prevent skin oils from contacting the glassware.
2. The ceramic tiles were scrubbed thoroughly with neutral pH liquid dish detergent commercially available as Express™ from Ecolab Inc. to remove dirt and oil.
3. The tiles were allowed to air dry.

Example 1

Four controls were prepared. For the first control (A), ceramic tiles were treated with only sodium hydroxide. For the second control (B), a tile was treated with 1000 ppm magnesium chloride, neutral pH. For the third control (C), the tile was treated with 1000ppm commercially purchased magnesium hydroxide/oxide nanoparticles. For the fourth control, tile (D) was treated with 1000ppm calcium chloride, neutral pH. Tiles (E) and (F) were treated according to the invention. Tile (E) was treated with 1000ppm water-soluble magnesium chloride under alkaline conditions to generate magnesium hydroxide *in situ*. Tile (F) was treated with

1000ppm water-soluble calcium chloride under alkaline conditions to generate magnesium hydroxide *in situ*. After treatment all tiles were rinsed with 17-grain hard water and dried with a paper towel. The contact angle of deionized water was measured using a goniometer. The lower the contact angle of deionized water, the better the wetting of the surface, and the less likely the surface will show water spotting. Results are shown in the table below:

Tile	Treatment	Contact Angle (degrees)
A	Sodium hydroxide	48
B	Magnesium chloride, neutral pH	28
C	Commercial magnesium hydroxide/oxide particles	15
D	Calcium chloride, neutral pH	35
E	*in situ* magnesium hydroxide	14
F	*in situ* calcium chloride	18

The results show that tiles E and F, treated according to the invention, performed substantially the same as the nanoparticle-treated tile C and better than tiles B & D that did not practice the invention.

WE CLAIM:

1. A composition useful in treating hard surfaces, comprising:

a substantially sequestrant-free source of at least one water-soluble cation selected from magnesium, titanium, and aluminum; and

a source of alkalinity including at least one hydroxide anion compound such that the cation and anion react to form a water-insoluble hydroxide precipitate that constitutes a conversion agent thereby softening the water.

2. A composition according to claim 1, wherein water-insoluble oxide precipitate is comprised of nanoparticles having an average particulate size of less than about 500 nanometers.

3. A composition according to claim 1, wherein the conversion agent causes calcium carbonate in hard water to precipitate as aragonite.

4. A composition according to claim 1, wherein the cation concentration is comprised of between about 10 ppm and about 1000 ppm.

5. A composition according to claim 1, wherein the composition is provided in solid form.

6. A composition according to claim 1, wherein the composition is substantially phosphate or phosphorous free.

7. A warewashing composition comprising:

(a) a substantially sequestrant-free source of between about 10 and 800 ppm of at least one water-soluble cation selected from magnesium, titanium, and aluminum,; and

(b) a source of alkalinity including at least one hydroxide anion compound such that the cation and anion react to form a conversion agent thereby softening the water.

8. The composition of claim 7, wherein the combination of the cation and the source of alkalinity causes a decrease in the contact angle of water on the surface of the wares to reduce spotting.

9. The composition according to claim 7, wherein a ware washed with the composition has a contact angle of water of less than 25 degrees.

10. The composition according to claim 7, wherein the conversion agent is comprised of water insoluble hydroxide precipitate causing calcium carbonate in hard water to precipitate as aragonite

11. The composition according to claim 7, wherein a ware treated with the composition has a contact angle of water of less than 20 degrees.

12. The composition according to claim 7, wherein the composition is a warewashing detergent further comprising about 0.5 wt.% to about 15 wt.% stabilizers.

13. The composition according to claim 7, wherein the composition further comprises about 0.5 wt.% and about 15 wt.% dispersant.

14. The composition according to claim 7, wherein the composition comprises about 5 wt.% to about 60 wt.% water.

15. The composition according to claim 7, wherein the composition comprises about 2 wt.% to about 8 wt.% water.

16. The composition according to claim 8, wherein the composition comprises a block having a size of at least about 5 grams.

17. The composition according to claim 7, further comprising a water-soluble packaging material enclosing the composition.

18. The composition according to claim 17, wherein the water-soluble packaging material comprises polyvinyl alcohol.

19. The composition according to claim 16, wherein the composition is provided within the water-soluble packaging material in an amount sufficient to provide a unit dose for application in a dishwashing machine.

20. The composition according to claim 7 wherein the composition comprises a rinse agent.

21. A composition according to claim 7, wherein the composition comprises is substantially phosphorous or phosphate free.

22. A method for using a warewashing composition, the method comprising:

(a) diluting the composition with water at a dilution ratio of water to composition of at least about 200:1, wherein the composition comprises:

(i) a substantially sequestrant-free source of at least one water-soluble cation selected from magnesium, titanium and aluminum; and

(ii) a source of alkalinity selected from at least one of hydroxide anion or carbonate anion such that the cation and anion react to form a conversion agent resulting in softened water; and

(b) washing ware with the use composition in an automatic dishwashing machine.

23. A method according to claim 22, wherein the use composition comprises a total of free cation concentration of greater than about 200 ppm.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2008/062546

A. CLASSIFICATION OF SUBJECT MATTER

C11D 3/04(2006.01)i, C11D 1/00(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 8 : C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKIPASS(KIPO internal), Espacenet

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X -------- Y	US 5,540,866 A (ASZMAN HARRY et al.) 30 JUL 1996 See abstract; column 1, line 7-column 3, line 41; column 5, line 43-column 6, line 13; examples; claims 1-4	1-11, 14, 15, 20-23 ---------- 12,13,16-19
Y ----- A	US 2005/0020464 A1 (SMITH, KIM R. et al.) 27 JAN 2005 See abstract; paragraphs [19]-[65]; claims 1-57	12,13,16-19 ---------- 1-11, 14, 15, 20-23
A	US 5,376,310 A (CRIPE THOMAS A. et al.) 27 DEC 1994 See abstract; column 2, lines 1-42; column 5, line 53-column 8, line 52; examples; claims 1-20	1-23
A	US 2006/0069001 A1 (SONG, BRIAN X.) 30 MAR 2006 See abstract; paragraphs [02]-[22], [35], [36], [44], [65]-[72]; examples; claims 1-22	1-23

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
22 OCTOBER 2008 (22.10.2008)	**22 OCTOBER 2008 (22.10.2008)**
Name and mailing address of the ISA/KR Korean Intellectual Property Office Government Complex-Daejeon, 139 Seonsa-ro, Seo-gu, Daejeon 302-701, Republic of Korea Facsimile No. 82-42-472-7140	Authorized officer LYU Eun Kyoung Telephone No. 82-42-481-8399

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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