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(54) **Titre : SYSTEME DE TRAITEMENT DE L'EAU, ET PROCEDES DE NETTOYAGE EN AVAL**  
 (54) **Title: WATER TREATMENT SYSTEM AND DOWNSTREAM CLEANING METHODS**

(57) **Abrégé/Abstract:**

The present invention provides methods for treating an aqueous system comprising contacting the aqueous system with a composition comprising a conversion agent. The methods of the present invention reduce the solubilized water hardness and/or reduce or inhibit scale formation in an aqueous system. Further, the methods of the present invention impact the chemistries needed in downstream cleaning processes employing water treated in accordance with the methods of the present invention.

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(54) **Title:** WATER TREATMENT SYSTEM AND DOWNSTREAM CLEANING METHODS

(57) **Abstract:** The present invention provides methods for treating an aqueous system comprising contacting the aqueous system with a composition comprising a conversion agent. The methods of the present invention reduce the solubilized water hardness and/or reduce or inhibit scale formation in an aqueous system. Further, the methods of the present invention impact the chemistries needed in downstream cleaning processes employing water treated in accordance with the methods of the present invention.

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## **WATER TREATMENT SYSTEM AND DOWNSTREAM CLEANING METHODS**

### **FIELD OF THE INVENTION**

5 The present invention relates to methods for treating an aqueous system, i.e., a water source or stream. In particular, methods for reducing solubilized water hardness using various conversion agents are provided. Methods for inhibiting or reducing scale formation are also provided. The present invention also relates to methods of employing treated water, for example, in cleaning processes.

### **BACKGROUND**

10 The level of hardness in water can have a deleterious effect in many systems. For example, when hard water alone, or in conjunction with cleaning compositions, contacts a surface, it can cause precipitation of hard water scale on the contacted surface. In general, hard water refers to water having a total level of calcium and magnesium ions in excess of about 100 ppm expressed in units of ppm calcium carbonate. Often, the molar ratio of  
15 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 hardness has been addressed in a number of ways. One method currently used to soften water is via ion exchange, e.g., by adding sodium to the water to exchange the calcium and magnesium ions in the water with sodium associated with a resin bed in a  
20 water softening unit. The calcium and magnesium adhere to a resin in the softener. When the resin becomes saturated it is necessary to regenerate it using large amounts of sodium chloride dissolved in water. The sodium displaces the calcium and magnesium, which is flushed out in a briny

25

solution along with the chloride from the added sodium chloride. When water softeners regenerate they produce a waste stream that contains significant amounts of chloride, creating a burden on the system, e.g., sewer system, in which they are disposed of, including a multitude of downstream water re-use applications like  
5 potable water usages and agriculture.

Hard water is also known to reduce the efficacy of detergents. One method for counteracting this includes adding chelating agents or sequestrants into deterative compositions that are intended to be mixed with hard water in an amount sufficient to handle the hardness. However, in many instances the water hardness exceeds the  
10 chelating capacity of the composition. As a result, free calcium ions may be available to attack active components of the composition, to cause corrosion or precipitation, or to cause other deleterious effects, such as poor cleaning effectiveness or lime scale build up.

15

### SUMMARY

In some aspects, the present invention provides a method for reducing solubilized water hardness in a water source. The method comprises contacting the water source having a pH of between about 6 and about 9 with a composition comprising a solid conversion agent. The conversion agent causes calcium hardness  
20 ions in the water source to substantially precipitate in a non-calcite crystalline form that does not need to be removed from the water source, such that the solubilized water hardness is substantially reduced.

In some embodiments, the conversion agent is selected from the group consisting of metal oxides, metal hydroxides, and combinations thereof. In other  
25 embodiments, the conversion agent is selected from the group consisting of magnesium oxide, aluminum oxide, titanium oxide, and combinations thereof. In still yet other embodiments, the conversion agent is selected from the group consisting of magnesium hydroxide, aluminum hydroxide, titanium hydroxide, and combinations thereof. In other embodiments, the conversion agent comprises  
30 magnesium oxide.

In some embodiments, the non-calcite crystalline form is aragonite. In other embodiments, the composition further comprises aragonite. In some embodiments, the composition comprises about 1 wt% to about 50 wt% of aragonite. In still yet

other embodiments, the conversion agent is insoluble in water. In some embodiments, the solubilized water hardness is reduced by about 15% or greater.

In some embodiments of the method of the present invention, the step of contacting the water with the conversion agent comprises running the water over the  
5 solid source of the conversion agent.

In other embodiments, the solid conversion agent is contained in a column. The column is agitated by a method selected from the group consisting of the flow of water through the column, by fluidization, mechanical agitation, high flow  
10 backwash, recirculation, and combinations thereof, in some embodiments. In still yet other embodiments, the temperature of the water source prior to contact with the conversion agent is between about 130°F and about 185°F. In some embodiments, the solubilized calcium ion water hardness is reduced.

In some aspects, the present invention provides a method of using a treated  
15 water source to clean an article. The method comprises treating a water source with a composition comprising a conversion agent, wherein the conversion agent causes calcium hardness ions in the water source to substantially precipitate in a non-calcite crystalline form that does not need to be removed from the water source, such that the solubilized hardness of the water is substantially reduced. A use solution is then  
20 formed with the treated water and a detergent. The article is then contacted with the use solution, such that the article is cleaned.

In some embodiments, the method further comprises the step of rinsing the article after it has been washed. In some embodiments, the article is rinsed using treated water. In other embodiments, the article is rinsed using untreated water.  
25

In some embodiments, the method further comprises applying a rinse aid to the article after it has been washed. In still yet other embodiments, the detergent used is substantially free of a chelant or sequestrant. In other embodiments, the detergent comprises an insoluble magnesium compound, an alkali metal carbonate, and water.  
30

In some aspects, the present invention provides an apparatus for treating a water source for use in an automatic warewashing machine. The apparatus comprises: an inlet for providing the water source to a treatment reservoir; a treatment reservoir comprising a conversion agent; an outlet for providing treated

water from the reservoir; and a treated water delivery line for providing the treated water to the automatic warewashing machine.

In some embodiments, the conversion agent in the treatment reservoir is a solid particle. In other embodiments, the solid conversion agent is selected from the group of metal oxides, metal hydroxides, and mixtures thereof. In still yet other  
5       embodiments, the metal oxide is selected from the group consisting of magnesium oxide, aluminum oxide, titanium oxide, and mixtures thereof. In other  
embodiments, the metal hydroxide is selected from the group consisting of  
magnesium hydroxide, aluminum hydroxide, titanium hydroxide, and mixtures  
10       thereof.

In still yet other embodiments, the solid conversion agent is an agitated bed in the treatment reservoir. In some embodiments, the bed of conversion agent is agitated by a method selected from the group consisting of the flow of water through the column, fluidization, mechanical agitation, high flow backwash, recirculation,  
15       and combinations thereof.

In some embodiments, the treatment reservoir comprises a portable, removable cartridge. In other embodiments, there is no filter between the outlet and the treated water delivery line.

In some aspects, the present invention provides a system for use in a cleaning  
20       process. The system comprises providing a water source to an apparatus for treating the water source. The apparatus comprises: an inlet for providing the water source to a treatment reservoir; a treatment reservoir comprising a conversion agent; an outlet for providing treated water from the reservoir; and a treated water delivery line for providing the treated water to the automatic washing machine. The treated  
25       water is provided to an automatic washing machine from the treated water delivery line of the apparatus. The treated water is combined with a deterative composition to provide a use composition.

In some embodiments, the automatic washing machine is selected from the group consisting of an automatic ware washing machine, vehicle washing system,  
30       instrument washer, clean in place system, food processing cleaning system, bottle washer, and an automatic laundry washing machine. In other embodiments, the deterative composition comprises a cleaning composition, a rinse agent composition or a drying agent composition. In some embodiments, the deterative agent is

substantially free of a chelant, builder, threshold agent, sequestrant or combination thereof. In still yet other embodiments, there is no filter between the outlet and the treated water delivery line.

5 In some aspects, the present invention provides a method for reducing scale formation in an aqueous system comprising contacting the aqueous system with a composition comprising a solid conversion agent, wherein the conversion agent causes calcium hardness ions in the water source to substantially precipitate in a non-calcite crystalline form that does not need to be removed from the water source, such that scale formation in the aqueous system is reduced.

10 These and other embodiments will be apparent to those of skill in the art and others in view of the following detailed description. It should be understood, however, that this summary and the detailed description illustrate only some examples, and are not intended to be limiting to the invention as claimed.

15 BRIEF DESCRIPTION OF DRAWINGS

Figure 1 is a schematic view of an apparatus for use in treating water according to the methods of the present invention.

Figure 2 is a photograph of glasses treated with varying ratios of magnesium oxide to calcite according to the methods of the present invention.

20 Figure 3 is a photograph of glasses rinsed with either treated or untreated water as described in Example 1(c).

Figure 4 is a photograph of glasses washed with either: a chelant free detergent and treated water; or a conventional detergent and untreated water, as described in Example 1(d).

25 Figure 5 is a photograph of glasses washed with either: a chelant free detergent treated water, and a rinse aid; or a conventional detergent, untreated water, and a rinse aid, as described in Example 1(d).

30 Figure 6 is a photograph of soiled glasses washed with either: a chelant free detergent and treated water; or a conventional detergent and untreated water, as described in Example 1(d).

Figure 7 is a graphical depiction of the effect of various conversion agents of the present invention on solubilized water hardness.

Figure 8 is a graphical depiction of the percent soil removal on various soils and textiles of either: a chelant free detergent and treated water; or a conventional detergent and untreated water, as described in Example 3.

Figure 9 is a graphical depiction of the percent ash left on wash cloths washed with either treated or untreated water as described in Example 3.

Figure 10 is a graphical depiction of the amount of calcium (ppm) left on wash cloths washed with either treated or untreated water as described in Example 3.

Figure 11 is a photograph of glasses contacted with either treated or untreated water at different temperatures as described in Example 4.

Figure 12 is a graphical depiction of the amount of Total Dissolved Solids (ppm), and  $\text{SiO}_3$  in untreated and treated water used in a vehicle washing facility.

#### DETAILED DESCRIPTION

The present invention relates to methods for treating water, such that the solubilized water hardness is reduced. In some embodiments, the solubilized calcium portion of water hardness is precipitated or reduced. In some aspects, a conversion agent, e.g., a metal oxide or hydroxide or a polymorph of calcium carbonate, is used to treat the water. In some embodiments, a solid source of an insoluble or slightly soluble conversion agent is used to treat the water. The water treated in accordance with the methods of the present invention has many beneficial effects, including, but not limited to, reduction of scale and soiling in areas where hard water can cause soiling, protecting equipment, e.g., industrial equipment, from scale build up, increased cleaning efficacy when used with conventional deterative compositions, and reducing the need for specific chemistries, e.g., those containing threshold agents, chelating agents, or sequestrants, or phosphorous, in downstream cleaning processes.

So that the invention may be more readily understood certain terms are first defined.

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 “free of chelating agent” or “substantially free of chelating agent” refers to a composition, mixture, or ingredients that does not  
5 contain a chelating agent or sequestrant or to which only a limited amount of a chelating agent or sequestrant has been added. Should a chelating agent or sequestrant be present, the amount of a chelating agent or sequestrant shall be less than about 7 wt%. In some embodiments, such an amount of a chelating agent or sequestrant is less than about 2 wt-%. In other embodiments, such an amount of a  
10 chelating agent or sequestrant is less than about 0.5 wt-%. In still yet other embodiments, such an amount of a chelating agent or sequestrant is less than about 0.1 wt-%.

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

As used herein, the term “conversion agent” refers to a species that causes solubilized calcium in water to substantially precipitate from solution as calcium carbonate in a form which is thought to be the thermodynamically unfavorable  
20 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.

As used herein, the term “solubilized water hardness” refers to hardness minerals dissolved in ionic form in an aqueous system or source, i.e.,  $\text{Ca}^{++}$  and  
25  $\text{Mg}^{++}$ . Solubilized water hardness does not refer to hardness ions when they are in a precipitated state, i.e., when the solubility limit of the various compounds of calcium and magnesium in water is exceeded and those compounds precipitate as various salts such as, for example, calcium carbonate and magnesium carbonate.

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

As used herein, the terms “slightly soluble” or “slightly 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-%. For example, magnesium oxide is considered to be insoluble as it has a water solubility (wt %) of about 0.00062 in cold water, and about 0.00860 in hot water. Other insoluble  
5 compounds for use with the methods of the present invention include, for example: magnesium hydroxide with a water solubility of 0.00090 in cold water and 0.00400 in hot water; aragonite with a water solubility of 0.00153 in cold water and 0.00190 in hot water; and calcite with a water solubility of 0.00140 in cold water and 0.00180 in hot water.

10 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.

15 As used herein, the term "free of threshold agent" or "substantially free of threshold agent" refers to a composition, mixture, or ingredient that does not contain a threshold agent or to which only a limited amount of a threshold agent has been added. Should a threshold agent be present, the amount of a threshold agent shall be less than about 7 wt%. In some embodiments, such an amount of a threshold agent  
20 is less than about 2 wt%. In other embodiments, such an amount of a threshold agent is less than about 0.5 wt%. In still yet other embodiments, such an amount of a threshold agent is less than about 0.1 wt%.

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

As used herein, the term "phosphate-free" or "substantially 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  
30 compound be present through contamination of a phosphate-free composition, mixture, or ingredients, the amount of phosphate shall be less than about 1.0 wt%. In some embodiments, the amount of phosphate is less than about 0.5 wt %. In

other embodiments, the amount of phosphate is less than about 0.1 wt%. In still yet other embodiments, the amount of phosphate is less than about 0.01 wt %.

As used herein, the term “phosphorus-free” or “substantially phosphorus-free” refers to a composition, mixture, or ingredient that does not contain  
5 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 about 1.0wt%. In some embodiments, the amount of phosphorus  
10 is less than about 0.5 wt %. In other embodiments, the amount of phosphorus is less than about 0.1 wt%. In still yet other embodiments, the amount of phosphorus is less than about 0.01 wt %.

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

15 As used herein, the term “ware” refers to items such as eating and cooking utensils and other hard surfaces such as showers, sinks, toilets, bathtubs, countertops, windows, mirrors, transportation vehicles, and floors. As used herein, the term “warewashing” refers to washing, cleaning, or rinsing ware.

As used herein, the term “hard surface” includes showers, sinks, toilets,  
20 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  
25 autoclaves and sterilizers, 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,  
30 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 using water treated according to the methods of the present invention.

As used herein, the phrases “medical instrument,” “dental instrument,”  
5 “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 using water treated according to the present invention. These various  
10 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,  
15 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, “weight percent (wt-%),” “percent by weight,” “% by weight,” and the like are synonyms that refer to the concentration of a substance as  
20 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  
25 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  
30 composition resulting from a particular initial mixture. Whether or not modified by the term “about,” the claims include equivalents to the quantities.

#### Compositions and Methods of Use

In some aspects, the present invention provides methods for treating water, comprising reducing the solubilized water hardness. In some embodiments, the solubilized calcium portion of water hardness is reduced. In some embodiments, the water is contacted with a composition comprising a conversion agent. In other  
5 aspects, the present invention provides methods for inhibiting or reducing scale formation in an aqueous system comprising contacting the aqueous system with a composition comprising a conversion agent. The conversion agent may be in any form, e.g., solid, particle, liquid, powder, nanoparticle, slurry, suitable for use with the methods of the present invention. In some embodiments, a solid source of a  
10 conversion agent is used.

Without wishing to be bound by any particular theory, it is thought that the conversion agents for use with the methods of the present invention cause solubilized calcium water hardness ions in water to substantially precipitate via an interfacial reaction from solution as calcium carbonate in the thermodynamically  
15 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. Thus, contacting water with a conversion agent of the present invention  
20 reduces the solubilized water hardness of the treated water, and leads to a reduction in scale formation on a surface in contact with the treated water. The aragonite crystals can also act as seed crystals for further reduction of solubilized calcium after contacting the conversion agent.

#### *Conversion agents*

25 Conversion agents suitable for use with the methods of the present invention include, but are not limited to metal oxides, metal hydroxides, polymorphs of calcium carbonate and combinations and mixtures thereof. In some embodiments, the conversion agent comprises a metal oxide. Metal oxides suitable for use in the methods of the present invention include, but are not limited to, magnesium oxide,  
30 aluminum oxide, titanium oxide, and combinations and mixtures thereof. Metal hydroxides suitable for use with the methods of the present invention include, but are not limited to, magnesium hydroxide, aluminum hydroxide, titanium hydroxide, and combinations and mixtures thereof. Polymorphs of calcium carbonate suitable

for use as a conversion agent with the methods of the present invention include, but are not limited to, aragonite. In some embodiments, magnesium oxide is used as a conversion agent to treat water. In some embodiments, magnesium hydroxide is used as a conversion agent to treat water. In still yet other embodiments, a  
5 combination of magnesium oxide and hydroxide are used as a conversion agent to treat water.

In some embodiments the conversion agent selected for use with the methods of the present invention is slightly soluble in water. In some embodiments, the conversion agent selected for use with the methods of the present invention is  
10 insoluble in water. In some embodiments, a conversion agent selected for use with the methods of the present invention has a solubility of less than about 0.01g /100 mL in water. In some embodiments, low solubility is preferred for longer conversion agent activity.

In some embodiments, water contacted with a conversion agent forms a  
15 calcium precipitate. The calcium precipitate formed using the methods of the present invention is such that the precipitate flows through the water source harmlessly. That is, in some embodiments, unlike conventional water treatment systems, there is not a need to filter or remove the precipitate from the treated water.

In some embodiments, the conversion agent used with the methods of the  
20 present invention is in solid form. By the term "solid" as used to describe the conversion agent 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  
25 like. The degree of hardness of the solid 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.

The composition comprising a conversion agent can further comprise  
30 additional functional ingredients. Additional functional ingredients suitable for use with the methods of the present invention include any materials that impart beneficial properties to the conversion agent, the water source being treated, or any combination thereof. For example, in some embodiments the conversion agent

comprises a solid media bed of particles, e.g., magnesium oxide particles. Additional functional ingredients may be added that aid in the prevention of “cementing” of the media bed, i.e., agglomeration of the particles, as it is contacted with a water source.

5           In some embodiments, the additional functional ingredient comprises a polymorph of calcium carbonate. Exemplary polymorphs of calcium carbonate suitable for use with the methods of the present invention include, but are not limited to, aragonite, calcite, vaterite and mixtures thereof. In some embodiments, the additional functional ingredient comprises aragonite. In other embodiments, the  
10 functional ingredient comprises calcite.

In some embodiments, the additional functional ingredient comprises a mixed cation compound of calcium and magnesium ions. In some embodiments, the additional functional material comprises calcium magnesium carbonate, some natural minerals of which may also be known by the name dolomite.

15           In some embodiments, the composition comprising a conversion agent further comprises about 10 wt% to about 90 wt% of an additional functional ingredient. In other embodiments, the composition comprising a conversion agent further comprises about 25 wt% to about 75 wt% of an additional functional  
20 ingredient. In still yet other embodiments, the composition comprising a conversion agent further comprises about 50 wt% of an additional functional ingredient. In some embodiments, the composition comprising a conversion agent further comprises about 25 wt% of aragonite. In some embodiments, the composition comprising a conversion agent further comprises about 25 wt% of calcite. It is to be  
25 understood that all values and ranges between these values and ranges are encompassed by the methods of the present invention.

#### *Water source*

In some aspects, the methods of the present invention comprise treating a water source such that the solubilized hardness of the water is reduced. The term “water source” as used herein, refers to any source of water having a hardness that  
30 would be benefited by treatment in accordance with the methods of the present invention. Exemplary water sources suitable for treatment using the methods of the present invention include, but are not limited to, water from a municipal water source, or private water system, e.g., a public water supply or a well. The water can

be city water, well water, water supplied by a municipal water system, water supplied by a private water system, and/or water directly from the system or well. In some embodiments, the water source is not an industrial process water, e.g., water produced from a bitumen recovery operation. In other embodiments, the water source is not a waste water stream.

In some embodiments the water source has a pH of about 6 to about 9 prior to treatment using the methods of the present invention. In some embodiments, the water source has a pH of between about 8 and about 12 prior to treatment using the methods of the present invention. In some embodiments, the water source will have a higher, i.e., more alkaline, pH after treatment in accordance with the methods of the present invention.

In some embodiments, the temperature of the water prior to contact with a conversion agent is at an ambient, i.e., room temperature, i.e., about 64 °F to about 75 °F. In some embodiments, the temperature of the water prior to contact with a conversion agent is at a temperature less than ambient temperature. In other embodiments the water source is heated prior to contact with a conversion agent. In some embodiments, heating the water source prior to contact with a conversion agent results in a greater reduction in the amount of scale formed on a surface, and a greater reduction in the solubilized water hardness than if the water source is not heated.

In some embodiments the temperature of the water prior to contact with a conversion agent is greater than about 100°F, greater than about 120°F, or greater than about 150°F. In some embodiments, the water temperature prior to contact with a conversion agent is between about 100°F and about 200°F. In other embodiments, the water temperature is between about 120°F and about 140°F, between about 140°F to about 160°F, or between about 65°F to about 180°F prior to contact with a conversion agent. It is to be understood that all values and ranges between these values and ranges are encompassed by the methods of the present invention.

In some aspects, the present invention provides methods for reducing solubilized water hardness comprising contacting a water source with a composition comprising a conversion agent. The step of contacting can include, but is not limited to, running the water source over or through a solid source, e.g., a column,



cartridge, or tank, comprising the conversion agent. The contact time is dependent on a variety of factors, including, for example, the pH of the water source, the hardness of the water source, and the temperature of the water source. In some embodiments, the water source has a contact time of between about 30 seconds and about 6000 seconds with the source of conversion agent. In some embodiments, the water source has a contact time of between about 120 seconds and about 1800 seconds with the source of conversion agent. In still yet other embodiments, the water source has a contact time of between about 200 seconds and about 1200 seconds with the source of conversion agent. It is to be understood that all values and ranges between these values and ranges are encompassed by the methods of the present invention.

In some embodiments, the methods of the present invention substantially reduce the solubilized hardness of the water source. The amount of water hardness reduction achieved is dependent on a variety of factors, including, but not limited to the pH of the water source, the temperature of the water source, and the initial water hardness.

For example, in some embodiments the solubilized water hardness is reduced by about 25%. In some embodiments, the solubilized water hardness is reduced by about 50%. In still yet other embodiments, the solubilized water hardness is reduced by about 75%. In still yet other embodiments, the solubilized water hardness is reduced by about 90%.

In some aspects, the present invention provides methods for reducing or inhibiting scale formation in an aqueous system. In some embodiments, an aqueous system, i.e., a water source, is contacted with a conversion agent, e.g., a metal oxide or hydroxide. Without wishing to be bound by any particular theory, it is thought, that the resulting treated aqueous system will have a reduced solubilized hardness. In some embodiments, the resulting treated aqueous system will have a reduced solubilized calcium hardness. This reduction in hardness will reduce the amount of scale formed on surfaces contacted by the water source. Thus, use of a water source treated in accordance with the methods of the present invention will inhibit or reduce the amount of water scale formed on a surface.

For example, in some embodiments the amount of scale formation is reduced by about 25%. In some embodiments, the amount of scale formation is reduced by

about 50%. In still yet other embodiments, the amount of scale formation is reduced by about 80%. In still yet other embodiments, the amount of scale formation is reduced by about 100%.

The methods of the present invention are especially effective at removing or preventing scale formation wherein the scale comprises calcium salts, e.g., calcium phosphate, calcium oxalate, calcium carbonate, calcium bicarbonate or calcium silicate. The scale which is intended to be prevented or removed by the present invention may be formed by any combination of the above-noted ions. For example, the scale may involve a combination of calcium carbonate and calcium bicarbonate. The scale typically comprises at least about 90 wt % of inorganic material, more typically at least about 95 wt % of inorganic material, and most typically at least about 99 wt % of inorganic material.

*Methods of Using a Treated Water Source in a Downstream Cleaning Process*

In some aspects, the present invention provides a method of using a treated water source to clean an article. It has been found that use of a treated water source has many advantages in downstream cleaning processes compared to use of a non-treated water source. For example, use of a water source treated in accordance with the methods of the present invention increases the efficacy of conventional detergents. Use of a treated water source also allows for the use of specific environmentally friendly deterative compositions, e.g., those free of chelants or sequestrants, or phosphorous.

In some embodiments, the methods of the present invention comprise treating a water source with a composition comprising a conversion agent, wherein the conversion agent causes calcium hardness ions in the water source to substantially precipitate in a non-calcite crystalline form that does not need to be removed from the water source, such that the solubilized hardness of the water is substantially reduced. A use solution can then be formed with the treated water and a deterative composition. The article or articles to be cleaned are then contacted with the use solution, such that the article(s) is cleaned.

In some embodiments, the method further comprises rinsing the article. The article can be rinsed with treated water, or with untreated water. In some

embodiments, the article is rinsed using treated water. A rinse aid can also be applied to the article after it has been washed.

Any conventional deterative composition can be used with the methods of the present invention. The deterative composition can comprise a cleaning composition, a rinse agent composition, a drying composition or any combination thereof.  
5 Without wishing to be bound by any particular theory, it is thought that use of a treated water source in a cleaning process increases the efficacy of the deterative composition due to the reduced amount of solubilized hardness minerals in the water source, e.g., solubilized calcium hardness ions. It is known that solubilized hardness  
10 ions combine with soap and detergents to form a scale or scum. Further, solubilized hardness ions limit the amount of lather formed with soaps and detergents. Reducing the amount of these solubilized hardness ions can therefore reduce the amount of these detrimental side effects.

Deterative compositions for use with the methods of the present invention can  
15 include, but are not limited to, detergent compositions, rinse agent compositions, or drying agent compositions. Exemplary detergent compositions include warewashing detergent compositions, laundry detergent compositions, CIP detergent compositions, environmental cleaning compositions, hard surface cleaning compositions (such as those for use on counters or floors), motor vehicle washing  
20 compositions, and glass cleaning compositions. Exemplary rinse agent compositions include those compositions used to reduce streaking or filming on a surface such as glass. Exemplary drying agent compositions include dewatering compositions. In the vehicle washing industry, it is often desirable to include a dewatering step where a sheeting or beading agent is applied to the vehicle exterior.

25 Exemplary articles that can be treated, i.e., cleaned, with the use solution comprising a deterative composition and treated water include, but are not limited to motor vehicle exteriors, textiles, food contacting articles, clean-in-place (CIP) equipment, health care surfaces and hard surfaces. Exemplary motor vehicle exteriors include cars, trucks, trailers, buses, etc. that are commonly washed in  
30 commercial vehicle washing facilities. Exemplary textiles include, but are not limited to, those textiles that generally are considered within the term "laundry" and include clothes, towels, sheets, etc. In addition, textiles include curtains. Exemplary food contacting articles include, but are not limited to, dishes, glasses, eating

utensils, bowls, cooking articles, food storage articles, etc. Exemplary CIP equipment includes, but is not limited to, pipes, tanks, heat exchangers, valves, distribution circuits, pumps, etc. Exemplary health care surfaces include, but are not limited to, surfaces of medical or dental devices or instruments. Exemplary hard surfaces include, but are not  
5 limited to, floors, counters, glass, walls, etc. Hard surfaces can also include the inside of dish machines, and laundry machines, in general, hard surfaces can include those surfaces commonly referred to in the cleaning industry as environmental surfaces.

In some embodiments, the deterative composition for use with the methods of the present invention comprises a detergent that is substantially free of a chelant sequestrant,  
10 and/or threshold agent, e.g., an aminocarboxylic acid, a condensed phosphate, a phosphonate, a polyacrylate, or the like. Without wishing to be bound by any particular theory, it is thought that because the methods of the present invention substantially reduce the solubilized hardness ions in the water source, when used with a detergent, there is a substantially reduced or eliminated need to include chelating agents, sequestrants, or  
15 threshold agents in the detergent composition in order to handle the hardness ions.

In some embodiments, the detergent for use with the methods of the present invention is substantially free of a chelating agent or sequestrant and comprises an insoluble magnesium compound, an alkali metal carbonate, and water. In some embodiments, the detergent composition for use with the methods of the present invention is a detergent  
20 composition described in U.S. Patent No.8,071,528, entitled "Cleaning Compositions with Water Insoluble Conversion Agents and Methods of Making and Using Them".

In some embodiments, the deterative composition may include other additives, including conventional additives such as bleaching agents, hardening agents or solubility modifiers, defoamers, anti-redeposition agents, threshold agents, stabilizers, dispersants,  
25 enzymes, surfactants, 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.

In some aspects, the present invention provides an apparatus for treating a water source used in a cleaning or washing process. The apparatus can be, for example, for use in an automatic warewashing machine, an automatic textile washing machine, and/or an automatic vehicle washing machine. The apparatus can be used both in commercial settings, e.g., at a restaurant, a hospital, and in residential settings, e.g., a private home, or apartment building.

Referring to Figure 1, a schematic of an apparatus of the present invention is shown at reference 10. The apparatus comprises: an inlet 12 for providing the water source to a treatment reservoir 14; a treatment reservoir 14 comprising a conversion agent 16; an outlet 18 for providing treated water from the treatment reservoir; and a treated water delivery line 20 for providing the treated water to the selected cleaning device. In some embodiments, there is no filter between the outlet and the treated water delivery line. A flow control device 22 such as a valve 24 can be provided in the treated water delivery line 18 to control the flow of the treated water into the selected end use device, e.g., a warewashing machine, a laundry washing machine.

In some embodiments, the conversion agent is contained in a treatment reservoir in the apparatus. The reservoir can be for example, a tank, a cartridge, a filter bed of various physical shapes or sizes, or a column. In some embodiments, the treatment reservoir comprising a conversion agent is resin free, i.e., it does not contain a material that contains univalent hydrogen, sodium or potassium ions, which exchange with divalent calcium and magnesium ions in the water source. In some embodiments, the reservoir is pressurized. In other embodiments, the reservoir is not pressurized. One reservoir or multiple reservoirs may be used with the methods of the present invention. For example, the water source may be passed over a plurality of reservoirs, in the same or in separate containers, comprising the same or different conversion agents. The reservoirs may be arranged in series or in parallel.

In some embodiments, the conversion agent is in the form of an agitated bed or column. The bed or column may be agitated to avoid "cementing," i.e., agglomeration of the solid conversion agent once contacted with the water source. The bed or column can be agitated by any known method including, for example, by

the flow of water through the column, fluidization, mechanical agitation, high flow backwash, recirculation, and combinations thereof. In some embodiments, the solid conversion agent comprises a fluidized bed, e.g., a column or a cartridge, in the treatment reservoir. Fluidization is obtained by an increase in the velocity of the fluid, e.g., water, passing through the bed such that it is in excess of the minimum fluidization velocity of the media.

In some embodiments, the entire treatment reservoir can be removable and replaceable. In other embodiments, the treatment reservoir can be configured such that the bed of conversion agent contained within the treatment reservoir is removable and replaceable. In some embodiments, the treatment reservoir comprises a removable, portable, exchangeable cartridge comprising a conversion agent, e.g., magnesium oxide.

In some aspects, the present invention provides a system for use in a cleaning process. The system comprises providing a water source to an apparatus for treating the water source. In some embodiments, the apparatus for treating the water source comprises: (i) an inlet for providing the water source to a treatment reservoir; (ii) a treatment reservoir comprising a conversion agent; (iii) an outlet for providing treated water from the treatment reservoir; and (iv) a treated water delivery line for providing the treated water to the automatic warewashing machine. In some embodiments, a device, e.g., a screen, is present in the treatment reservoir in order to keep the conversion agent contained within the treatment reservoir as the fluid is passing over or through it. In some embodiments, there is no filter between the outlet and the treated water delivery line. Once the water has been treated, the treated water is provided to an automatic washing machine, e.g., an automatic ware washing machine, a vehicle washing system, an instrument washer, a clean in place system, a food processing cleaning system, a bottle washer, and an automatic laundry washing machine, from the treated water delivery line of the apparatus. Any automatic washing machine that would benefit from the use of water treated in accordance with the methods of the present invention can be used. The treated water is then combined with a deterative composition in the washing machine to provide a use composition. Any deterative composition can be used in the system of the present invention, for example, a cleaning composition, a rinse agent composition or

a drying agent composition. The articles to be cleaned are then contacted with the use solution in the automatic washing machine such that they are cleaned.

The water treatment methods and systems of the present invention can be used in a variety of industrial and domestic applications. The water treatment  
5 methods and systems can be employed in a residential setting or in a commercial setting, e.g., in a restaurant, hotel, hospital. For example, a water treatment method, system, or apparatus of the present invention can be used in: ware washing applications, e.g., washing eating and cooking utensils and other hard surfaces such as showers, sinks, toilets, bathtubs, countertops, windows, mirrors, and floors; in  
10 laundry applications, e.g., to treat water used in an automatic textile washing machine at the pre-treatment, washing, souring, softening, and/or rinsing stages; in vehicle care applications, e.g., to treat water used for pre-rinsing, e.g., an alkaline presoak and/or low pH presoak, washing, polishing, and rinsing a vehicle; industrial applications, e.g., cooling towers, boilers, industrial equipment comprising heat  
15 exchangers; in food service applications, e.g., to treat water lines for coffee and tea brewers, espresso machines, ice machines, pasta cookers, water heaters, steamers and/or proofers; in healthcare instrument care applications, e.g., soaking, cleaning, and/or rinsing surgical instruments, treating feedwater to autoclave sterilizers; and in feedwater for various applications such as humidifiers, hot tubs, and swimming  
20 pools

In some embodiments, the water treatment methods and systems of the present invention can be applied at the point of use. That is, a water treatment method, system, or apparatus of the present invention can be applied to a water source immediately prior to the desired end use of the water source. For example, an  
25 apparatus of the present invention could be employed to a water line connected to a household or restaurant appliance, e.g., a coffee maker, an espresso machine, an ice machine. An apparatus employing the methods of the present invention can also be included as part of an appliance which uses a water source, e.g., a water treatment system built into a coffee maker, or ice machine.

30 Additionally, an apparatus for employing the water treatment methods of the present invention can be connected to the water main of a house or business. The apparatus can be employed in line before the hot water heater, or after the hot water

heater. Thus, an apparatus of the present invention can be used to reduce solubilized water hardness in hot, cold and room temperature water sources.

### EXAMPLES

The present invention is more particularly described in the following examples that are intended as illustrations only, since numerous modifications and variations within the scope of the present invention will be apparent to those skilled in the art. Unless otherwise noted, all parts, percentages, and ratios reported in the following examples are on a weight basis, and all reagents used in the examples were obtained, or are available, from the chemical suppliers described below, or may be synthesized by conventional techniques.

*Example 1- Water Treatment with a Conversion Agent Comprising Low Water Soluble Magnesium Media*

The following experiments were performed to evaluate the effect of various conversion agents on water hardness, and ware washing applications.

*(a) Ability of a Conversion Agent Comprising a Solid Source of Magnesium Oxide to Reduce Solubilized Water Hardness*

The ability of a conversion agent comprising a solid source of insoluble magnesium oxide to treat water, e.g., reduce solubilized water hardness was evaluated. For this experiment water was passed through a media bed of magnesium oxide particles. The particles had an average size of about 900 microns. The media was held in a tank.

The amount of calcium and magnesium ions in the water was measured before and after passing over the bed comprising the conversion agent. The total dissolved solids (TDS), water hardness, and pH were also measured both before and after treatment. The table below summarizes the results.

Table 1.

	Before Treatment	After Treatment
pH	7.6	9.3
TDS (ppm)	360.5	201.4
Water Hardness (grains)	18	12
Ca <sup>++</sup> ions present (ppm)	66	9
Mg <sup>++</sup> ions present (ppm)	28	48



As can be seen from this table, the pH of the treated water rose slightly after treatment. Without wishing to be bound by any particular theory, it is thought that this is due to the magnesium oxide in the media bed dissolving into  $Mg^{++}$  and  $OH^{-}$  once contacted by the water. It was also observed that the total solubilized water hardness decreased by about 35%, and the total solubilized  $Ca^{++}$  decreased by about 86%. Overall, it was observed that the treatment of a water source with the solid conversion agent, i.e., magnesium oxide, provided beneficial effects, e.g., reduced solubilized water hardness, and reduced amounts of total dissolved solids, to the treated water source.

10 *(b) Addition of Calcite to a Conversion Agent*

Another test was run to determine the effect of adding calcite to the media bed comprising the conversion agent, i.e., magnesium oxide. It was theorized that the calcite would prevent “cementing” of the magnesium oxide during use over time, as magnesium oxide is known to agglomerate and form a solid mass. The amount of magnesium ions and calcium ions in the treated water were measured after treatment with various concentrations of magnesium oxide and calcium. The table below summarizes the results.

Table 2.

Percent Make-Up in Treatment Tank (%)					
MgO/Calcite	100/0	75/25	50/50	25/75	0/100
Treated Water Composition					
$Mg^{++}$ (ppm)	48.3	45.3	39.0	36.8	26.0
$Ca^{++}$ (ppm)	8.96	13.5	25.1	37.3	63.9

20 Drinking glasses were also washed in a ware washing machine using water treated with the above MgO/Calcite formulations. After 100 cycles the glasses were evaluated for spotting and filming, although filming was taken to be a more reliable indicator of glass appearance in the test. Heavily filmed glasses do not show spots well because a heavy film prevents appearance of spots. Figure 2 shows the glasses treated in this experiment. It was observed that the glasses washed with the water comprising 100% MgO and no calcite had little to no spotting. It was observed that

the amount of spotting and filming increased on the glasses as the amount of MgO used decreased, and the amount of calcite increased.

*(c) Addition of a Conversion Agent During a Ware Washing Process*

Another ware washing test on drinking glasses was run using a tank  
5 comprising a conversion agent, i.e., magnesium oxide, and no calcite. For this test, a Hobart AM-14 automatic ware washing machine was used. The water prior to treatment had a hardness of 17 grains. The magnesium oxide treated water was supplied before the sump in the machine, thereby also having an effect during the rinse cycle. No detergent or rinse aid was applied to the glasses. As a control, a  
10 glass was washed for 100 cycles with untreated water. After 100 cycles the glasses were evaluated for spotting and filming. Figure 3 shows the results of this experiment. It was observed that the glass ware treated with water and a conversion agent had no filming or scaling, unlike the control glass which had substantial filming and spotting.

15 *(d) Addition of a Conversion Agent During a Ware Washing Process with Detergent Formulations with and without a Chelant or Sequestrant*

A water treatment system comprising a solid source of a conversion agent was attached to an automatic ware washing system. The conversion agent used in this study comprised magnesium oxide. For this test, a Hobart AM-14 machine was  
20 used. The water prior to treatment had a hardness of 17 grains.

Two detergent formulations were tested. The first comprised about 1000ppm of a commercially available detergent with about 35% chelant, Apex Power®, available from Ecolab Inc. A rinse aid was applied after the glasses were washed with this detergent.

25 The second detergent was free of a chelant or sequestering agent, and comprised about 32% NaOH, about 35% RU silicate (a sodium silicate available from Philadelphia Quartz), about 0.6% polyether siloxane, about 2% Plurionic N3® (a copolymer available from BASF), about 1% of a nonionic defoaming agent, about 9.5% soda ash, about 12% sodium sulfate, and about 1% water. About 650ppm of  
30 the chelant free detergent was used. No rinse aid was used with the chelant free detergent. The glasses were washed with either formulation for 100 cycles.

The glasses washed with the chelant free detergent were washed using water treated with a conversion agent of the present invention, i.e., magnesium oxide. The

glasses washed with the commercially available detergent comprising a builder, i.e., Apex Power®, were washed using untreated water.

Figure 4 shows the glasses after completion of the 100 cycle test. As can be seen from this figure, the glass washed using a chelant free detergent and treated  
5 water, had substantially less filming and spotting than the glasses washed with Apex Power® and a rinse aid, but with untreated water. Further, it was observed that after the 100 cycles were completed, the inside of the machine used with the chelant free detergent and the treated water visually looked better than the machine used with the Apex Power® and the untreated water.

10 This test was repeated, however, a rinse aid was added after the wash cycle. About 2.33 mL of the rinse aid was added per cycle. Figure 5 shows the glasses after washing with each formulation. As can be seen in this figure, when a rinse aid was added, both glasses had an improved visual appearance. However, the glass treated with the chelant free detergent, and the treated water, still had substantially  
15 less spotting and filming than the glass washed with untreated water, and Apex Power®.

The same test was performed, this time using soiled glassware. Glasses were soiled with 100% whole milk and a dried protein/starch/grease combined soil. Soiled glasses were washed for 10 cycles, as described above, with either Apex  
20 Power®, or the chelant free detergent composition described above. The glasses were re-soiled between each cleaning cycle with additional starch and protein soil. The glasses washed with Apex® were washed with untreated water, and the glasses washed with the chelant free detergent were washed with water treated with a conversion agent, i.e., magnesium oxide.

25 The results are shown in Figure 6. As can be seen from this figure, the glasses washed with the chelant free detergent and the treated water had less spotting and filming than those washed using Apex Power®. It was also observed that the glasses washed with Apex Power® and untreated water had a slightly bluish tint, and those washed with the treated water had no visual blue spotting.

30

#### *Example 2- Effect of Various Metal Oxides and Salts on Hard Water*

A variety of tests were run to determine the effect various metal oxides and salts have on water hardness.

*(a) Effect of Various Metal Complexes on Hard Water*

The following test was run to determine the effect of various metal complexes, i.e., oxides, carbonates, and hydroxides, with or without calcite or aragonite, on water hardness. The starting water had a hardness of about 23 grains.

- 5 Different metal complexes were added to the water, and the hardness of the water was measured thereafter. For these experiments, about 216g of treatment agent was added to a beaker containing about 500mL of hard water. After stirring the contents the beaker for 20 minutes, an aliquot was removed and filtered through a 0.2 micron syringe filter to remove any suspended particulate. Then the filtered sample was
- 10 titrated for total water hardness ( $\text{Ca}^{++}$  and  $\text{Mg}^{++}$ ) using a water test kit. The following table summarizes the results. Table 3.

Treatment	Water Hardness after treatment (grains)
starting water	23
alum. oxide	6
alum. oxide + aragonite	8
alum. oxide + calcite	4
iron oxide	24
iron oxide + aragonite	26
iron oxide + calcite	24
mag. carbonate	24
mag. carbonate + aragonite	50
mag. carbonate + calcite	23
mag. hydroxide + aragonite	26
mag. oxide	8
titanium oxide	3
titanium oxide + aragonite	12
titanium oxide + calcite	9
zinc oxide	23
zinc oxide + aragonite	22
zinc oxide + calcite	23

These results are also graphically depicted in Figure 7. As can be seen from the table above, and Figure 7, addition of aluminum oxide, magnesium oxide, or titanium oxide reduced the water hardness more than the other metal oxides tested.

- 5 For example, the addition of aluminum oxide resulted in more than about a 70% reduction in the water hardness, the addition of titanium oxide resulted in more than about an 80% reduction in water hardness, and the addition of magnesium oxide resulted in more than about a 60% reduction in water hardness.

10 It was also found that the addition of aragonite and calcite with a metal oxide did not increase the reduction in the water hardness as much when aluminum oxide, magnesium oxide or titanium oxide was added to the water alone. However, the use of aluminum oxide, titanium oxide or magnesium oxide with calcite or aragonite still reduced the water hardness more than the other metal oxides tested, i.e., iron oxide, and zinc oxide.

15 *(b) Evaluation of Potential Water Softening Agents by Wetting Effect Change*

Various metal oxides, hydroxides, and salts were tested to determine their ability to act as water softeners. Solutions of about 1000ppm of the various compositions were prepared. Smooth ceramic tiles were rinsed with the solutions and wiped dry. The contact angle of deionized water on the surface of the tiles was measured. The tiles were then rinsed under 17 grain water hardness, dried, and the contact angle was re-measured. The results are shown in the table below.

20

Table 4.

Treatment	before hard water rinse	after hard water rinse	ratio after/before hard water rinse
0.1% titanium oxide	24	17	0.7
0.1% aluminum oxide	26	19	0.7
1% magnesium oxide	18	15	0.8
1% magnesium oxide nanoparticles	18	15	0.8
1% magnesium hydroxide	22	19	0.9

0.001% magnesium hydroxide	23, 17, 25	15	0.7
0.01% magnesium hydroxide	13, 18, 18	15	0.9
0.1% magnesium hydroxide	18, 16	16, 18	0.9, 1.1
untreated	37, 36	48	1.3
0.1% magnesium chloride	21	28	1.3
0.1% zinc oxide	16	22	1.4
0.1% calcium chloride	20	35	1.8
0.1% magnesium sulfate	11	24	2.2
0.1% silicon oxide nanoparticles (Snowtex N, Nissan Chemical)	9	23	2.6
0.1% silicon oxide nanoparticles (Snowtex 40, Nissan Chemical)	10	26	2.6
0.1% silicon oxide nanoparticles (Snowtex ZL, Nissan Chemical)	6	22	3.7
0.1% sodium hydroxide	2	21	10.5

It was theorized that a lower ratio of the contact angle of water before and after hard water rinsing of the substrate correlates to improved protection of the substrate from the hard water as it shows less impact of water hardness ions on the surface wetting. As can be seen from this table, the ratio of the contact angle after/before the hard water rinse was about 1 or less for the titanium oxide, aluminum oxide, and the magnesium oxide and hydroxide solutions tested. Based on these results, it was theorized that these solutions would likely soften water. The silicon oxide nanoparticles and sodium hydroxide had the highest change in contact angle.

*(c) Evaluation of Potential Water Softening Agents by Calcium Selective Electrode*

Various metal oxides, hydroxides, and salts were tested to determine their ability to act as water softeners. Solutions of the various compositions were prepared. To prepare the solutions, equal volumes of the treatment were mixed with about 17 grain hard water which is about 400ppm water hardness. The mixtures were allowed to stand for 10 minutes. An aliquot was removed and filtered through

a 0.2 micron syringe filter to remove any non-solubilized material. The level of dissolved calcium remaining in solution was determined using a calcium selective electrode (e.g., model 9720BNWP from ThermoScientific). The table below shows the results of this test.

5 Table 5.

Treatment	Ca Remaining from 400ppm Starting Solution (ppm)
untreated	400
calcite	300
aragonite	275
dolomite	300
magnesium oxide	275
magnesium hydroxide	275
aluminum oxide	150
iron oxide	300
silicon oxide	300
titanium oxide	250
clay (sodium/magnesium/calcium aluminosilicate)*	50

\*turned to gel; measured Ca level after filtration with a 0.2 micron filter.

As can be seen from this table, the solutions treated with magnesium oxide and hydroxide, aluminum oxide, and titanium oxide yielded the greatest reduction in the amount of calcium remaining in the solution after treatment. The iron oxide and silicon oxide decreased the amount of calcium remaining in the solution, at a lower level than the other metal oxides tested.

### *Example 3- Use of a Conversion Agent in a Laundry Application*

The effect of an inline conversion agent in a laundry application was determined. To determine the effect of the conversion agent on soil removal, soiled swatches are washed in a device such as a Terg-o-tometer (United States Testing

Co., Hoboken, N.J.). The Terg-o-tometer is a laboratory washing device that consists of multiple pots that reside in a single temperature-controlled water bath, with overhead agitators under time and speed control. Wash test parameters include: wash temperature, wash duration, pH, mechanical agitation, dose of cleaning  
5 composition, water hardness, wash formula, and cloth/liquor ratio. For this test, a pair of cylinders comprising a conversion agent, i.e., magnesium oxide, was mounted inline, upstream of a wash wheel in both hot and cold 17 grain water lines.

After completing the appropriate exposure times the fabric samples were removed. The detergent chemistries were immediately flushed, and the swatches  
10 rinsed with cold synthetic 5 grain water until 5 cycles of fills and rinses are complete. The swatches were then laid flat and dried overnight on white polyester-cotton towels before reflectance readings were taken using a spectrophotometer, e.g., Hunter ColorQuest XE (reflectance) Spectrophotometer.

To determine the % soil removal (SR), the reflectance of the fabric sample is  
15 measured on a spectrophotometer. The "L value" is a direct reading supplied by the spectrophotometer. L generally is indicative of broad visible spectrum reflectance, where a value of 100% would be absolute white. The % soil removal is calculated from the difference between the initial (before washing) lightness (L) value and the final L value (after washing):

$$20 \quad SR = ((L_{\text{final}} - L_{\text{initial}}) / (96 - L_{\text{initial}})) \times 100\%$$

Two detergent compositions were used in this study. The first comprised a mixture of chelant/sequestrant i.e., polyacrylate polymer and sodium citrate, and the second was substantially free of any chelant/sequestrant. Other than the presence or absence of a chelant or sequestrant, the two detergent compositions were equivalent  
25 and comprised about 3-75 wt% surfactant (if present), about 5-50 wt% sequestrant (if present), about 0-50 wt% alkalinity source and about 0-30wt% of an active enzyme composition.

The detergent composition with no chelant or sequestrant was used with treated water, i.e., water contacted with the conversion agent, and the detergent with  
30 the chelant/sequestrant mixture was used with untreated water. The results are shown in Figure 8. As can be seen in this figure, the treated water/chelant free detergent composition had a higher percent soil removal for the carbon cotton blood milk soiled swatch. For the other swatches tested, the detergent comprising a



chelant/sequestrant used with untreated water had a higher percent soil removal than the treated water/chelant free detergent composition. However, for most of the soils tested, the results were similar between both test groups.

Another test was run to evaluate the encrustation of linens when using a conversion agent of the present invention. For this test, face cloths were washed for 20 cycles in the wash wheel using 17 grain water. Single face cloths were removed for analysis at 0, 5, 15, and 20 cycles. Two tests were run. For both tests, the chelant/sequestrant free detergent described above was used. The first test included an inline cylinder comprising a conversion agent, and the second test used untreated water. The amount of total ash and calcium content for the wash cloths were measured using Inductively Coupled Plasma (ICP), and the results are shown in the table below.

Table 6.

Percent Ash					
Number of wash cycles	0	5	10	15	20
Untreated water	0.13	0.36	0.79	1.45	2.58
Treated water	0.13	0.19	0.65	0.76	0.83
Calcium (ppm)					
Number of wash cycles	0	5	10	15	20
Untreated water	121	1120	2750	5240	10100
Treated water	125	750	3080	3570	4120

These results are also graphically depicted in Figures 9 and 10. As can be seen from these results, the wash cloths washed using the treated water had a much lower

amount of ash remaining on the cloths at each test point. For example, after 20 washes, the cloths washed with treated water had about 32% of the amount of ash as those washed with the untreated water. With respect to the amount of calcium present on the wash clothes, at all test points other than the 10 cycle test point, there was less calcium on the wash cloths washed with treated water than those washed with untreated water.

The amount of other metals on the wash cloths was also measured. These results are shown in the table below.

Table 7.

Copper (ppm)					
Number of wash cycles	0	5	10	15	20
Untreated water	37.7	18.4	25.2	27.4	35.1
Treated water	37.7	16.6	16	15.3	16
Magnesium (ppm)					
Number of wash cycles	0	5	10	15	20
Untreated water	23.9	146	198	242	295
Treated water	22.8	176	408	460	543
Phosphorus (ppm)					
Number of wash cycles	0	5	10	15	20
Untreated water	10.3	18.6	29.1	42.2	61.5
Treated water	7.56	22.3	73.1	77.7	97

Iron (ppm)					
Number of wash cycles	0	5	10	15	20
Untreated water	4.73	3.81	3.88	3.67	3.69
Treated water	5.21	4.23	3.7	3.44	3.53

As can be seen from this chart, there was less copper in the samples washed with the treated water than the untreated water. However, there was more magnesium in the samples washed with the treated water than the untreated water.

- 5 This was to be expected, as the conversion agent used for this study comprised magnesium, and it may have partially dissolved over time.

*Example 4- Effect of Water Temperature on Conversion Agents*

The effect of the temperature of the water contacted by a conversion agent on  
 10 filming or spotting of glassware was determined. Water with a hardness of 17 grains per gallon was connected to a tank comprising a conversion agent of the present invention, i.e., magnesium oxide. The tank was then connected to an automatic dishwashing machine. Glasses in a glassware rack were set into the dish machine. The dish machine was set to automatically run 100 cycles back to back. A cycle is a  
 15 complete wash, rinse, and 15 second pause. After 100 cycles the test was stopped and the glasses were observed. No detergents were used for this test. The test was repeated with hot water, i.e., about 140°F to about 150°F, and cold water. A control of untreated water, i.e., no contact with the conversion agent was also run. The glasses were visually inspected for spotting and filming. The results are shown in  
 20 Figure 11.

In Figure 11, the glass on the left was the glass treated with a conversion agent and hot water, the glass in the middle of the picture was treated with a conversion agent and cold water, and the glass on the right was the control in cold water, i.e., not contacted with the conversion agent. As can be seen from this figure,  
 25 the glass washed with the hot water contacted with the conversion agent yielded

substantially spotless glasses. The glass treated with the cold water contacted with the conversion agent, showed less filming than the control glass, but was not as clean or clear as the hot water treated glass. These results were surprising as calcium becomes less soluble, i.e., precipitates more, when heated.

5

*Example 5- Use of a Conversion Agent to Prevent Soap Scum*

A test was run to determine the effect of treated water, i.e., water contacted with a conversion agent, on the formation of soap scum. The cold water stream to two showers was attached to a tank comprising a solid source of a conversion agent, i.e., magnesium oxide. The cold water had 17 grain hardness before treatment. The hot water was blended at the shower temperature control knob, and comprised softened water.

After two months of running, the showers with and without treatment were inspected. It was observed that the tiled shower walls were more easily cleaned in the treated shower stalls, compared to the non-treated shower stalls. The white film, i.e., soap scum, that formed was much more easily removed by wiping in the shower stall that had treated water running in it. The untreated stalls had a gummy soap scum that was sticky and harder to wipe off. It was also noted that the shower heads in the un-treated stalls had a much more visible white scale present than those in the treated shower stalls.

The shower stalls were also subjected to a fizz test. An acid was sprayed onto the shower walls and observed to see if there was any fizzing upon contact. Fizzing indicates the presence of calcium carbonate. The treated shower stalls showed no fizz when sprayed with an acid. However, the shower stall without the treatment showed a pronounced fizz when contacted by the acid.

*Example 6- Use of a Water Treatment System for Vehicle Care*

A test was run to determine the effect of using treated water in a vehicle washing facility. Two tanks comprising a solid source of magnesium oxide as a conversion agent were installed in an automatic vehicle washing facility. The first tank (Tank 1) was installed on the first presoak arch. The second tank (Tank 2) was installed on the second presoak arch. The pH, TDS, and temperature of the untreated hot water, treated water from Tank 1, and treated water from Tank 2 were

measured. The amount of  $\text{SiO}_3$  in the untreated and treated waters was also measured.

Figure 12 is a graphical depiction of the results of this test. As can be seen in this figure, the tanks (Tank 1 and Tank 2) were installed on Day 22. The TDS increased on this day. However, by Day 32, the levels of TDS in the treated water were less than the level of  
5 TDS in the untreated water. As can also be seen in this figure, after the tanks were installed, the amount of  $\text{SiO}_3$  in the water dropped significantly in the treated water samples. It was also observed that the vehicles washed with treated water during the pre-soak had a much lower amount of scaling after being washed than those that had been washed using untreated water during the presoak stage. Overall, using water treated in accordance with  
10 the methods of the present invention had beneficial effects when used at a vehicle washing facility.

#### *Other Embodiments*

It is to be understood that while the invention has been described in conjunction with the detailed description thereof, the foregoing description is intended to illustrate, and  
15 not limit the scope of the invention, which is defined by the scope of the appended claims. Other aspects, advantages, and modifications are within the scope of the following claims.

It is to be understood that wherever values and ranges are provided herein, all values and ranges encompassed by these values and ranges, are meant to be encompassed within the scope of the present invention. Moreover, all values that fall within these ranges, as well  
20 as the upper or lower limits of a range of values, are also contemplated by the present application.

## We Claim:

1. A method for reducing solubilized water hardness in a water source, said method comprising:
  - (a) contacting the water source having a pH of between about 6 and about 9 with a composition comprising a solid conversion agent selected from the group consisting of metal oxides, magnesium hydroxide, aluminum hydroxide, titanium hydroxide, and combinations thereof, wherein the conversion agent causes calcium hardness ions in the water source to substantially precipitate in a non-calcite crystalline form that does not need to be removed from the water source, such that the solubilized water hardness is substantially reduced.
2. The method of claim 1, wherein the conversion agent is selected from the group consisting of magnesium oxide, aluminum oxide, titanium oxide, and combinations thereof.
3. The method of claim 1, wherein the non-calcite crystalline form is aragonite.
4. The method of claim 1, wherein the composition further comprises aragonite.
5. The method of claim 4, wherein the composition comprises about 1 wt% to about 50 wt% of aragonite.
6. The method of claim 1, wherein the conversion agent is insoluble in water.
7. The method of claim 1, wherein the solubilized water hardness is reduced by about 15% or greater.
8. The method of claim 1, wherein the step of contacting the water with the conversion agent comprises running the water over the solid source of the conversion agent.
9. The method of claim 1, wherein the solid conversion agent is contained in a column.
10. The method of claim 9, wherein the column is agitated by a method selected from the group consisting of the flow of water through the column, by fluidization, mechanical agitation, high flow backwash, recirculation, and combinations thereof.
11. The method of claim 1, wherein the temperature of the water source prior to contact with the conversion agent is between about 130°F and about 185°F.

12. The method of claim 1, wherein the solubilized calcium ion water hardness is reduced.
13. A method of using a treated water source to clean an article said method comprising:
  - (a) treating a water source with a composition comprising a conversion agent selected from the group consisting of metal oxides, magnesium hydroxide, aluminum hydroxide, titanium hydroxide, and combinations thereof, wherein the conversion agent causes calcium hardness ions in the water source to substantially precipitate in a non-calcite crystalline form that does not need to be removed from the water source, such that the solubilized hardness of the water is substantially reduced;
  - (b) forming a use solution with the treated water and a detergent; and
  - (c) contacting the article with the use solution such that the article is cleaned.
14. The method of claim 13, wherein the metal oxide is selected from the group consisting of magnesium oxide, aluminum oxide, titanium oxide, and mixtures thereof.
15. The method of claim 13, wherein the composition further comprises aragonite.
16. The method of claim 13, wherein the water source has a neutral pH prior to treatment.
17. The method of claim 13, wherein the water hardness decreases by about 15% or greater after treatment.
18. The method of claim 13, wherein the method further comprises the step of rinsing the article after it has been washed.
19. The method of claim 18, wherein the article is rinsed using treated water.
20. The method of claim 18, wherein the article is rinsed using untreated water.
21. The method of claim 13, wherein the amount of calcium hardness ions in the treated water source is lower than the amount of calcium hardness ions in the water source prior to the treatment step.
22. The method of claim 13, wherein the method further comprises applying a rinse aid to the article after it has been cleaned.

23. The method of claim 13, wherein the detergent is substantially free of a chelant or sequestrant.
24. The method of claim 13, wherein the detergent comprises an insoluble magnesium compound, an alkali metal carbonate, and water.
25. An apparatus for treating a water source for use in an automatic warewashing machine comprising:
- (a) an inlet for providing the water source to a treatment reservoir;
  - (b) the treatment reservoir comprising a conversion agent selected from the group consisting of metal oxides, magnesium hydroxide, aluminum hydroxide, titanium hydroxide, and combinations thereof, wherein the conversion agent causes calcium hardness ions in the water source to substantially precipitate in a non-calcite crystalline form that does not need to be removed from the water source, such that the solubilized hardness of the water is substantially reduced;
  - (c) an outlet for providing treated water from the reservoir; and
  - (d) a treated water delivery line for providing the treated water to the automatic warewashing machine.
26. The apparatus of claim 25, wherein the conversion agent in the treatment reservoir is a solid particle.
27. The apparatus of claim 25, wherein the metal oxide is selected from the group consisting of magnesium oxide, aluminum oxide, titanium oxide, and mixtures thereof.
28. The apparatus of claim 26, wherein the solid conversion agent is an agitated bed in the treatment reservoir.
29. The apparatus of claim 28, wherein the bed of conversion agent is agitated by a method selected from the group consisting of the flow of water through the column, fluidization, mechanical agitation, high flow backwash, recirculation, and combinations thereof.
30. The apparatus of claim 25, wherein the treatment reservoir comprises a portable, removable cartridge.



31. The apparatus of claim 25, wherein there is no filter between the outlet and the treated water delivery line.
32. A system for use in a cleaning process, said system comprising:
- (a) providing a water source to an apparatus for treating the water source said apparatus comprising:
    - (i) an inlet for providing the water source to a treatment reservoir;
    - (ii) the treatment reservoir comprising a conversion agent selected from the group consisting of metal oxides, magnesium hydroxide, aluminum hydroxide, titanium hydroxide, and combinations thereof, wherein the conversion agent causes calcium hardness ions in the water source to substantially precipitate in a non-calcite crystalline form that does not need to be removed from the water source, such that the solubilized hardness of the water is substantially reduced;
    - (iii) an outlet for providing treated water from the reservoir; and
    - (iv) a treated water delivery line for providing the treated water to an automatic washing machine; and
  - (b) providing treated water to the automatic washing machine from the treated water delivery line of the apparatus; and
  - (c) combining the treated water with a deterative composition to provide a use composition.
33. The system of claim 32, wherein the automatic washing machine is selected from the group consisting of an automatic ware washing machine, vehicle washing system, instrument washer, clean in place system, food processing cleaning system, bottle washer, and an automatic laundry washing machine.
34. The system of claim 32, wherein the deterative composition comprises a cleaning composition, a rinse agent composition or a drying agent composition.
35. The system of claim 32, wherein the deterative agent is substantially free of a chelant, builder, threshold agent, sequestrant or combination thereof.

36. The system of claim 32, wherein there is no filter between the outlet and the treated water delivery line.

37. A method for reducing scale formation in an aqueous system comprising contacting the aqueous system with a composition consisting essentially of a solid conversion agent selected from the group consisting of metal oxides, magnesium hydroxide, aluminum hydroxide, titanium hydroxide, and combinations thereof, wherein the conversion agent causes calcium hardness ions in a water source to substantially precipitate in a non-calcite crystalline form that does not need to be removed from the water source, such that scale formation in the aqueous system is reduced.

38. The method of claim 37, wherein the metal oxide is selected from the group consisting of magnesium oxide, aluminum oxide, titanium oxide, and mixtures thereof.

39. The method of claim 37, wherein the composition further comprises aragonite.

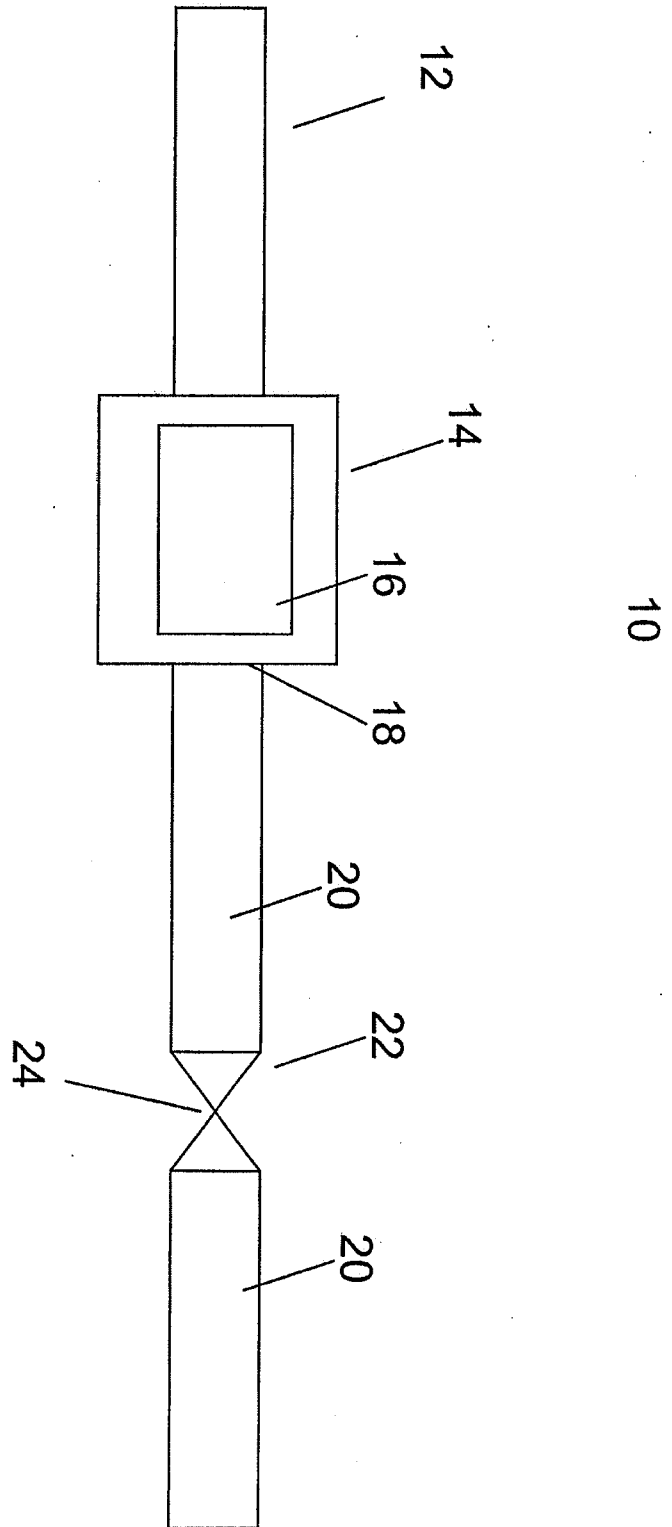


Figure 1

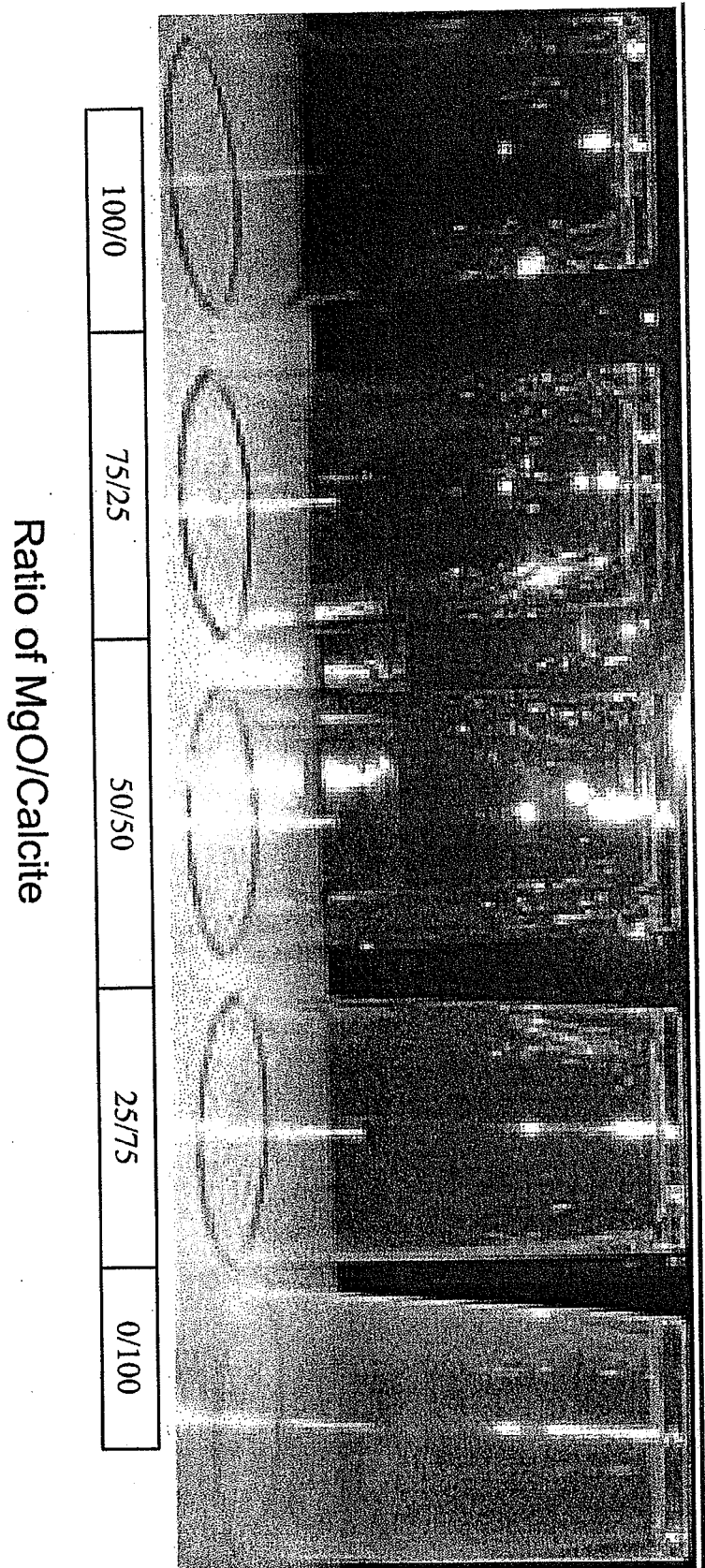


Figure 2

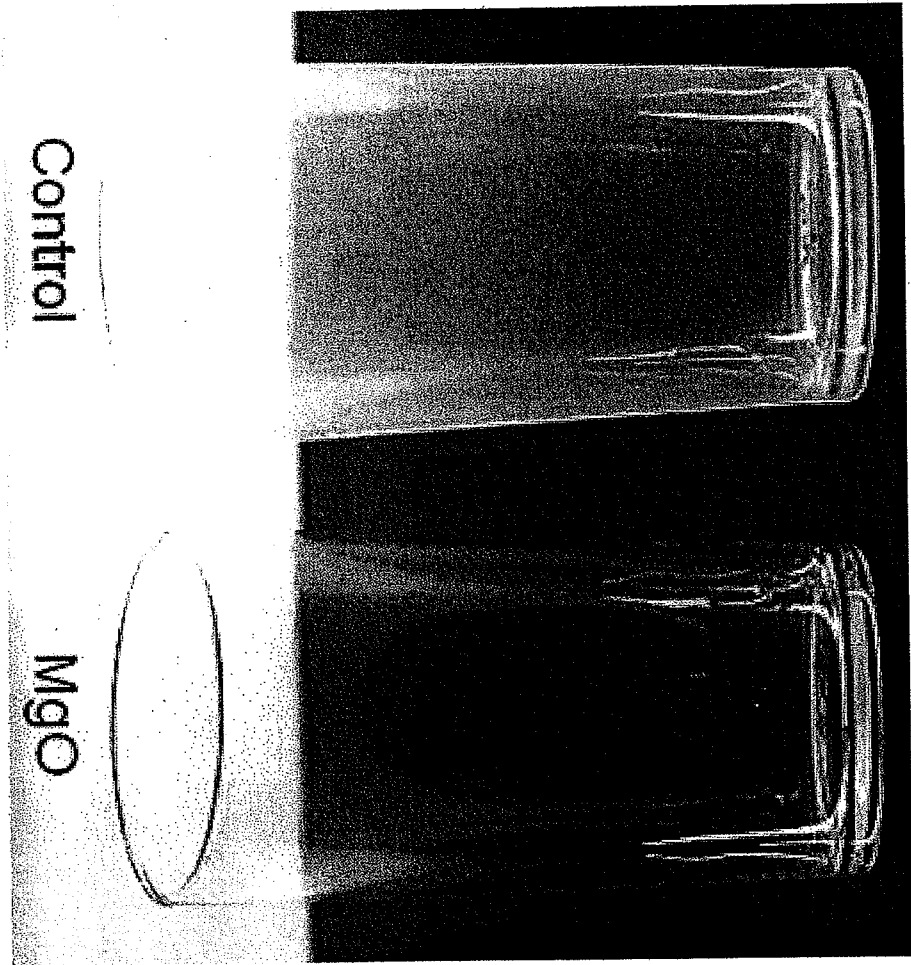


Figure 3

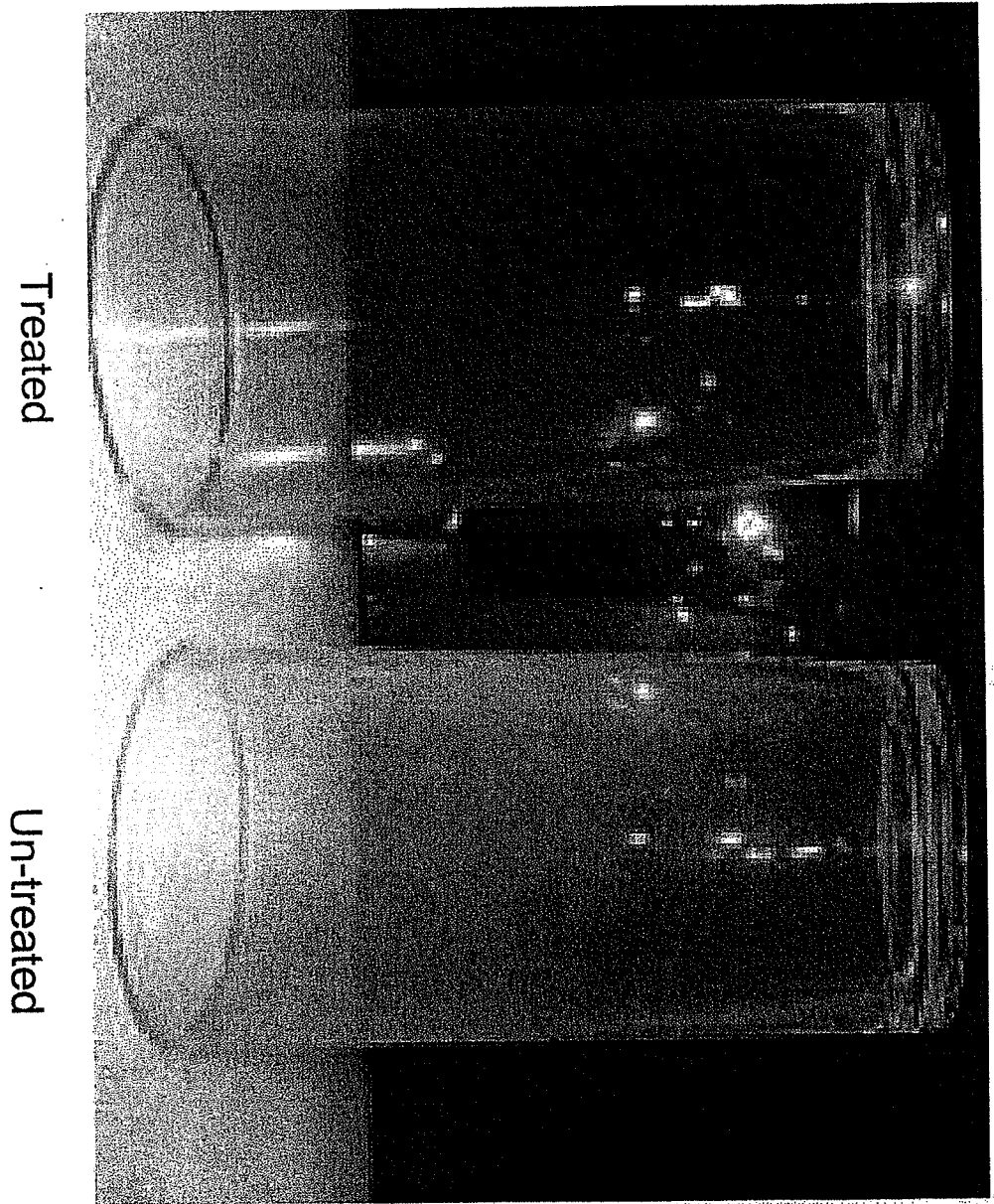
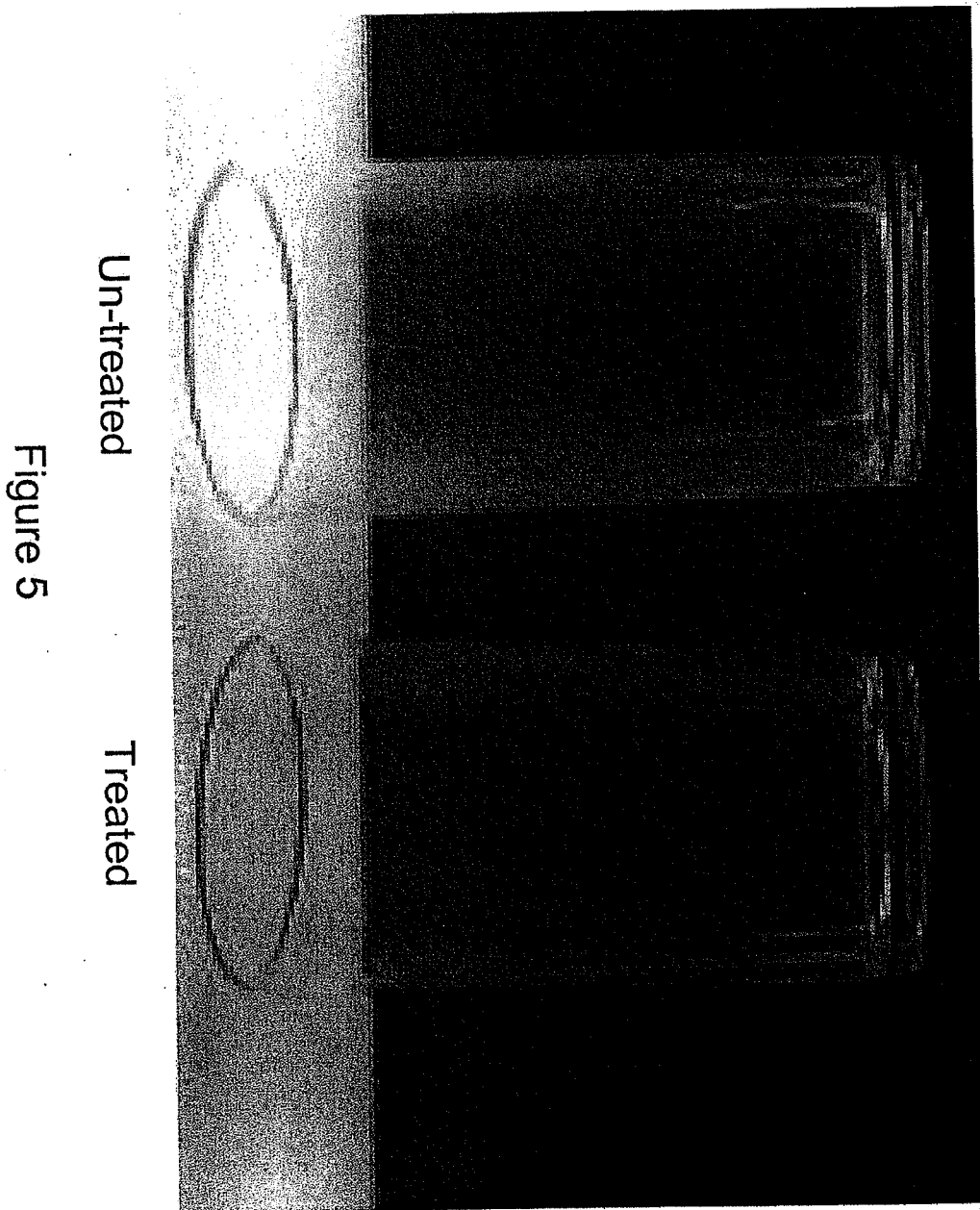
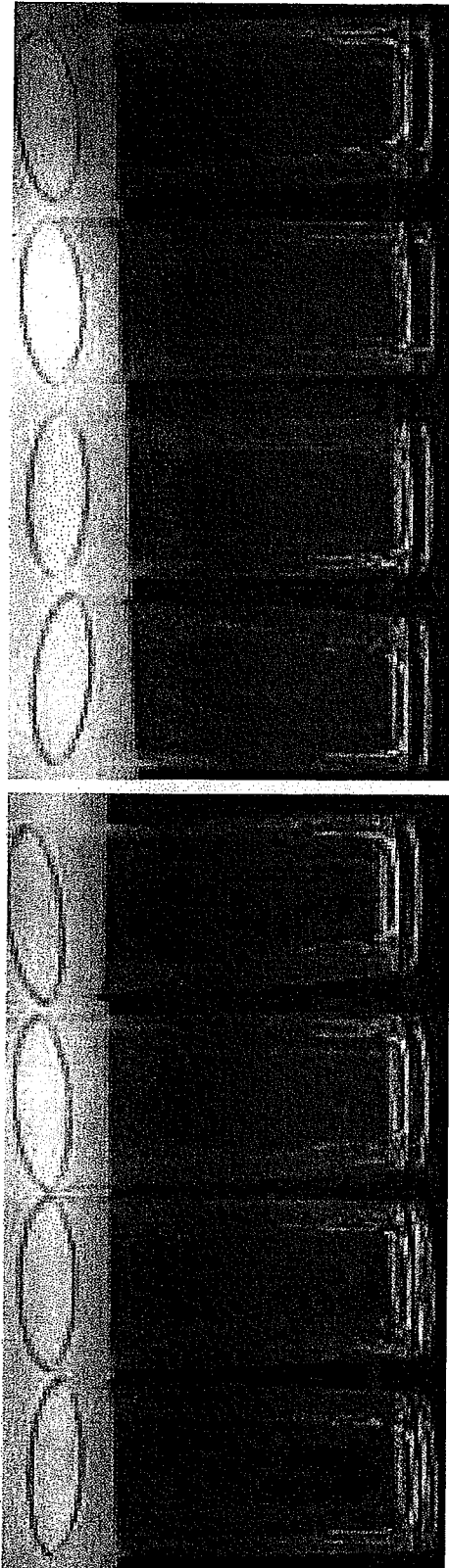


Figure 4



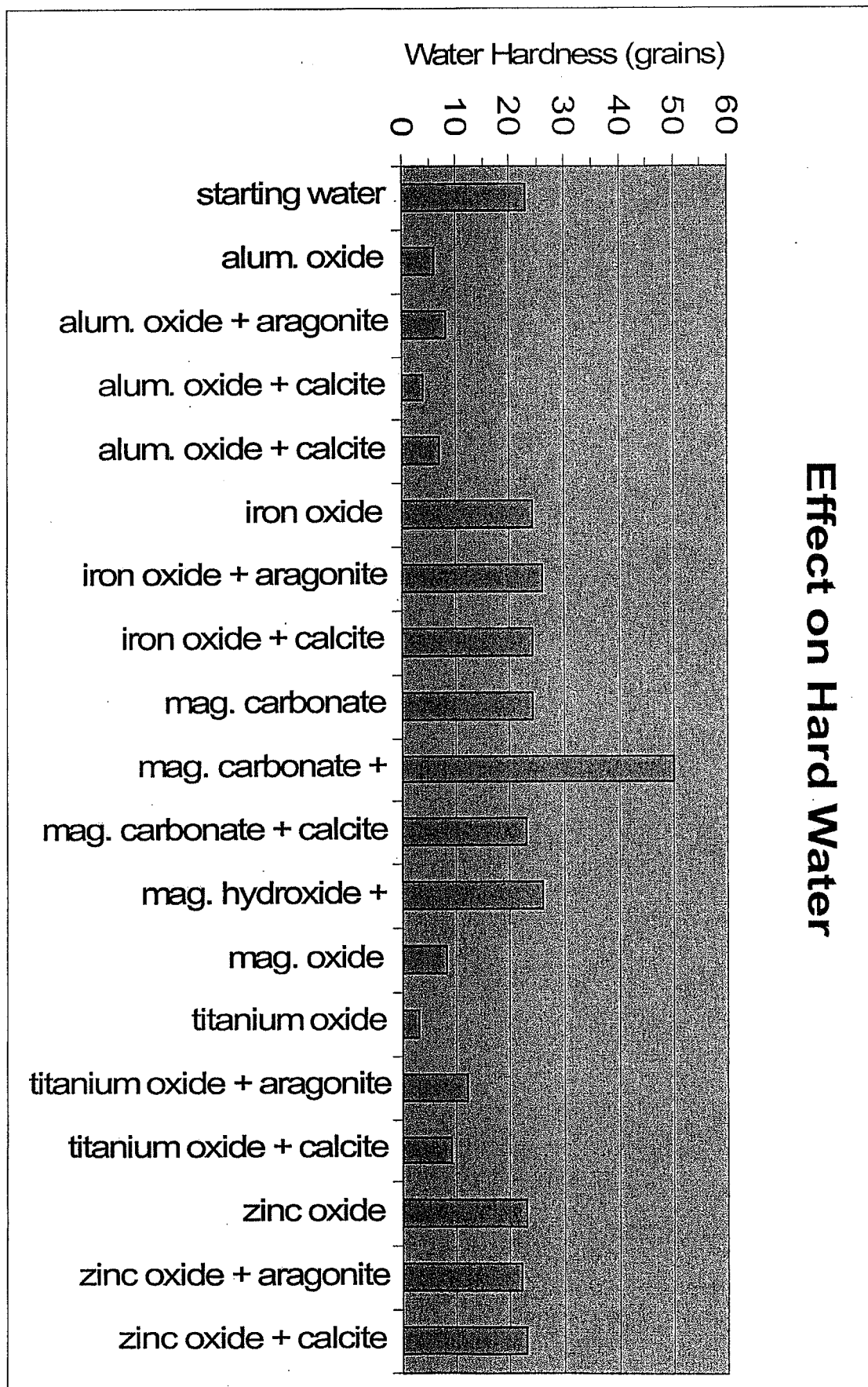


Un-treated

Treated

Figure 6





Effect on Hard Water

Figure 7

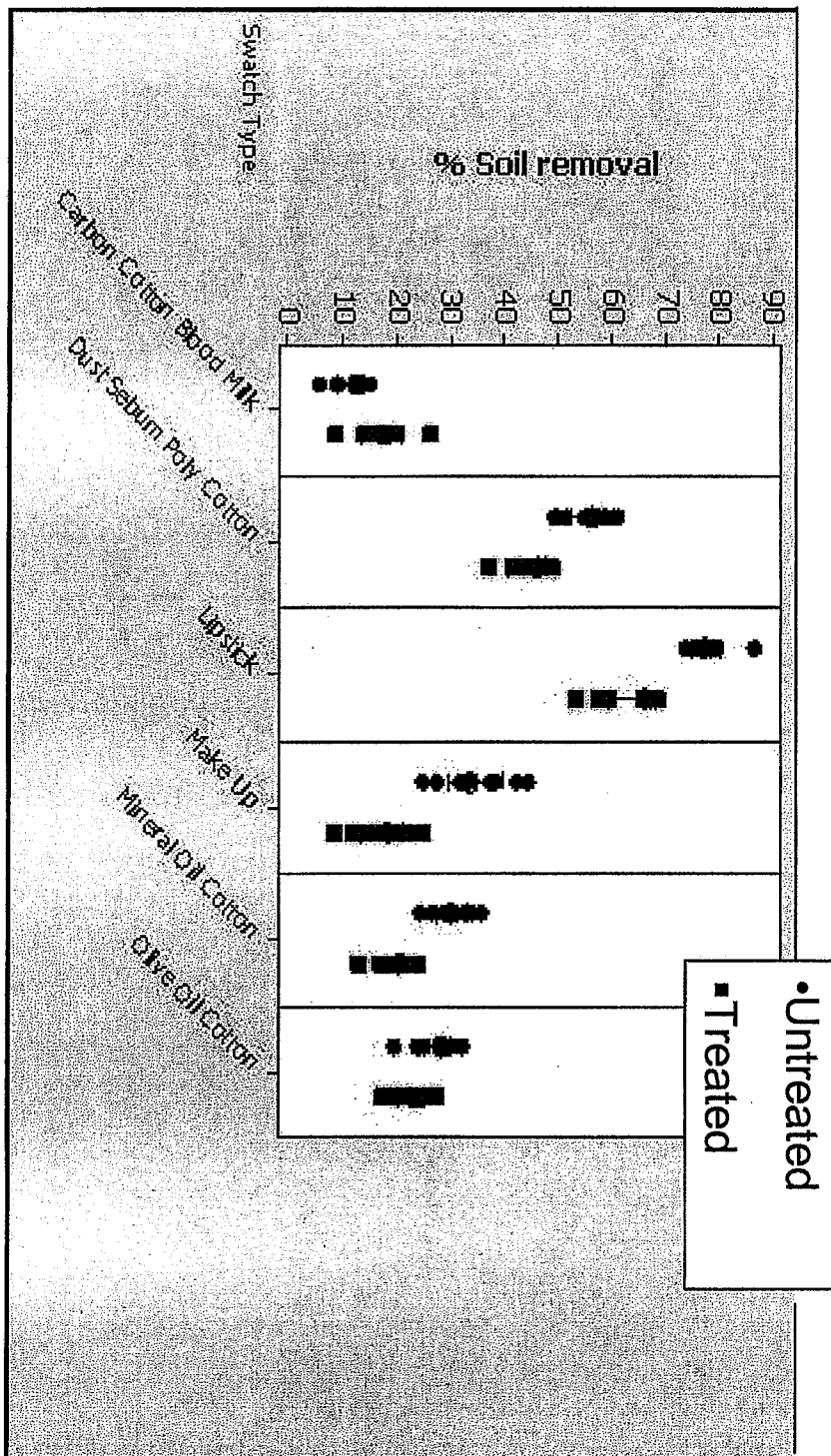


Figure 8

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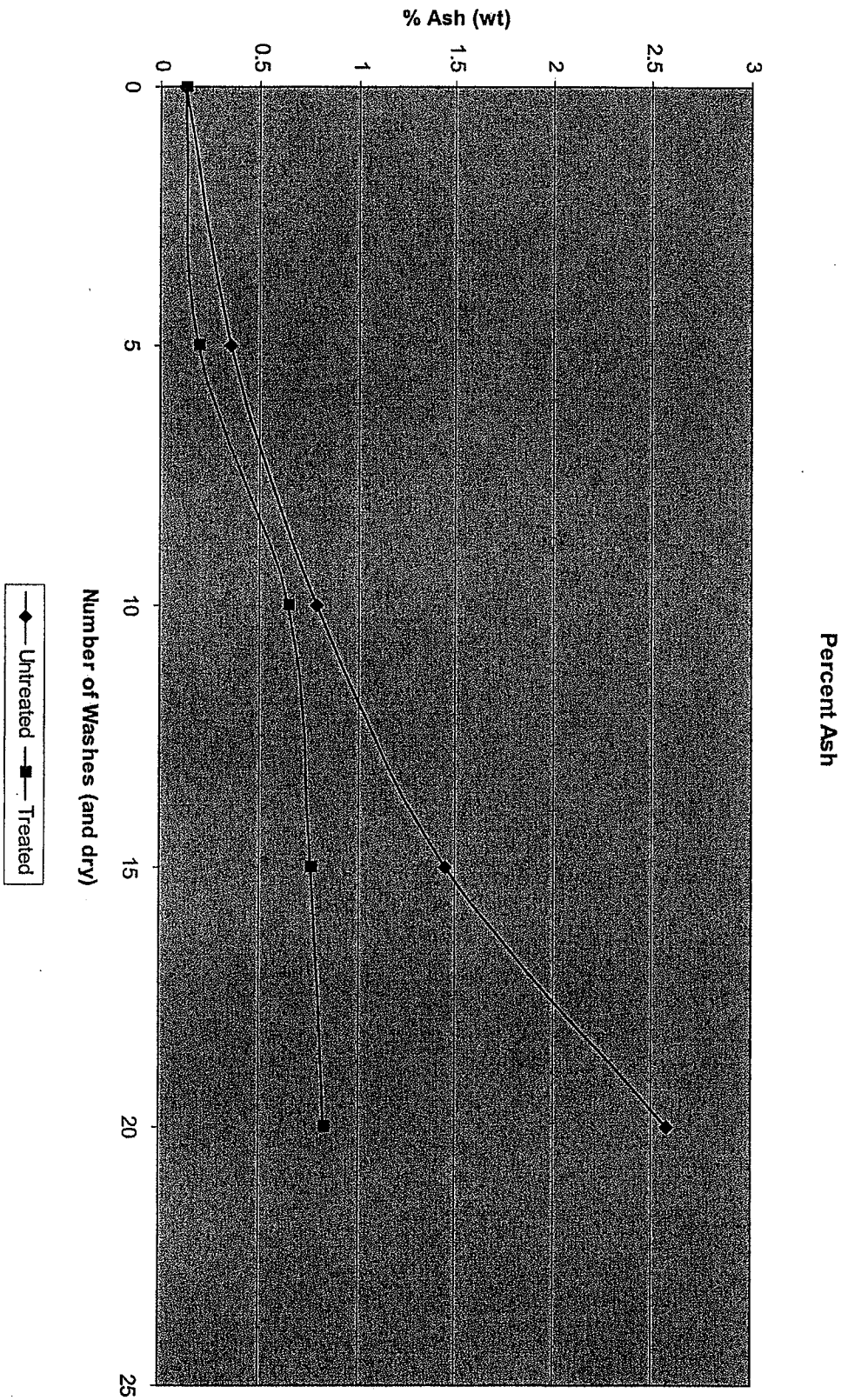


Figure 9

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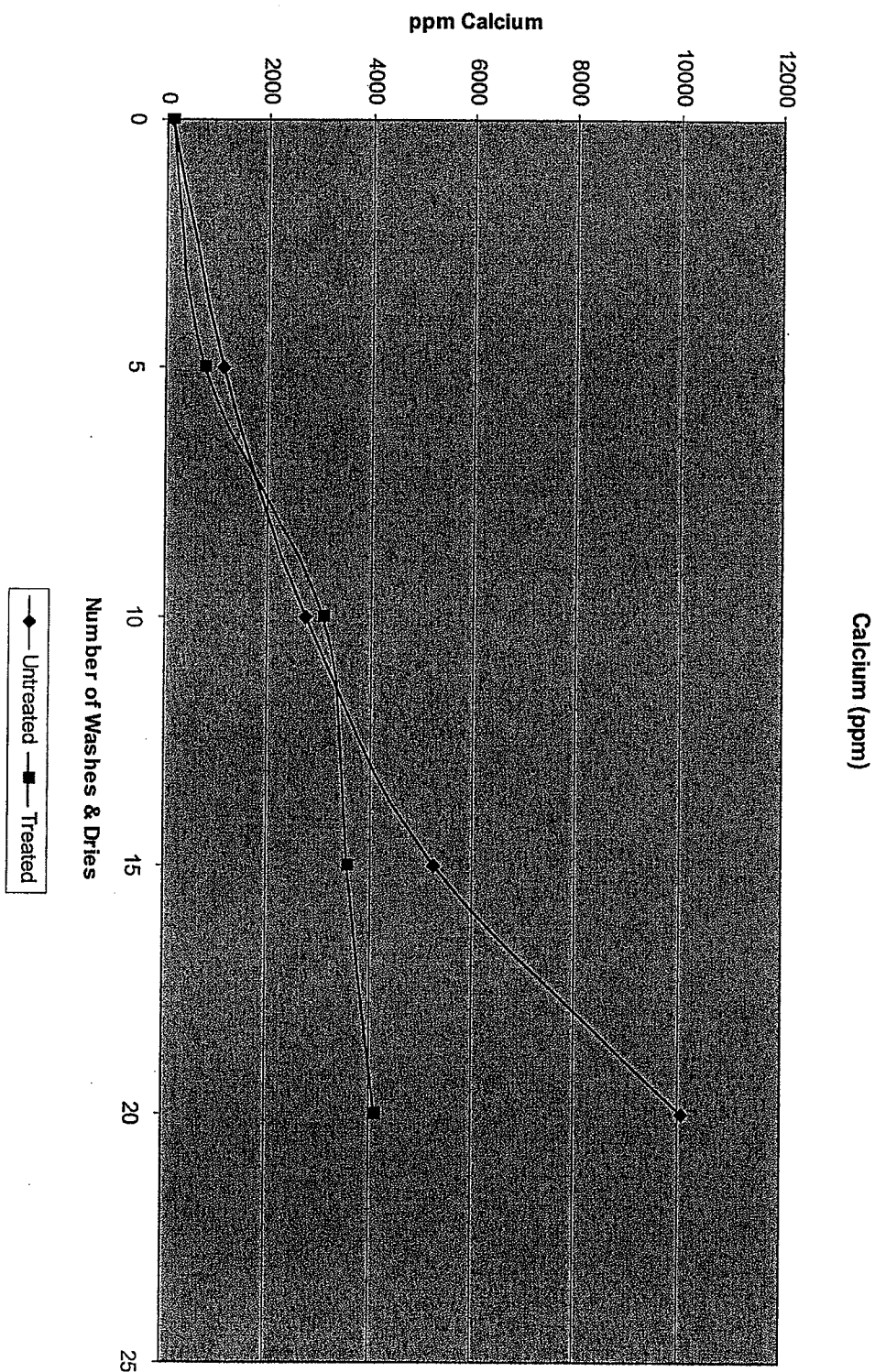


Figure 10

Hot water-  
treated      Cold water-  
treated      Cold water-  
untreated

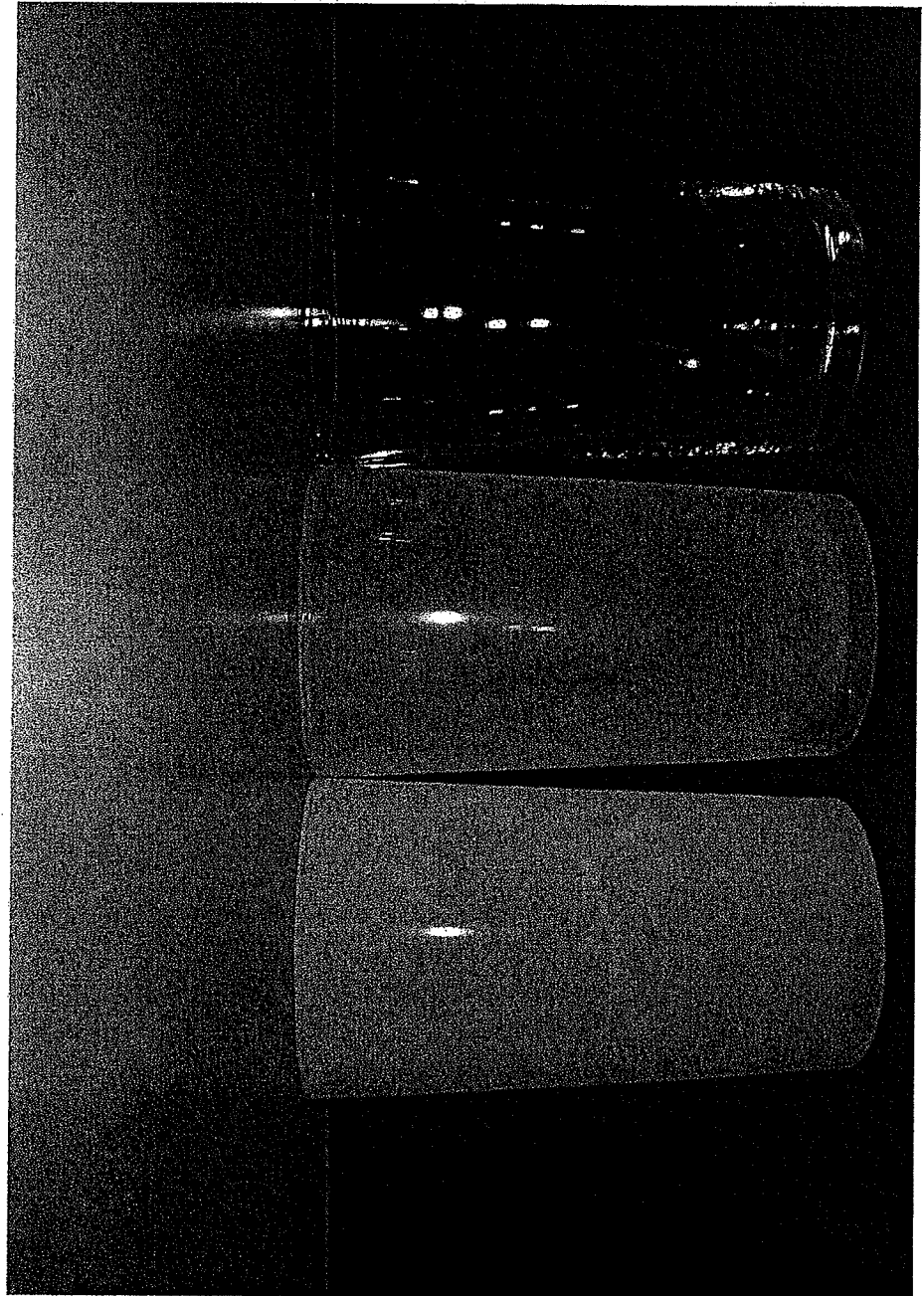


Figure 11

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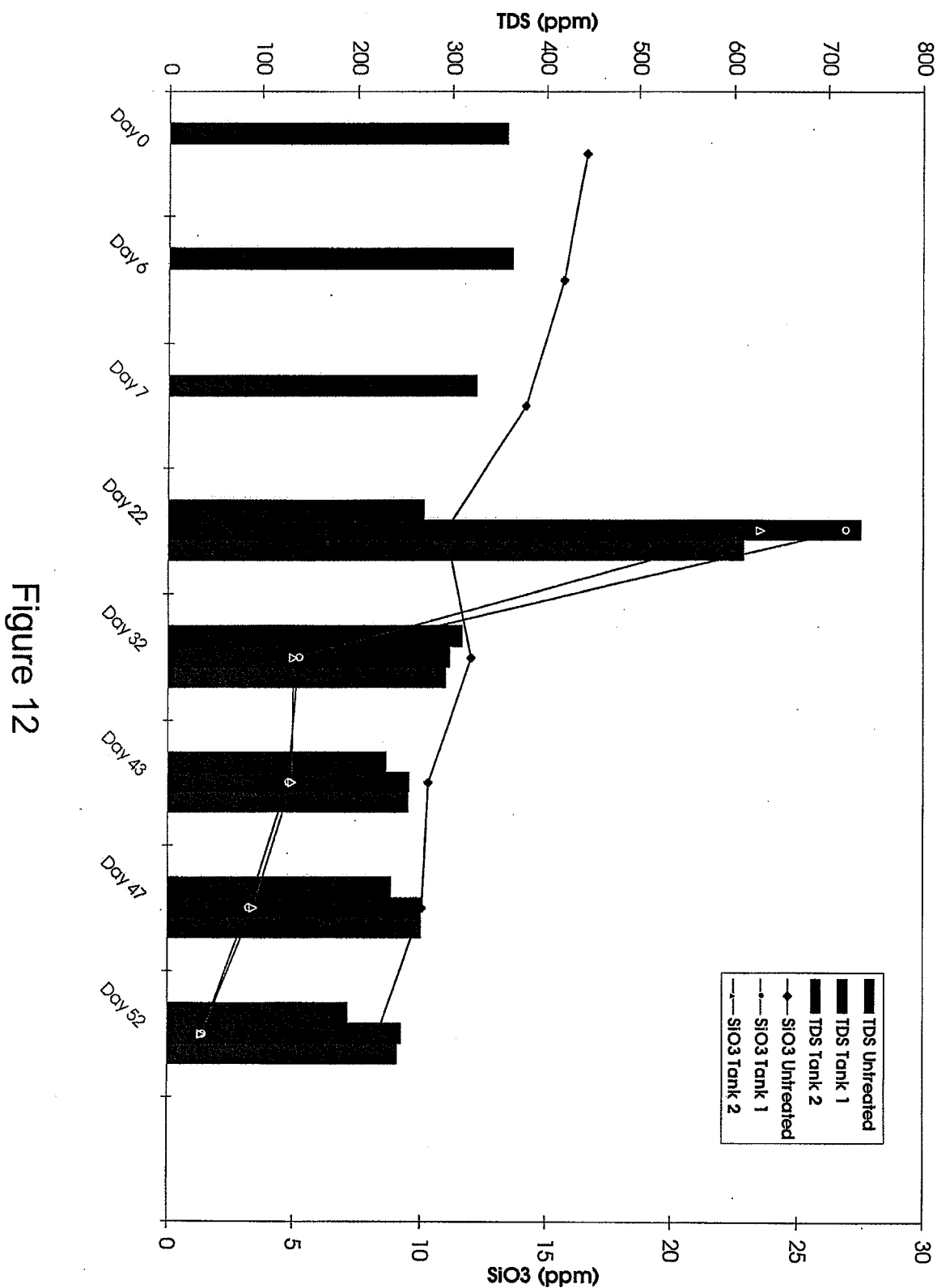


Figure 12