

ELECTROCHEMICAL GENERATION OF QUATERNARY AMMONIUM COMPOUNDS

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CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims priority to and the benefit of filing of U.S. Provisional Patent Application Serial No. 61/450,735, entitled "Electrochemical Generators for the Production of Quaternaryammonium Hypohalites from Quaternaryammonium Halide Salts", filed on March 9, 2011, the specification of which incorporated herein by reference.

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BACKGROUND OF THE INVENTIONField of the Invention (Technical Field):

The present invention is related to electrochemical conversion of quaternary ammonium halide salts to quaternary ammonium hypohalite salts preferably through the anodic oxidation of the halide anions of the quaternary ammonium halide salts.

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Background Art:

Note that the following discussion may refer to a number of publications and references. Discussion of such publications herein is given for more complete background of the scientific principles and is not to be construed as an admission that such publications are prior art for patentability determination purposes.

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Disinfectants and biocides are used to control microorganisms which may be present either in air, on a surface, or in a bulk liquid. Common chemicals that are used as disinfectants include alcohols, aldehydes, oxidizing chemicals (including halogens, hypohalous acids, hypohalite anions, chloramines, hydrogen peroxide, and ozone), phenols, and quaternary ammonium compounds. Some disinfectants, including quaternary ammonium compounds, can also serve as surfactant cleaners or corrosion inhibitors. Each of these chemicals have unique and specific properties which make them suitable for many applications, but preferential for certain applications. Aqueous chlorine is perhaps the most prominent and universally applied

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biocide. While aqueous chlorine is typically produced either through bubbling chlorine gas into water (as in disinfection of potable water) or delivered to a point-of-use in the form of concentrated aqueous solutions, it can also be generated electrochemically from sodium chloride (salt). Electrolysis of aqueous sodium chloride solutions, and brines containing other alkali metal halide salts, has long been used in the production of halogen, hypohalous acid, and hypochlorite solutions. Typically, dimensionally stable anodes are used in the electrolytic production of halogen solution that can be used for disinfection, sanitization, cleaning and other applications.

Quaternary ammonium halide salts are a commonly used alternative biocide to aqueous halogen solutions in non-drinking water applications. The general chemical structure of a quaternary ammonium halide salt is NR_4X , where N is a central nitrogen atom, R denotes an organic hydrocarbon functional group, and X represents a halide (Cl^- , Br^- , or I^-). Examples of quaternary ammonium halides commonly used for disinfection and sanitization include: benzalkonium chloride (N-alkyl-N-benzyl-N-dimethylammonium chloride where the alkyl chain contains between 8 and 18 carbon atoms), benzethonium chloride, centrimonium chloride or bromide (cetyltrimethylammonium chloride or bromide), cetylpyridium chloride, dequalinium, and didecyldimethylammonium chloride. The quaternary ammonium cation is the main active component, capable of killing microorganisms by perforating the cell membrane. Quaternary ammonium cations are environmentally stable, providing a long-lived residual disinfection capability in a given application. Quaternary ammonium halide compounds are often used to disinfect surfaces, especially in the medical, food, and beverage industries. Quaternary ammonium compounds are also used for disinfection and sanitization in other applications, including but not limited to treatment of oil/gas drilling hydraulic fracturing or process waters, as components of antibacterial consumer products, and treatment of cooling tower water. They are also used as corrosion inhibitors of iron and steel in acidic solutions or as part of an important part of a corrosion inhibition formulation.

Combinations of aqueous chlorine and/or mixed oxidant solution and quaternary ammonium salts, effectively producing quaternary ammonium hypohalite salts, may be used to enhance the germicidal properties of a disinfecting or sanitizing solution. However, the combined solution typically degrades quickly. It is believed the organic portion of the compound will react

with the hypohalite portion, decreasing the efficacy of the overall combination for disinfection and sanitization, thereby adversely affecting stability of the compounds and solutions. Thus, a method by which quaternary ammonium hypohalite compounds can be generated on-site and on-demand is desirable, so the biocides may be produced just before use, particularly since the precursors
5 (for example a halogen salt or brine and quaternary ammonium salts) are highly stable and can be stored for long periods of time. There are no known processes by which quaternary ammonium cations and either hypohalite anions or halogens with enhanced antimicrobial activity combinations can be made from quaternary ammonium halide salts at the point of use.

Electrochemical oxidation of halide ions is one such method by which quaternary
10 ammonium hypohalite compounds can be produced on-site and on-demand. Electrochemical production of aqueous solutions of halogens (chlorine, bromine, or iodine) from the respective halide ions through electrochemical oxidation of the halide is a well known technology. However, electrochemistry may also destroy (through oxidation or reduction processes at electrode surfaces) organic compounds dissolved in water, such as aqueous solutions of quaternary
15 ammonium compounds. Thus it is advantageous to develop a process for electrochemical oxidizing such compounds, either alone or in combination with additional alkali halide components, without destroying them, in order to produce quaternary ammonium hypohalite compounds that can act as an effective disinfectant, sanitizer, cleaner, surfactant, and/or corrosion inhibitor.

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SUMMARY OF THE INVENTION (DISCLOSURE OF THE INVENTION)

An embodiment of the present invention is a method for producing a solution, the method comprising electrolyzing a first solution comprising a quaternary ammonium compound in solution and producing a second solution comprising a quaternary ammonium hypohalite in solution. The
25 quaternary ammonium compound preferably comprises a quaternary ammonium halide. The first solution optionally further comprises a halide salt, preferably an alkali metal halide salt, in solution. The first solution optionally comprises a compound selected from the group consisting of surfactant, organic surfactant, colorant, perfume, disinfectant, germicide, and biocide. The second solution preferably further comprises an additional oxidant species, optionally selected

from the group consisting of halide based oxidant, halogen, hydrogen peroxide, ozone, chlorine dioxide, and combinations thereof. The combination of the quaternary ammonium hypohalite and the additional oxidant species in the second solution preferably substantially increases the disinfection efficacy of the second solution over an unelectrolyzed solution comprising the quaternary ammonium hypohalite and the additional oxidant species mixed together in solution. The second solution preferably does not substantially comprise a halide salt.

Another embodiment of the present invention is a method of producing a solution, the method comprising electrolyzing a first solution comprising a first quaternary ammonium compound in solution and a second component and producing a second solution comprising a second quaternary ammonium compound in solution and a second compound. The second component optionally comprises ammonia or an ammonium salt and the second compound comprises a haloamine. Alternatively, the second component comprises a chlorite salt and the second compound comprises chlorine dioxide. Alternatively, the second component comprises dissolved oxygen at a greater concentration than a naturally occurring dissolved oxygen concentration of the first solution and the second compound comprises hydrogen peroxide. In this case the electrolyzing step is preferably performed in a divided electrolytic cell and the second quaternary ammonium compound and hydrogen peroxide is produced in the cathodic compartment of the divided electrolytic cell. If the first solution comprises a quaternary ammonium halide or a halide salt, the second solution preferably further comprises a quaternary ammonium hypohalite produced in the anodic compartment of the divided electrolytic cell.

Another embodiment of the present invention is a device for dispensing the solution produced in any of claims 1-16, the device comprising a flow through electrolytic cell comprising an anode and a cathode and a spray nozzle for dispensing the solution. The device may optionally comprise a spray bottle configuration, wherein electrolysis of the solution is activated by a user squeezing a trigger. The device may alternatively comprise a hand washing station, wherein electrolysis of the solution is activated by a user moving a lever or a user placing at least one hand under the device.

Another embodiment of the present invention is a device for dispensing wipes comprising a solution, the device comprising a supply of wipes comprising a quaternary ammonium

compound, an anode, and a cathode, wherein the wipes are disposable between the anode the said cathode, at which time the quaternary ammonium compound is electrolyzed. The anode may optionally comprise a drum anode and the cathode may optionally comprise a drum cathode.

Alternatively, the anode and cathode comprise flat plates, and the device further comprises a

5 mechanism for pressing a wipe between the anode and the cathode. The wipes preferably comprise a compound selected from the group consisting of quaternary ammonium halide, halide salt, surfactant, organic surfactant, colorant, perfume, disinfectant, germicide, and biocide.

Another embodiment of the present invention is a method for on demand generation of a quaternary ammonium hypohalite solution, the method comprising signaling a desired amount of a first solution comprising a quaternary ammonium hypohalite in solution to be produced; mixing a
10 second solution comprising a quaternary ammonium compound in solution with a third solution comprising a halogen solution, the amounts of the second solution and third solution corresponding to the desired amount of the third solution; producing the desired amount of the third solution; and dispensing the desired solution immediately or prior to significant degradation
15 of the third solution. The halogen solution preferably comprises a compound selected from the group consisting of bleach, hypochlorous acid, hypobromous acid, hypoiodous acid, hypochlorite, hypobromite, hypoiodite, and hypohalite.

Objects, advantages, novel features, and further scope of applicability of the present invention will be set forth in part in the detailed description to follow, taken in conjunction with the
20 accompanying drawings, and in part will become apparent to those skilled in the art upon examination of the following, or may be learned by practice of the invention. The objects and advantages of the invention may be realized and attained by means of the instrumentalities and combinations particularly pointed out in the appended claims.

25 BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings, which are incorporated into and form a part of the specification, illustrate an embodiment of the present invention and, together with the description, serve to explain the principles of the invention. The drawings are only for the purpose of

illustrating various embodiments of the invention and are not to be construed as limiting the invention. In the drawings:

FIG. 1 is a schematic drawing showing an electrochemical process by which a quaternary ammonium halide salt is converted to a quaternary ammonium hypohalite salt.

5 FIG. 2 is a schematic drawing of an embodiment of a batch electrochemical cell for the conversion of quaternary ammonium halide salts to quaternary ammonium hypohalite salts.

FIG. 3 is a schematic drawing of an embodiment of a flow through generator system for the conversion of quaternary ammonium halide salts to quaternary ammonium hypohalite salts.

FIG. 4 is a schematic drawing of an embodiment of a flow-through electrochemical cell for
10 the conversion of quaternary ammonium halide salts to quaternary ammonium hypohalite salts.

FIG. 5 is a schematic drawing of an embodiment of the invention for use as part of a surface disinfection delivery system.

FIG. 6 is a schematic drawing showing an embodiment of the invention used to electrolyze a solution of quaternary ammonium halide salts to produce a solution that is then used
15 for hand sanitization.

FIG. 7 is a schematic drawing of showing an embodiment of the invention used to electrolyze quaternary ammonium halide salts that are incorporated into wipes that are subsequently used to disinfect or sanitize surfaces.

FIG. 8 is a schematic drawing showing an embodiment of the invention whereby a
20 solution of quaternary ammonium hypohalite is produced through the combination of an aqueous solution of halogen and an aqueous solution of quaternary ammonium halides.

FIG. 9 shows how the solution resulting from the electrolysis of a quaternary ammonium halide salt results in the formation of a product that reacts with diethyl-p-phenylene diamine (DPD) to produce a magenta color.

25 FIGS. 10a and 10b show the foaming that sometimes occurs during the electrolysis of a quaternary ammonium halide solution or a quaternary ammonium halide/alkali metal halide solution.

FIG. 11 is a graph showing the enhanced microbial inactivation achieved by a solution of a quaternary ammonium hypochlorite compound produced through the electrolysis of the corresponding quaternary ammonium chloride compound.

FIG. 12 is a graph showing the differences between quaternary ammonium hypochlorite compounds prepared by electrolysis of a quaternary ammonium halide compound and the mixing solutions of a quaternary ammonium halide compound with an alkali (or alkaline) metal hypochlorite compound.

FIG. 13 is a graph illustrating the impact of solution pH on the inactivation of *B. globigii* spores using electrolyzed solutions of cetyltrimethylammonium chloride (CTAC).

FIG. 14 is a graph illustrating inactivation efficacies for an electrolyzed mixture of CTAC and sodium chloride at different free available chlorine (FAC) concentrations.

FIG. 15 is a graph illustrating the inactivation efficacy of unelectrolyzed, electrolyzed, and electrolyzed/quenched tetramethylammonium chloride (TMAC) solutions.

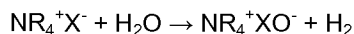
DESCRIPTION OF THE PREFERRED EMBODIMENTS

(BEST MODES FOR CARRYING OUT THE INVENTION)

Embodiments of the present invention are unique electrochemical cells and processes by which quaternary ammonium halide salts are preferably dissolved into solution and converted, preferably electrochemically, into quaternary ammonium hypochlorite salts in solution, preferably in bulk, such as part of a delivery system (for example, a spray bottle) or as part of a dispensing system whereby quaternary ammonium halide salts absorbed onto wipes can be dispensed as quaternary ammonium hypochlorite salts. Other blends between quaternary ammonium cations and halogen based disinfectants (such as diatomic halogens, hypohalous acids, or hypochlorite anions) may be produced. By choosing an appropriate quaternary ammonium halide salt, a corresponding quaternary ammonium hypochlorite salt solution can be formed that has one or more desired properties, such as corrosion inhibition, scale formation inhibition, surfactant, or cleaning properties.

In an embodiment of the present invention, an aqueous solution comprising dissolved quaternary ammonium salts is electrolyzed, which converts the halide component of the quaternary ammonium salt to the corresponding halogen. The halogen dissolves in the aqueous

solution producing hypohalous acid and hypohalite anion. The general electrochemical reaction can be described by the simplified equation:



where NR_4^+ is the quaternary ammonium ion containing a central nitrogen atom connected to four hydrocarbon functional groups (denoted R), X^- is a halide ion (eg. Cl^- , Br^- , or I^-), and XO^- is a hypohalite ion (e.g. ClO^- , BrO^- , or IO^-). Examples of quaternary ammonium compounds that could be utilized in this process include, but are not limited to, benzalkonium chloride, didecyldimethylammonium chloride, cetyltrimethylammonium chloride, octyltrimethylammonium chloride, tetramethylammonium chloride, tetraethylammonium chloride, tetrapropylammonium chloride, tetrabutylammonium chloride, cetylpyridinium chloride, benzalkonium bromide, didecyldimethylammonium bromide, cetyltrimethylammonium bromide, octyltrimethylammonium bromide, tetramethylammonium bromide, tetraethylammonium bromide, tetrapropylammonium bromide, tetrabutylammonium bromide, cetylpyridinium bromide, benzalkonium iodide, didecyldimethylammonium iodide, cetyltrimethylammonium iodide, octyltrimethylammonium iodide, tetramethylammonium iodide, tetraethylammonium iodide, tetrapropylammonium iodide, tetrabutylammonium iodide, and cetylpyridinium iodide. Polymeric quaternary ammonium compounds, for example, but not limited to, the polyquaternium polymers, can also be used as the quaternary ammonium halide source in these reactions.

Embodiments of the present invention utilize an electrochemical process by which a quaternary ammonium halide salt is converted to a quaternary ammonium hypohalite salt; one such process is shown in FIG. 1. In aqueous solution, halide anions **14** of quaternary ammonium halide salt **10** partially separate from, but are still associated with, quaternary ammonium cations **16**. When the electrochemical cell is energized, the halide anions **14** are oxidized to halogen **22** at the surface of the anode plates **18**. Halogen **22** then dissolves in water to yield hypohalous acid **24** and hydrohalic acid **26**. On the surface of cathode **20**, water molecules **28** are converted to hydrogen gas **30** and hydroxide anions **32**. Hypohalous acid **24**, hydrohalic acid **26**, hydroxide ions **32**, and quaternary ammonium cations **16** preferably associate to form a quaternary ammonium hypohalite salt **12**.

There are a variety of solution compositions and operational conditions which can be employed for this invention. The quaternary ammonium halide salt used can be a singular salt or a mixture containing one or more quaternary ammonium moieties combined with one or more halide anions. Similarly, the counterions for the quaternary ammonium cations could be chloride, bromide, or iodide. In addition to the quaternary ammonium compound, the solution used in this electrolysis process may comprise additional halides such as alkali metal halide salts, which increase halogen, hypohalous acid, and hypohalite ion production capacity. In this case, the feed salts include, but are not limited to, sodium chloride, sodium bromide, sodium iodide, potassium chloride, potassium bromide, and potassium iodide. For example, NaCl and a quaternary ammonium halide salt can be electrolyzed simultaneously, producing a combined biocidal solution comprising quaternary ammonium hypohalite salt and one or more chlorine based oxidants. Moreover, the solution used during the electrolytic process described herein may comprise other germicidal components in addition to the quaternary ammonium cations, such as additional germicidal agents, colorants, and perfume components.

Halides, surfactants (e.g. linear alkyl benzene sulfonates), and/or other germicidal compounds such as biocides may optionally be dissolved with the quaternary ammonium halide into solution (such as a brine) prior to electrolysis. If a halide such as an alkali metal halide salt (e.g. NaCl) is added, then any quaternary ammonium compound, not just a quaternary ammonium halide, may be used, since the halide salt can contribute the halide to the solution. Embodiments of the present invention also encompass methods to control or tune the concentrations of different disinfectants or surfactants, thereby controlling synergy for a specific disinfection or cleaning application.

Other compounds may be added to the solution or brine used to feed the electrochemical cell. If ammonia or an ammonium salt (such as ammonium chloride, ammonium sulfate, ammonium bromide, ammonium iodide, etc) is added, solutions are produced that comprise both quaternary ammonium compound(s) and haloamine(s) such as monochloramine, dichloramine, trichloramine, monobromamine, dibromamine, tribromamine, monoiodamine, diiodamine, or triiodamine. If a chlorite (ClO_2^-) salt (such as sodium chlorite) is added, solutions are produced that comprise both quaternary ammonium compound(s) and chlorine dioxide. If the solution being

fed into the electrochemical cell contains increased dissolved oxygen, solutions are produced that comprise both quaternary ammonium compound(s) and hydrogen peroxide. In this case it is preferable that the electrolytic cell is divided (i.e. the cathodic and anodic compartments are separate). The quaternary ammonium compound and hydrogen peroxide will be produced in the cathodic compartment. Additionally, quaternary ammonium hypohalites may simultaneously be produced on the anodic compartment of such a cell (if the feed stream comprises a quaternary ammonium halide and/or a halide salt).

One embodiment of the present invention is a batch electrochemical cell as depicted in FIG. 2. Here, the electrochemical cell preferably comprises one primary anode **40**, one primary cathode **42**, and any number of intermediate electrodes **44**. This cell is immersed into a container **46** which contains aqueous solution **48** that comprises a single quaternary ammonium halide salt or multiple quaternary ammonium salts, optionally in combination with various alkali metal halide salts and/or other inorganic and organic biocides, dissolved in water. The cell is then energized by power supply **50** through electrical connections **52** to produce a solution of the desired quaternary ammonium hypohalite salt.

Another embodiment of the present invention is a flow through electrochemical cell as depicted in FIG. 3. Initial solution tank **60** contains the aqueous solution **62** to be electrolyzed. In practice, this solution may comprise any variety of organic quaternary ammonium cations, halide anions, added alkali metal halides, surfactants and/or other disinfectants. Solution **62** is then transferred preferably using pump **64** through pipe **66** to generator assembly **68** and into electrochemical cell **70**. Generator assembly **68** preferably comprises other operational and control features such as power supply **72**, operations system controls **74**, and operational display and user interface **76**. After the solution is electrolyzed and halide ions have been converted to halogen, hypohalous acid, and hypohalite species, the generated solution leaves generator **68** through pipe **78** and is disposed in tank **80**, where it collects as the product solution **82**. Product solution **82** may optionally be transferred using pump **84** and pipe **86** to meet the needs of the desired application.

Details of an embodiment of electrochemical cell **70** are given in FIG. 4. In this cell, the incoming solution **90**, which may comprise various quaternary ammonium cations, halide anions,

alkali metal cations, surfactants, and/or other germicidal agents, enters cell housing **92**. Inside of cell housing **92** is the electrochemical cell which preferably comprises primary anode **94**, primary cathode **96**, and intermediate plates **98**. The product stream **100** then leaves cell housing **92**.

Practical operation of all types of cells will vary depending on a number of factors, such as the chemical nature of the quaternary ammonium halide salt, the concentration of all halide salts in solution, the desired level of halogen, hypohalous acid, and hypohalite ion in the product, the type of halide ion to be oxidized, and the presence of additional germicidal agents. Cell operational parameters that may be varied include, but are not limited to, cell voltage, electrode spacing, cell current, solution flow rate, and/or cell operating temperature. Additionally, other factors involved in cell construction may vary depending on the operating conditions, including but not limited to the spacing of the electrodes, the nature of the coating on the anode surfaces, and/or the nature of the coating on the cathode surfaces.

An embodiment of the present invention is a cell combined in a solution delivery system such as the spray bottle shown in FIG. 5. Solution housing **110** is filled with solution **112** which comprises quaternary ammonium cations, alkali metal cations, halide anions, surfactants, and/or other germicidal agents. This solution is drawn through tube **114**, preferably as a result of the pumping mechanism of trigger **116**, and enters head housing **118**. Inside of head housing **118** is flow-through electrochemical cell **120** (similar to the one described in FIG. 4) where the halide ions in solution are converted to halogens, hypohalous acids, and hypohalite anions, thus producing a quaternary ammonium hypohalite salt solution, which exits head housing **118** through nozzle **122** as a spray **124**. Similar embodiments of this invention may comprise a spray bottle that is connected to a small batch cell or flow-through cell type generator which fills the spray bottle housing with the electrolyzed solution.

An embodiment of the present invention is a hand wash station as shown in FIG. 6. This embodiment consists of housing **130** which contains a reservoir of solution **132** that comprises quaternary ammonium cations, alkali metal cations, halide anions, surfactants, and/or other germicidal agents. Solution **132** is pumped through the action of mechanism **134** by way of tube **136** through electrolytic cell **138**, where the halides are converted to halogens, hypohalous acids, and hypohalite ions to produce a quaternary ammonium hypohalite salt solution **140**, which is

then dispensed through nozzle **142**. Solution **132** may optionally comprise a liquid, gel, foam, or other medium that can be pumped through cell **136** to undergo electrolysis prior to dispensing. A similar embodiment of the present invention comprises an electrochemical generation system attached to a janitorial bucket that produces quaternary ammonium hypohalite solution to be used
5 for cleaning floors.

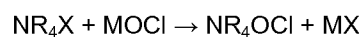
An alternative embodiment of the invention is a cell capable of oxidizing the halide component of quaternary ammonium halide salts impregnated onto wipes used for sanitizing various surfaces, as shown in FIG. 7. Device housing **150** holds a supply of wipes **152** that have been impregnated or saturated with quaternary ammonium halide salts. Other germicidal agents
10 may optionally or additionally be incorporated into the matrix of these wipes. Wipes **152** are then dispensed from housing **150** by passing through drum electrodes consisting of anode drum **154** and cathode drum **156**. As wipes **152** pass through drum electrodes **154** and **156**, electrolysis of the impregnated halide anions occur, thereby producing quaternary ammonium hypohalite salts on electrolyzed wipes **158** that can be used for disinfection and sanitization of various surfaces.

Possible variations on this embodiment of the present invention include, but are not limited to, drum electrodes where a single drum contains anodic and cathodic regions that are separated by non-electrolyzed regions, a similar device that manually dispenses electrolyzed wipes, a similar device that automatically dispenses electrolyzed wipes, and a similar device in which wipes are electrolyzed by placing them between two electrodes that are pressed together.
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Another embodiment of the present invention is a device that can combine separate aqueous solutions of quaternary ammonium halide salts and halogen(s) to provide the quaternary ammonium hypohalite solution without the use of electrolysis. One example of such a device is illustrated in FIG. 8. Here, tank **160** contains aqueous quaternary ammonium halide salt solution **162**, which is preferably pumped from tank **160** with pump **164** along tube **166**. Similarly, tank **168**
20 contains aqueous halogen solution (for example, but not limited to, bleach, hypochlorous acid, hypobromous acid, hypoiodous acid, hypochlorite, hypobromite, hypoiodite, or any hypohalite) **170**, which is preferably pumped from tank **168** with pump **172** along tube **174**. Pumps **164** and **172** are connected to control box **176** through connections **178**. Control box **176** is used to control the relative amounts of aqueous quaternary ammonium halide salt solution **162** and aqueous
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halogen solution **170** to be combined. These solutions are preferably combined in a mixing element (such as a tank) **180** and are further transferred along tube **182** as quaternary ammonium hypohalite solution **184** which is stored in tank **186**. Quaternary ammonium hypohalite solution **184** can then be dispensed from tank **186** through the action of pump **188** to be
5 transferred along tube **190**. Possible variations on this embodiment include, but are not limited to, a device that can combine more than two solutions in combinations of aqueous quaternary ammonium halide salts or aqueous halogens, additional chemical dosing pumps to alter the final solution pH or other characteristics, and devices that do not contain an intermediate storage capability. In the latter embodiment, the solution containing quaternary ammonium hypohalite
10 salts is preferably dispensed immediately after solution combination. Because this system uses stable chemicals in an on site generation process to produce the quaternary ammonium hypohalite solution on demand, degradation of the final product is no longer an issue.

Electrochemical processes such as the ones described herein may produce products that are substantively different than a process whereby two components are simply mixed together. In
15 the case of quaternary ammonium hypohalite salts, the comparative processes are the physical combination of an aqueous solution of an alkali metal hypohalite with an aqueous solution of a quaternary ammonium halide without electrolysis, and the electrochemical oxidation of the halide portion of a quaternary ammonium halide salt. One major distinction between these processes is that the physical combination of the two individual components also produces a quantity of
20 undesirable alkali metal halide salt, as is illustrated with the following chemical equation:



Here, NR_4X is the quaternary ammonium halide salt, MOCl is the metal hypohalide, NR_4OCl is the quaternary ammonium hypohalite compound that is the intended product of the chemical reaction, and MX is the alkali metal halide byproduct, such as NaCl . Comparatively, the
25 electrochemical process involves only the oxidation of the halide component of the quaternary ammonium halide salt, and therefore, essentially no excess alkali metal halide is present in the resulting disinfection solution. This distinction is critical in a number of applications, and expressly so in the case of surface disinfection. The extra salts produced through physical combinations of a quaternary ammonium halide salt and an alkali metal hypohalite can lead to the excessive

formation of residual solids on the surface to be cleared, thus necessitating a secondary cleaning step or agent to be used to remove the excess salts. Moreover, alkali metal halide salts are well known to be corrosive agents against stainless steels as well as other materials, and therefore limiting the exposure of corrosion-susceptible materials is a critical factor in the selection of surface disinfectants.

Another difference between simple combination of quaternary ammonium halide salts with alkali (or alkaline) metal hypochlorite and the electrochemical production of quaternary ammonium hypochlorite compounds is that the electrolysis process may produce other oxidative species beyond just the aqueous halogen, which species can demonstrate synergistic inactivation properties. Electrochemical cells exist, for example, that can produce a mixed oxidant solution, comprised primarily of aqueous chlorine but also having other oxidative species, that has been shown to be more effective at inactivating a wide range of microorganisms. Similarly, an electrochemical cell designed to produce quaternary ammonium hypochlorite compounds may also produce other oxidant species, resulting in a disinfecting solution that is more effective for microbial inactivation than simply physically mixing the two corresponding components together.

Example 1

An aqueous solution of benzalkonium chloride was prepared by dissolving 10 grams of benzalkonium chloride in 1000 mL of deionized water to give a 1% (10,000 mg/L) solution. 200 mL of this solution was transferred to a 250 mL beaker, and a three electrode cell was immersed in the solution. The cell was then energized to 12 volts for 20 minutes. During this time, extensive bubbling was observed on the cathodic electrodes, producing a foam above the surface of the solution (similar to that shown in FIGS. 10a and 10b). After 20 minutes, a sample of the electrolyzed solution was withdrawn and the free available chlorine (FAC) content of the solution was determined to be 332 mg/L using the diethyl-p-phenylene diamine (DPD) method.

Example 2

An aqueous solution of cetyltrimethylammonium chloride was prepared by adding 20 mL of a 25% by weight cetyltrimethylammonium solution to 1000 mL of deionized water to give a

0.5% (5,000 mg/L) solution. 200 mL of this solution was transferred to a 250 mL beaker, and a three electrode cell was immersed in the solution. The cell was then energized to 12 volts for 60 minutes. During this time, extensive bubbling was observed on the cathodic electrodes, producing a foam above the surface of the solution (similar to that shown in FIGS. 10a and 10b). After 60 minutes, a sample of the electrolyzed solution was withdrawn and the free available chlorine content of the solution was determined to be 360 mg/L using the DPD method.

Example 3

A solution containing 100 mg/L benzalkonium chloride and 5,000 mg/L sodium chloride was prepared by dissolving 0.1 g benzalkonium chloride and 5 g sodium chloride in 1000 mL deionized water. 200 mL of this solution was transferred to a 250 mL beaker, and a three electrode cell was immersed in the solution. The cell was then energized to 12 volts for 20 minutes. During this time, extensive bubbling was observed on the cathodic electrodes, producing a foam above the surface of the solution (similar to that shown FIGS. 10a and 10b). After 20 minutes, a sample of the electrolyzed solution was withdrawn and the free available chlorine content of the solution was determined to be 3,000 mg/L using the DPD method.

Example 4

A solution containing 100 mg/L cetyltrimethylammonium chloride and 1,000 mg/L sodium chloride was prepared by dissolving 0.4 mL of a 25% cetyltrimethylammonium chloride solution and 1 g sodium chloride in 1000 mL deionized water. 200 mL of this solution was transferred to a 250 mL beaker, and a three electrode cell was immersed in the solution. The cell was then energized to 12 volts for 20 minutes. During this time, extensive bubbling was observed on the cathodic electrodes, producing a foam above the surface of the solution (similar to that shown in FIGS. 10a and 10b). After 20 minutes, a sample of the electrolyzed solution was withdrawn and the free available chlorine content of the solution was determined to be 850 mg/L using the DPD method.

Example 5

FIG. 9 shows how the solution resulting from the electrolysis of a quaternary ammonium halide salt results in the formation of a product that reacts with DPD to produce a magenta color.

In the example, the reaction was the electrolysis of a 1% benzalkonium chloride solution in

5 deionized water. This solution was electrolyzed for 5 minutes with 12 volts applied to the cell. The magenta color is consistent with the presence of free available chlorine resulting for the oxidation of the chloride associated with the benzalkonium cation at the anode of the cell.

Example 6

10 FIGS. 10a and 10b are photographs showing the foaming that sometimes occurs during the electrolysis of a quaternary ammonium halide solution or a quaternary ammonium halide/alkali metal halide solution. In these photographs, the solution being electrolyzed is a 100 mg/L benzalkonium chloride and 20 g/L sodium chloride solution, and the electrolysis is at 12 volts applied to the cell. Similar results were observed during electrolysis of brines comprised of

15 cetyltrimethylammonium chloride, octyltrimethylammonium chloride, or didecyldimethylammonium chloride, either alone combined with sodium chloride. Solutions of tetraalkylammonium chlorides (such as tetramethylammonium chloride, tetraethylammonium chloride, tetrapropylammonium chloride, and tetrabutylammonium chloride), either alone or in sodium chloride based brines, produced chlorine when electrolyzed but the production of foam during electrolysis was

20 minimized.

Example 7

FIG. 11 is a graph showing the enhanced microbial inactivation achieved by a solution of a quaternary ammonium hypochlorite compound produced through the electrolysis of the

25 corresponding quaternary ammonium chloride compound. Here, an aqueous solution of cetyltrimethylammonium chloride (CTAC) at a concentration of 250 mg/L was divided into two portions. One portion was passed through an electrochemical cell operating at an applied cell voltage of 12 V. After electrolysis the concentration of free available chlorine, measured using the DPD methodology, was determined to be 6.8 mg/L. A sample of this solution was then mixed with

sodium thiosulfate, which was used to quench the free available chlorine but does not react with the quaternary ammonium component of the solution. Similarly, a solution of sodium hypochlorite was prepared by the dilution of commercial bleach to have a free available chlorine concentration of 6.5 mg/L. All four solutions (6.5 mg/L FAC sodium hypochlorite, 250 mg/L unelectrolyzed CTAC, 250 mg/L electrolyzed CTAC, and 250 mg/L electrolyzed and quenched CTAC) were then used to inactivate a suspension of *Bacillus globigii* spores. After a five minute contact time with the *B. globigii* spores, the resulting solutions were enumerated for viable spore counts (colony forming units (CFU)) using the dilution plate method. Briefly, specific volumes of the solution are spread onto agar plates and allowed to incubate at 35 °C for 24 hours, after which, the number of surviving spores are quantified in terms of log reduction from the initial spore concentration. Results from this experiment are given in FIG. 11, where it is clear that the electrolyzed solution of 250 mg/L CTAC exhibited the highest degree of spore inactivation. Further, the inactivation was synergistic, not additive, indicating that the freshly produced quaternary ammonium hypohalite is important for efficacy. Additionally, the solutions of unelectrolyzed and electrolyzed/quenched 250 mg/L CTAC produced approximately the same degree of *B. globigii* inactivation, indicating that the quaternary ammonium functionality of the molecule was unaffected due to the electrolysis process.

Example 8

The differences between quaternary ammonium hypohalite compounds prepared by electrolysis of a quaternary ammonium halide compound and the mixing solutions of a quaternary ammonium halide compound with an alkali (or alkaline) metal hypochlorite compound were examined. Here, a 500 mg/L CTAC solution was electrolyzed as described above, producing a solution with a measured FAC of 32 mg/L. Similarly, a solution containing 500 mg/L CTAC and 31.2 mg/L FAC was prepared by combining CTAC and commercial bleach solutions. As a control, a 500 mg/L CTAC solution was prepared without either electrolysis or added bleach. All three solutions were then used to inactivation *B. Globigii* spores with a contact time of 2, 5, and 10 minutes, and the results from this test are shown in FIG. 12. As can be seen, the un-electrolyzed (with no bleach added) 500 mg/L CTAC solution resulted in a 1.25-1.29 log inactivation of *B.*

Globigii spores, depending on contact time. In the case of CTAC mixed with bleach, slightly higher spore log inactivations were observed, with a maximum log inactivation of 1.86 found for the 10 min contact time. Electrolyzed CTAC, however, produced much higher log inactivation, with a maximum log inactivation of 3.87 observed for the 10 minute contact time. The differences between the disinfectant produced by electrolysis and the one produced through the combination of CTAC and bleach may possibly be related to the cogeneration of oxidants other than free available chlorine species, which then work with both the quaternary ammonium and FAC components of the solution to produce a significant enhancement of microbial inactivation efficacy.

Example 9

FIG. 13 illustrates the impact of solution pH on the inactivation of *B. globigii* spores using electrolyzed solutions of CTAC. It is well known that pH has a dramatic impact on the ability of free chlorine to inactivate microorganisms. This is due to the fact that hypochlorous acid (HOCl) is more effective at inactivating microorganisms than the hypochlorite (ClO^-) anion. The relative amount of these species present in solution is pH dependent: when the pH is below 7.5, HOCl is the major species; when the pH is higher than 7.5, ClO^- predominates. Therefore, aqueous chlorine solutions are more effective disinfectants when the pH is lower than 7.5. To test the impact of pH on quaternary ammonium hypochlorite compounds, a solution containing 250 mg/L CTAC was electrolyzed and divided up into several portions. The pH of these portioned solutions of CTAC was then adjusted to between 6.5 and 9, and these solutions were used to inactivate a suspension of *B. globigii* spores. A similar variable pH series of solutions was prepared from unelectrolyzed CTAC also at 250 mg/L, and these solutions were also used to inactivate *B. globigii* spores. As can be seen in FIG. 12, pH had very little impact on the inactivation efficacy of electrolyzed CTAC, a surprising result given what is known about the disinfection actions of aqueous chlorine and other aqueous halogen solutions. These data indicate that the quaternary ammonium hypochlorite product resulting from the electrolysis may be stabilized in a beneficial fashion that would not be possible without the electrolysis step.

Example 10

As an example of the differences between quaternary ammonium hypochlorite solutions that are produced through the combination of a solution containing quaternary ammonium halide compounds with a solution containing an alkali (or alkaline) metal hypochlorite as compared to the direct electrolysis of a quaternary ammonium halide compound, solutions based on CTAC were prepared by combining CTAC (150 mg/L) and sodium hypochlorite (variable FAC concentration between 1 and 50 mg/L FAC). Similarly, CTAC (167 mg/L) was electrolyzed in an electrochemical cell, producing a solution that had a FAC concentration of 4.2 mg/L. Alone, CTAC at 167 mg/L was able to achieve a 0.90 ± 0.14 log inactivation of *B. globigii* spores while that same solution, after electrolysis, achieved a 2.93 ± 0.19 log inactivation of *B. globigii* spores. In comparison, the mixed CTAC and bleach solutions had lower log inactivation of *B. globigii* spores until the FAC concentration was at least 20 mg/L, and at that concentration, the solution was only able to achieve a log inactivation of 1.23 ± 0.17 . Similar results were observed when comparing other concentrations of mixed and electrolyzed solutions using other CTAC concentrations as well as other quaternary ammonium compounds. Enhanced spore inactivation associated with quaternary ammonium hypochlorite produced through electrolysis as opposed to quaternary ammonium produced through blending the individual components is consistent with the presence of other oxidizing biocides, possibly including hydrogen peroxide.

Example 11

In some applications of the present disclosure, it may be necessary to vary the relative amounts of FAC and quaternary ammonium components in a produced quaternary ammonium hypochlorite solution. This can be readily achievable using the present invention by blending an alkali metal halide salt with a quaternary ammonium halide compound to produce a mixed brine that is then electrolyzed. In one specific example, CTAC was blended with sodium chloride to produce a series of brines with varying concentration of CTAC, with the concentration of sodium chloride being constant at 20 g/L. Here the concentration of CTAC in the brines was set to be 50, 100, 500, 1000, and 5000 mg/L. These solutions were then electrolyzed, and FAC concentrations of the electrolyzed solutions was found to be 4550, 4000, 3000, 2650, and 1600 mg/L

respectively. These solutions were then diluted so that the FAC concentration was either 5 or 10 mg/L, resulting in an equivalent cetyltrimethylammonium concentration of 0.06, 0.13, 0.83, 1.9, and 16 mg/L for the 5 mg/L FAC solutions and 0.11, 0.25, 1.67, 3.78, and 31 mg/L for the 10 mg/L FAC solutions respectively. These solutions were then used to inactivate *B. globigii* spores and the results of this test are shown in FIG. 14 and TABLE 1.

NaCl concentration in the brine (g/L)	CTAC concentration in the brine (mg/L)	FAC concentration of the electrolyzed CTAC/NaCl brine (mg/L)	Electrolysis solution diluted to a FAC concentration of 5 mg/L		Electrolysis solution diluted to a FAC concentration of 10 mg/L	
			Quaternary ammonium concentration (mg/L)	Log inactivation	Quaternary ammonium concentration (mg/L)	Log inactivation
20	50	4550	0.06	1.17	0.11	3.5
20	100	4000	0.13	1.18	0.25	3.5
20	500	3000	0.83	1.16	1.67	3.5
20	1000	2650	1.9	1.18	3.78	3.5
20	5000	1600	16	1.51	31	3.5

TABLE 1

As can be seen, the log inactivation of solutions based on a 5 mg/L FAC concentration were typically around 1.1 with the highest log inactivation of 1.51 seen with an equivalent cetyltrimethylammonium concentration of 16 mg/L. However, when the FAC concentration was 10 mg/L, all solutions independent of cetyltrimethylammonium concentration demonstrated a log inactivation of 3.5 (the maximum observable under this test design). Unelectrolyzed CTAC solutions under similar concentrations and exposure times typically resulted in log inactivation of around 0.27-0.30 while FAC alone solutions under these conditions typically result in a log inactivation of less than 1. This data indicates that it is possible to achieve a biocide of the desired strength by choosing the appropriate blend ratio of a quaternary ammonium halide compound

with an alkali metal halide salt into the brine used for electrolysis. Moreover, these results are surprising in that only small amounts of CTAC were necessary to achieve the synergistic disinfection in the electrolyzed quaternary ammonium hypochlorite compound solution. Other concentrations of CTAC, as well as other concentrations of sodium chloride and other quaternary ammonium compounds, produced similar results with the main difference being actual ratios of quaternary ammonium compound to FAC in the produced solutions, which showed differing inactivation efficacy depending on the chemical nature of the quaternary ammonium compound.

Example 12

For some quaternary ammonium halide compounds, electrooxidation of the halide component of the compounds can install an unexpected biocidal capability. One example is the case of tetramethylammonium chloride (TMAC), a quaternary ammonium compound that is not traditionally effective as a microbiocide. When a 500 mg/L TMAC solution was electrolyzed, thereby producing tetramethylammonium hypochlorite, and the unelectrolyzed, electrolyzed, and electrolyzed/quenched TMAC solutions were then used to inactivate *B. globigii* spores. FIG. 15 shows the results of these inactivation tests. The unelectrolyzed and electrolyzed/quenched TMAC solutions both produced about a 0.27 and 0.36 log inactivation with contact times of 2 and 5 minutes, respectively. These observations are consistent with the low biocidal efficacy of TMAC in the quaternary ammonium chloride form. However, electrolyzed TMAC resulted in a 3.6 log inactivation independent of exposure time.

Although the invention has been described in detail with particular reference to these preferred embodiments, other embodiments can achieve the same results. Variations and modifications of the present invention will be obvious to those skilled in the art and it is intended to cover all such modifications and equivalents. The entire disclosures of all patents and publications cited above are hereby incorporated by reference.

CLAIMS

What is claimed is:

- 5 1. A method for producing a solution, the method comprising:
electrolyzing a first solution comprising a quaternary ammonium
compound in solution; and
producing a second solution comprising a quaternary ammonium
hypohalite in solution.
- 10 2. The method of claim 1 wherein the quaternary ammonium compound comprises
a quaternary ammonium halide.
- 15 3. The method of claims 1 or 2 wherein the first solution further comprises a halide
salt in solution.
4. The method of claim 3 wherein the halide salt comprises an alkali metal halide
salt.
- 20 5. The method of claims 1, 2, 3, or 4 wherein the first solution comprises a
compound selected from the group consisting of surfactant, organic surfactant, colorant, perfume,
disinfectant, germicide, and biocide.
- 25 6. The method of any of claims 1-5 or 9 wherein the second solution further
comprises an additional oxidant species.
7. The method of claim 6 wherein the additional oxidant species is selected from
the group consisting of halide based oxidant, halogen, hydrogen peroxide, ozone, chlorine
dioxide, and combinations thereof.

8. The method of claim 6 wherein a combination of the quaternary ammonium hypohalite and the additional oxidant species in the second solution substantially increases the disinfection efficacy of the second solution over an unelectrolyzed solution comprising the quaternary ammonium hypohalite and the additional oxidant species mixed together in solution.

9. The method of any of claims 1-8 wherein the second solution does not substantially comprise a halide salt.

10. A method of producing a solution, the method comprising:
electrolyzing a first solution comprising a first quaternary ammonium compound in solution and a second component; and
producing a second solution comprising a second quaternary ammonium compound in solution and a second compound.

11. The method of claim 10 wherein the second component comprises ammonia or an ammonium salt and the second compound comprises a haloamine.

12. The method of claim 10 wherein the second component comprises a chlorite salt and the second compound comprises chlorine dioxide.

13. The method of claim 10 wherein the second component comprises dissolved oxygen at a greater concentration than a naturally occurring dissolved oxygen concentration of the first solution and the second compound comprises hydrogen peroxide.

14. The method of claim 13 wherein the electrolyzing step is performed in a divided electrolytic cell and the second quaternary ammonium compound and hydrogen peroxide is produced in the cathodic compartment of the divided electrolytic cell.

15. The method of claim 14 wherein the first solution comprises a quaternary ammonium halide or a halide salt.

16. The method of claim 15 wherein the second solution comprises a quaternary ammonium hypohalite produced in the anodic compartment of the divided electrolytic cell.

17. A device for dispensing the solution produced in any of claims 1-16, the device comprising:
a flow through electrolytic cell comprising an anode and a cathode; and
a spray nozzle for dispensing the solution.

18. The device of claim 17 comprising a spray bottle configuration, wherein electrolysis of the solution is activated by a user squeezing a trigger.

19. The device of claim 18 wherein electrolysis of the solution is activated by a user moving a lever or a user placing at least one hand under said device.

20. A device for dispensing wipes comprising a solution, the device comprising:
a supply of wipes, said wipes comprising a quaternary ammonium compound;
an anode; and
a cathode;
wherein said wipes are disposable between said anode and said cathode, at which time the quaternary ammonium compound is electrolyzed.

21. The device of claim 20 wherein said wipes comprise a compound selected from the group consisting of quaternary ammonium halide, halide salt, surfactant, organic surfactant, colorant, perfume, disinfectant, germicide, and biocide.

22. The device of claims 20 or 21 wherein said anode comprises a drum anode and said cathode comprises a drum cathode.

23. The device of claims 20 or 21 wherein said anode and said cathode each
5 comprise a flat plate, said device further comprising a mechanism for pressing a wipe between said anode and said cathode.

24. A method for on demand generation of a quaternary ammonium hypohalite solution, the method comprising:
10 signaling a desired amount of a first solution comprising a quaternary ammonium hypohalite in solution to be produced;
mixing a second solution comprising a quaternary ammonium compound in solution with a third solution comprising a halogen solution, the amounts of the second solution and third solution corresponding to the desired amount of the third solution;
15 producing the desired amount of the third solution; and
dispensing the desired solution immediately or prior to significant degradation of the third solution.

25. The method of claim 24 wherein the halogen solution comprises a compound
20 selected from the group consisting of bleach, hypochlorous acid, hypobromous acid, hypoiodous acid, hypochlorite, hypobromite, hypoiodite, and hypohalite.