# (19) World Intellectual Property Organization

International Bureau





(43) International Publication Date 28 July 2005 (28.07.2005)

**PCT** 

# (10) International Publication Number WO 2005/068378 A1

(51) International Patent Classification<sup>7</sup>:

C02F 1/76

(21) International Application Number:

PCT/US2004/036080

(22) International Filing Date: 28 October 2004 (28.10.2004)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

10/740,982

19 December 2003 (19.12.2003) US

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

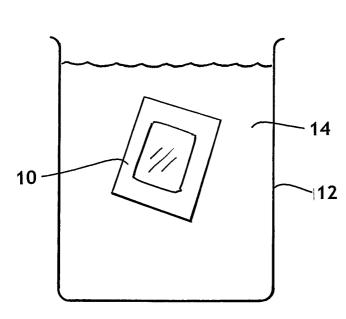
(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

#### **Published:**

with international search report

[Continued on next page]

(54) Title: PROCESS AND ARTICLE FOR DISINFECTING WATER



(57) Abstract: There is provided a water disinfectant article (10) and process in which iodine or another halogen disinfectant such as chlorine, bromine, or fluorine is released in free form only when it is needed for disinfection and which provides an increased shelf life and effectiveness. The instant invention uses a halogen in a captive form, and releases it in a free form as a result of a redox reaction upon mixing with water (14). After a time sufficient to allow the halogen to disinfect the water (14), a second component is released to reduce or neutralize the free halogen back to the captive halogen form. An optional visual indicator may be included to signal to the consumer of the water that the process has been completed.

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

# PROCESS AND ARTICLE FOR DISINFECTING WATER

# **BACKGROUND OF THE INVENTION**

The invention concerns processes and articles adapted for water purification.

Purification is broadly interpreted to include disinfection or removal of harmful contaminants or both.

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The growth in world population, industrialization, along with natural disasters has caused world supplies of safe drinking water to dwindle. Key pollutants that pose a threat to humans via polluted water consumption are pathogens (bacteria and viruses), organics, halogenated organics and heavy metals.

Conventional water filters are commonly used to remove water impurities and to provide cleaner, more aesthetically pleasing drinking water. They are, however, expensive, bulky, difficult to install and replace. They can harbor harmful organisms, are inconvenient, and do not claim to remove or kill 100 percent of all pathogens, although most are effective in removing some organics (including halogenated organics) as well as some heavy metals.

Small disposable filters are expensive by world standards. They can also be somewhat cumbersome to use. A distinct drawback to these types of filtration devices is that they are designed for use in water which is microbiologically safe. That is, the devices are not designed to remove pathogens because it is assumed that the water is pathogen free. Additionally, these devices have only limited utility in the removal of harmful substances such as, for example, heavy metals.

It is difficult for many people in the world to obtain safe drinking water without having the inconvenience of disinfecting it by either boiling it or through the use of iodine-based disinfectants. In many places, however, iodine-based disinfectants are not readily available. When available, it is well known that some of the iodine-based disinfectant systems

currently being deployed leave a distinctively bad taste in the mouth. Additionally, due to the fact that the iodine is consumed, potentially adverse medical effects can arise, especially for individuals having thyroid problems. Further, it is known that iodine and other halogen disinfectants, by virtue of their appreciable vapor pressure, are fugitive substances that escape easily from a package. Iodine in teabag-type disinfecting systems have been found to have a reduced shelf life or storage time because of this phenomenon. In disinfecting systems including other components like gelatin capsules and activated carbon, the free iodine may be absorbed by those components, or may escape to the air as vapor.

Chlorine dioxide, which may also be used as a disinfectant for water, may be generated by reacting sodium chlorite with sodium dichloroisocyanurate. There is however, no visual indication that disinfection is taking place, or whether disinfectant is still present in the water when disinfection is complete.

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It is clear that there exists a distinct need for a one-step process and article that allows a consumer to disinfect or otherwise purify water without having to resort to an independent timing mechanism. There is a distinct need for a process and article which provides a visual indication after the purification process is complete and that the water may be drunk.

#### **SUMMARY OF THE INVENTION**

In response to the foregoing difficulties encountered by those of skill in the art, we have discovered a process for disinfecting water which provides increased shelf life and effectiveness. The instant invention uses a halogen in a captive form, and releases it in a free form as a result of a redox reaction upon mixing with water. After a time sufficient to allow the halogen to disinfect the water, a second component is released to reduce or neutralize the free halogen back to the captive halogen form. An optional visual indicator

may be included to signal to the consumer of the water that the process has been completed.

The halogen disinfectant may be iodine, chlorine, bromine, or fluorine and is released in free form only when it is needed for disinfection.

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The invention includes a method of disinfecting water including the steps of providing water, intermixing the water with captive halogen and an oxidizing agent for a time sufficient to allow the mixture to render harmless substantially all pathogens present in the water and intermixing the water with an agent that adapted to substantially remove the disinfectant. The agent that removes the disinfectant may be a reducing agent adapted to remove substantially all of the free halogen from the water, or a material adapted to remove the disinfectant by physical adsorption.

### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 illustrates a disinfectant, colorant and removing material contained in a small pouch.

Figure 2 is a drawing of a pouch or teabag having two pockets.

#### **DETAILED DESCRIPTION OF THE INVENTION**

Water disinfection is a critical need for much of the world, especially those beset with overpopulation, poverty, and war. Clean water is increasingly becoming scarce even in developed countries as population and pollution make increased demands on this limited resource. The invention described herein can disinfect water rapidly and inexpensively and so improve the quality and length of peoples' lives.

The invention is directed toward a single-use, disposable product and process which provides the user with disinfected water and also provides the user with an indication visible to the unaided eye after the disinfection process has been completed and the water is safe

to drink. The water may be drunk immediately or stored for many hours before consuming, though it is desirable that it be stored in a closed container to reduce the risk of recontamination.

Pathogens which may be targeted for destruction are gram negative bacteria like Actinomyces, Bacillus, Bifodobacterium, Cellulomonas, Clostridium, Corynebacterium, Micrococcus, Mycobacterium, Nocardia, Staphylococcus, Streptococcus and Streptomyces and gram positive bacteria like Acetobacter, Agrobacterium, Alcaligenes, Bordetella, Brucella, Campylobacter, Caulobacter, Enterobacter, Erwinia, Escherichia, Helicobacterium, Legionella, nesseria, Nitrobact, Pasteurelia, Pseudomas, Rhizobium, Rickettsia, Salmonella, Shigella, Thiobacilus, Veiellonealla, Vibrio, Xanthomonas and Yersinia. In addition, water-10 borne viruses, protozoa and nematodes may also be targeted for destruction. Examples of water borne pathogens include viruses and cysts such as vibrio cholerea, giardia lamblia, cryptosporidium, retrovirsus, adenoviruses and human enteric viruses such as polio, hepatitis A, and coxsackie.

Gram negative bacteria have cell walls that are mainly lipopolysaccharide. Additionally there is present phospholipid, protein, lipoprotein and a small amount of peptidoglycan. The lipopolysaccharide consists of a core region to which are attached repeating units of polysaccharide moieties. A component of the cell wall of most Gramnegative bacteria is associated with endotoxic activity, with which are associated the pyrogenic effects of Gram-negative infections. On the side-chains are carried the bases for the somatic antigen specificity of these organisms. The chemical composition of these side chains both with respect to components as well as arrangement of the different sugars determines the nature of the somatic or O antigen determinants, which are such an important means of serologically classifying many Gram-negative species. In many cases it has been shown that the reason for certain organisms belonging to quite different 25 species, giving strong serological cross-reactivity, is due their having chemically similar

carbohydrate moieties as part of their lipopolysaccharide side chains, which generally have about 30 repeating units.

Gram positive bacteria are characterized by having, as part of their cell wall structure, peptidoglycan as well as polysaccharides and/or teichoic acids. The peptidoglycans which are sometimes also called murein are heteropolymers of glycan strands, which are cross-linked through short peptides.

The basis of the murein are chains of alternating residues of N-acetylglucosamine and N-acetyl muramic acid which are Beta -1,4-linked. The muramic acid is a unique substance associated with bacterial cell walls. These chains are cross-linked by short polypetide chains consisting of both L- and D-aminoacids. While in Gram-negative bacteria the peptidoglycan is simple in structure and comparatively uniform throughout most genera, in Gram-positive bacteria there is a very big variation in structure and composition. In general the peptidoglycan is multilayered. There have also been recorded some minor variations in composition in some groups. Thus, in Mycobacterium and Nocardia the N-acetyl moiety of the muramic acid is replaced by the oxidized form Nglycolyl. The amino acid composition of the both the cross-linking as well the stem polypeptides can vary extensively with different groups. These differences form the basis for the taxonomy of these organisms.

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The inventors have found that a system in which iodine or another halogen disinfectant such as chlorine, bromine, or fluorine is generated only when it is needed for disinfection provides a way to increase the shelf life effectiveness of the system. The instant invention uses a halogen in a captive or non-reactive form, and releases it in a free or reactive form as a result of a redox reaction upon mixing with water. After a time sufficient to allow the halogen to disinfect the water, a second component is released to reduce or neutralize the free halogen back to the captive halogen form. An optional visual indicator may be included to signal to the consumer of the water that the process has

been completed. Prior studies have shown that exposure to a concentration of 60 ppm of iodine for four minutes was sufficient to neutralize several common pathogens. It is desirable in the practice of this invention that the water be disinfected in less than 10 minutes, more desirably less than 4 minutes and still more desirably less than 2 minutes.

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The redox or reduction-oxidation reaction involves the transfer of electrons between at least one element or substance and another. In a redox reaction, the element that loses electrons increases in valency and so is said to be oxidized and the element gaining electrons is reduced in valency and so is said to be reduced. Conversely, an element that has been oxidized is also referred to as a reducing agent since it must necessarily have reduced another element, i.e., provided one or more electrons to the other element. An element that has been reduced is also referred to as an oxidizing agent since it must necessarily have oxidized another element, i.e., received one or more electrons from the other element. Note that since redox reactions involve the transfer of electrons between at least two elements, it is a requirement that one element must be oxidized and another must be reduced in any redox reaction.

Reduction potential refers to the voltage that a redox reaction is capable of producing or consuming. Much effort has gone into the compilation of reduction potential for various redox reactions and various published sources, such as "Handbook of Photochemistry" by S. Murov, I. Carmichael and G. Hug, published by Marcel Dekker, Inc. N.Y. (1993), ISBN 0-8247-7911-8, are available to those skilled in the art for this information.

In one example of the redox reaction of the invention, the captive halogen potassium iodide (KI) is oxidized by sodium periodate to produce iodine. In the process of oxidizing iodide to iodine, the sodium periodate is itself reduced to iodine. An excess of potassium iodide may react with the free iodine to form polyiodides, such as  $Kl_3^+$ ,  $Kl_5^+$ , etc. which have a pale brown color. The resulting iodine and / or polyiodide disinfects the

water. Potassium iodide and sodium periodate, also known as sodium metaperiodate and periodic acid sodium salt and which has the chemical formula NaIO<sub>4</sub>, are commercially available from many sources, including Sigma-Aldrich Chemical Company of Milwaukee, WI, USA and Mallinckrodt Baker Inc., of Phillipsburg, NJ, USA.

In order to provide an enhanced visual indication that disinfection is in progress, a small amount of water-soluble starch may be included in the device to make the halogen more visible. The water-soluble starch dissolves in the water and interacts with the iodine to form a blue-colored complex.

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A reducing or neutralizing agent may be added to the water after a time sufficient to disinfect the water to reduce the iodine back to the captive halogen iodide form. The resulting water would not have the off-taste associated with residual iodine. In addition, the disappearance of iodine causes the blue complex formed with the starch to disappear. The water sample is therefore eventually rendered colorless by the reducing agent to indicate that the disinfecting is complete.

Alternatively, a physical adsorbent, such as activated carbon, may be added to the water after a time sufficient to disinfect the water, in order to remove iodine. Suitable activated carbons include PCB 6x16 Coconut Activated Carbon, available from Calgon Carbon Corporation, Pittsburgh PA. A combination of a physical adsorbent and a reducing agent could also be used to neutralize the disinfectant.

Other suitable redox systems that may be used to produce iodine include an oxychloride (such as calcium oxychloride) and an iodide (such as potassium iodide), a peroxide (such as calcium peroxide) and an iodide (such as potassium iodide), a chlorate (such as sodium chlorate) and an iodide (such as potassium iodide), a manganese (III) salt (such as manganese (III) hydroxide) in combination with an iodide (such as potassium iodide) and an acid (such as phosphoric acid).

If chlorine is chosen as the disinfectant, it may be generated in situ using, for example, an oxidizing agent such as calcium oxychloride and an acid, such as sodium hydrogen sulfate. The chlorine may be detected using for instance, 3,3',5,5'-tetramethylbenzidine which produces a red color upon reaction with chlorine. Alternatively, the presence of the chlorine disinfectant may be detected by inclusion of a small quantity of potassium iodide and starch to produce a deep blue color. If chlorine is the principle disinfectant used, the neutralizing agent released into the system after a predetermined time may include ascorbic acid or a salt thereof or sodium thiosulfate — both of these materials reduce free chlorine to chloride salts. Alternatively, activated carbon may be used to adsorb the halogen and / or the colorant from the water.

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Chlorine dioxide, which may be also used as a disinfectant for water, may be generated by reacting sodium chlorite with sodium dichloroisocyanurate dehydrate though such a system does not provide a visual indication that disinfection is taking place, or whether disinfectant is still present in the water when disinfection is complete. As above, if a small amount of an iodide (for instance, potassium iodide) and an indicator (such as starch) is included in the disinfectant system, the chlorine dioxide produced by the reaction of sodium chlorite with sodium dichloroisocyanurate dihydrate may be used to oxidize an iodide (e.g. potassium iodide) to iodine; the iodine may in turn be used to produce an intense color to indicate disinfection by the addition of water soluble starch.

Bromine is another halogen that may be used to disinfect water. Bromine may be formed in situ from the reaction between calcium oxychloride and a bromide (such as sodium bromide). The presence of free bromine in the water being disinfected may be detected using 3,3',5,5'-tetramethylbenzidine, which reacts with bromine to produce a red color. Alternatively, a small amount of sodium iodide and a water soluble starch may be included in the disinfecting article to produce a blue – black color through oxidation of iodide to iodine by bromine, and subsequent combination of the iodine with starch to

produce a deeply colored complex. If bromine is the principle disinfectant used, the neutralizing agent released into the system after a predetermined time may include ascorbic acid or a salt thereof or sodium thiosulfate. Alternatively, activated carbon could be used to adsorb the halogen and colorant from the water.

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Ascorbic acid is suitable for use as the reducing or neutralizing agent for this system. The inventors have found, for example, that a gelatin capsule containing ascorbic acid will dissolve in warm water at a rate such as to allow a sufficient time for the disinfection of water by the iodine in most circumstances. An alternative to using a reducing agent to remove malodorous iodine is to use an adsorbent, such as activated carbon, available from Calgon Carbon Corp. under the tradename Carbsorb®, zeolites, or molecular sieves, available in a range of cavity sizes from Sigma-Aldrich. Adsorbent materials remove the disinfectant such as iodine by physically adsorbing it.

The inventors also discovered that pharmaceutical grade capsules made from hydroxypropylmethyl cellulose and sold by Torpac Inc. of Fairfield, NJ, USA under the name "vegi capsule", dissolve in cold water after allowing sufficient time for iodine to disinfect a volume of water. Other suppliers of capsules include GS Technologies, Eli Lilly, Pharmaphil, Now Foods of Bloomington, II and Warner Lambert. Any other water soluble polymers that are safe for the consumer may be used to form the capsule, such as, for example, starch, polyvinylalcohol, polyethylene oxide, hydroxypropyl cellulose, carboxymethyl cellulose, cellulose sulfate, gelatin, and sulfonated cellulose. The time may be extended for larger volumes of water by increasing the thickness of the water soluble capsule walls, for example. Ascorbic acid (also known as vitamin C) is commonly available from many suppliers including Sigma-Aldrich. An alternative reducing agent for removing halogens from water is sodium thiosulfate, also available from Sigma-Aldrich.

A suitable starch for use as the visual indicator in the practice of this invention is a cold water soluble starch, also known as pre-gelatinized starch, precooked starch, pre-

gelled starch and instant starch. Such starches are available from National Starch and Chemical Company of Bridgewater, NJ, USA. A commercial example of a suitable starch is known as STRUCTURE® ZEA or hydroxypropyl starch phosphate, from National Starch. Other suitable commercial starches include the TIStar series of tapioca starch from the Multi-Kem Corporation of Ridgefield, NJ, USA. The presence of starch in the water to be disinfected or otherwise purified greatly magnifies the intensity of color present as a result of iodine being present. At low concentrations of iodine, the water may appear to be color-free even though trace amounts of iodine are, in fact, present. Addition of starch magnifies and increases the color to a level detectable by normal eye sight. Naturally, other colorants or different materials may be utilized to enhance the color of iodine, such as the dye fluorescein, which slowly turns from yellowish green to pink in the presence of free iodine.

The inventors believe, though they do not wish to be limited by this belief, that an excess amount of free halogen in the amount of at least about 20 ppm should be sufficient to disinfect water, desirably at least about 40 ppm and more desirably at least about 60 ppm. It is believed that the higher the concentration of free halogen used, the less time is needed to achieve disinfection of the water. A large excess amount of free halogen, however, may be discernable by the consumer, so the excess should be kept below 250 ppm, desirably less than 150 ppm to prevent a strong iodine odor from being detectable.

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The ingredients of the invention may be assembled for use in a number of configurations. One that is satisfactory and very familiar to consumers is that of a teabag or pouch. Figure 1 illustrates a disinfectant, colorant and removing material contained in a small pouch 10 formed from a water-pervious, hydrophilic material. The pouch is similar to a conventional tea bag in construction and function in that it is water-pervious. The water 14 is disinfected substantially like tea is brewed with the exception that external heat is not

necessary. More specifically, the pouch 10 is dipped into a container 12 of water 14 which is to be disinfected, the water 14 may be slightly agitated by stirring or swirling to facilitate intermixing, and the pouch 10 is removed upon completion of the disinfection reaction. The teabag-like structure or pouch contains the reactants necessary for the oxidation and reduction reactions.

Figure 2 shows a pouch or teabag 20 having two pockets 22, 24. In one pocket 22 in the pouch 20 is the sodium periodate 26, in the other 24, the ascorbic acid in a capsule 28, potassium iodide 32 and optional visual indicator 34. The pouch 20 may be optionally folded along the dashed line 36 and sealed along the entire periphery 38 of the water pervious material 40 resulting in a smaller form of the bag.

The material from which the pouch may be made is, as mentioned above, water pervious. The material is desirably heat sealable, or sealable by crimping, or sealable by stitching or folding so that a pouch may be formed. The pouch may also be formed from the water pervious material using glue to stick the walls of the pouch together. Suitable paper material is commercially available as tea-bag material from Melitta USA, Inc. of Clearwater, FL, USA, which may be crimped to form a pouch. The pouch material could also be made using a woven or knitted fabric, such as woven or knitted cotton. The pouch could also be made from a laboratory filter paper, such Whatman ® Qualitative Filter Paper Grade 3 available from Sigma-Aldrich, and made into a pouch using adhesive, crimping, stapling, etc to join faces of the material together, or folding in such a way to contain the contents. The material may also be made from abaca pulp, rayon or nonwoven fabrics such as meltblown polypropylene fabric.

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It may also be possible to contain some of the components within (that is incorporate into) the water-pervious, desirably hydrophilic material so that these components will be near the surface of the pouch and will be able to more readily escape into the water. In this manner the other components will be able to disperse throughout the water to a greater

degree and thereby perform their intended function before coming into contact with the reducing agent. Inclusion of the oxidizing agent in the water-pervious material may allow the oxidizing agent to more rapidly increase in concentration upon contact with water. In such an embodiment, more rapid disinfection will likely occur as a result of the higher initial concentration of oxidizing agent in the water. The oxidizing agent may be printed onto the surface of the water pervious material by conventional printing techniques using the oxidizing agent in an aqueous phase and allowing it to dry.

In addition, it is possible to build devices of the present invention that utilize water soluble materials to contain the captive halogen and oxidizing agent prior to use. Indeed, the iodine-roducing system may be contained in a water soluble capsule, such as a gelatin or other water soluble polymer capsule such as those available from Torpac, Inc., Fairfield, NJ.

It should also be realized that, in some simple embodiments, all of the ingredients may simply be contained within an open-mouthed pouch with the contents being dumped into a container of water when it is desired to disinfect the water. Those of skill in the art will readily recognize that a large number of variations and modifications to the present invention can be made. For example, the process may include the additional step of treating the water during the time of disinfection in some manner. If such is the case, the article for achieving the disinfection of the water must be modified accordingly.

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In this regard, the treatment may add substances to the water which are useful, for example, in promoting good health. Alternatively, the treatment may be directed toward the removal of substances other than the disinfectant and colorant where the substances to be removed are potentially harmful if ingested. That is organics, heavy metals, halogenated organics, polyaromatics, halogenated polyaromatics, pesticides, herbicides and the like.

If it is desired to add a substance, the substance to be added need only be added as an additional component of the tea bag in a form which is water-soluble. Thus, when the

article comes into contact with the water during the disinfecting process, the substance to be added will dissolve into the water and be ingested by the consumer. Of course, care needs to be taken to make sure that the removing material does not remove the added substance to any great extent. If a substance is to be added by the treating step, the substance may be water-soluble vitamins, minerals, trace nutrients and colorant enhancers. If gelatin is used as the dissolving capsule containing the neutralizing agent, then protein may be added to the water as the capsule dissolves. Exemplary water-soluble vitamins which may be added include one or more vitamins like, for example, B vitamins and vitamin C. Exemplary minerals which may be added include one or more minerals like calcium, magnesium, potassium, sodium, iron or phosphorous. Exemplary trace nutrients which may be added include one or more trace nutrients, like, for example, zinc or copper. An exemplary colorant enhancer is starch when the colorant is iodine.

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If a substance is to be removed by the treating step, the removing material present to remove the disinfectant and the colorant may also be effective in removing additional substances. Alternatively, if it is desired to remove an additional substance which the removing material does not effectively remove by, for example, absorption, adsorption or neutralization, additional different removing material(s) may be added which specifically target such additional substance(s).

If a substance is to be removed by the treating step, the substance may be for example, heavy metals, organics, halogenated organics, polyaromatics, and halogenated polyaromatics. It is desirable to remove pesticides and herbicides where they are present as a result of run-off contamination or other causes. Exemplary heavy metals which may be removed by the treating step include lead, nickel, mercury, copper and arsenic.

Other additives may include binders, selected vitamins, minerals and/or flavors.

During the several minutes that the water is gently stirred, the disinfectant kills bacteria, cysts, and viruses while the solid sorbent adsorbs organics, including halogenated organics.

Heavy metals may also be adsorbed if an appropriate solid sorbent is chosen. The solid sorbent also serves to remove, by adsorption, the residual disinfectant and any color indicator if present. The color indicator's disappearance (at the point when the water appears clear to the unaided eye) indicates that substantially all the germs have been killed, substantially all disinfectant has been adsorbed or neutralized, and substantially all organic contaminants have been removed. The article may also release calcium, magnesium, vitamin C or any other chosen healthful vitamins or minerals or flavors at appropriate times in the cycle via a controlled release mechanism or other mechanism.

Those of skill in the art will recognize that the sequencing of the release of the disinfectant, colorant, removing material and treating material, if present, can be engineered as desired. For example, the removing material and/or treating material may be encapsulated within a substance which slowly dissolves in water so that the removing material and/or treating material is exposed to the water in a predetermined timed fashion depending upon the thickness and water-solubility rate of the encapsulating coating. In particular, the disinfectant and colorant could first be released to indicate to the consumer that the disinfecting process was under way. Release of the removing material would be delayed until such time as the disinfectant has achieved the concentration and exposure time desired. If present, release of treating materials that are additives could be delayed until a time shortly prior to the colorant being absorbed or neutralized by the removing material. This would lessen the likelihood of the removing material also removing the additive.

The following examples aid in understanding the invention.

#### Example 1

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An amount of material sufficient to disinfect 1 liter of water by the provision of 60 ppm of iodine was calculated using the equation:

$$KIO_4 + 4 H_2O + 11 KI \rightarrow 4KI_3 + 8 KOH$$

Sodium periodate was substituted for potassium periodate, however the difference between the molecular mass of sodium periodate and potassium periodate is low (near 5%) and as such has only a small bearing on the quantity of iodine produced by the reaction. Sodium periodate from Sigma-Aldrich in the amount of 0.0135 g, potassium iodide from Sigma-Aldrich in the amount of 0.113 g (an excess), cold water-soluble starch (National Starch Sample) in the amount of 0.05 g, and ascorbic acid in a Torpac Inc. size 00 capsule in an amount of 0.113 g (an approximately 50% mole excess, to ensure rapid neutralization of iodine) were added to water though exact amounts for three repetitions are shown below.

# Actual Quantities used for samples of Example 1:

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| Material         | Nominal  | Actual, Sample 1 | Actual, Sample 2 | Actual, Sample 3 |
|------------------|----------|------------------|------------------|------------------|
| Sodium periodate | 0.0135 g | 0.0146 g         | 0.0149 g         | 0.0172 g         |
| Potassium iodide | 0.1130 g | 0.1182 g         | 0.1179 g         | 0.1182 g         |
| Starch           | 0.050 g  | 0.0524 g         | 0.0582 g         | 0.0528 g         |
| Ascorbic Acid    | 0.113 g  | 0.1136 g         | 0.1175 g         | 0.1146 g         |

Heat sealable, water pervious material as described in US Patents 5,662,808 and 5,538,629, which are incorporated herein in their entirety by reference thereto for all purposes, was cut into strips approximately 4 inches (10 cm) wide and folded down the middle. A hemming iron was used to heat-seal sections of the folded strip to form two open pouches. The sodium periodate was accurately weighed and placed in one pocket. The other materials were placed in the other pocket. Ascorbic acid was placed into a pharmaceutical grade hydroxypropylmethyl cellulose size 00 capsule before being placed into the second pocket. Specification for size 00 is a capsule of volume 0.033 oz. (0.9759 cc), outer diameter 0.34 inches (0.86 cm) and locked length of 0.92 inches (2.3 cm). Finally,

both pockets were sealed to form an article. The thus-prepared "teabag-like device" was place in 1 liter of water at room temperature and gently agitated using a glass rod. When the teabag was placed in the water, the water quickly turned blue and stayed blue until the rupture of the ascorbic acid capsule. The capsule ruptured at 4 minutes, making the water colorless.

#### Example 2

An amount of material sufficient to disinfect 1 liter of water by the provision of 60 ppm of iodine was calculated. This included sodium periodate from Sigma-Aldrich in the amount of 0.0135 g, potassium iodide from Sigma-Aldrich in the amount of 0.113 g (an excess), cold water soluble starch (National Starch) in the amount of 0.05 g, and ascorbic acid in a Torpac Inc. capsule in an amount of 0.113 g (an approximately 50% mole excess, to ensure rapid neutralization of iodine). Ten repetitions were performed with exact amounts below:.

Actual Quantities used for samples of Example 2:

|                  | Actual Mass Measurements |          |          |          |          |  |
|------------------|--------------------------|----------|----------|----------|----------|--|
| Material         | Sample 1                 | Sample 2 | Sample 3 | Sample 4 | Sample 5 |  |
| Sodium periodate | 0.0147 g                 | 0.0171 g | 0.0188 g | 0.0152 g | 0.0153 g |  |
| Potassium iodide | 0.1176 g                 | 0.1168 g | 0.1168 g | 0.1171 g | 0.1154 g |  |
| Starch           | 0.054 g                  | 0.055 g  | 0.0496 g | 0.051 g  | 0.0503 g |  |
| Ascorbic Acid    | 0.1160 g                 | 0.1137 g | 0.1189 g | 0.1129 g | 0.1185 g |  |

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|                  | Actual Mas | ctual Mass Measurements |          |          |           |  |
|------------------|------------|-------------------------|----------|----------|-----------|--|
| Material         | Sample 6   | Sample 7                | Sample 8 | Sample 9 | Sample 10 |  |
| Sodium periodate | 0.0162 g   | 0.0168 g                | 0.0169 g | 0.0164 g | 0.0175 g  |  |
| Potassium iodide | 0.1169 g   | 0.1142 g                | 0.1143 g | 0.1177 g | 0.1153 g  |  |
| Starch           | 0.0497 g   | 0.0538 g                | 0.0488 g | 0.0547 g | 0.0509 g  |  |
| Ascorbic Acid    | 0.1178 g   | 0.1153 g                | 0.1145 g | 0.1127 g | 0.1145 g  |  |

The sodium periodate was place in one pocket in a heat sealable, water pervious material as described in Example 1. The other materials were placed in the other pocket. Ascorbic acid was placed into a pharmaceutical grade hydroxypropylmethyl cellulose size 00 capsule before being heat sealed into the article. In addition, approximately 3 grams of soda lime glass beads of 3 mm diameter (available from Sigma-Aldrich) were included in the bag to ensure that the bag sank and could be dunked easily. Johnson & Johnson Reach® mint waxed dental floss was rinsed under a cold running faucet to remove the mint flavor and dried using a paper towel. The floss was included between the "teabag-like device" layers before heat sealing such that the end of the floss could be held and used to assist in dunking the disinfecting device. The thus-prepared "teabag-like device" was placed in 1 liter of water at room temperature and gently agitated using a glass rod. When the teabag was placed in the water, the water quickly turned blue and stayed blue until the rupture of the ascorbic acid capsule. The capsule ruptured at 4 minutes, making the water colorless. Prior studies have shown that exposure to a concentration of 60ppm of iodine for four minutes was sufficient to neutralize several common pathogens.

These teabag water disinfectants were easier to use since they sank more rapidly because of the glass beads, and could be dunked like a regular teabag to provide agitation using the dental floss. The water became a deep blue color within one minute from first immersing the tea-bag and at four minutes, the capsule burst, releasing the ascorbic acid into the water, which neutralized the iodine. No iodine odor or color was observed in the water after 6 minutes from initial immersion of the tea-bag.

# Example 3

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One Katadyne ® Micropur ® Emergency Drinking Water Tablet was added to 1 liter of water at ambient temperature and stirred. Katadyne tablets weigh 0.4g each, and contain 6.4% sodium chlorite and 1.0% sodium dichlorocyanurate dihydrate, as well as

92.6% of inert ingredients. Approximately 0.3 g potassium iodide was added to the solution, which turned a faintly brown color due to the production of iodine. Addition of approximately 0.3 g of cold water soluble starch (National Starch) produced a blue color.

After 5 months storage in a polyethylene bag, the paper of the teabag, and the plastic bag remained white, indicating that iodine was not escaping from the device and that the devices had not lost their efficacy.

# Comparative Example 1 (not an example of the invention)

Regular iodine Potable Aqua® tablets (distributed by WPC Brands, Jackson WI) were crushed and stored in a paper packet in a polyethylene bag. Potable Aqua tablets contain iodine in a fast dissolving form (tetraglycinehydroperiodide) and are commonly used to disinfect water in camping & hiking situations. Within a few days, the paper was heavily stained from iodine as was a closed plastic storage bag and any surrounding containers, indicating leakage of volatile iodine and loss of efficacy.

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#### Comparative Example 2 (not an example of the invention)

Four tablets, or 0.476g of Potable Aqua ® tablets were crushed and placed in a pouch formed from heat sealable tea-bag material described in example 1. 0.1 g of cold water soluble starch (National Starch) was also added to the pouch. 17.5g of activated carbon (untreated, 8-20 mesh, from Sigma-Aldrich) was used to fill two porcine gelatin capsules of size SU-7 from Torpac, Inc. The capsules were then locked closed by pressing the two interlocking sections of each capsule together. Size SU-7 capsule specification is 1 oz (29.6cc) volume with an outer diameter of 0.9 inches (2.3cm) and a length when locked closed of 3.5 inches (8.9 cm). The carbon-filled capsules were placed into the pouch and the remaining surfaces of the opening were heat-sealed closed. Thus, all materials were sealed into the water permeable pouch.

The device was placed into 1 liter of warm (37°C) water and agitated using a glass rod. Within a short period of time, a blue color developed in the water. While it was difficult to observe activity within the paper pouch, after 5-6 minutes, the gelatin capsules dissolved sufficiently to break open and allow the carbon to adsorb the iodine. After 15 minutes, the water appeared to have lost the blue color of the starch-iodine complex. A significant amount of carbon fines were observed in the water.

# Comparative Example 3 (not an example of the invention)

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Two devices were made in the following manner:

Four tablets, or 0.476g of Potable Aqua ® tablets were crushed and placed in a pouch formed from heat-sealable tea-bag material described in example 1. 0.1 g of cold water-soluble starch (National Starch) was also added to the pouch. 17.5g of activated carbon (Type APA 12x40 from Calgon Carbon Corp, Pittsburg PA) was used to fill two porcine gelatin capsules of size SU-7 from Torpac, Inc. The capsules were then locked closed by pressing the two interlocking sections of each capsule together. Size SU-7 capsule specification is 1 oz (29.6 cc) volume with an outer diameter of 0.9 inches (2.3 cm) and a length when locked closed of 3.5 inches (8.-9). The carbon-filled capsules were placed into the pouch and the remaining surfaces of the opening were heat sealed closed. Thus, all materials were sealed into the water-permeable pouch.

One device was placed into 1 liter of warm (37°C) water and agitated using a glass rod. Within a short period of time, a blue color developed in the water. While it was difficult to observe activity within the paper pouch, after 5-6 minutes, the gelatin capsules dissolved sufficiently to break open and adsorb the iodine. After 15 minutes, the water appeared to have lost the blue color of the starch-iodine complex. A significantly lower amount of carbon fines were observed in the water compared to comparative example 2.

The second device was placed in a plastic bag for storage. Within a few days, the paper was heavily stained from iodine as was a closed plastic storage bag and any surrounding containers, indicating leakage of volatile iodine and loss of efficacy.

### Comparative Example 4 (not an example of the invention)

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Two tablets of Potable Aqua ® (0.238 g) were crushed and placed into a size 000 porcine gelatin capsule (Now Foods) along with 0.05 +/- 0.005g cold water-soluble starch (National Starch). Size 000 specification is volume 0.05 oz (1.48cc) (, outer diameter of 0.39 inches (0.99cm), capsule length when locked closed of 1.03 inches (2.62 cm). A size 00 capsule (Torpac, Inc.) was opened, and the longer section was shortened using scissors in such a manner that the closed capsule would fit inside the size 000 gelatin capsule. Ascorbic acid was added to the modified size 00 by crushing two P.A.Plus® neutralizing tablets (WPC Brands, Inc. Jackson WI). In total, 90mg of ascorbic acid was added to the modified size 00 capsule containing the ascorbic acid was placed inside the size 000 capsule that already contained soluble iodine and starch indicator.

The capsule based device was dropped into 500ml warm water at 40°C and stirred. After 4 minutes, the gelatin outer capsule began to rupture, forming black blobs of iodine / starch / gelatin. A strong iodine odor was observed. After 6 minutes, the water was colored blue. The ascorbic acid appeared to be released after 7 1/2 minutes, as the color began to fade rapidly. The water became colorless after 8 minutes.

As will be appreciated by those skilled in the art, changes and variations to the invention are considered to be within the ability of those skilled in the art. Examples of such changes are contained in the patents identified above, each of which is incorporated herein by reference in its entirety to the extent it is consistent with this specification. Such changes and variations are intended by the inventors to be within the scope of the invention.

#### What is claimed is:

- 1) An article for disinfecting water comprising:
  - a captive halogen;
  - an oxidizing agent that reacts with said captive halogen to form free halogen;
- a reducing agent adapted to react with said free halogen after a predetermined time.
  - 2) The article of claim 1 wherein said halogen is selected from the group consisting of iodine, chlorine, bromine, fluorine and mixtures thereof.
  - 3) The article of claim 1 further comprising a visual indicator.
- 4) The article of claim 3 wherein said indicator is a cold water soluble starch that turns

  blue in the presence of iodine.
  - 5) The article of claim 1 wherein the reducing agent is selected from the group consisting of ascorbic acid, activated carbon, zeolites, molecular sieves, and mixtures thereof.
  - 6) The article of claim 1 wherein said free halogen is present in an amount of at least 20 ppm and less than 250 ppm prior to reaction with said reducing agent.
    - 7) The article of claim 1 wherein said free halogen is present in an amount of at least 40 ppm and less than 250 ppm prior to reaction with said reducing agent.
    - 8) The article of claim 1 wherein said free halogen is present in an amount of at least 60 ppm and less than 250 ppm prior to reaction with said reducing agent.
- 20 9) The article of claim 1 wherein said predetermined time is less than 10 minutes.
  - 10) The article of claim 1 wherein said predetermined time is less than 4 minutes.
  - 11) The article of claim 1 wherein said predetermined time is less than 2 minutes.
  - 12) The article of claim 1 wherein said oxidizing agent is printed onto said article.
- 13) The article of claim 1 wherein said reducing agent is encapsulated in a water-soluble coating.
  - 14) A teabag-like article for disinfecting water and providing a visual indication after the

disinfection is complete, the article comprising:

a bag formed from a water-pervious material and defining two interior chambers, wherein a first chamber contains potassium iodide and a second chamber contains a visual indicator, an oxidizing agent and a reducing agent encapsulated in a water soluble coating.

- 15) The article of claim 14 wherein the water-pervious bag material is formed from a material selected from the group consisting of abaca pulp or rayon.
- 16) The article of claim 14 wherein said oxidizing agent is printed onto said material.
- 17) A process for disinfecting water including the steps of:

# 10 providing water;

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intermixing the water with a captive halogen and an oxidizing agent for a time sufficient to form free halogen and allow the mixture to render harmless substantially all pathogens present in the water; and,

intermixing the water with a reducing agent adapted to remove substantially all of the free halogen from the water.

- 18) The process of claim 17 wherein said captive halogen is potassium iodide.
- 19) The process of claim 17 further comprising indicating the presence of free halogen with a visual indicator which changes color again upon reacting with said reducing agent.
- 20) The process according to claim 19, wherein the visual indicator is selected from the group consisting of starch and cold-water soluble starch, fluorescene and mixtures thereof.



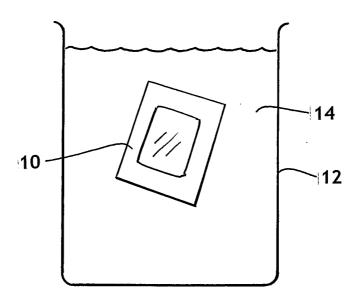


FIG. 1

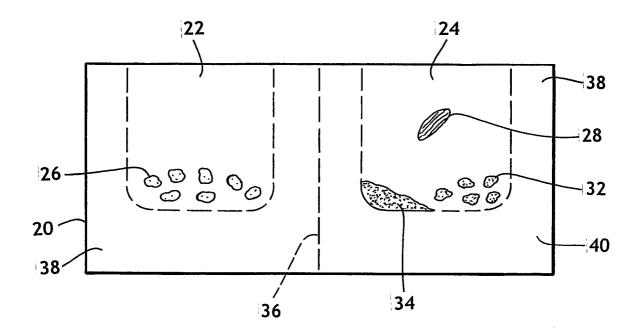


FIG. 2

# INTERNATIONAL SEARCH REPORT

ional Application No PCT/US2004/036080

# A. CLASSIFICATION OF SUBJECT MATTER IPC 7 CO2F1/76

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

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