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(71) Applicant: **3M INNOVATIVE PROPERTIES COMPANY** [US/US]; 3M Center, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US).

(72) Inventor; and

(71) Applicant : **SIEDLE, Allen R.** [US/US]; 3M Center, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US).

(74) Agents: **LAPOS-KUCHAR, Julie A.** et al.; 3M Center Office of Intellectual Property Counsel Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US).

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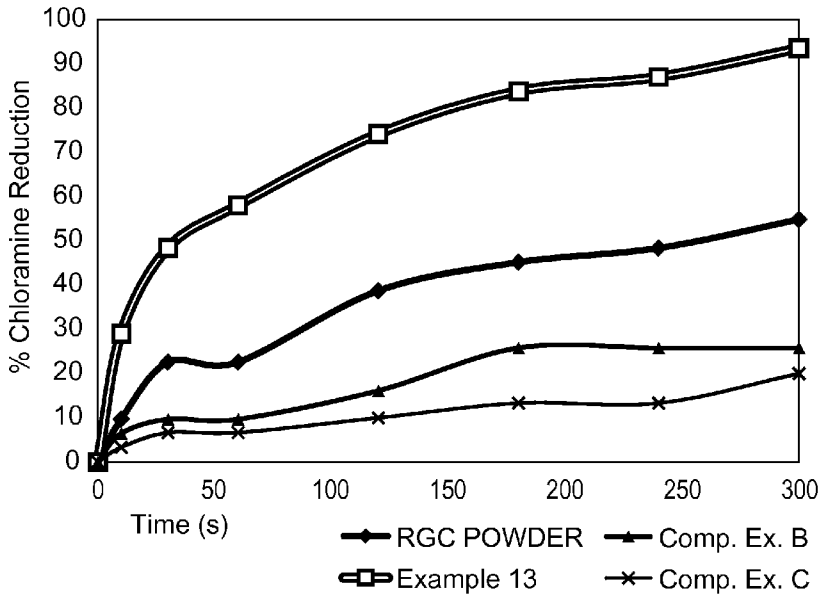
(54) **Title**: FILTRATION MEDIUM COMPRISING PLATINUM AND/OR PALLADIUM



(57) **Abstract**: Described herein is a method for removing chloramines from aqueous solutions by contacting the aqueous solution with a solid, wherein the surface of the solid comprises a metal or metal-containing compound, wherein the metal is selected from the group consisting of palladium and platinum.

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FILTRATION MEDIUM COMPRISING PLATINUM AND/OR PALLADIUM

TECHNICAL FIELD

[0001] A method for removing chloramine from an aqueous solution using palladium, platinum or a combination thereof.

BACKGROUND

[0002] Chloramine is commonly used in low concentration as a secondary disinfectant in municipal water distribution systems as an alternative to chlorination with free chlorine. Concerns over taste and odor of chloramine treated water have led to an increase in the demand for water filters with chloramine removal capabilities.

[0003] Carbon particles, such as activated carbon particles, have been used to remove chloramine from aqueous streams. Improvements in removal of chloramine can be achieved by reducing the mean particle diameter of the carbon and by increasing the carbon bed contact time. Although parameters such as contact time and mean particle diameter are known to affect chloramine removal efficiencies, more significant improvements are desired without significantly increasing the pressure drop of filtration media.

[0004] U.S. Pat. No. 5,338,458 (Carrubba et al.) discloses an improved process for the removal of chloramine from gas or liquid media by contacting the media with a catalytically-active carbonaceous char.

[0005] U.S. Pat. No. 6,699,393 (Baker et al.) shows improved chloramine removal from fluid streams, when the fluid stream is contacted with an activated carbon, which has been pyrolyzed in the presence of nitrogen-containing molecules, versus a catalytically-active carbonaceous char.

[0006] WO 2011/125504 (Hitomi et al.) discloses an activated carbon containing 1.40-4.30 mass % oxygen, 0.90-2.30 mass % nitrogen, 0.05-1.20 mass % sulfur, and 0.40-0.65 mass % hydrogen, which is said to effectively break down chloramines.

SUMMARY

[0007] There is a desire to provide a filtration medium, which is less expensive and/or more efficient at the removal of chloramine than currently available filtration media.

[0008] In one aspect, a method for removing chloramine from aqueous solutions is described comprising: providing an aqueous solution comprising chloramine and contacting the aqueous

solution with a solid, wherein the surface of the solid comprises a metal or metal-containing compound, and wherein the metal is selected from the group consisting of palladium and platinum.

[0009] In one embodiment, the solid comprises a support having a surface, wherein the surface comprises the metal or metal-containing compound.

[0010] In one embodiment, a metal-containing particulate is mixed with a support particulate, wherein the D_{50} of the metal-containing particulate is at least 5 times smaller than the D_{50} of the support particulate.

[0011] The above summary is not intended to describe each embodiment. The details of one or more embodiments of the invention are also set forth in the description below. Other features, objects, and advantages will be apparent from the description and from the claims.

DESCRIPTION OF THE FIGURES

[0012] Fig. 1 is a chart of the percent chloramine reduction versus time for Substrate B and Examples 1-4.

[0013] Fig. 2 is a chart of the percent chloramine reduction versus time for Substrate B and Examples 5-6.

[0014] Fig. 3 is a chart of the percent chloramine reduction versus time for Substrate B, and Example 7.

[0015] Fig. 4 is a chart of the percent chloramine reduction versus time for Substrate B, Comparative Example A, and Example 8.

[0016] Fig. 5 is a chart of the percent chloramine reduction versus time for Substrate B and Examples 9-12

[0017] Fig. 6 is a chart of the percent chloramine reduction versus time for Substrate B, Comparative Examples B-C, and Example 13.

DETAILED DESCRIPTION

[0018] As used herein, the term

"D_{10}" refers to the particle size for which only 10 percent by volume of the particles in a particle distribution are smaller;

"D_{50}" refers to the particle size for which 50 percent by volume of the particles in a particle distribution are smaller (also commonly referred to in the art as the average or mean particle size);

"D_{90}" refers to that particle size for which 90 percent by volume of the particles in a particle distribution are smaller;

“a”, “an”, and “the” are used interchangeably and mean one or more; and

"and/or" is used to indicate one or both stated cases may occur, for example A and/or B includes, (A and B) and (A or B).

[0019] Also herein, recitation of ranges by endpoints includes all numbers subsumed within that range (e.g., 1 to 10 includes 1.4, 1.9, 2.33, 5.75, 9.98, etc.).

[0020] Also herein, recitation of "at least one" includes all numbers of one and greater (e.g., at least 2, at least 4, at least 6, at least 8, at least 10, at least 25, at least 50, at least 100, etc.).

[0021] The present disclosure is directed to a filtration medium comprising a solid wherein the solid comprises platinum, palladium, and combinations thereof (herein referred to as noble metals), or compounds containing these particular noble metals. Filtration media comprising these noble metals may be used for the removal of chloramine from aqueous solutions.

[0022] In one embodiment, a solid comprising the noble metal may be contacted with an aqueous solution comprising the chloramine. Such solids may include for example, platinum solid, platinum oxide, platinum hydroxide, platinum hydride, palladium solid, palladium oxide, palladium hydroxide, palladium hydride, and combinations thereof.

[0023] Although not wanting to be limited by theory, it is believed that platinum and palladium react with chloramine in a catalytic fashion. In such a catalytic process, the chemical reaction with chloramine occurs predominately and/or exclusively on the surface of the media. Therefore, small quantities of these noble metals may be utilized. One aspect of the present disclosure is to provide supports comprising these noble metals.

[0024] The noble metal (or compound comprising the noble metal) is added to the surface of the support (or substrate) to form, what is being referred to herein as the activated support. The supports of the present disclosure include both carbon-based and inorganic supports.

[0025] The carbon-based support may be a granular material, a powder material, a fiber, a tube, a web, or a foam.

[0026] The morphology of the carbon-based support is not particularly limited and may include a non-particulate, a particulate, or an aggregate. Additional exemplary morphologies include: a carbon block, a carbon monolith, foams, films, fibers, nanoparticulates, such as nanotubes and nanospheres. A non-particulate carbon-based support is a support that is not composed of discernable, distinct particles. A particulate carbon-based support is a support that has discernable particles, wherein the particle may be spherical or irregular in shape and has an average diameter of at least 0.1, 1, 5, 10, 20, or even 40 micrometers (μm) to at most 75 μm, 100 μm, 500 μm, 1 millimeter (mm), 2 mm, 4mm, 6.5 mm, or even 7 mm. An aggregate (or a composite) is formed by the joining or conglomeration of smaller particles with one another or with larger carrier particles or surfaces. The aggregates may be free standing (self-supporting against gravity).

[0027] Typically, the morphology of the carbon-based support will be selected based on the application. For example, particulate with a large particle size is desirable when the supports of the present disclosure are used in applications requiring low pressure drops such as in beds through which gases or liquids are passed. In another example, particle sizes of 20 to 200 μm may be preferable when used in a carbon block monolith.

[0028] In one embodiment, the carbon-based support is comprised of activated carbon, in other words carbon that has been processed to make it highly porous (i.e., having a large number of pores per unit volume), which thus, imparts a high surface area.

[0029] Commercially available carbon-based supports include: granular activated carbon available under the trade designation "RGC" by Mead Westvaco Corp, Richmond, VA may be preferred in water treatment. Activated coconut carbon available under the trade designation "KURARAY PGW" by Kuraray Chemical Co., LTD, Okayama, Japan may also be used.

[0030] The morphology of the inorganic support is not particularly limited and may include a non-particulate, a particulate, or an aggregate. Exemplary morphologies include: fibers and nanoparticules such as nanotubes and nanospheres.

[0031] The inorganic support may comprise, for example, silicon dioxide (silica), zirconia, titania, ceria, alumina, iron oxide, zinc oxide, tin oxide, alumina/silica, zirconia-silica, clays, talc-containing materials, spinel-structured oxides such as magnesium aluminate or cobalt iron oxide or the like, and other binary or ternary oxides of aluminum or silicon with other metal oxide materials. Although the inorganic support may be essentially pure, it may contain small amounts of stabilizing ion such as ammonium and alkaline metal ions, or it may be a combination of oxides such as a combination of titania and zirconia.

[0032] The choice of support materials is quite broad and can include without limitation calcium carbonate, alumina, silica, zeolites, ion exchange resins and porous organic materials, activated carbon, metal oxides and metal oxide framework (MOF) materials, and inorganic oxides. All of these materials can be used in combination with one another or in combination with a carbon-based support.

[0033] The size of the pores of the support can be selected based on the application. The support may be microporous, macroporous, mesoporous, or a mixture thereof.

[0034] In one embodiment, it is preferable for the support to be porous. The porous nature will enable, for example, more surface area for chloramine removal. Particularly useful are supports that have high surface area (e.g., at least 100, 500, 600 or even 700 m^2/g; and at most 1000, 1200, 1400, 1500, 1800, or even 2000 m^2/g based on BET (Brunauer Emmet Teller method) nitrogen adsorption).

[0035] In one embodiment, the solid comprises more than 0.1, 0.2, 0.5, 1, 1.5, 2, 2.5, 4, 5, 10, 15, or even 20% by mass of the noble metal. Larger values may be envisioned, however due to cost and the presumption of catalytic activity with chloramine, values less than 50%, 40%, 30%, or even 25% by mass of the noble metal are preferred.

[0036] In the present disclosure, the surface of the support comprises platinum and/or palladium (or a compound containing such metals). The platinum and/or palladium is adherent to the surface of the support. In other words, when the activated support is gently stirred with water, there is no apparent separation of the noble metal from the activated support. It is advantageous for the noble metal to be adherent to the support to contain the noble metal, preventing loss of the noble metal from the filtration media e.g., during washing of the filtration media.

[0037] In the present disclosure, if a support is used, it is preferable that the platinum and palladium (or a compound comprising the noble metal) be located at the surface of the activated support to enable contact with the chloramine. The platinum and/or palladium (or a compound comprising the noble metal) may be applied to the surface of the support, using techniques known in the art. Such techniques include, for example, physical mixing, vacuum deposition, and wet impregnation.

[0038] In one embodiment, the activated support may be made by physical blending of the noble metal and the support involving mechanical and/or electrostatic mixing. Physical blending can be carried out by dry blending. "Dry blending" refers to blending the support particle and the noble metal in the absence of water and organic solvents. Dry blending can be carried out, for example, via convective mixing, diffusive mixing, and shear mixing mechanisms. For example, contacting a support particle with the noble metal particulates can be carried out by tumbling the support particle and the noble metal (or compound comprising the noble metal) using conventional tumbling mixers (e.g., V-blender, double cone, or rotating cube); convective mixers (e.g., ribbon blender, nautamixer); fluidized bed mixers; or high-shear mixers. Such techniques should, in the process of mixing, cause the noble metal (or compound comprising the noble metal) to become adherent to the surface of the support.

[0039] In one embodiment, the noble metal or a compound comprising the noble metal, is mechanically mixed with the support to impinge the noble metal (or compound comprising the noble metal) onto the support. Such mechanical mixing is known in the art and includes for example, tumbling the components together with for example balls, magnetically-assisted impact coating, or exposing the support to a high velocity fluid comprising the noble metal (or compound comprising the noble metal).

[0040] In one embodiment, such mechanical mixing, not only impinges the noble metal onto the surface of the support, but also decreases the particle size of the resulting activated support, thus

creating metal-containing particulates. The metal-containing particulate may have a particle size of no more than 100, 50, 25, 20, 15, 10, 5 or even 1 micrometers.

[0041] In one embodiment, a noble metal-containing particulate is mixed with a support, which is a particulate, wherein the D_{50} of the noble metal-containing particulate is at least 5, 10, 15, or even 20 times smaller than the D_{50} of the support. If the support is a highly porous substrate, such as an activated carbon, such a technique would provide and activated support that had a high loading of the noble metal-containing particulate.

[0042] In one embodiment, the activated support may be made by applying the noble metal, or a compound comprising the noble metal, to the surface of the support via a vacuum deposition method, including physical deposition and chemical deposition. Such techniques are known in the art.

[0043] Physical vapor deposition (PVD) of metals is a well-established practice in the coating art. Physical vapor deposition of the conductive layer can be carried out in various different ways. Representative approaches include sputter deposition, evaporation, laser ablation, and cathodic arc deposition. Any of these or other PVD approaches can be used in the process of the present disclosure, although the nature of the PVD technique can impact the resulting activity. For example, the energy of the PVD technique can impact the mobility of the deposited metal and hence its tendency to coalesce and form a continuous thin film.

[0044] In another embodiment, the activated support may be made by impregnating a support with the noble metal followed by reduction. For example, a compound comprising the noble metal, is mixed with solvent (e.g., water, or an organic solvent such as alcohol) to form a solution, which is used to impregnate the support. After impregnation, the impregnated support is reduced (e.g., using hydrogen) to generate the activated supports of the present disclosure. Such techniques are known in the art.

[0045] In one embodiment, it is desirable to achieve high local loading of the platinum and palladium. In other words, the surface of the support instead of comprising a uniform distribution of the noble metal, forms localized clusters (or aggregates) that are 1 nn or larger on the surface, or even 5 nm or larger on the surface.

[0046] The platinum and palladium-containing compounds may be selected based on the technique used to treat the surface of the support. Exemplary platinum and palladium-containing compounds include for example, the corresponding metal hydrides, oxides, or hydroxides, chloroplatinic acid, palladium chloride, palladium nitrate, and combinations thereof.

[0047] In one embodiment, the platinum and palladium-containing compounds have a molecular weight less than 500 g/mol, 200 g/mol, or even less than 100 g/mol.

[0048] In one embodiment, the platinum and palladium-containing compounds do not substantially comprise a nitrogen-containing oxyanion, sulfur-containing anion, chloride, phosphate, or carboxylate.

[0049] In one embodiment, the noble metal-containing solid or activated support is disposed in a matrix. The matrix may be a web, a polymer-containing composite block, on the surface of a tube, or in another structure that enables aqueous solutions to pass therethrough. In one embodiment, the filtration medium may be a compressed blend of the solid or activated support and a binder material, such as a polyethylene, e.g., an ultra high molecular weight polyethylene, or a high-density polyethylene (HDPE). In another embodiment, the solid or activated support may be loaded into web, such as a blown microfiber, which may or may not be compacted such as described in U.S. Publ. No. 2009/0039028 (Eaton et al.), herein incorporated in its entirety.

[0050] The loading, expressed as weight of the solid or activated support by the total weight of the filtration media, can vary depending on matrix used. In one embodiment, the amount of activated support (or the solid) comprises is at least 10, 25, 40, 50, 60, 75, or even 80 %; at most 90, 92, 95, 97, or 99%, or even 100% mass of the filtration media. For example, when carbon blocks are used, the filtration media may comprise about 50-85% mass of the activated support (or the solid), while for a carbon loaded web, the filtration media may comprise about 80-95% mass of the activated support (or the solid).

[0051] In one embodiment, the solid or activated support is disposed in a fluid conduit, wherein the fluid conduit is fluidly connected to a fluid inlet and a fluid outlet. Such systems may include packed beds.

[0052] In one embodiment, the solid or activated support may be used to remove chloramines from a fluid stream, particularly a liquid fluid stream, more specifically, an aqueous fluid stream. Chloramines are formed from the aqueous reaction between ammonia and chlorine (hypochlorite). Thus, adding ammonia (NH_3) to a chlorination system converts chlorine to chloramines. Specifically, monochloramine, hereafter referred to as "chloramine," in low concentrations arise from the disinfection of potable water sources. In one embodiment, after contacting the aqueous solution with a support comprising a carbon, sulfur, and nitrogen, as disclosed herein, the resulting aqueous solution comprises a reduced amount of chloramines.

EXAMPLES

[0053] Advantages and embodiments of this disclosure are further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as

other conditions and details, should not be construed to unduly limit this invention. In these examples, all percentages, proportions and ratios are by weight unless otherwise indicated.

[0054] All materials are commercially available, for example from Sigma-Aldrich Chemical Company; Milwaukee, WI, or known to those skilled in the art unless otherwise stated or apparent.

[0055] These abbreviations are used in the following examples: g = gram, hr = hour, in = inch, kg = kilograms, min = minutes, mol = mole, mm = millimeter, mL = milliliter, L = liter, psi=pressure per square inch, mPa = milliPascals, Pa = Pascals, and wt = weight.

[0056] Testing Methods

[0057] Chloramine Test

[0058] The chloramine content of water samples was determined from the total chlorine content in the samples. Total chlorine (OCl^- and chloramines) concentration was measured by the DPD Total Chlorine Method, Hach Method 8167, which Hach Company claims to be equivalent to USEPA Method 330.5. The free chlorine (OCl-) concentration was periodically measured by the DPD Free Chloramine Analysis, Hach Method 8021, which Hach company claims is equivalent to EPA Method 330.5. Free chlorine was maintained at a negligible concentration (< 0.2 ppm), thus, the total chlorine analysis was considered a good approximation of the concentration of chloramines in the water. All reagents and the instruments were those described in the standard Hach Method and can be obtained from Hach Company, Loveland, CO.

[0059] Chloramine Preparation

[0060] 3 ppm choramine was prepared by adding the appropriate amount of commercial bleach (5.25% NaOCl) to deionized water. While stirring, 1.5 equivalents of a solution of ammonium chloride in water was added to the bleach solution and stirred for 1 hour. The pH was adjusted to 7.6 by the addition of NaOH or HCl and tested using a pH meter (obtained from Thermo Fisher Scientific, Inc., Waltham, MA, under the trade designation "ORION 3-STAR").

[0061] Chloramine Removal Test

An aqueous chloramine test solution was prepared comprising 3 ppm NH_2Cl (prepared as described above) at a pH 7.6 at 27°C. Immediately prior to the test, the initial total chlorine content of the aqueous chloramine test solution was measured as described in the Chloramine Test above. With continuous stirring, a 0.46g aliquot of a carbon substrate sample (i.e. a sample prepared according to Comparative Examples or the Examples according to the disclosure) was added to the aqueous chloramine test solution. For the commercially available metal or metal oxides shown in Table 1, the samples were compared on a per volume basis, measuring 1.5 cc. Immediately after mixing, a timer was started. After 30 sec, a 5 mL-aliquot of mixture was removed and within 5 sec of removal, the mixture was passed through a 1-micrometer syringe filter to remove suspended

solids. The chloramine content of the filtered aliquot was measured within 30 sec of taking the 5-mL aliquot as described above. Aliquots from the mixture were taken periodically over the course of 5 minutes and analyzed using the Chloramine Test as described above. The efficiency of the chloramine removal is reported as the % chloramine reduction determined by the equation:

$$\left(1-\frac{[NH2Cl]filteredaliquot}{[NH2Cl]initial}\right)\times 100$$

[0062] Substrates

[0063] Substrate A: Activated carbon (80 x 325) was obtained from MeadWestvaco Specialty Chemicals, North Charleston, SC, under the trade designation "RGC 325".

[0064] Substrate B: was an activated carbon powder with an ash content of 2.9 wt% (obtained under the trade designation "RGC POWDER", -325 mesh, from MeadWestvaco Specialty Chemicals, North Charleston, SC).

[0065] Example 1

[0066] A mixture of 0.04 g. platinum black (obtained from Aldrich Chemical Co., Milwaukee, WI) and 0.1 g of Substrate A was placed in a 10 x 25 mm stainless steel cylinder that contained two 6 mm stainless steel ball bearings and then milled for 1 min in a dental amalgamator (Wig-L-Bug, Crescent Dental Manufacturing Co., Elgin, IL). After milling, the finely powdered sample was intimately mixed by tumbling with 0.9 g of Substrate A. The Pt loading in the composite so produced was 4 wt %.

[0067] When Substrate A was milled in a separate experiment under identical conditions the particle size distribution of the Substrate A powders was reduced as a function of milling time. The average particle size of milled Substrate A powders for various milling times was determined with a particle size analyzer (MASTERSIZER 2000, Malvern Instruments, Worcestershire, UK). Results are shown in Table 1, where for example, after 30 seconds of milling, 10% by volume of the particles are smaller than 2.2 μm in diameter.

Table 1

Milling time (sec)	Particle size		
	D_{10}	D_{50}	D_{90}
0	71 μm	130 μm	226 μm
30	2.5 μm	15 μm	44 μm
60	2.2 μm	10.7 μm	32 μm

[0068] Example 2

[0069] Example 2 was prepared in the same manner as Example 1, except that 4 wt % PdO (obtained from Aldrich Chemical Co., Milwaukee, WI) was used in place of the platinum black.

[0070] Example 3

[0071] Example 3 was prepared in the same manner as Example 1, except that 0.5 wt % of Pd (obtained from Aldrich Chemical Co., Milwaukee, WI) was used instead of platinum black.

[0072] Example 4

[0073] Example 4 was prepared in the same manner as Example 1, except that 4 wt % of Pd was used instead of platinum black.

[0074] Examples 1-4 and Substrate B (RGC POWDER) were tested for chloramine removal using the Chloramine Removal Test described above. The results are shown in Figure 1.

[0075] Example 5

[0076] 40 cc (13.89g) of Substrate A was dried in a convection oven at 150°C for 24 hours. The dried carbon was placed into a particle agitator apparatus in a vacuum chamber of sputtering apparatus as described in U.S. Pat. No. 7,727,931 (Brey et al.). The vacuum chamber was evacuated to less than 1 x 10^{-5} torr (1 mPa), and an argon- hydrogen mix containing 15% hydrogen and 85% argon sputtering gas was introduced to reach a pressure of about 10 millitorr (0.7 Pa). Palladium deposition was then started by applying a cathodic sputter power of 150 watts. The particle agitator shaft was rotated at about 6 rpm (revolutions per minute) during the palladium deposition process. The power was stopped after 2 hours. The chamber was backfilled with air and the palladium coated particles were removed and sieved through an 80 mesh screen. The palladium sputter target weight loss was 3.72 g. Based on the metal vapor capture efficiency of the agitator, the amount of palladium coated on the carbon particles was calculated to be approximately 1.8% by weight.

[0077] Example 5 was analyzed by inductively coupled plasma mass spectrometry and found to have 1.5% wt palladium loading.

[0078] Example 6

[0079] Example 6 was prepared similarly to Example 5, except Substrate B was used in place of Substrate A. The palladium sputter target weight loss was 3.77g. Based on the metal vapor capture efficiency of the agitator, the amount of palladium coated on the carbon particles was calculated to be approximately 2.3 % by weight.

[0080] Example 6 was analyzed by inductively coupled plasma mass spectrometry and found to have 2.2% wt palladium loading.

[0081] Examples 5-6 and Substrate B (RGC POWDER) were tested for chloramine removal using the Chloramine Removal Test described above. The results are shown in Figure 2.

[0082] Example 7

[0083] Example 7 was a commercially available catalyst, 5% wt Pt on carbon (obtained from Engelhard Co., Iselin, NJ) and was used as received.

[0084] Example 7 and Substrate B (RGC POWDER) were tested for chloramine removal using the Chloramine Removal Test described above. The results are shown in Figure 3.

[0085] Example 8

[0086] Example 8 was a commercially available catalyst, 5% wt Pd on carbon (obtained from Engelhard Co., Iselin, NJ) and was used as received.

[0087] Comparative Example A

[0088] Comparative Example A was a commercially available catalyst, 5 wt % rhodium on charcoal (Cat. No 83711, obtained from Aldrich Chemical Co., Milwaukee, WI) and was used as received.

[0089] Examples 8, Comparative Example A (Comp. Ex. A), and Substrate B (RGC POWDER) were tested for chloramine removal using the Chloramine Removal Test described above. The results are shown in Figure 4.

[0090] Example 9

[0091] Example 9 was 5 wt % Pd on graphite (obtained from Johnson Matthey Co., Westchester, PA) and was used as received.

[0092] Example 10

[0093] Example 10 was 5 wt% Pd on CaCO3 (obtained from Strem chemicals, Inc., Newburyport, MA) and was used as received.

[0094] Example 11

[0095] Example 11 was 5 wt % Pd/Al2O3 (Cat. No 205710, obtained from Aldrich Chemical Co., Milwaukee, WI) and was used as received.

[0096] Example 12

[0097] Example 12 was PtO2 (83.7 wt% Pt, obtained from Engelhard Co., Iselin, NJ) and was used as received.

[0098] Examples 9-12 and Substrate B (RGC POWDER) were tested for chloramine removal using the Chloramine Removal Test described above. The results are shown in Figure 5. Although the surface areas for Examples 9-12 were not measured, it is believed that the supports used in Examples 9-11 did not have a high surface area.

[0099] Example 13

[00100] Example 13 was 20 wt % palladium hydroxide on carbon (Pearlman's catalyst, Cat. No. 212911, obtained from Aldrich Chemical Co., Milwaukee, WI) and was used as received.

[00101] Comparative Example B

[00102] Comparative Example B was 5 wt% ruthenium on carbon (Cat. No.206180, obtained from Aldrich Chemical Co., Milwaukee, WI) and was used as received.

[00103] Comparative Example C

[00104] Comparative Example C was 5 wt % iridium on carbon (Cat. No.38330, obtained from Alfa-Aesar, Ward Hill, MA) and was used as received.

[00105] Example 13, Comparative Examples B-C (Comp. Ex. B-C), and Substrate B (RGC POWDER) were tested for chloramine removal using the Chloramine Removal Test described above. The results are shown in Figure 6.

[00106] Foreseeable modifications and alterations of this invention will be apparent to those skilled in the art without departing from the scope and spirit of this invention. This invention should not be restricted to the embodiments that are set forth in this application for illustrative purposes. To the extent that there is a conflict or discrepancy between this specification and the disclosure in any document incorporated by reference herein, this specification will control.

What is claimed is:

1. A method for removing chloramine from aqueous solutions comprising: providing an aqueous solution comprising chloramine and contacting the aqueous solution with a solid, wherein the surface of the solid comprises a metal or metal-containing compound, wherein the metal is selected from the group consisting of palladium and platinum.

2. The method of claim 1, wherein the solid comprises a support having a surface, wherein the surface comprises the metal or metal-containing compound.

3. The method of claim 2, wherein the support has a high surface area.

4. The method of any one of claims 2-3, wherein the solid comprises more than 0.1% by mass of the metal.

5. The method of any one of claims 2-4, wherein the solid comprises a carbon-based support selected from a carbon particle, a polymer containing composite block, and combinations thereof.

6. The method of any one of claims 2-5, wherein the surface of the solid comprises a metal-containing particulate, wherein the metal-containing particulate comprises a metal selected from the group consisting of palladium and platinum.

7. The method of claim 6, wherein the metal-containing particulate is mixed with a support particulate, wherein the D_{50} of the metal-containing particulate is at least 5 times smaller than the D_{50} of the support particulate.

8. The method of any one of claims 6-7, wherein the metal-containing particulate is adherent to the support.

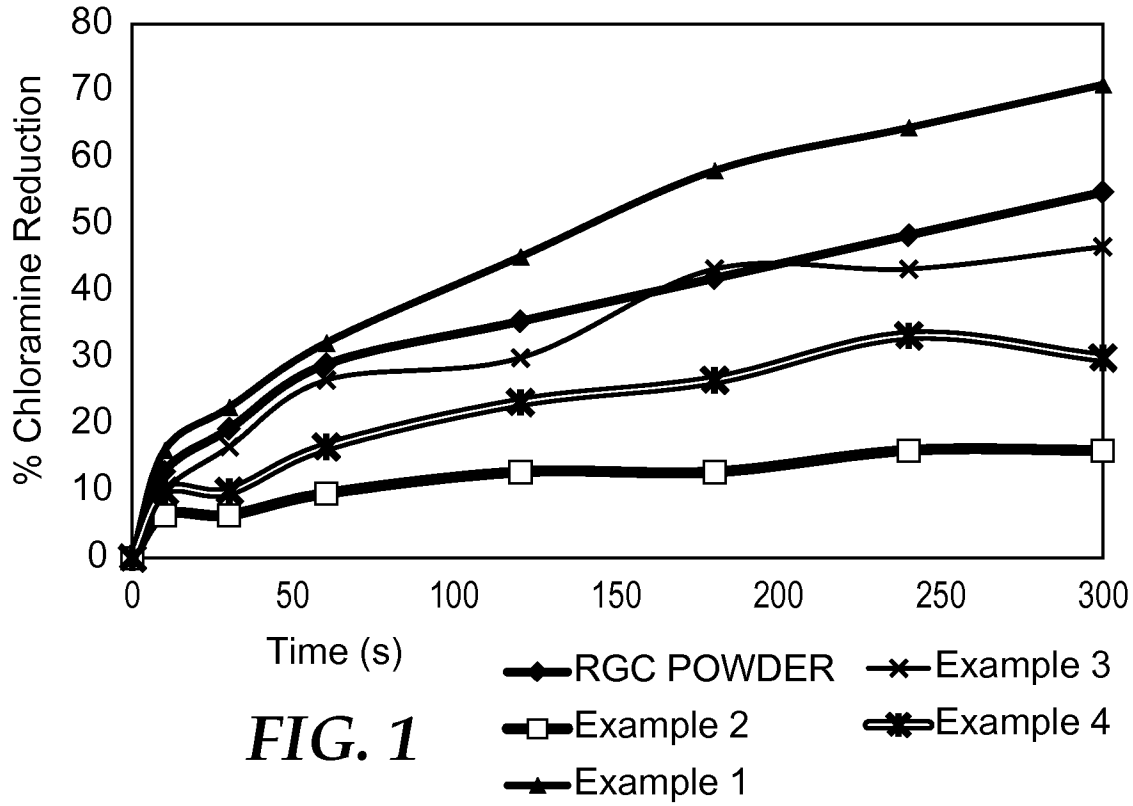
% Chloramine Reduction
0
10
20
30
40
50
60
70
80
0
50
100
150
200
250
300
Time (s)
RGC POWDER
Example 3
Example 2
Example 4
Example 1

FIG. 1

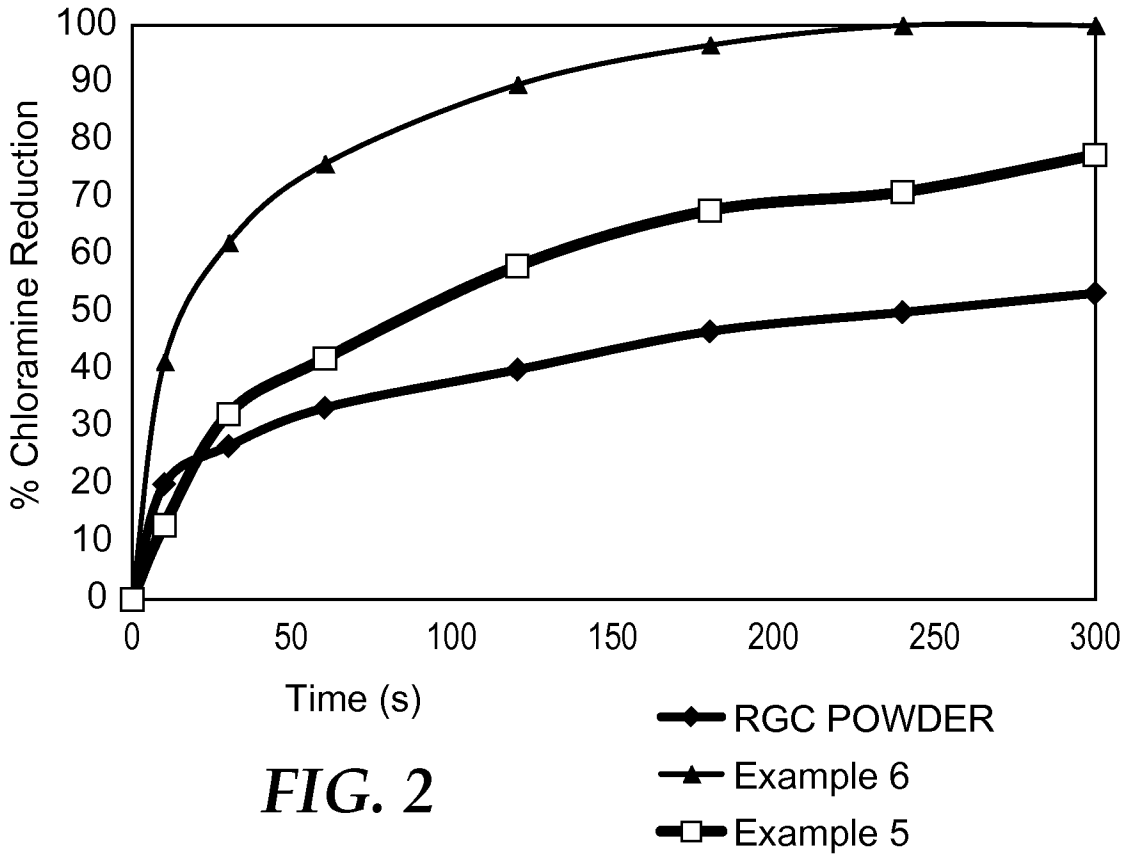
% Chloramine Reduction
0
10
20
30
40
50
60
70
80
90
100
0
50
100
150
200
250
300
Time (s)
RGC POWDER
Example 6
Example 5

FIG. 2

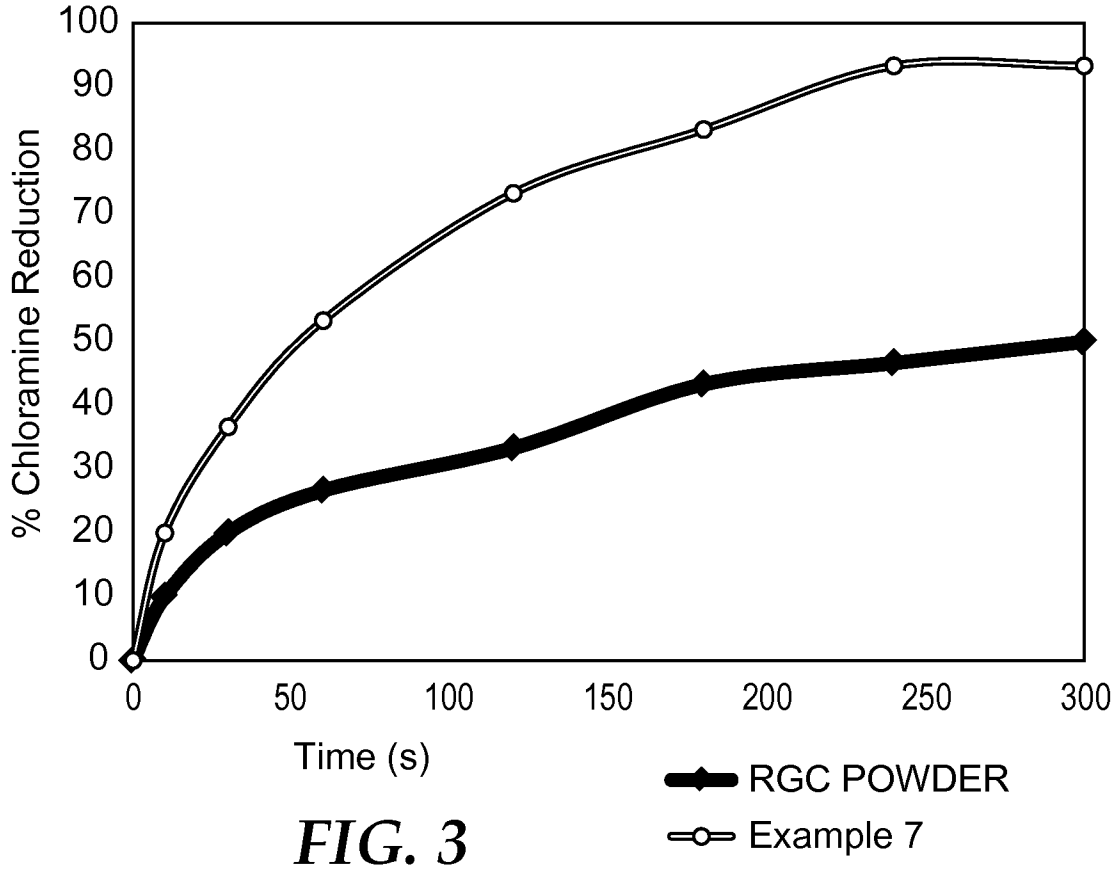
100
90
80
70
60
50
40
30
20
10
0
% Chloramine Reduction
0
50
100
150
200
250
300
Time (s)
RGC POWDER
Example 7

FIG. 3

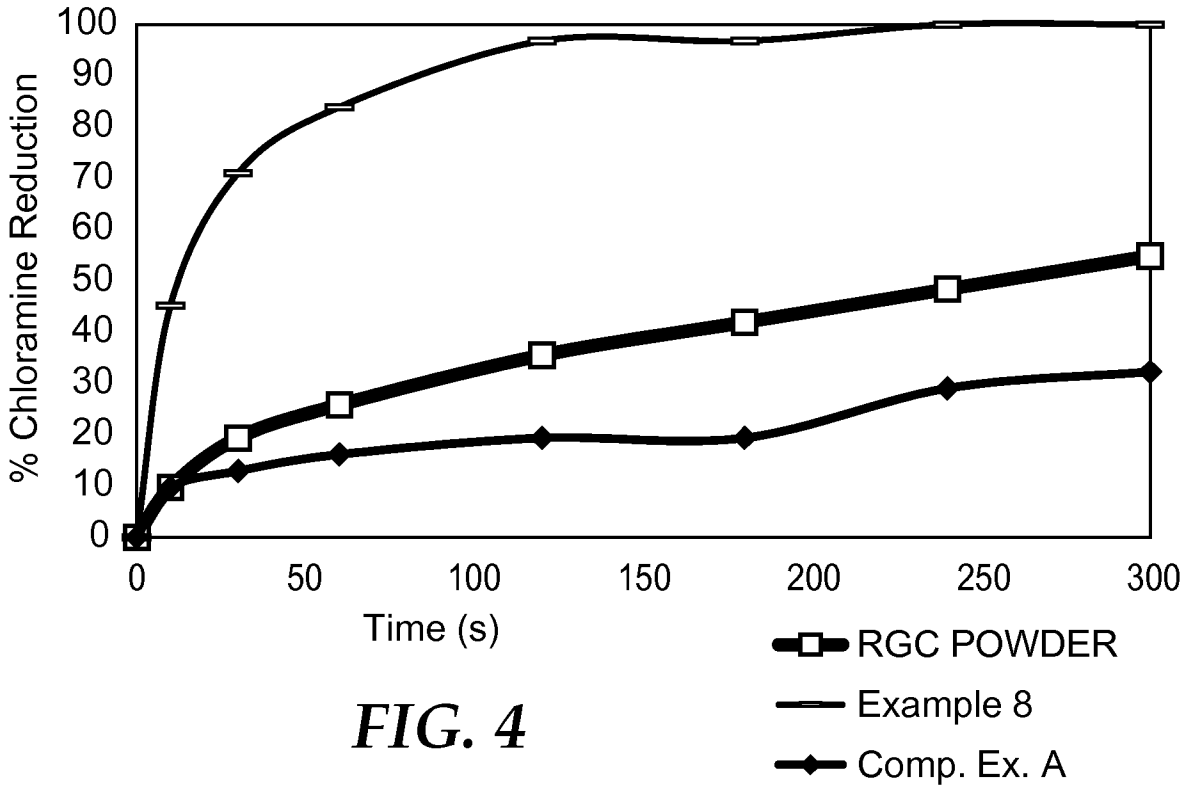
100
90
80
70
60
50
40
30
20
10
0
% Chloramine Reduction
0
50
100
150
200
250
300
Time (s)
RGC POWDER
Example 8
Comp. Ex. A

FIG. 4

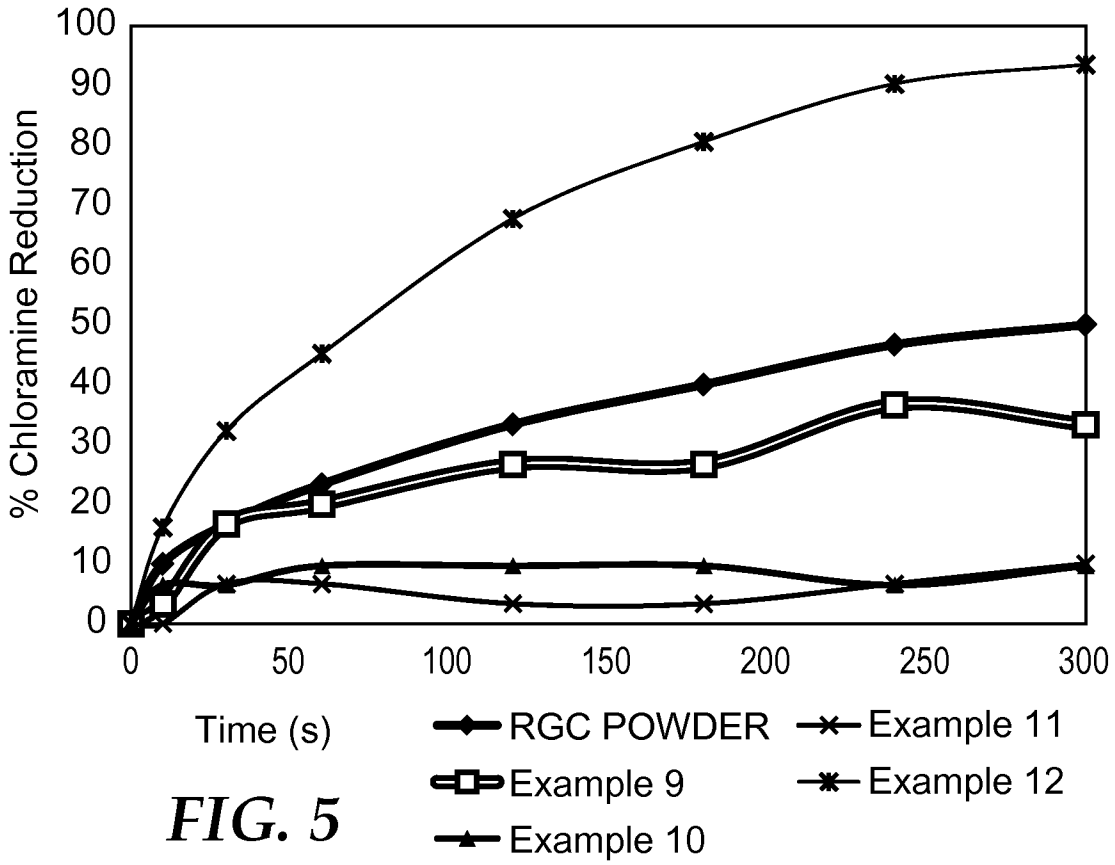
100
90
80
70
60
50
40
30
20
10
0
% Chloramine Reduction
0
50
100
150
200
250
300
Time (s)
RGC POWDER
Example 11
Example 9
Example 12
Example 10

FIG. 5

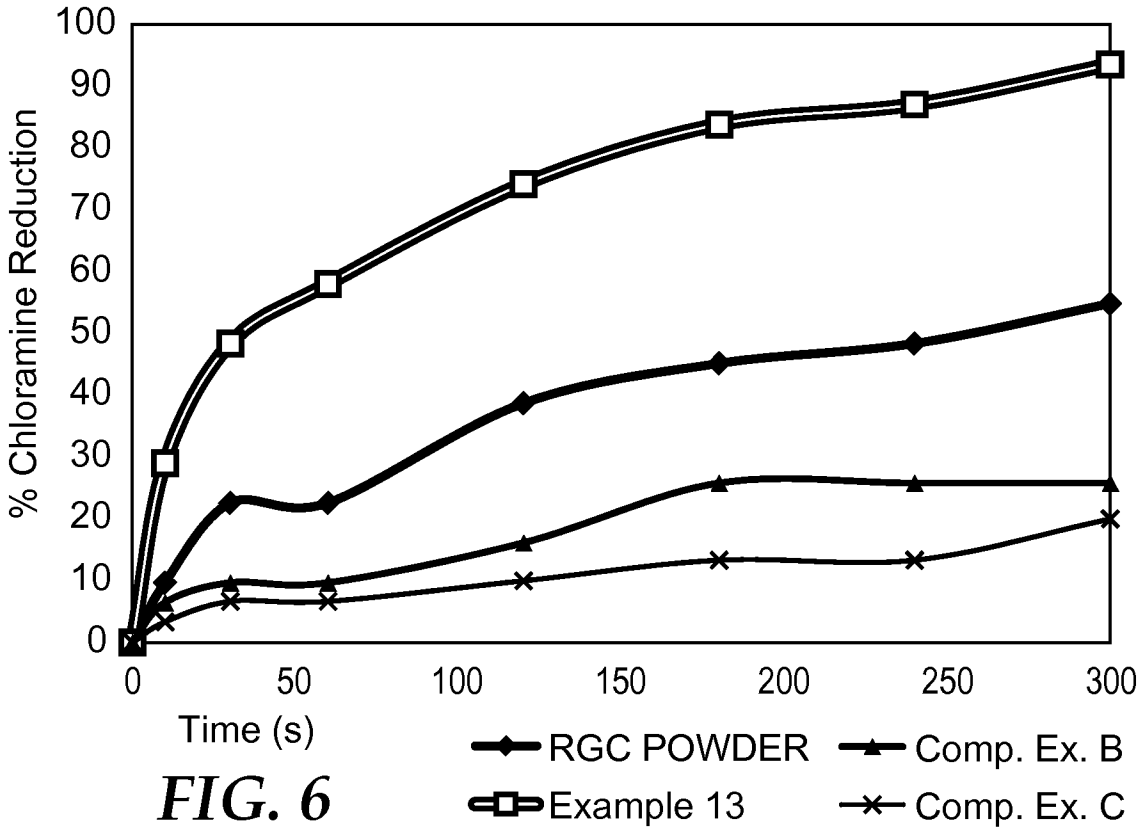
100
90
80
70
60
50
40
30
20
10
0
% Chloramine Reduction
0
50
100
150
200
250
300
Time (s)
RGC POWDER
Comp. Ex. B
Example 13
Comp. Ex. C

FIG. 6

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/044894

A. CLASSIFICATION OF SUBJECT MATTER

C02F 1/58(2006.01)i, C02F 1/28(2006.01)i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C02F 1/58; C02F 1/32; C02F 1/20; C02F 5/02; C02F 1/44; C02F 1/70; C02F 1/00; C02F 1/28

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & keywords: chloramines, palladium,platinum

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 7097773 B1 (FURLOUGH, TIFFANI et al.) 29 August 2006 See abstract, column 7, lines 19-58 and claims 16, 18.	1-4
A	US 2005-0127323 A1 (TYLER, MICHAEL et al.) 16 June 2005 See abstract, paragraphs [0013]-[0016] and claim 1.	1-4
A	US 6451209 B1 (KAAS, POVL) 17 September 2002 See abstract, column 3, lines 14-44 and claim 1.	1-4
A	US 4666610 A (KUHNS, JOHN F.) 19 May 1987 See abstract and claims 1-4.	1-4
A	US 6419837 B1 (AKSE, JAMES R.) 16 July 2002 See abstract and claims 1-4.	1-4

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

☒ See patent family annex.

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

Date of the actual completion of the international search	Date of mailing of the international search report
11 November 2013 (11.11.2013)	**12 November 2013 (12.11.2013)**

Name and mailing address of the ISA/KR
Korean Intellectual Property Office
189 Cheongsa-ro, Seo-gu, Daejeon Metropolitan City, 302-701, Republic of Korea
Facsimile No. +82-42-472-7140

Authorized officer
LEE, Dong Wook
Telephone No. +82-42-481-8163

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/044894

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 7
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
Claim 7 is unclear since it refers to claim which is not searchable due to not being drafted in accordance with the second and third sentence of Rule 6.4(a).

3. ☒ Claims Nos.: 5, 6, 8
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required addtional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2013/044894

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 7097773 B1	29/08/2006	None	
US 2005-0127323 A1	16/06/2005	US 6989109 B2	24/01/2006
US 6451209 B1	17/09/2002	AT 209611 T	15/12/2001
		AU 1869399 A	19/07/1999
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		DE 69802716 D1	10/01/2002
		DE 69802716 T2	08/05/2002
		DK1042237T3	02/04/2002
		EP 1042237 A1	11/10/2000
		EP 1042237 B1	28/11/2001
		NO 20003376 A	25/08/2000
		NO 20003376 D0	28/06/2000
		NO 320514 B1	12/12/2005
		WO 99-33752 A1	08/07/1999
US 4666610 A	19/05/1987	EP 0203741 A2	03/12/1986
		EP 0203741 B1	28/02/1990
		JP 05066198 B	21/09/1993
		JP 1850992 C	21/06/1994
		JP 61-271086 A	01/12/1986
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		EP 1117619 A1	25/07/2001
		EP 1117619 A4	05/12/2001
		WO 00-07943 A1	17/02/2000