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(54) Title: FILTRATION MEDIUM COMPRISING A METAL-CONTAINING PARTICULATE

(57) Abstract: Described herein is a liquid filtration device disclosed comprising a fluid conduit fluidly connecting a fluid inlet to a fluid outlet; and a water filtration medium disposed in the fluid conduit; the water filter medium comprising a metal-containing particulate, wherein the metal-containing particulate comprises a thermolysis product of a metal salt wherein the salt is selected from nitrogen-containing oxyanions, sulfur-containing anions, chlorides, phosphates, and combinations thereof; and methods of removing chloramines from aqueous solutions.



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FILTRATION MEDIUM COMPRISING A METAL-CONTAINING PARTICULATE**TECHNICAL FIELD**

5 [0001] A filtration medium comprising a metal-containing particulate is described, wherein the metal-containing particulate comprises a thermolysis product of a metal salt, wherein the salt is selected from nitrogen-containing oxyanions, sulfur-containing anions, chlorides, phosphates, and combinations thereof.

BACKGROUND

10 [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.

15 [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.

20 [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.

25 [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.

SUMMARY

30 [0006] 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. In some instances, there is also a desire to provide a solid block of carbon to remove chloramine. In other instances, there is a desire to have a granular material that may be used in a packed bed. In still other instances, there is a desire to provide a material that may be used in a web-form.

35 [0007] In one aspect, a liquid filtration device is disclosed comprising a fluid conduit fluidly connecting a fluid inlet to a fluid outlet; and a liquid filtration medium disposed in the fluid conduit; the liquid filter medium comprising a metal-containing particulate, wherein the metal-containing particulate comprises a

thermolysis product of a metal salt, wherein the salt is selected from nitrogen-containing oxyanions, sulfur-containing anions, chlorides, phosphates, and combinations thereof.

[0008] In another aspect, a method for removing chloramine from aqueous solutions is disclosed comprising: providing an aqueous solution comprising chloramine and contacting the aqueous solution with a composition comprising a metal-containing particulate, wherein the metal-containing particulate comprises a thermolysis product of a metal salt, wherein the salt is selected from nitrogen-containing oxyanions, sulfur-containing anions, chlorides, phosphates, and combinations thereof.

[0009] In yet another aspect, a method of removing chloramine from aqueous solutions is disclosed comprising: heating a metal salt wherein the salt is selected from nitrogen-containing oxyanions, sulfur-containing anions, chlorides, phosphates, and combinations thereof to form a thermolysis product; cooling the thermolysis product; and contacting the cooled thermolysis product with an aqueous solution comprising chloramine.

[0010] In yet another aspect, a method of making a composite carbon article is described comprising: providing a mixture comprising (a) a metal-containing particulate wherein the metal-containing particulate comprises a thermolysis product of an iron salt, wherein the salt is selected from nitrogen-containing oxyanions, sulfur-containing anions, chlorides, phosphates, and combinations thereof; and (b) a melt-processable polymer; contacting the mixture with a high-frequency magnetic field, wherein the high-frequency magnetic field oscillates in a range from about 10^3 Hz to about 10^{15} Hz.

[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.

DETAILED DESCRIPTION

[0012] As used herein, the term

"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).

[0013] 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.).

[0014] 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.).

[0015] The present disclosure is directed to a composition comprising a thermolysis product of a metal salt, wherein the salt is selected from nitrogen-containing oxyanions, sulfur-containing anions, chlorides, phosphates, and combinations thereof.

[0016] It has been found that such compositions may be useful for the removal of chloramine from aqueous solutions.

[0017] Thermolysis Product of Metal Salts

[0018] The metal salts of the present disclosure include those wherein the salt is selected from nitrogen-containing oxyanions, sulfur-containing anions, chlorides, phosphates, and combinations thereof.

Preferable metal salts include those that are water soluble and have a thermal decomposition temperature below 1000°C, however higher temperatures may be employed.

[0019] The nitrogen-containing oxyanion salt may comprise a nitrate and/or a nitrite ion.

[0020] The sulfur-containing anions including oxyanions. The sulfur-containing salts may comprise sulfates, sulfamates, sulfites, bisulfates, bisulfites, and/or thiosulfates.

[0021] A chloride salt is a salt comprising a chloride anion, and a phosphate salt is a salt comprising a phosphate ion.

[0022] The metal portion of the metal salt may include any metal, however, metals that are acceptable for presence in drinking water are preferred. Exemplary metals include: copper, iron, silver, and manganese.

[0023] Exemplary metal salts of the present disclosure include: ferric nitrate, manganous sulfate, manganese nitrate, copper sulfate, and combinations thereof.

[0024] The present disclosure is directed toward the thermolysis product of a metal salt. Thermolysis involves heating the metal salt at or above the temperature at which the metal salt begins to lose metal-bound water, if present, and at which the anionic portion of the compound begins to decompose. As used herein a "thermolysis product" refers to a product that results from the dissociation or decomposition of a compound by heat. This thermolysis process is believed to change the nature of the metal salt to a material having a different stoichiometry, composition, and/or different chemical properties, wherein at least a portion of the salt is thermally decomposed and is removed by volatilization as a gas.

[0025] In one embodiment, upon thermolysis, the oxidation state of the metal changes. For example, in one embodiment of the present disclosure, the metal in the thermolysis product comprises at least a portion of the metal with an oxidation state of, for example, Cu^0 , Cu^{+1} , or Fe^{+2} .

[0026] Although not wanting to be bound by theory, in another embodiment, the thermolysis of the metal salt is thought to produce a material having active surface sites that exhibit enhanced activity for catalyzing the decomposition of chloramines. The production of these surface sites by thermolysis of the metal salt results in materials (such as are observed by X-ray diffraction analysis of the thermolysis product) with chloramine removal properties superior to those that result from utilizing similar metal compounds produced by non-thermolysis methods, e.g., metal oxides derived from more traditional methods or finely divided metals. In the present disclosure, the metal-containing particulate comprises the thermolysis product of a metal salt, wherein the salt is selected from nitrogen-containing oxyanions, sulfur-containing anions, chlorides, phosphates, and combinations thereof.

[0027] In one embodiment, the metal salt is thermally treated to form the thermolysis product.

[0028] In another embodiment, the metal salt is thermally treated in the presence of a support, for example, carbon substrates or inorganic oxide substrates. The metal salt may be impregnated into the support prior to thermolysis. For example, a metal salt may be dissolved in a solvent and the resulting solution contacted with the support. The impregnated support then may be heated to form a thermolysis product disposed on the surface (or surface of the pores) of a support.

[0029] In another embodiment, metal salts, which are not sufficiently soluble to dissolve in the solvent (i.e., do not completely dissolve in the volume of solvent used in the experiment) may be impregnated into the support by adding the metal salt and the support to the solvent. In time, the metal salt that is dissolved in the solvent can diffuse into the support and deposit thereon, so that the metal salt is incorporated into or onto the support over time.

[0030] As used herein "metal-containing particulate" includes both the thermolysis product of the metal salt and the thermolysis product of the metal salt disposed (continuously or discontinuously) on a carbon substrate or inorganic oxide substrate, such substrates can include granular materials, powder materials, fibers, tubes, and foams.

[0031] In one embodiment, it is preferable for the metal-containing particulate product to be porous. The porous nature will enable, for example, more surface area for chloramine removal. Preferably having a high surface area (e.g., at least 100, 500, 600 or even 700 m²/g; and at most 1000, 1200, 1400, 1500, or even 1800 m²/g based on BET (Brunauer Emmet Teller method) nitrogen adsorption). Such high surface areas may be accomplished by using a highly porous carbon substrate or inorganic oxide substrate and/or by applying a physical technique applied (such as crushing or pulverizing) to decrease the particle size of the resulting product.

[0032] Carbon Substrates and Inorganic Oxide Substrates

[0033] In one embodiment, the thermolysis product is disposed on the surface of the support such as a carbon or inorganic oxide substrate. This may be advantageous because the carbon or inorganic oxide substrate can provide a support for the thermolysis product, which may penetrate into the substrate or reside at the surface of the substrate. Further the carbon or inorganic oxide substrate may also provide additional removal capabilities complementary to the chloramines removal, for example providing removal of organics, free chlorine, or metals.

[0034] The morphology of the carbon substrate 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, and nanoparticulates, such as nanotubes and nanospheres. A non-particulate is a substrate that is not composed of discernable, distinct particles. A particulate substrate is a substrate 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).

[0035] Typically, the morphology the carbon substrate will be selected based on the application. For example, particulate with a large particle size is desirable when the compositions 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 micrometers, may be preferable when used in a carbon block monolith.

[0036] Commercially available carbon substrates 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.

[0037] The size of the pores of the carbon substrate can be selected based on the application. The carbon substrate may be microporous carbon, macroporous carbon, mesoporous carbon, or a mixture thereof.

[0038] The carbon substrates can contain larger regions of crystalline, graphitic domains or they can be substantially disordered. Particularly useful are carbon substrates that are substantially disordered and have high surface areas. As used herein, substantially disordered means that the carbon substrate has in-plane domain sizes of about 1-10 nm.

[0039] In one embodiment, the carbon substrate 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.

[0040] The morphology of the inorganic oxide substrate 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.

[0041] The inorganic oxide substrate 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 oxide 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.

[0042] The size of the pores of the inorganic oxide substrate can be selected based on the application. The inorganic oxide substrate may be microporous, macroporous, mesoporous, or a mixture thereof. Particularly useful are inorganic oxide substrates that have high surface areas.

[0043] The choice of support materials is quite broad and can include without limitation 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 substrate.

[0044]

[0045] Preparation of the Thermolysis Product

5 [0046] As previously mentioned, the metal salt is thermally treated alone or in the presence of a support to form the thermolysis product.

[0047] The thermal treatment may be conducted in an air environment or in an inert environment, such as in a nitrogen or argon environment.

10 [0048] The thermolysis temperature, the temperature at which the thermolysis reaction is conducted, may be conducted at a temperature of at least 200, 250, 300, 400, or even 500°C; and at most 650, 700, 800, 900, 1000, 1200, or even 1400 °C. Generally the temperature at which thermolysis is conducted may be determined, by first analyzing the material (e.g., the metal salt or the metal salt impregnated support) to be treated by differential thermal analysis/thermal gravimetric analysis (DTA/TGA) performed under controlled conditions (atmosphere and heating rate) to determine its thermal decomposition behavior.

15 Then trials are performed by thermolyzing the material at various temperatures beginning with the onset temperature of decomposition to determine at what point and under what conditions (temperature, time and atmosphere) the most active material is formed.

[0049] In one embodiment, as the reaction temperature changes the thermolysis product of the metal salt changes and there may be a select temperature based on the metal salt and support used, if any, which

20 offers a more efficient removal of chloramine. For example, excessive heating of the metal salt can result in "over-firing" of the reaction product, and the activity of the material can diminish. In one embodiment, the presence of a carbon support during the thermolysis treatment can alter the decomposition temperature.

[0050] Although the thermolysis product should only comprise elements present in the metal salt, small

25 amounts of other elements may be present, due to impurities present in the metal salt, the support used, if any, and/or in atmosphere used during the thermal treatment. In one embodiment, the metal-containing particulate is substantially free (i.e., less than 5%, 2%, 1%, 0.1%, 0.05%, or even 0.01% of sulfur atoms based on the weight of the metal-containing particulate).

[0051] In one embodiment, the thermolysis product comprises sulfur. The addition of sulfur may be

30 advantageous in some embodiments for the removal of chloramines. In one embodiment, the metal-containing particulate comprises a sulfur atom, which is derived from the sulfur-containing anion.

[0052] In one embodiment, the metal-containing particulate comprises more than 1.2, 1.3, 1.5, 1.8, 2.0, 4.0, 6.0, 8.0 or even 10.0 mass % sulfur based on the total mass of the metal-containing particulate.

[0053] In one embodiment, the metal-containing particulate of the present disclosure comprises less than

35 0.90, 0.80, 0.70, 0.50, 0.30, 0.10, 0.05, 0.01, or even 0.005 mass % nitrogen based on the total mass of the metal-containing particulate.

[0054] In one embodiment, the metal-containing particulate of the present disclosure comprises nitrogen and less than 0.50, 0.30, 0.10, 0.05, 0.01, or even 0.005 mass % sulfur based on the total mass of the carbon substrate.

[0055] In one embodiment, the metal-containing particulate of the present disclosure is substantially free of hydrogen, comprising less than 0.40, 0.30, 0.20, 0.10, 0.05, or even 0.01 mass % hydrogen based on the total mass of the metal-containing particulate.

[0056] Use

[0057] In one embodiment of the present disclosure, the metal-containing particulate is used as a filter medium. Because of the ability of the compositions of the present disclosure to remove chloramine, the compositions of the present disclosure may be used as a filtration media. Filtration methods as known in the art can be used.

[0058] Although the metal-containing particulate may be used in an uncontained (bulk-fashion), it is preferable that the metal-containing particulate be contained in some sort of support matrix and/or vessel for ease of use.

[0059] The metal-containing particulate of the present disclosure may be used in a powdered form, a granular form, or shaped into a desired form. For example, the metal-containing particulate may be a compressed blend of a carbon substrate, the thermolysis product of the metal salt 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 metal-containing particulate of the present disclosure 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 by reference.

[0060] Because the metal-containing particulate may comprise a ferromagnetic material, in one embodiment, the metal-containing particulate may be part of a carbon support such as carbon particles, which can be heated by induction heating to form composite blocks. Typically in making a carbon block monolith, carbon particles are heated in an oven to fuse the carbon particles together. When using ferromagnetic material, a high frequency magnetic field may be used to heat the metal-containing particulate, causing the carbon support to become fused and form a carbon block monolith. In one embodiment, the magnetic field may oscillate at a frequency in a range from about 10^3 Hz to about 10^{15} Hz.

[0061] The use of induction heating to prepare a composite block, may allow more uniform heating and better heat penetration to the core of the composite carbon block and/or increase manufacturing throughput of the carbon block composites. The levels of iron salts versus other metal salts may be varied to optimized the ferromagnetic properties and the chloramine removal properties of the material.

[0062]

[0063] In one embodiment, the metal-containing particulate 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 (NH₃) 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 composition comprising a metal-containing particulate, as disclosed herein, the resulting aqueous solution comprises a reduced amount of chloramines, for example, at least a 10, 20, 25, 30, 50, 70, 80, 90, 95, or even 100 % chloramine reduction as measured by the Chloramine Removal Test, at 180 seconds described in the Example Section below. Note that as the particle size decreases, in general, the amount of removal of chloramine will increase due to the increase in surface area. For example, the percent removal of chloramines is at least 50, 70, 90, or even 99% reduction in 180 seconds with a median particle size of about 50 micrometers.

[0064] Previous publications, such as Vikesland, et al. in Environmental Science and Technologies, 200, 34, 83-90 have shown that the water soluble forms of the ferrous ion are responsible for the removal of chloramines in their materials. Unlike the prior art, in one embodiment of the present disclosure, the metal responsible for the chloramine removal activity in the metal-containing particulate has limited solubility in water (in other words, a solubility producing metal ion concentrations of less than 20 ppm, 10 ppm, 5 ppm, 2 ppm, 1 ppm, 0.5 ppm, or even 0.1 ppm). When the metal-containing particulate is washed with water, little to no metal is present in the wash water and the washed metal-containing particulate retains its activity for chloramine removal. In one embodiment, when the thermolysis product of a metal carboxylate is washed, it does not lose more than 5, 10, 15, 20, 30, 40, 50, or even 60% of its original activity for the removal of chloramines. Having an insoluble or limited solubility thermolysis product may be advantageous, because the metal would be immobilized, preventing leaching into the treated water, enable the metal-containing particulate to be conditioned prior to use, and/or generate longer lifetimes of the filtration media.

[0065] A non-limiting list of exemplary embodiments and combinations of exemplary embodiments of the present disclosure are disclosed below.

[0066] Embodiment 1. A liquid filtration device comprising a fluid conduit fluidly connecting a fluid inlet to a fluid outlet; and a liquid filtration medium disposed in the fluid conduit; the liquid filter medium comprising a metal-containing particulate, wherein the metal-containing particulate comprises a thermolysis product of a metal salt, wherein the salt is selected from nitrogen-containing oxyanions, sulfur-containing anions, chlorides, phosphates, and combinations thereof.

[0067] Embodiment 2. The liquid filtration device of embodiment 1, wherein the nitrogen-containing oxyanions comprise a nitrate, a nitrite, and combinations thereof.

[0068] Embodiment 3. The liquid filtration device of embodiment 1, wherein the sulfur-containing anions comprise a sulfate, sulfamate, sulfite, bisulfate, bisulfite, thiosulfate, and combinations thereof.

[0069] Embodiment 4. The liquid filtration device of any one of the previous embodiments, wherein the metal-containing particulate is substantially free of sulfur atoms.

[0070] Embodiment 5. The liquid filtration device of embodiments 1 or 3, wherein the metal-containing particulate comprises a sulfur atom and the sulfur atom is derived from the sulfur-containing anion.

5 [0071] Embodiment 6. The liquid filtration device of any one of the previous embodiments, wherein the metal of the metal salt is copper, iron, manganese, silver, and combinations thereof.

[0072] Embodiment 7. The liquid filtration device of any one of the previous embodiments, wherein water filtration medium comprises a support.

10 [0073] Embodiment 8. The liquid filtration device of embodiment 7, wherein the thermolysis product is disposed on the surface of the support.

[0074] Embodiment 9. The liquid filtration device of any one of embodiments 7 to 8, wherein the support is selected from a carbonaceous solid, an inorganic oxide particle, or a fibrous particle.

[0075] Embodiment 10. The liquid filtration device of anyone of embodiments 8 or 9, wherein the support is an activated carbon.

15 [0076] Embodiment 11. The liquid filtration device of any one of the previous embodiments, wherein the thermolysis product of a metal salt is immobilized in the fluid conduit.

[0077] Embodiment 12. The liquid filtration device of any one of the previous embodiments, wherein the metal-containing particulate is porous.

20 [0078] Embodiment 13. The liquid filtration device of any one of the previous embodiments, wherein the metal-containing particulate comprises less than 0.90, mass % nitrogen based on the total mass of the metal-containing particulate.

[0079] Embodiment 14. The liquid filtration device of any one of the previous embodiments, wherein the metal-containing particulate comprises greater than 2.0 mass % sulfur based on the total mass of the metal-containing particulate.

25 [0080] Embodiment 15. A method for removing chloramine from aqueous solutions comprising: providing an aqueous solution comprising chloramine and contacting the aqueous solution with a composition comprising a metal-containing particulate, wherein the metal-containing particulate comprises a thermolysis product of a metal salt, wherein the salt is selected from nitrogen-containing oxyanions, sulfur-containing anions, chlorides, phosphates, and combinations thereof.

30 [0081] Embodiment 16. The method of embodiment 15, wherein the nitrogen-containing oxyanions comprise a nitrate, a nitrite, and combinations thereof.

[0082] Embodiment 17. The method of embodiment 15, wherein the sulfur-containing anions comprises a sulfate, sulfamate, sulfite, bisulfate, bisulfite, thiosulfate, and combinations thereof.

35 [0083] Embodiment 18. The method of any one of embodiments 15 or 16, wherein the metal-containing particulate is substantially free of sulfur atoms.

[0084] Embodiment 19. The method of any one of embodiments 15 or 17, wherein the metal-containing particulate comprises a sulfur atom and the sulfur atom is derived from the sulfur-containing anion.

[0085] Embodiment 20. The method of any one of embodiments 15 to 19, wherein the metal of the metal salt is copper, iron, manganese, silver, and combinations thereof.

5 [0086] Embodiment 21. The method of any one of embodiments 15 to 20, wherein after contacting the aqueous solution with a composition comprising a metal-containing particulate, the resulting aqueous solution comprises a reduced amount of chloramine.

[0087] Embodiment 22. The method of any one of embodiments 15 to 21, wherein the metal-containing particulate comprises less than 0.90, mass % nitrogen based on the total mass of the metal-containing
10 particulate.

[0088] Embodiment 23. The method of any one of embodiments 15 to 22, wherein the metal-containing particulate comprises greater than 2.0 mass % sulfur based on the total mass of the metal-containing particulate.

[0089] Embodiment 24. A method for removing chloramine from aqueous solutions comprising:
15 heating a metal salt wherein the salt is selected from nitrogen-containing oxyanions, sulfur-containing anions, chlorides, phosphates, and combinations thereof to form a thermolysis product;
cooling the thermolysis product; and
contacting the cooled thermolysis product with an aqueous solution comprising chloramine.

20 [0090] Embodiment 25. The method of embodiment 24, wherein the heating is conducted at a temperature of at least 200°C.

[0091] Embodiment 26. The method of any one of embodiments 24 to 25, wherein at least a portion of the metal salt is disposed on a support during the heating step.

[0092] Embodiment 27. The method of any one of embodiments 24 to 26, wherein the heating is
25 conducted in an inert atmosphere.

[0093] Embodiment 28. The method of any one of embodiments 24 to 27, wherein the thermolysis product comprises less than 0.90, mass % nitrogen based on the total mass of the thermolysis product.

[0094] Embodiment 29. The method of any one of embodiments 24 to 28, wherein the thermolysis product comprises greater than 2.0 mass % sulfur based on the total mass of the thermolysis product.

30 [0095] Embodiment 30. A carbon block comprising: (a) a carbon support, (b) a metal-containing particulate, wherein the metal-containing particulate comprises a thermolysis product of a metal salt, wherein the salt is selected from nitrogen-containing oxyanions, sulfur-containing anions, chlorides, phosphates, and combinations thereof, and (c) a binder.

[0096] Embodiment 31. The carbon block of embodiment 30, wherein the binder is selected from
35 polyethylene.

[0097] Embodiment 32. A method of making a composite carbon article comprising:

providing a mixture comprising (a) a metal-containing particulate wherein the metal-containing particulate comprises a thermolysis product of a metal salt, wherein the salt is selected from nitrogen-containing oxyanions, sulfur-containing anions, chlorides, phosphates, and combinations thereof; and (b) a melt-processable polymer;

contacting the mixture with a high-frequency magnetic field, wherein the high-frequency magnetic field oscillates in a range from about 10^3 Hz to about 10^{15} Hz.

[0098] Embodiment 33. The method of embodiment 32, wherein the melt-processable polymer is an ultra high molecular weight polyethylene.

EXAMPLES

[0099] 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.

[00100] 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.

[00101] These abbreviations are used in the following examples: cc = cubic centimeters, g = gram, hr = hour, in = inch, kg = kilograms, min = minutes, mol = mole; M = molar, cm = centimeter, mm = millimeter, ml = milliliter, L = liter, N = normal, psi = pressure per square inch, MPa = megaPascals, and wt = weight.

[00102] Testing Methods

[00103] Apparent Density Determination

[00104] The apparent density of a sample (prepared according to Comparative Examples or the Examples according to the disclosure) was determined by tapping a weighed sample in a graduated cylinder until closest packing was achieved. The closest packing was deemed to occur when tapping did not produce a further decrease in volume of the carbon substrate sample.

[00105] Chloramine Test

[00106] 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.

[00107] Chloramine Preparation

[00108] 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").

[00109] Chloramine Removal Test

[00110] An aqueous chloramine test solution was prepared comprising 3 ppm +/- 0.3 ppm NH_2Cl (prepared as described above) at a pH about 7.6 at about 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 1.5 cc 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. Aliquots were measured by mass knowing the apparent density. 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:

$$\left(1 - \frac{[\text{NH}_2\text{Cl}]_{\text{filtered aliquot}}}{[\text{NH}_2\text{Cl}]_{\text{initial}}} \right) \times 100$$

Materials

Material	Description
Carbon Substrate A	Activated carbon powder obtained from MeadWestvaco Specialty Chemicals, North Charleston, SC, under the trade designation "AQUAGUARD Powder". This carbon is sold specifically for chloramine reduction.
Carbon Substrate B (RGC)	Wood-based activated carbon powder MeadWestvaco Specialty Chemicals, North Charleston, SC, under the trade designation "RGC Powder".
Carbon Substrate C	Coconut-shell-based activated carbon powder, obtained from Kuraray Chemical, Osaka Japan under the trade designation "PGWH-100MD".
Carbon Substrate D	Wood-based activated carbon powder MeadWestvaco Specialty Chemicals, North Charleston, SC, under the trade designation "RGC 80 x 325 mesh".
$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	Ferric Nitrate 9-Hydrate Crystal, ACS Reagent grade, obtained from J.T. Baker, a division of Covidien, Phillipsburg, NJ.
$\text{MnSO}_4 \cdot \text{H}_2\text{O}$	Manganous Sulfate Monohydrate Powder, ACS Reagent grade obtained from J.T. Baker.
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	Copper Sulfate Pentahydrate, Purified Grade, obtained from VWR International LLC, Tadnor, PA.
$\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$	Cupric Nitrate, 2.5-Hydrate, J-T Baker, Mallinckrodt Baker, Inc, Phillipsburg, NJ

[00111] Comparative Examples A-C

[00112] Carbon Substrates A, B, and C were tested, without further treatment, using the Chlroamine Removal Test. The results are shown in Table 1.

[00113] Example 1

[00114] $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (6.75 g) was added to deionized water (35 g) with vigorous stirring. The aqueous manganese sulfate solution was added to 17.5 g of Carbon Substrate B with stirring. The impregnated carbon was placed in a crucible (with lid) and was then heated in a nitrogen-purged muffle furnace at 875 °C for 15 minutes. The crucible was then removed to cool under a nitrogen purge. The impregnation resulted in approximately 12.5%wt manganese (as Mn) on the carbon. The sample was then tested using the Chlroamine Removal Test. The result is shown in Table 1.

[00115] Example 2

[00116] An impregnated carbon sample was prepared by the method of Example 1, but using a lower amount of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, such that the impregnation resulted in approximately 6.3 wt% manganese (as Mn) on the carbon. The sample was then tested using the Chlroamine Removal Test. The result is shown in Table 1.

[00117] Example 3

[00118] An impregnated carbon sample were prepared by the method of Example 1, but using a larger amount of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, such that the impregnation resulted in approximately 18.9 wt% manganese (as Mn) on the carbon. The sample was then tested using the Chlroamine Removal Test. The result is shown in Table 1.

[00119] Example 4

[00120] Following the same procedure outlined in Example 1, an aqueous manganese sulfate solution was added to Carbon Substrate C such that the impregnation resulted in approximately 19 wt% manganese (as Mn) on the carbon. The sample was then tested using the Chlroamine Removal Test. The result is shown in Table 1.

[00121] Example 5

[00122] Copper sulfate pentahydrate (5 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) was dissolved in 15 g water. The solution was added to the Carbon Substrate B (8.5 gram) with stirring such that the impregnation resulted in approximately 12.5% copper (as Cu) on the carbon. The impregnated carbon was placed in a crucible (with lid) and was then heated in a nitrogen-purged muffle furnace at 800 °C for 15 minutes. The crucible was then removed to cool under a nitrogen purge. The sample was then tested using the Chlroamine Removal Test. The result is shown in Table 1.

Table 1

Example	Carbon Substrate	% by wt metal impregnate	% Chloramine Reduction	
			At 150 sec	At 180 sec
Comp. Example A	A	0	83	89
Comp. Example B	B	0	39	42
Example 1	B	12.5 (Mn)	78	87
Example 2	B	6.3 (Mn)	69	72
Example 3	B	18.9 (Mn)	98	99
Example 5	B	15 (Cu)	96	98
Example 6	B	20 (Fe)	76	80
Comp. Example C	C	0	41	52
Example 4	C	19 (Mn)	74	79

[00123] Example 6

[00124] Iron nitrate (14.5 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) was dissolved in 20 g water. Half of the solution was added to the Carbon Substrate B (8 gram). The impregnated carbon substrate was then dried at 100 °C. The remainder of the iron salt solution was added to the impregnated carbon resulting in approximately 20% iron on the carbon. The impregnated carbon was then heated at 900 °C in N_2 for 15 minutes (in closed crucibles in a nitrogen purged muffle furnace). The sample was then tested using the Chloramine Removal Test. The result is shown in Table 1 above.

[00125] Example 6 was tested for ferromagnetism. A small bar magnet was held above Example 6. When the magnet was about 0.25 inches (0.6 centimeters) from the sample, the carbon particles comprising the thermolysis product of the iron nitrate were attracted to the magnet.

[00126] Example 6

[00127] 0.374 g $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ was dissolved in 8 mL of deionized water. The solution was added to Carbon Substrate B (5.0 g). The sample was dried in an oven at 90° C and subsequently heated to 300° C in a tube furnace purged with N_2 . The sample was cooled in N_2 to room temperature prior to removing from the furnace.

[00128] Example 7

[00129] The same process and disclosed in Example 6 was used except that 0.960 g of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ was used.

[00130] Example 8

[00131] The same process and disclosed in Example 6 was used except that 2.03 g of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ was used.

[00132] Example 9

[00133] The same process and disclosed in Example 6 was used except that 3.23 g of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ was used.

[00134] Example 10

[00135] The same process and disclosed in Example 6 was used except that Carbon Substrate **D** was used in place of Carbon Substrate **B**.

[00136] Example 11

[00137] The same process and disclosed in Example 7 was used except that Carbon Substrate **D** was used in place of Carbon Substrate **B**.

[00138] Example 12

[00139] The same process and disclosed in Example 8 was used except that Carbon Substrate **D** was used in place of Carbon Substrate **B**.

[00140] Example 13

[00141] The same process and disclosed in Example 9 was used except that Carbon Substrate **D** was used in place of Carbon Substrate **B**.

[00142]

[00143] Examples 6-13 and Carbon Substrate D (comparative Example D) were then tested using the Chlroamine Removal Test. The results are shown in Table 2.

Table 2

Example	Carbon Substrate	% by wt copper impregnate	% Chloramine Reduction	
			At 120 s	At 180 s
6	B	2	65	74
7	B	5	81	84
8	B	10	84	90
9	B	15	81	87
10	D	2	45	55
11	D	5	45	58
12	D	10	42	55
13	D	15	42	52
Comp. Example D	D	0	7	7

[00144] 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 liquid filtration device comprising a fluid conduit fluidly connecting a fluid inlet to a fluid outlet; and a liquid filtration medium disposed in the fluid conduit; the liquid filter medium comprising a metal-containing particulate, wherein the metal-containing particulate comprises a thermolysis product of a metal salt, wherein the salt is selected from nitrogen-containing oxyanions, sulfur-containing anions, chlorides, phosphates, and combinations thereof.

2. The liquid filtration device of claim 1, wherein the nitrogen-containing oxyanions comprise a nitrate, a nitrite, and combinations thereof.

3. The liquid filtration device of claim 1, wherein the sulfur-containing anions comprise a sulfate, sulfamate, sulfite, bisulfate, bisulfite, thiosulfate, and combinations thereof.

4. The liquid filtration device of any one of the previous claims, wherein the metal-containing particulate is substantially free of sulfur atoms.

5. The liquid filtration device of claims 1 or 3, wherein the metal-containing particulate comprises a sulfur atom and the sulfur atom is derived from the sulfur-containing anion.

6. The liquid filtration device of any one of the previous claims, wherein the metal of the metal salt is copper, iron, manganese, silver, and combinations thereof.

7. A method for removing chloramine from aqueous solutions comprising: providing an aqueous solution comprising chloramine and contacting the aqueous solution with a composition comprising a metal-containing particulate, wherein the metal-containing particulate comprises a thermolysis product of a metal salt, wherein the salt is selected from nitrogen-containing oxyanions, sulfur-containing anions, chlorides, phosphates, and combinations thereof.

8. A method for removing chloramine from aqueous solutions comprising:

heating a metal salt wherein the salt is selected from nitrogen-containing oxyanions, sulfur-containing anions, chlorides, phosphates, and combinations thereof to form a thermolysis product;

cooling the thermolysis product; and

contacting the cooled thermolysis product with an aqueous solution comprising chloramine.

9. A carbon block comprising: (a) a carbon support, (b) a metal-containing particulate, wherein the metal-containing particulate comprises a thermolysis product of a metal salt, wherein the salt is selected from nitrogen-containing oxyanions, sulfur-containing anions, chlorides, phosphates, and combinations thereof, and (c) a binder.

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10. A method of making a composite carbon article comprising:

providing a mixture comprising (a) a metal-containing particulate wherein the metal-containing particulate comprises a thermolysis product of a metal salt, wherein the salt is selected from nitrogen-containing oxyanions, sulfur-containing anions, chlorides, phosphates, and combinations thereof; and (b)

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a melt-processable polymer;

contacting the mixture with a high-frequency magnetic field, wherein the high-frequency magnetic field oscillates in a range from about 10^3 Hz to about 10^{15} Hz.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2012/069414**A. CLASSIFICATION OF SUBJECT MATTER****BOW 39/14(2006.01)i, C02F 1/58(2006.01)I, C02F 1/28(2006.01)I, BOW 15/00(2006.01)I, BOW 35/00(2006.01)I**

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B01D 39/14; B01J 21/18; C02F 1/28; C01B 31/02; C02F 1/58; B01D 39/02; C01B 31/10

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 modelsElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & keywords: medium, metal salt, thermolsys, chloramine, filtration**c. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2005-0011827 A1 (KOSLOW, EVAN E.) 20 January 2005	1-6
Y	See abstract, paragraphs [0034], [0041] and claims 1, 7, 15, 53, 57, 72-74.	7-10
Y	US 6699393 B2 (BAKER, FREDERICK STANLEY et al.) 2 March 2004 See example 1 and claim 1.	7-8
Y	US 7361280 B2 (BAKER, FREDERICK STANLEY) 22 April 2008 See example 7 and claims 1, 13.	9-10
A	US 4624937 A (CHOU, SHINE K.) 25 November 1986 See abstract and claim 1.	1-10
A	US 6342129 B1 (VAUGHN, ROBERT H. et al.) 29 January 2002 See abstract and claims 1, 4.	1-10

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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Date of the actual completion of the international search

20 MARCH 2013 (20.03.2013)

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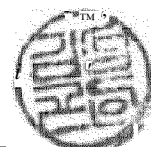


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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2012/069414

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2005-001 1827 A 1	20.01.2005	AU 2000-36034 A 1	14.09.2000
		AU 2003-202859 A 1	02.09.2003
		AU 2003-202859 B2	31.01.2008
		AU 2003-202860 A 1	02.09.2003
		AU 2003-202860 B2	23.08.2007
		AU 2003-209 149 A 1	02.09.2003
		AU 2003-209 149 B2	14.02.2008
		AU 2003-210565 A 1	02.09.2003
		AU 2003-210565 B2	13.03.2008
		AU 2003-293205 A 1	23.06.2004
		AU 2003-293205 A8	23.06.2004
		AU 2004-230869 A 1	28.10.2004
		AU 2004-230869 B2	31.05.2007
		CA 2444808 A 1	07.08.2003
		CA 2474854 A 1	07.08.2003
		CA 2474858 A 1	07.08.2003
		CA 2474980 A 1	07.08.2003
		CA 2522052 A 1	28.10.2004
		CA 2528435 A 1	03.02.2005
		CA 2752109 A 1	28.10.2004
		CA 2770444 A 1	03.02.2005
		CN 1232333 CO	21.12.2005
		CN 1278757 CO	11.10.2006
		CN 1280001 CO	18.10.2006
		CN 1625428 A	08.06.2005
		CN 1625428 CO	11.10.2006
		CN 1625429 A	08.06.2005
		CN 1625429 CO	18.10.2006
		CN 1625434 A	08.06.2005
		CN 1625434 CO	18.10.2006
		CN 1795148 A	28.06.2006
		CN 1795148 CO	13.08.2008
		CN 1891325 A	10.01.2007
		CN 1891325 CO	08.10.2008
		EP 1159624 A 1	05.12.2001
		EP 1159624 B 1	02.01.2004
		EP 1470083 A 1	27.10.2004
		EP 1470083 B 1	26.03.2008
		EP 1483028 A2	08.12.2004
		EP 1483028 B 1	19.03.2008
		EP 1483034 A 1	08.12.2004
		EP 1483034 B 1	28.07.2010
		EP 1483039 A 1	08.12.2004
		EP 1483039 B 1	23.04.2008
		EP 1578693 A2	28.09.2005
		EP 1578693 B 1	08.08.2012
		EP 1628922 A 1	01.03.2006
		EP 1646438 A 1	19.04.2006
		EP 1646438 A4	08.10.2008

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2012/069414

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		EP 1694905 A2	30.08.2006
		EP 1703955 A2	27.09.2006
		JP 2002-538435 A	12.11.2002
		JP 2005-515879 A	02.06.2005
		JP 2005-515880 A	02.06.2005
		JP 2005-515892 A	02.06.2005
		JP 2005-527344 A	15.09.2005
		JP 2007-178440 A	12.07.2007
		JP 2007-524500 A	30.08.2007
		JP 2008-2296 19 A	02.10.2008
		JP 2010-279945 A	16.12.2010
		JP 2010-284649 A	24.12.2010
		JP 4726415 B2	20.07.2011
		KR 10-0757577 B1	10.09.2007
		KR 10-0757578 B1	10.09.2007
		KR 10-079350 1 B1	14.01.2008
		KR 10-086328 1 B1	15.10.2008
		KR 10-0917075 B1	15.09.2009
		KR 10-0982596 B1	15.09.2010
		TW 284055 B	21.07.2007
		TW 514733 B	21.12.2002
		us 2001-0035800 A1	01.11.2001
		us 2003-00673 16 A1	10.04.2003
		us 2003-0140785 A1	31.07.2003
		us 2003-014126 1 A1	31.07.2003
		us 2003-016840 1 A1	11.09.2003
		us 2003-0177909 A1	25.09.2003
		us 2003-0196963 A1	23.10.2003
		us 2003-0196964 A1	23.10.2003
		us 2003-0200868 A1	30.10.2003
		us 2003-020 123 1 A1	30.10.2003
		us 2003-0205529 A1	06.11.2003
		us 2003-0205530 A1	06.11.2003
		us 2003-020553 1 A1	06.11.2003
		us 2003-02 13750 A1	20.11.2003
		us 2004-003 1749 A1	19.02.2004
		us 2004-0084378 A1	06.05.2004
		us 2004-0140822 A1	22.07.2004
		us 2004-0178 142 A1	16.09.2004
		us 2005-005 1487 A1	10.03.2005
		us 2007-0298064 A1	27.12.2007
		us 2010-0044289 A1	25.02.2010
		us 201 1-01 155 12 A1	19.05.2011
		us 6218910 B1	17.04.2001
		us 6501343 B2	31.12.2002
		us 6630016 B2	07.10.2003
		us 6660172 B2	09.12.2003
		us 6686754 B2	03.02.2004
		us 683531 1 B2	28.12.2004
		us 6866704 B2	15.03.2005

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2012/069414

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		US 687231 1 B2	29. 03.2005
		US 6913154 B2	05. 07.2005
		US 6917210 B2	12. 07.2005
		us 6953604 B2	11. 10.2005
		us 6959820 B2	01. 11.2005
		us 6998058 B2	14. 02.2006
		us 7008537 B2	07. 03.2006
		us 701 1753 B2	14. 03.2006
		us 7144533 B2	05. 12.2006
		us 7241388 B2	10. 07.2007
		us 7276166 B2	02. 10.2007
		us 7287650 B2	30. 10.2007
		us 7296691 B2	20. 11.2007
		us 76551 12 B2	02. 02.2010
		us 8056733 B2	15. 11.2011
		Wo 00-50905 A1	31. 08.2000
		Wo 03-063996 A2	07. 08.2003
		wo 03-064006 A1	07. 08.2003
		wo 03-0640 13 A1	07. 08.2003
		wo 03-064330 A1	07. 08.2003
		wo 2004-050205 A2	17. 06.2004
		wo 2004-050205 A3	17. 06.2004
		wo 2004-092076 A1	28. 10.2004
		wo 2005-009589 A1	03. 02.2005
		wo 2005-018769 A2	03. 03.2005
		wo 2005-018769 A3	03. 03.2005
		wo 2005-035866 A2	21. 04.2005
		wo 2005-035866 A3	21. 04.2005
US 6699393 B2	02. 03.2004	AU 2003-225306 A1	11. 11.2003
		AU 2003-225306 A8	11. 11.2003
		CA 2485103 A1	20. 11.2003
		CA 2485103 C	14. 07.2009
		CN 1288094 CO	06. 12.2006
		EP 1503959 A1	09. 02.2005
		EP 1503959 B1	23. 08.2006
		JP 2005-52523 1 A	25. 08.2005
		US 2003-0209497 A1	13. 11.2003
		us 2003-0209498 A1	13. 11.2003
		us 2004-0124152 A1	01. 07.2004
		us 2005-0167367 A1	04. 08.2005
		us 6706194 B2	16. 03.2004
		us 7361280 B2	22. 04.2008
		wo 03-095368 A1	20. 11.2003
US 7361280 B2	22. 04.2008	AU 2003-225306 A1	11. 11.2003
		AU 2003-225306 A8	11. 11.2003
		CA 2485103 A1	20. 11.2003
		CA 2485103 C	14. 07.2009
		CN 1288094 CO	06. 12.2006

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2012/069414

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		EP 1503959 A1	09. 02. 2005
		EP 1503959 B1	23. 08. 2006
		JP 2005-52523 1 A	25. 08. 2005
		US 2003-0209497 A1	13. 11. 2003
		US 2003-0209498 A1	13. 11. 2003
		US 2004-0124152 A1	01. 07. 2004
		US 2005-0167367 A1	04. 08. 2005
		US 6699393 B2	02. 03. 2004
		US 6706194 B2	16. 03. 2004
		Wo 03-095368 A1	20. 11. 2003
US 4624937 A	25. 11. 1986	EP 0162035 A2	21. 11. 1985
		EP 0162035 B1	20. 12. 1989
		JP 1680242 C	13. 07. 1992
		JP 60-246328 A	06. 12. 1985
		KR 10-1987-000 1854 B1	17. 10. 1987
		KR 10-1989-000 1298 B1	29. 04. 1989
		US 4696772 A	29. 09. 1987
US 6342129 B1	29. 01. 2002	AT 275436 T	15. 09. 2004
		AU 2000-60789 A1	05. 02. 2001
		DE 69920005 D1	14. 10. 2004
		DE 69920005 T2	15. 09. 2005
		EP 1079925 A1	07. 03. 2001
		EP 1079925 B1	08. 09. 2004
		EP 1200342 A1	02. 05. 2002
		EP 1200342 B1	26. 05. 2004
		ES 2228041 T3	01. 04. 2005
		US 6534442 B1	18. 03. 2003
		Wo 01-05704 A1	25. 01. 2001
		wo 99-58240 A1	18. 11. 1999