(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
13 October 2005 (13.10.2005)

PCT

(10) International Publication Number
WO 2005/095285 A1

(51) International Patent Classification[7]: C02F 1/50, 1/28

(21) International Application Number:
PCT/US2005/009812

(22) International Filing Date: 23 March 2005 (23.03.2005)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/555,766 24 March 2004 (24.03.2004) US

(71) Applicant *(for all designated States except US)*: **CUNO INCORPORATED** [US/US]; 400 Research Parkway, Meriden, CT 06450 (US).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **YEH, Eshan, B.** [US/US]; 7 Larchwood West, Unionville, CT 06085 (US). **GOVERNAL, Robert, A.** [US/US]; 8332 Town Brooke, Middletown, CT 06457 (US). **HAMLIN, Thomas, J.** [US/US]; 37 Eliot Drive, Vernon, CT 06066 (US). **PATEL, Hemang** [IN/US]; 144 Knollwood Drive, Wallingford, CT 06492 (US). **BUCHOLZ, Marjorie** [US/US]; 15 Sylvester Street, Meriden, CT 06450 (US).

(74) Agents: **PAYNE, R., Thomas** et al.; Cuno Incorporated, 400 Research Parkway, P.O. Box 1018, Meriden, CT 06450-1018 (US).

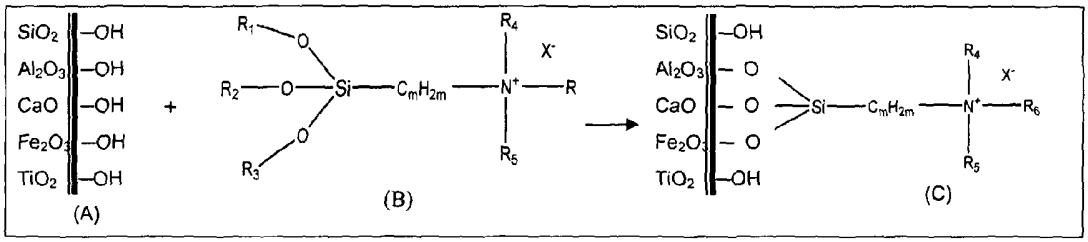
(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR,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

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

Published:
— *with international search report*

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

(54) Title: ANTI-MICROBIAL MEDIA AND METHODS FOR MAKING AND UTILIZING THE SAME



where, m = 1 to 10;
R_1, R_2, R_3 are hydrogen or alkyl groups with 1 to 5 carbon atoms;
R_4, R_5, R_6 are alkyl groups with at least one of them with 5 to 25 carbon atoms;
$X^{\ominus}$ is a counter anion, such as $Cl^{\ominus}$ or $Br^{\ominus}$.

(57) Abstract: An improved fluid filtration media having anti-microbial properties and methods for producing and utilizing improved fluid filtration media having anti-microbial properties and employing the same in fluid filtration applications wherein one representative separation media for fluids comprises a base mixture of organic and inorganic components comprising at least one anti-microbial component; and at least one component of the base mixture comprises a charge-modified group covalently bonded to the surface of the at least one anti-microbial component is disclosed.

WO 2005/095285 A1

ANTI-MICROBIAL MEDIA AND METHODS FOR MAKING AND UTILIZING THE SAME

Related Applications

This application is a continuation-in-part of commonly owned U.S. Provisional Patent Application Serial No. 60/555,766, filed March 24 ,2004, of Yeh et al., entitled "ANTI-MICROBIAL MEDIA AND METHODS FOR MAKING AND UTILIZING THE SAME," the disclosure of each is herein incorporated by reference to the extent not inconsistent with the present disclosure.

Background of the Disclosure

The present disclosure relates to fluid filtration media and methods for producing and utilizing fluid filtration media, and more particularly, to fluid filtration media having anti-microbial properties and methods for producing fluid filtration media having anti-microbial properties and employing the same in fluid filtration applications.

Often in both consumer and industrial fluid filtration applications a fluid is filtered prior to its use in an intended application. As a result, fluid filtration systems are installed either internally or externally within the industrial system or consumer appliance.

It is quite possible that fluids, such as, for example, household water contains various levels of microorganisms even after municipal water treatment. Microorganisms, such as protozoan cysts, bacteria and viruses (hereinafter collectively referred to as "microbes"), which may have existed in the water supply, can remain in water intended for drinking. This is particularly true for well water that has not gone through the municipal water treatment.

In some instances, disinfection agents such as chlorine or chlorine compounds, ozone, UV, other halogens such as iodine and bromine, and transition metals are used to reduce the concentration of such bacteria and viruses, while mechanical separation may be used for protozoan cyst reduction. However, a significant number of drinking water systems do not use chemicals, such as, for example, chlorine and chloramine, for disinfection in order to reduce the smell and/or health risk due to such chemicals being present in water. The lack of such chemicals in water could result in increased levels of microorganisms and biofilm build-up in the water.

Chlorine or chlorine compounds used for disinfection must often be removed from water supplies prior to use in drinking water systems, food service beverage systems and ice dispensing equipment. The reasons for removal of the above compounds vary depending on the specific application or system. For example, the presence of chlorine in the water supply to certain beverage systems may negatively impact a particular aesthetic quality of the beverage product, such as its taste. The removal of the chlorine or chlorine compounds from the water supply to certain beverage systems, however, can result in the return of harmful microorganisms to the point of use of the beverage systems.

Furthermore, a build-up of microorganisms can occur within dechlorination filters, resin beds, and other finely divided fluid media filters when water is not flowing for some period of time. The build-up of high levels of microorganisms can then be released downstream at causing health concerns, as well as severe off-tastes and odors when the water arrives for use at the intended location. Over a prolonged period of time the buildup of microorganisms may coat water lines and wetted parts of dispensing equipment to form layers of biofilm, thus compounding the microorganism build-up problem.

Known high levels of microorganism build-up have caused many in the food service, beverage processing and drinking water industry to periodically sanitize water lines. Thus, it is important to consider such sanitization processes. Many of the sanitization processes currently available are difficult to administer, costly, service intensive, and use highly toxic chemicals that invoke toxic chemical handling and disposal difficulties that cause further adverse economic consequences. Since the water supply system must also be shut down or bypassed while administering the sanitization treatment processes, the economic burden is increased as well as being disruptive to the end user. For example, a water line may be coated with biofilms and an extended flush with water containing a disinfectant agent such as, for example, chlorine is needed to remove such biofilm coating followed by at least an additional flush with potable water before the water line can be used again for its intended purpose.

The EPA Water Purifier Standard requires that a filtration device for drinking water applications remove microorganisms at greater than 6 log for bacteria, 4 log for virus and 3 log for protozoan cysts ("Guide Standard and Protocol for Testing Microbiological water purifiers", 1987 the disclosure of which is herein incorporated by reference to the extent not inconsistent with the present disclosure).

Filter media (hereinafter referred to as "anti-microbial filtration media") currently available for the management of microorganisms in potable water environments contain appreciable concentration of materials that can leach into the effluent to levels that are unacceptable from a regulatory standpoint, have poor efficacy (*e.g.*, limited to claims of bacteriastasis and/or cyst reduction only), and can contain or use hazardous materials within their materials of construction or employ a unsafe and costly mode of operation (*e.g.*, mercury-arc UV lamps, ozone).

Furthermore, microbial contamination is not only a problem in water supplies used for human consumption, but also is a major concern for industries that require purified water for production of microelectronics, pharmaceuticals, and biopharmaceutical processes, among others.

As is known in the art, there are a number of ways water can be purified. For example, one article "A technique for injecting Ag^+ Ions as Biocide into H_2O", NASA Tech Briefs, 51, November 2001, the disclosure of which is hereby incorporated by reference to the extent not inconsistent with the present disclosure, disclosed the information of injecting 0.5 mg/L silver ion in drinking water. US patent 6,248,342 B1 disclosed an antimicrobial high pressure laminate which contained Ag, Zn, etc. for counter top surface treatment. Iodinated resin developed by Pentapure Inc. and others has been commercially used. The iodinated resin works by eluting iodine into the water at a controlled rate. However, the response time is unacceptably long and there is a health concern relating to the iodine leaching into the fluid, which renders the application more favorable for short term use or under emergency situations. Additionally, persons with certain thyroid conditions may also be sensitive to iodine consumption.

Bon Del Water Filters has a process of treating drinking water, and one of the key components is silver impregnated granular activated carbon. There are many other companies that have silver based antimicrobial technology including Agion, British Berkefeld and Surfacine. KDF® claims it has a process by the redox reaction by using bi-metallic Cu-Zn alloy to reduce metal and to control microorganisms. Among the disadvantages of these treatments are the lack of data that show the required bacterial and viral removal criteria set by EPA, as mentioned above, and the potential leak of potentially hazardous concentration of silver or iodine components into the water stream.

An article "TiN Electrode Reactor for Disinfection of Drinking Water" appeared in Water Research (Vol. 34, Issue 12, page 3117, 2000,) disclosed a method

to reduce microbes by using titanium nitride (TiN) electrodes. By applying an electrical potential across the electrodes, it was shown that the microbial cell concentration can be reduced down to 7%. Although this may be a novel method to eliminate microbes, the concentration of remaining microbes may still be too high to meet the EPA's guideline as mentioned above.

Biomaterials (Vol. 22, page 2239, 2001) taught a method to synthesize polyurethanes that contained quaternized pyridine, and these polymers showed antimicrobial property. However, this method involved an extensive use of potentially toxic organic solvents in the polymer synthesis and quaternization. Further, only a few selected polymers showed bactericidal activity against *E. coli*, according to the report.

All the methods described above have had some success in one area but none of the above methods provides any information or data that demonstrates that they were effective in reaching the microbial reduction requirements set by EPA, as discussed above.

Considerable information is available concerning the use of UV and oxidants such as ozone and hydrogen peroxide for drinking water treatment. However, safety concerns related to using UV light or ozone, plus the initial capital cost for the required equipment and the ensuing maintenance considerations make these methods less attractive.

Additionally, microbial control may be desirable in already existing water supply systems that currently possess fluid filtration devices having mechanical screening membranes and adsorption fluid filtration using activated carbon, such as, for example, systems that employ disposable filter cartridges. However, the complication of adding further fluid filtration devices to an existing water supply system, and the cost associated with the additional plumbing work, or just general nuisance of having multiple fluid filtration devices for one system, create inconvenience for the average residential consumer by adding additional required space and installation and maintenance cost, among many.

Additional approaches to solving related problems for specific applications include, the disclosure contained in US patent 5,145,596, wherein octadecylaminodimethyl trimethoxysilylpropyl ammonium chloride was added directly to a washing machine in order to eliminate odor from fabrics, US patents 4,406,892 and 4,282,366, wherein octadecylaminodimethyl trimethoxysilylpropyl ammonium chloride was used to treat cellulose fabrics to inhibit the growth of disease

causing microorganisms, US patent 5,013,459, wherein octadecylaminodimethyl trimethoxysilylpropyl ammonium chloride was used to treat PE, PP, glass beads, cellulose triacetate, styrene maleic anhydride beads, and #1 Whatman filter paper, which reported 100% reduction of microbes. An antimicrobial form such as one from polyurethane was treated with such octadecylaminodimethyl trimethoxysilylpropyl ammonium chloride, as was disclosed in US patent 4,631,297 to reduce or eliminate microorganisms. European Application WO87/00006 disclosed the application of such octadecylaminodimethyl trimethoxysilylpropyl ammonium chloride in a surfactant to kill microorganisms on multi-cellular plants. US patent 4,835,019 disclosed a process of making Nylon 6 yarn antimicrobial by adhering such octadecylaminodimethyl trimethoxysilylpropyl ammonium chloride in the presence of surfactants on the fiber surface. Wet wipers of cellulosic fiber were made antimicrobial as was disclosed in US patent 4,781,974.

However, none of the above mentioned disclosures immobilizes octadecylaminodimethyl trimethoxysilylpropyl ammonium chloride on a solid support to reduce extractables of octadecylaminodimethyl trimethoxysilylpropyl ammonium chloride, which has, thus far, an unknown effect to human consumers.

US patent 4,682,992 disclosed spherical glass beads or silica gel beads being rendered antimicrobial by reacting with such octadecylaminodimethyl trimethoxysilylpropyl ammonium chloride. US patents 4,414,268 and 4,395,454 teach the use of additional silicon wetting agents to render such octadecylaminodimethyl trimethoxysilylpropyl ammonium chloride non-leachable. Similar octadecylaminodimethyl trimethoxysilylpropyl ammonium chloride to indicate algae growth inhibition was disclosed in US patents 3,817,739, and 3,730,701.

None of the above disclosed prior patents or publications described the use of octadecylaminodimethyl trimethoxysilylpropyl ammonium chloride to treat diatomaceous earth, a very versatile component in fluid filter media, or the treatment of diatomaceous earth in combination with activated carbon, another versatile component in fluid filter media, in drinking water or other water purification applications.

US Patent application 0009239 A1, in which 10-20 mesh sand were used as a substrate to remove microorganisms based on the use of octadecylaminodimethyl trimethoxysilylpropyl ammonium chloride. However, sand

lacks the preferred size, shape, and surface morphology to be used as an effective fluid filtration media.

An article "The Quest for the Holy Grail: Microbiological Carbon Block Filters", WC&P, August 2002, pp. 42 mentioned the use of "two chemicals" that are "bonded to the carbon." There is no disclosure of such chemicals, the bonding techniques, and no mention of additional filter aid, such as diatomaceous earth used in the referenced article.

An article "Activated Carbon Treatment of Drinking Water" from "Water Treatment Notes", December 1995 indicated that activated carbon is very effective in reducing certain organic chemicals and chlorine in water, but only from "microbiologically safe water."

There are other types of antimicrobial modification of fluid filter media and one example of these is the use of polyionene. Information released from Buckman Laboratories disclosed the use of a group of sulfur-nitrogen compounds and polyionene for water treatment, "A new registered Combination of Microbial Actives: Mixed Isothiazolinones and a Polymeric Ionene". But both polyionene and isothiazolinones are not listed in CFR 21 for direct addition to food for human consumption In addition, there is a concern that a concentration of 10 ppb of isothiazolinone may have toxicity to aquatic organisms per EPA's premanufacturer notices (PMNs) P-95-116/96-1250 and P-96-117/96-1251.

US patent 4,980,067 taught a method of removing microorganisms from biological fluids by nylon membranes grafted with polyionene. The grafting method required a great deal of synthetic chemistry to achieve the stated results, in addition to the expensive membrane used as the filtration media, which could make the process uneconomical.

An article from Journal of Controlled Release (Vol. 50, issue 145, 1998, disclosed a polymer that had quaternary ammonium and phosphonium groups, and these polymers showed antimicrobial activity. However, there was no description of how to immobilize such polymer for practical consumer applications.

In order to meet the EPA's requirement of microbial reduction, there may be a need to have multiple active ingredients. US patent publication 2003/0168401 A1 disclosed that both silver species and a quaternary ammonium salt were useful for antimicrobial application. Silver was disclosed as being the preferred metal species used to disinfect the drinking water. However, as disclosed in US patent publication 2003/0168401 A1, the silver species were closely clustered around

quaternary ammonium charge center, instead of evenly distributed over the substrate. In addition, there is no mention of any chemical method to immobilize the disclosed quaternary ammonium salt, poly(diallyldimethylammonium chloride), which could make the extractable level unacceptably high.

Concerning the dispersion of metal, metal oxide, or metal halide (collectively called metal species, for instance, silver species), all procedures presently known to the inventors of the present disclosure are based on the dissolution of metal salt such as silver nitrate in aqueous media. Working with aqueous solution of silver nitrate is operationally simple, and can form silver halide as has been disclosed in the afore mentioned patent publication. However, this treatment makes the silver species physically clustered around quaternary ammonium charge center due to charge interactions without a true covalent bond. When there is no halide present, these silver nitrate particles grow into larger size after water is evaporated due to the high surface tension of water. Thus, there is a need to increase the dispersion of silver species particles without involving sophisticated molecular phase or nano phase silver species particles, which are understood by those skilled in these arts.

Therefore, there is a need for a fluid filtration media and an incorporating device which can effectively meet microbial reduction standards such as those presented by the EPA without use of hazardous materials or unsafe techniques, vary for use in diverse fluid filtration applications, fulfill multiple fluid filtration needs, and satisfy these needs while minimizing capital, operating and management costs so that they are acceptable to the consumer. Furthermore, there is an additional need to immobilize the antimicrobial components to eliminate unacceptable leaching of such potentially hazardous components. Even further, there is a need to significantly reduce if not minimize the particle size of metal species that have antimicrobial properties in order to maximize the effect of such metal species and to reduce the possibility of these metal species particles dislodging from the fluid filtration media device surface. Even further that there is a need to at least minimize, if not eliminate, significant clustering of metal species so that these metal species can be substantially, uniformly distributed with high dispersion over the entire filter surface.

Summary of the Disclosure

The new and innovative separation media for fluids, which includes the principals of the present disclosure, provides a solution to many of the problems described above. One representative separation media for fluids according to the present disclosure comprises a base mixture of organic and inorganic components comprising at least one anti-microbial component; and at least one component of the base mixture comprises a charge-modified group covalently bonded to the surface of the at least one anti-microbial component.

In another representative embodiment, the charge-modified group covalently bonded to at least one component of the base mixture and is selected from the group comprising: charge-carrying monomers, charge-carrying macromolecules, charge-carrying polymers and mixtures thereof, the charge-modified group listed above containing a functional group selected from the group comprising: alkoxy, azeridinium, epoxy, reactive hydrogens, and mixtures thereof.

In yet another representative embodiment, the base mixture is selected from the group comprising: diatomaceous earth, activated carbon, polymers, perlite, porous and non-porous ceramic materials, glass fibers, glass spheres, and combinations thereof.

In still another representative embodiment, the covalently bonded charge-modifying group is permanently associated with at least one component of the base mixture.

In another representative embodiment, separation the anti-microbial component has a positive zeta potential at pH from about 5 to about 9.

In yet another representative embodiment, the molecular mass of charge-carrying monomers, charge-carrying macromolecules, and charge-carrying polymers is less than about 5,000.

In still another representative embodiment, the base mixture includes a polymer of olefin, or polymer having functional groups of $-NH_2$, -OH, -NH, C=O, -C(=O)-O-, and combinations thereof.

In another representative embodiment, the polymers are selected from the group comprising: cellulose, nylon, polyester, polyurethane, modified polyethylene and polypropylene, and combinations thereof.

In yet another representative embodiment, the charge-carrying monomer comprises: an organo-silane having alkoxy groups and having the following formula:

$A_1A_2A_3SiC_pH_{2p}B^{\oplus}(C_lH_{2l+1})\ (C_mH_{2m+1})\ (C_nH_{2n+1})X^{\ominus}$;

wherein A_1, A_2, and A_3 are independently $C_rH_{2r+1}O$ or OH, where r is in the range of 1 to 5, p is in the range of 1 and 10, B comprises nitrogen or phosphorus, *l*, *m*, and *n* are individually in the range of 1 and 32, and $X^{\ominus}$ is an anion, selected from the group comprising:

Cl, Br, I, NO_3, OH, ClO_3, SO_3, SO_4, MnO_4, PF_6, or BF_4, and combinations thereof.

In another representative embodiment, the charge-carrying monomer comprises an organo-silane having an alkoxy group according to the following formula:

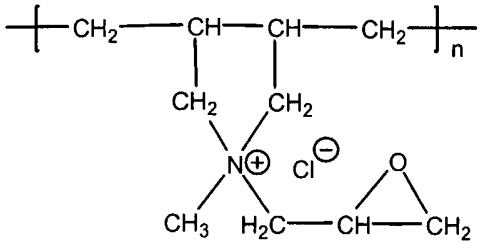
$A_1A_2A_3SiC_pH_{2p}N^{\oplus}(C_5H_5)\ X^{\ominus}$;

wherein A_1, A_2, and A_3 are independently $C_rH_{2r+1}O$ or OH, r is in the range of 1 to 5, p is in the range of 1 to 30, $N^{\oplus}(C_5H_5)$ is a pyridinium group, and X is Cl, Br, I, NO_3, ClO_3, SO_3, SO_4, MnO_4, PF_6, or BF_4 and combinations thereof.

In another representative embodiment, the at least one charge-carrying macromolecule has branch structure including a plurality of terminals.

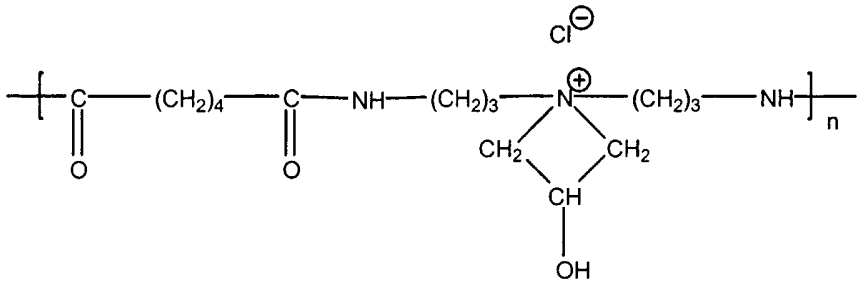
In still another representative embodiment, the at least one of the charge carrying macromolecules includes a quaternary ammonium or phosphonium group operatively connected to one or more of the branch terminals.

In yet another representative embodiment, the at least one of the charge carrying macromolecules includes the following repeat unit:



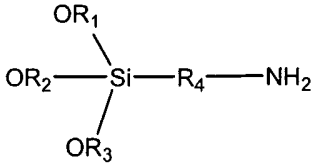
where n is between about 5 and about 24.

In another representative embodiment, the at least one of the charge carrying macromolecules includes the following repeat unit:



where n is between about 5 and about 16.

In still another representative embodiment , the charge carrying macromolecules include a linking molecule according to the following structure for covalently bonding to at least one component of the base mixture:



where, R_1, R_2, and R_3 are H's or C_1 to C_5 alkyl groups, R_4 is an aliphatic or aromatic hydrocarbon chain, or the combination of the two, or amino-aliphatic chain, with carbon atoms up to 30.

In yet another representative embodiment, the base inorganic component further comprises: a compound selected from the group comprising: a single transition metal compound or mixtures of transition metal compounds, incorporated therewith by an incipient-wetness impregnation method.

In another representative embodiment, the transition metal compound includes transition metal oxide, halide, and sulfide.

In yet another representative embodiment, the transition metal compound includes:

Ag_2O, AgO, Ag_2S and AgCl.

In still another representative embodiment, at least one of the transition metal compounds is dissolved in a solvent having an equal or a lower surface tension than water.

In another representative embodiment, the low surface tension solvent includes organic and inorganic solvents.

In yet another representative embodiment, the low surface tension solvent includes surfactants.

In still another representative embodiment, the transition metal compound is substantially evenly distributed over the surface and in the pores of the inorganic and organic base mixture.

In another representative embodiment, the inorganic base mixture component comprises:

silica, alumina, aluminosilicate, magnesia, titania, diatomaceous earth, perlite, and combinations thereof.

In still another representative embodiment, the inorganic base mixture comprises synthetic or naturally occurring inorganic material.

In yet another representative embodiment, the polymeric base mixture comprises:

water insoluble polymers.

In another representative embodiment, the base mixture comprises:

a composite of two or more components of organic or inorganic nature.

In still another representative embodiment, the base mixture composite includes a polypyrrole coated base mixture wherein *in situ* polymerization of pyrrole is accomplished by the incipient-wetness impregnation method.

In yet another representative embodiment, the porous and non-porous ceramic material comprises:

zeolite.

In another representative embodiment, the transition metal component comprises:

an oxide selected from the group comprising: silver, copper, zinc, titanium, zirconium, manganese, tungsten, iron, vanadium, and combinations thereof.

In still another representative embodiment, the organo-silane includes a crosslinked polymer covalently bonded to the surface of the base mixture.

In yet another representative embodiment, the component of the base mixture that has a charge-modified group covalently bonded to the surface of the component has a cationic surface at a pH from about 5 to about 9.

Brief Description of the Drawings

Figure 1 is a schematic illustration of one known process for depositing a metal species on the surface of a solid filter medium substrate;

Figure 2 is a schematic illustration of a representative process for depositing a relatively thin layer of substantially uniform distribution of a metal species on the surface of a filter medium according to the present disclosure;

Figure 3 illustrates a representative reaction of three methoxyl groups of octadecylaminodimethyl trimethoxysilylpropyl ammonium chloride with the hydroxyl groups of DE to form a chemical linkage between DE and the antimicrobial octadecylaminodimethyl trimethoxysilylpropyl ammonium chloride;

Figure 4 illustrates the DE surface after reaction of a representative form of any one a plurality of possible forms that such substituted quaternary silane could take in accordance with the present disclosure;

Figure 5 illustrates another representative possible form of linkage of a plurality of possible leakage forms between the DE substrate and the charged silane species;

Figure 6 illustrates another of the plurality of possible representative functional groups that can react with DE, specifically epoxy groups, in accordance with the present disclosure;

Figure 7 illustrated the use of coupling agents to enhance the reactivity of the groups to the surface of DE, in accordance with the present disclosure;

Figure 8 is an illustration of representative examples of the surface modification of DE utilizing the coupling agents of Figure 7; and

Figure 9 illustrates one representative surface modification of one representative filter media in accordance with the present disclosure.

Detailed Description of the Disclosure

Unless otherwise indicated, all numbers expressing quantities of ingredients, properties such as molecular weight, reaction conditions, and so forth used in the specification and claims are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that may vary depending upon the desired properties sought to be obtained by the present disclosure. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value,

however, inherently contain certain errors necessarily resulting from the standard deviation found in their respective testing measurements.

The representative fluid filter medium used in the present disclosure includes, but is not limited to activated carbon (AC), diatomaceous earth (DE), powders of polyethylene, fibers of polyethylene and polypropylene, and a lead adsorption component such as titanium silicate (ATS, Engelhard Corp, Iselin, NJ). Both AC and DE are active components and are major fluid filtration components, as they allow fluids, such as, for example, water to flow through and mechanically separate and/or adsorb undesired species present in influent fluid, such as, for example, water used for drinking purposes, from being present in the effluent fluid stream by at least one or more of the following mechanisms: mechanical sieving, adsorption and charge interactions.

While the specific examples and details of the present disclosure relates to microbial reduction in water, it is believed that the technical principles and the specific chemical concepts discussed herein will most likely apply to microbial reduction in the gas phase as well. Thus, whenever the term fluid is used in the present disclosure, it is understood to mean fluid in the conventional sense including liquids, such as for example, water and gas, such as for example, air.

Filter medium block

As used in the present disclosure, the term "green strength" means the strength a block structure has when the block is compressed without baking. A minimum of such green strength is needed when the block is subjected to human or robotic handling when preparing for the process of baking.

The filter medium block used in the following examples of the present disclosure was made based on US patent 5,882,517 issued to CUNO, Incorporated, the disclosure of which is herein incorporated by reference, to the extent not inconsistent with the present disclosure. US patent 5,882,517 describes a porous structure based on activated carbon (hereafter AC) and various powder and fibrous components. The green strength is maintained by a rod-shaped fiber. The remaining components described in US patent 5,882,517 act as binders. The binders, especially the one that melts during baking, provide the strength after the block is subjected to a pressure of about 2000 psi at room temperature and then baked at a temperature of about 142° C for about 45 minutes, as described in US patent 5,882,517. While there are many binders used by those skilled in the art, the presently preferred binder used

in this disclosure is micron sized polyethylene powders having a melting point of about 110° C. In the present disclosure, at least part of the AC is replaced with diatomaceous earth (hereafter DE) and the DE is then subjected to modifications in order to provide antimicrobial activities.

Metal Particle Dispersion

One of a plurality of possible modifications to filter mediums to impart anti-microbial activity is to disperse a uniformly thin layer of a transition metal species, (where a transition metal is, presently preferably, defined herein as an element from the 'B' group of the periodic table which forms one or more stable ions which have incompletely filled 'd' sublevels or orbitals, and does not include lanthanides and actinides) such as, for example, zinc, copper, iron, silver species, on the medium. The process of depositing a metal species on the surface of a solid filter medium substrate is known in the art as "impregnation". In the present disclosure, the metal species can be impregnated on AC and/or DE. One effective method to impart a metal species, such as, for example, silver is via a silver nitrate solution.

As illustrated in Figure 1, in one known practice, silver nitrate is dissolved in water to a predetermined concentration and then added to AC or DE to the point of incipient wetness, which is a subjective judgment when the flow of AC or DE powder begins to slow down (as an example a visually detectable resistance to rolling of the media within a jar mill), but before the formation of any appreciable agglomerate. By the term "incipient wetness" is meant the state when a particle of porous or nonporous nature is at least partially, and presently preferably, fully coated with a layer of wetting liquid. For practical purpose, a later stage of incipient wetness, i.e., before the formation of any agglomerate, is preferred.

Since water has a very high surface tension (72.0 dynes/cm at 25° C), which not only is expected to form localized large silver nitrate particles when water is evaporated, but also hinders the accessibility of water to the smaller areas of the filter medium. Given this process, one possible approach to at least significantly reducing if not substantially eliminating the accessibility problem is to use benign non-aqueous solvents of low surface tension that can dissolve silver salts to solve this wetting and dispersion problems in order to provide both highly dispersed smaller particle size silver species that can evenly distribute over the entire liquid-wetted surface of the filter medium substrate. These preferred solvents include, but are not limited to, low molecular weight alcohols, such as, for example, methanol, ethanol,

propanol, isoproanol, and the like having the general structure of $C_n H_{2n+1}$ –O-H with ethanol being presently preferred which has a surface tension of about 22.0 dynes/cm at about 25 °C. Other solvents including supercritical fluids (SCF) and surfactants in water or other solvent systems, with a final surface tensions range from about 1 dyne/cm to about 72 dynes/cm at 25 °C shall be included (water, for example has a surface tension of about 72 dynes/cm at 25 °C. The solvent system with presently preferred final surface tension of 15 to 50 dynes/cm, including for example trimethylamine (13.4 dynes/cm), diethyl ether (16.7 dynes/cm), 2-methyl-2-proponal (20.0 dynes/cm), all C1 to C6 alcohols in this range for example: 1-hexanol (25.8 dynes/cm), diethylene glycol (44.8 dynes/cm) and the most presently preferred surface tension of 20 to 30 dynes/cm is included in this disclosure.

Using the benign solvents or other similar mechanisms, a thin layer of substantially uniform distribution of silver nitrate particles is formed when the benign solvent, such as, for example, ethanol is evaporated. The above two processes are illustrated by the figures discussed below.

As illustrated in Figure 2, using a benign solvent having a surface tension of about 20 to about 40 dynes/cm at about 20 to about 25° C, such as, for example, an ethanol solution of silver nitrate, provides at least three benefits: 1) small but uniformly distributed silver nitrate particles provide greater surface area coverage of the filter medium substrate, 2) maximum coverage of the filter medium substrate surface includes, but is not limited to, micro pores where only a relatively low surface tension liquid can penetrate and subsequently wet such micro pores, and 3) small but uniformly distributed silver nitrate particles have a higher adhesion to the filter medium substrate surface, as compared to the water based system. The better adhesion of small particles to the substrate surface will reduce the possibility of particle leach into effluent stream.

Modification of AC and DE surfaces

As is known by those skilled in the art, AC has a very complicated molecular structure. Due to the thermal treatments during processing, the AC surface has mostly oxygen-containing groups such as –OH, -CO, and –COOH. Since these oxygen-containing groups are positioned on fused rings, their concentrations are believed rather low. This relatively low concentration of these oxygen-containing groups reduces the reactivity of the activated carbon (AC). Highly oxidized surface can be achieved by reacting nitric acid or sulfuric acid, or this highly oxidized surface

can be achieved in the presence of ozone or oxygen plasma, UV, or other methods to oxidize the surface. In addition to oxidation, the surface can be treated to provide amine groups for further surface modification. One example of such modification is to react surface amine or surface hydroxyl groups with chemical species that has reactive epoxy or other active groups available for reaction, or can be linked through an agent that has epoxy or other active groups available for reaction, such as alkoxy, azeridinium, reactive hydrogens (hydrogen atoms linked to atoms with greater elecronegativity (>0.4 on the electronegatively scale) than elemental hydrogen, beyond that of a weak polar covalent bond), and mixtures thereof. Unless the concentration of surface amines or hydroxyls is high enough so that the surface modification shows its antimicrobial effect, such modification generally does not give a significant result for this application. As explained above, there may not be enough surface modification on activated carbon. Thus, there is a need to include a second active component in the filtration medium.

DE is a naturally occuring material, composed of skeletal remains of single-celled plants called diatoms. In the diatoms' lifetimes, the diatoms abstract silica and other minerals from water, and when the diatoms die, only the diatoms skeleton shapes remain. Since DE has a mixture of minute particles of different size, shape and structure, it has been used for many years as a filter media or as a filter aid. The composition of un-processed DE is mostly silica, with some alumina, calcium oxide, iron oxide, titania, etc. Despite its compositional complexity, the surface of DE is covered with hydroxyl groups when in a moisturized environment. The present disclosure describes, among other features, the use of such surface hydroxyl groups to react with charged antimicrobial species so as to charge modify the surface to process antimicrobial ability. It is believed that activated carbon, polymers, ceramics, and transition metals once treated, if necessary, to generate surface hydroxyl groups, may also be reacted in this way to generate antimicrobial activity.

In the early 1970's, a group of organosilicon quaternary ammonium compounds was developed by Dow Corning, and many have been studied with respect to showing antimicrobial properties. Out of those studied, octadecylaminodimethyl trimethoxysilylpropyl ammonium chloride (DC-9-6346) is one of the most cited in the antimicrobial literature (for example, US patent 3,560,385). The three methoxyl groups of octadecylaminodimethyl trimethoxysilylpropyl ammonium chloride can react with the hydroxyl groups of DE to form a chemical linkage between DE and the antimicrobial

octadecylaminodimethyl trimethoxysilylpropyl ammonium chloride. The reaction is generally illustrated in Figure 3.

As illustrated in Figure 3, (A) represents DE including the major constituents in DE and the surface hydroxyl groups. (B) represents the generalized form of organosilicon quaternary ammonium compounds. (C) represents the attachment of (B) on the surface of (A) without implying a specific attachment location.

One representative example of such quaternary ammonium salt of a substituted silane is octadecylaminodimethyl trimethoxysilylpropyl ammonium chloride, which is commercially available from Dow Corning Corporation (DC-9-6346) or Aegis Environmental Management Inc. (AEM 5700).

There are many forms that such substituted quaternary silane can take. For example, the quaternary nitrogen atom is in a ring so that, after reaction, the DE surface will have a structure similar to the structure illustrated in Figure 4.

There are other possible forms of linkage between the DE substrate and the charged silane species, such as, but not limited to, the linkage illustrated in Figure 5 where two adjacent silane groups linked to DE are coupled together via the alkyloxy linkage.

In addition to the reactions of quaternary amine substituted silanes with DE via hydroxyl or alkyloxyl groups, there are other functional groups that can react with DE. One representative example of such reaction is via, but not limited to, the epoxy groups as illustrated in Figure 6.

In case the reactivity of such reaction is low, coupling agents can be used to chemically link such epoxy-carrying quaternary ammonium species onto the surface of DE. These coupling agents include, but are not limited to, a coupling agent having a structure similar to that illustrated in Figure 7.

Representative examples of such surface modification of DE include, but are not limited to, the structure as illustrated in Figure 8.

Whether these charge-modifying compound are polymers as shown in (D) of Figure 6, or macromolecules as shown in (B) of Figure 3 with a large m number, such as greater than about 10, or a monomer such as shown in (D) of Figure 6, where n is equal to one, they all can absorb small negatively charged species, such as, but not limited to, bacteria and viruses. But not all charge-carrying species described above possess the ability to inactivate the life processes of microbes. It seems that a unique combination of the size and/or the shape of such charge-carrying

species will possess such function to inactivate the life processes of microbes. It is particularly interesting to explore the interactions between microbes and a charged compound, where the charged compound has a branched structure with a charged center, such as, but not limited to, quaternary amine at the terminal of each branch.

Antimicrobial Testing

In addition to performing testing conforming in order to closely follow the "Guide Standard and Protocol for Testing Microbiological Water Purifiers" issued by the United States Environmental Protection Agency (US EPA) in 1987, an equivalent low biohazard test method was developed and revealed in this disclosure. *Brevundimonas diminuta* (ATCC-19146) shall be used as the bacterial surrogate, the bacteriophage MS-2 (ATCC-15597-B1) shall be used as a viral surrogate for poliovirus, and the bacteriophage PRD-1 shall be used as a viral surrogate for rotavirus SA-11.

The methods that are used for suspension preparation, density determination, negative control and analysis of the challenge organisms for use/testing are presented below:

Test water requirements:

A treated water that meets the following characteristics was used as the water for both 'seeded' testing (microorganisms added to challenge levels) as well as 'unseeded' testing (no additional microorganisms):

Chlorine or other disinfectant residual	Free of any
Hardness (as $CaCO_3$)	Not more than 170 mg/L
pH	7.5 ± 0.5
Temperature	20 °C ± 2.5 °C
Total Organic Carbon (TOC)	0.5 ± 0.1 mg/L
Total dissolved solids (TDS)	200-500 mg/L
Turbidity	< 1 NTU

Any measurable amount of chlorine was removed by sodium thiosulfate, which is a known art in this field. Prior to the seeding treatment, the water shall be pre-filtered with an NSF standard 42 filtration device that has been properly flushed as per the manufacturer's instructions.

Another water supply was used for leaching purposes. The water supply used for leaching purposes was similar to the one described above with the pH being in the range of about 5.0 ± 0.2 pH units and the TDS value less than about 100 mg/L.

Microorganisms

As used in the following examples, all organisms were obtained from: American Type Culture Collection, 19301 Parklawn Drive, Rockville, Maryland 20852-1776.

Test Organisms with associated hosts used in the examples are *Brevundimonas diminuta* (ATCC #19146), *MS-2* (ATCC #15597 – B1), and *E. coli* (ATCC # 15597, host organism for bacteriophage MS-2).

Bacterial challenge 'seeded' test water

A water supply with the following characteristics was used in the following examples.

Bacterial challenge level	>100,000,000 (1 x 10^8) cfu/L
Hardness (as $CaCO_3$)	Not more than 170 mg/L
pH (NaOH adjusted)	9.0 ± 0.2
Temperature	4 °C ± 1 °C
Humic acid (Sigma- Aldrich) as Total Organic Carbon (TOC)	> 10 mg/L
Sea salt (Sigma-Aldrich) or NaCl (Reagent Grade) as Total dissolved solids (TDS)	1500 mg/L ± 150 mg/L
Turbidity (test dust of <5 micron size with 20% to 40% (volume) >2.5 micron)	> 30 NTU

Viral challenge 'seeded' test water

A water supply with the following characteristics was used during the following testing examples.

Viral challenge level	>10,000,000 (1×10^7) pfu/L
Hardness (as $CaCO_3$)	Not more than 170 mg/L
pH (NaOH adjusted)	9.0 ± 0.2
Temperature	4 °C ± 1 °C
Humic acid (Sigma-Aldrich) as Total Organic Carbon (TOC)	> 10 mg/L
Sea salt (Sigma-Aldrich) or NaCl (Reagent Grade) as Total dissolved solids (TDS)	1500 mg/L ± 150 mg/L
Turbidity (test dust of <5 micron size with 20% to 40% (volume) >2.5 micron)	> 30 NTU

Although a turbidity of greater than about 30 NTU was used for this testing, it is believed that since the test dust is quickly removed on a filtration surface through mechanical reduction, that the internal structure of a filter will be exposed to lower turbidity water. It is believed that the results shown may be obtained irrespective of the concentration of test dust used in the challenge water as specified above.

Buffer Solutions Preparation:

Sterile buffered dilution water (SBDW) was prepared according to the Standard Methods for the Examination of Water and Wastewater (dilution water: buffered water). Two buffer solutions are used and prepared as defined below: Phosphate buffer saline (PBS) with about a pH 7.4, and Trizma (Tris) buffered saline (TBS) with about a pH 7.3.

- Phosphate buffer saline (PBS) – a stock solution was prepared by dissolving 80 g sodium chloride (NaCl), 2 g potassium dihydrogen phosphate (KH_2PO_4), 29 g hydrated disodium hydrogen phosphate ($Na_2HPO_4 \cdot 12\ H_2O$) and 2 g potassium chloride (KCl) in water to a final volume of 1 L. A working solution was prepared from the stock solution by diluting 1 volume of the stock with 9 volumes of water. The pH was adjusted using a pH meter to 7.4 with 0.1 N HCl or 0.1 N NaOH before use.

- Trizma (Tris) buffered saline (TBS): Sigma-Aldrich Chemical, St. Louis, MO, USA. A stock solution was prepared by dissolving 2.42 g Tris and 29.24 g NaCl in water to a final volume of 1 L. the pH was adjusted using a pH meter to 7.3 with 0.1 N HCl.

Growth medium

The following representative growth medium was used in the examples described below.

TSB (Tryptic Soy Broth)

Tryptone	1.7 g
Soytone	0.3 g
Dextrose	0.25 g
Sodium chloride	0.5 g
Dipotassium phosphate	0.25 g
DI water	100 mL
pH	7.3 +/- 0.2

The solid phase chemicals such as tryptone, soytone, dextrose, sodium chloride and dipotassium phosphate are dissolved in the DI water through boiling, then adjusted to final pH, then about 8 mL aliquots are dispensed into covered 16 x 150 mm test tubes. The resulting broth is then sterilized through an autoclaving process utilizing steam under pressure with a temperature of no less than about 121 °C +/- 1 °C at about 15 psi for about 20 minutes. The cooled broth is then stored at about 5 °C +/- 3 °C F to minimize the potential for re-growth of bacteria.

TSA (Tryptic Soy Agar)

Tryptone	7.5 g
Soytone	2.5 g
Sodium chloride	2.5 g
Bacto-agar	7.5 g
DI water	500 mL
pH	7.3 +/- 0.2

The solid phase chemicals such as tryptone, soytone, dextrose, sodium chloride and dipotassium phosphate are dissolved in the DI water through boiling, then adjusted to final pH, then sterilized through an autoclaving process utilizing steam under pressure with a temperature of no less than about 121 °C +/- 1 °C at about

15 psi for about 20 minutes. Pour tempered media into sterile petri dishes. Store the agar plates at about 5 °C +/- 3 °C F to minimize the potential for re-growth of bacteria, until use. Allow plates to warm to room temperature before use.

SLB (Saline Lactose Broth)

Sodium chloride	7.6 g
DI water	1000 mL
Lactose Broth	0.39 g
0.25 M Potassium Phosphate Monobasic	2 mL

Dissolve the solids shown in the table above in the DI water and adjust the pH to about 6.9 – 7.0 using about 0.1 N sodium hydroxide.

Preparation of Challenge Suspension:

The methods used for preparing the various challenge solutions used in the examples described below and detailed as follows.

Preparation of Challenge Suspension of *B. diminuta*:

About Two days prior to preparing the challenge suspension thaw a cryogenically frozen *B. diminuta* strain and inoculate one TSB tube with the stock suspension. Incubate at about 30 °C ± 2 °C for about 24 hours. About Twenty-four hours before the test challenge inoculate appropriate amount of SLB with 1 mL of *B. diminuta* seed culture per liter of SLB. Incubate at about 30 °C ± 2 °C for about 24 hours. On the day of preparing challenge suspension, allow TSA plates to warm to room temperature prior to use. Aseptically remove an aliquot of the SLB culture and determine density via optical density or epifluorescence.

Based on the determined density of the SLB culture, prepare a suspension of about 1 x 10^8 cfu/ L organisms with the General test Water. Remove a 10-mL aliquot from the challenge suspension and set aside for density verification.

Preparation of Challenge Stock MS-2:

All stocks to be grown by a method described by Smith and Gerba (1982, in Methods in Environmental Virology, pp. 15-47) and purified by the procedure of Sharp, *et al.* (1975, Applied Microbiology, 29:94-101), or similar

procedure (Berman and Hoff, 1984, Applied Environmental Microbiology, 48:317-323), as these methods will produce largely monodispersed virion particles, the disclosure of each is herein incorporated by reference to the extent not inconsistent with the present disclosure.

About Two days prior to preparing the challenge suspension thaw a cryogenically frozen *E. coli* (ATCC # 15597) sample and inoculate one TSB tube with the stock suspension. Incubate at about 35 °C ± 2 °C for about 18 hours without shaking. Inoculate another TSB tube with culture from (a) and incubate for about six (6) hours at about 35 °C ± 2 °C with shaking to obtain fresh cultures. After these steps, thaw and dilute stock MS-2 and serially dilute in Tris-buffered saline to approximate concentrations of 10^5 pfu/ml. Add about 0.1 ml of MS-2 phage dilution and 1 ml *E. coli* culture to tubes of molten overly agar (TSB with about 1% agar) and mix. After mixing, pour mixture into petri dishes containing TSA and incubate for about 18-24 hours at about 35 °C ± 2 °C . Should confluent plaques be observed, add about 6-7 mL Tris buffer to the plates as previously prepared and allow to sit for a maximum of about 1 hour. Recover the liquid fraction and centrifuge (about 15000 xg for about 20 minutes at about 10 °C). Recover liquid fraction and filter through a 0.2 micron SterAssure membrane disc (from Cuno Incorporated, Meriden, CT.) to eliminate bacterial contamination. Recover pellet and resuspend in sterile Tris buffer. Store at about 5 °C ± 3 °C .

Addition of Tris buffer and allowing the plates to remain static for one hour allows the bacteriophage such as MS-2 to diffuse through the agar surface and into the liquid buffer for capture and transfer of the bacteriophage from the agar surface to the test tubes as the concentrated stock solution from which all bacteriophage injections will be made during seeded injections into the test filters.

Preparation of Challenge suspension of MS-2:

On the day of preparing the challenge suspension, inoculate the appropriate amount of sterile Trizma base (amount to be determined during validation) with an appropriate amount (amount to be determined during validation) of MS-2 seed culture per liter of Tris. Store at about 23 °C ± 1 °C. Allow TSA plates to warm to room temperature (range for room temp) prior to use. Aseptically remove an aliquot of the culture and determine density via optical density or epifluorescence. After these steps, vortex and dilute the cell suspension with the appropriate Test

Water to obtain a minimum suspension target of about 1 x 10^7 cfu / L. Remove about a 10-mL aliquot from the challenge suspension and set aside for density verification.

Determination of the concentration of the challenge organism

This determination was based upon the unit flow rates, injection feed pump rate, suspension density, and the final challenge organism concentration for the unit challenge. The suspension will have to be of adequate volume to deliver the challenge organism to two complete ON/OFF cycles at each sample point.

For example, for a unit flow rate of about 1.0 gallon per minute (gpm) and a duplicate unit tested so a total of about 2.0 gpm (7,560 mL/min) would be required. When the injection rate is about 10 mL/min and the suspension density is about 1 x 10^9 / mL, the final concentration would be about 7.0 x 10^4 / mL. The ON/OFF cycle could be 10 min ON / 10 min OFF (20 minutes ON for two complete cycles).

Density Determination of *B. diminuta*

Make appropriate serial dilutions using sterile SDBW. Plate appropriate (10^0 – 10^{-5}) dilutions in duplicate on TSA plates. Invert and incubate at about 35 °C ± 0.5 °C for about 48 hours. After incubation, enumerate plates containing about 30-300 distinct colony forming units (cfu) using a Colony Counter. Calculate the density of the *B. diminuta* suspension by multiplying the number of CFU obtained by the inverse of the dilution factor. Express results as the number of CFU / L.

Density Determination of MS-2

Make serial dilutions (10^0 – 10^{-4}) using sterile SDBW. Plate (10^0–10^{-5}) dilutions in duplicate on TSA plates using *E. coli* as the host organism. Invert and incubate at about 35 °C ± 0.5 °C for about 48 hours. After incubation, enumerate plates containing 30-300 distinct plaque forming units (pfu) using a Colony Counter. Calculate the density of the MS-2 suspension by multiplying the number of PFU obtained by the inverse of the dilution factor. Express results as the number of PFU / L

Analysis of negative control, influent and effluent samples

Negative Control

Plate is heated to about 10^0 of each bacterial strain in duplicate on TSA for *B. diminuta*. Invert and incubate at about 35 °C ± 0.5 °C for about 24 hours. Plate 10^0 the viral strain in triplicate on TSA using *E. coli* (ATCC # 15597) as the host bacteria for the MS-2 bacteriophage. Incubate at about 35 °C ± 0.5 °C for about 24 hours.

B. diminuta

Influent samples

Make serial dilutions of the influent samples (10^0 – 10^{-4}) using sterile SDBW. Plate 10^0 – 10^{-5} dilutions in duplicate on TSA plates. Invert and incubate at about 35 °C ± 0.5 °C for about 48 hours. After incubation, enumerate plates containing 30 – 300 distinct colony forming units (CFU) using a Colony Counter. Calculate the influent of the *B. diminuta* suspension by multiplying the number of CFU obtained by the inverse of the dilution factor. Express results as the number of CFU / L.

Effluent samples

Aseptically conduct the standard plate count method using a 0.20 micron membrane and plate on TSA. Invert and incubate at about 35 °C ± 0.5 °C for about 48 hours. If there is no growth present, continue to incubate for up to about 7 days. After incubation, enumerate plates containing about 20 – about 200 distinct colony forming units (CFU) using a Colony Counter. Express results as the number of CFU / L.

MS-2

The influent and effluent sample treatments are similar to *B. diminuta* except that no membrane is used in the effluent samples because plaques are not detectable on the membrane disc; membrane filtration method is not appropriate for plaque count.

Non-pathogenic bacteria commonly found in drinking water systems, also referred to as Heterotrophic Plate Counts (HPC) may interfere with *B. diminuta* analysis, as *B. diminuta* is part of the broad classification of organisms contained

within the classification 'HPC'; it is required to eliminate HPC interference to avoid false positive results.

Results

Following incubation, count colonies on all of the influent sample plates. Calculate the mean of colony forming units (cfu) per L for plates with 30 – 300 colonies or plaque forming units (pfu) per L for plates with 30 – 300 plaques for viruses. This is the 'N_0' value.

Following incubation, count colonies on all of the effluent sample plates. Calculate the mean of colony forming units (cfu) per L for plates with 30 – 300 colonies or plaque forming units (pfu) per L for plates with 30 – 300 plaques for viruses. This is the 'N_s' value.

Following incubation, confirm that all effluent bacterial colonies are the test organisms by Gram stain and the biochemical tests specific for *B. diminuta*. If there are no colonies on the filter(s) corresponding effluent sample(s) plate, then the Log Reduction (LR) for each test filter is approximated using the following formula:

$$LR \sim Log_{10} (N_o)$$

If there are one or more colonies on the effluent sample plate, this filter's LR is calculated from the equation:

$$LR = Log_{10} (N_o / N_s)$$

If the effluent sample plate has confluent growth, the LR cannot be determined and is recorded as such.

EXAMPLES

A general procedure for the preparation of the representative filter medium blocks used in the examples of the present disclosure is described as follows.

About 28 grams of DE is blended with about 28 grams activated carbon (Barneby & Sutcliffe, Activated Carbon Type 1184), about 16 grams of polyethylene binder (FN510 available from Equistar), about 8 grams of fibrillated polyethylene fiber (UL410 available from Minifiber), about 2 grams of polypropylene unfibrillated fibers (3DPP ¼" available from Minifiber), about 4 grams of fibrillated polyethylene fibers of smaller size (ESS-5F available from Minifiber), and about 14 grams of Pb reduction media (ATS, from Engelhard) in a uniform manner by a V-shaped blender (Littleford Day, Inc., Polyphase mixers, Model #: FM 130 DX). The components are mixed for about 30 seconds, then mixed and chopped for about 10

minutes. The blended mixture, called "flock", is fed into a standard 6" block mold via the shaking table, vibration chute and vacuum line, as would be understood by one skilled in the art. The mold is compressed (Conoflow, ITT Fluid Tech Corporation, Loomis Hydraulic Press) isopiestically to about 750 psi at about room temperature to obtain the green strength. After the compression operation, the resultant is known as a "block". The block is then oven (Lunair Limited, Gruenberg Oven, Model #: C35V31.50M) baked at about 60°C for about 1-hour, then at about 114°C for about 40-minutes. The block underwent subsequent OD (outer dimension) lathing on the Central Machinery Bench Lathe to obtain an average OD of about 1.5". Each lathed block was subsequently cut on the Rigid Saw to a length of about 6".

Impregnation of silver species onto DE.

The procedure used to impregnate the silver species into DE was as follows. The silver nitrate (available from J. T. Baker), 1.6 grams, was added to 1 liter ethanol and stirred until complete dissolution. The solution was added to 1 kg DE (Celite® 501 available from World Minerals) in a 2-liter container in a dropwise manner until incipient wetness stage was reached, while continually stirring the mixture. The impregnated Celite® 501 was transferred to a shallow tray and spread evenly so that the powder depth is about half inch. The tray with the content was rested in a fume hood, with occasional agitating the Celite® 501 powder, for a period of about 15 hours or longer until no detectable ethanol evaporation, as evidenced in Figure 9.

The contents of the tray were then transferred to a muffle furnace (Lindberg Blue M oven Model #: MO1440A-1) and then heated at about 440 °C for about 30 minutes. After cooling to room temperature, the impregnated Celite® 501 is ready for further treatment.

Modification of DE surface with octadecylaminodimethyl trimethoxysilylpropyl ammonium chloride.

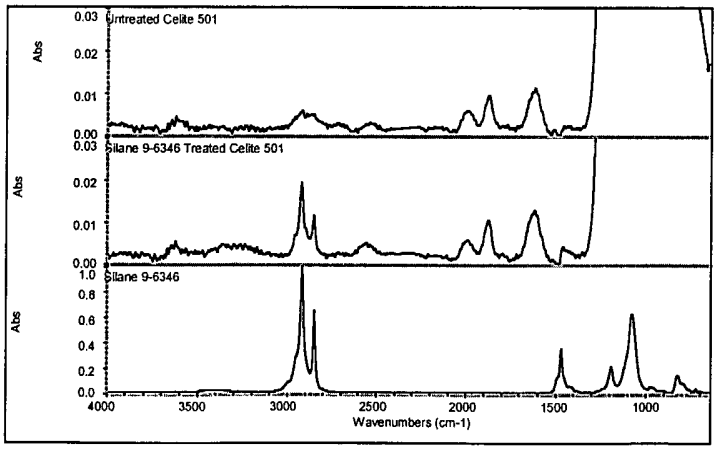
The modification of the surface of DE with octadecylaminodimethyl trimethoxysilylpropyl ammonium chloride was accomplished as follows. One hundred g of DE (Celite® 501 available from World Minerals) was weighed out into a glass beaker and a 110g water solution of 2g octadecylaminodimethyl trimethoxysilylpropyl ammonium chloride (available from Dow Corning Corporation as DC9-6346) was slowly (about 1 gram per minute) added while the beaker was

subject to slow tumbling (about 2 revolutions per second) to reach a uniform mixing and distribution of added liquid to the solid DE powders. After finishing the addition, the content was transferred to a tray and was placed in an about 80°C oven for about four hours and then about 120°C for about four hours. Longer time treatment didn't seem to affect the results. The DE was rinsed 4 times with 1L DI water in a screw-top jar and tumbled on a roller mill to ensure uniform wetting and rinsing, then the content was vacuum filtered through a Whatman paper before being placed in a about 120°C oven for about 4 hours or until the treated DE was fully dried.

The following tests demonstrate the presence of a representative modifying agent on the surface of Celite 501, even after very extensive washing of this DE, by using the example of DC9-6346 as the modifying agent.

Fourier Transform Infra-Red (FTIR) Spectroscopy

FTIR spectra of untreated and DC9-6346 treated DE are shown below:



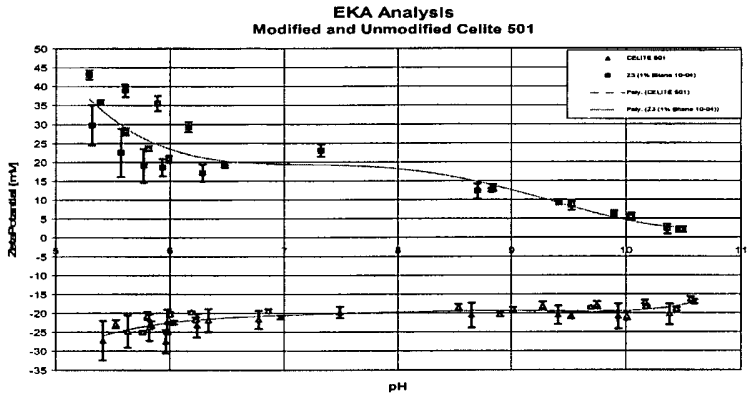
The top and the middle spectra show the untreated Celite 501 and the DC9-6346 treated Celite 501. Both spectra show strong Si-O bands at about 1070 & 790 cm^{-1} as well as smaller bands at about 1990, about 1870, & about 1620 cm^{-1}. The spectra of the silane treated Celite 501 also displays aliphatic bands at about 2920 & about 2850 cm^{-1} not present in the untreated Celite 501 spectrum.

The bottom spectrum is DC9-6346. The absorption bands at about 2920 & about 2850 cm^{-1} seen in the treated Celite 501 spectrum (but not in the untreated Celite 501 spectrum) match up well with similar bands in the spectrum of DC9-6346.

An absorption band at about 1460 cm^{-1} in the spectrum of the DC9-6346 treated Celite 501 (but not in the untreated Celite 501 spectrum) is close, but not an exact match, to a band at about 1470 cm^{-1} in the spectrum of the DC9-6346.

Zeta potential

Zeta potential of this study was conducted with Electro Kinetic Analyzer (EKA) from Anton Paar. For the untreated and DC9-6346 treated Celite 501, the difference is that the treated DE possesses positive charge even when the pH is as high as about 10. The untreated DE has a negative zeta potential in the pH range of about 5.5 to about 10.5.



Each DC9-6346 treated DE has been washed extensively to remove any free silane molecules. One such washing method is to wash about 50 grams of treated DE with about 0.8 liters of water followed by about 0.2 liters of a water rinse after filtration. The table below shows that after 5 sequential washes, the silane concentration is below the limit of quantitation (<0.40 mg/L).

Sample ID	Nitrogen (mg/L)
1st liter rinse	4.3
2nd liter rinse	3.2
3rd liter rinse	0.63
4th liter rinse	0.56
5th liter rinse	<0.40
6th liter rinse	<0.40
7th liter rinse	<0.40
DI water control	N.D.

Modification of DE with a linker and Solfix E.

The modification of the surface of DE with a linker and Solfix E was accomplished as follows. One hundred g of DE (Celite® 501 available from World Minerals) was weighed out into a glass beaker and about 110g water solution of about 1.2 g 3-aminopropyltriethoxysilane (available from Gelest, Inc.) was slowly (about 1 gram per minute) added while the beaker was subject to slow tumbling (about 2 revolutions per second) to reach a uniform mixing and distribution of added liquid to the solid DE powders. After finishing the addition, the content was transferred to a tray and was placed in an about 115°C oven for about four hours. Longer time treatment didn't seem to affect the results. The treated DE was rinsed 4 times with about 1L DI water in a screw-top jar and tumbled on a roller mill to ensure uniform wetting and rinsing, then the content was vacuum filtered through a Whatman paper before being placed in an about 115°C oven for about 4 hours or until the treated DE was fully dried. A caustic Solfix E (available as 20% concentration from Ciba Specialty Chemicals, Inc.) solution was prepared by dissolving about 33.75 g 20% Solfix E and about 33.75 g 5N NaOH into about 575 g DI water and mixed well. The resulted Solfix E solution was added to the previously treated DE in a similar manner. After washing, the content was transferred to a tray and dried as before.

It is believed that a range of anionic counter ion to the catatonically modified DE may be used, where an anion is defined as an atom or a group of atoms that possess a net negative charge.

Once the preparatory work described above that is required to conduct the experiments was completed, the feasibility of the new and innovative filter media was tested. The procedures followed during the conduct of these experiments are discussed below in Examples 1-3.

Example 1: Antimicrobial reduction test with unmodified filter media

A representative filter block that was composed of about 28% AC, about 28% unmodified DE, about 16% polyethylene binder FN510, about 8% polyethylene fiber UL410, about 2% polypropylene fiber 3DPP ¼", about 4% polyethylene ESS-5F, and about 14% ATS. The block was fitted into a filter housing

with a fluid inlet and a fluid outlet to constitute a filter device similar to those filter devices used in water filtration applications.

The filter device was then tested as per the USEPA Guide Standard and Test Protocol (1987), the disclosure of which is hereby incorporated by reference.

The 20 gallon challenge test water made with unfiltered tap water was refrigerated overnight. Residual chlorine was left in the tank to inhibit bacterial growth during the overnight cool down. The general test water was made with tap water filtered by an Aqua Pure™ AP117 chlorine reduction filter available from Cuno, Inc. Both tanks were tested for total chlorine by a Hach™ DR/700 Colorimeter with the AccuVac™ DPD Total Chlorine Reagent. If the total chlorine was greater or equal to about 0.02 mg/L, about 3% sodium thiosulfate solution (w/v) was added to each tank (about 0.1 mL of about 3% sodium thiosulfate per about 1200 mL of water). After the agitation, the tanks were then resampled and retested for total chlorine. Sodium thiosulfate was added, as stated above, until the total chlorine was below about 0.02 mg/L.

During the course of the test, MS-2 (ATCC 15597-B1) was used to seed the general test water tank to a concentration of about 10^6 PFU/mL, and Klebsiella terrigena (ATCC-33257) was used to seed the water tank to a concentration of about 10^8/l. (The following table shows the result of this example:

Time	Influent concentration (pfu/l)	Effluent concentration (pfu/l)	Log reduction value
Day 1	1.0E+07	1.04E+05	2.0
Day 3	1.45E+07	7.35E+05	1.3
Day 6	1.44E+07	1.22E+06	1.1

As can be seen from the results, the influent challenge of the bacteriophages has been maintained in the specified concentrations of approximately 1.0E+07 pfu/l; this is referred to as the 'N_o' value. The effluent concentration, or the concentration of the bacteriophage MS2 detected in the water exiting the filter, is shown to be between 1.5E+05 pfu/l and 1.22E+06 per l; these would be referred to as the 'N_s' values. As described previously in this disclosure the log of the ratio of the influent concentration N_o to the effluent concentration N_s is the Log Reduction Value (also referred to as the 'LRV') as shown in the above table; this is the direct measure of the viral reduction capability of the filter. According to the calculation detailed earlier in this disclosure, there was a reduction of from about 1 to about 2 log of the bacteriophage MS-2 in the general test water environment utilizing just the filter block alone without any modifications thereto. This is insufficient to address the viral

reduction requirements as prescribed by the EPA Protocol, as one point in the test was two orders of magnitude below the minimum four-log viral reduction requirement.

Example 2 Antimicrobial reduction test with modified filter media

A filter block that was composed of the same ingredients as used in Example 1 except that DE was modified based on the methods described above. The results are illustrated utilizing the bacteriophage MS-2 as the test organism seeded into the general test water environment in the following table:

Time	Influent concentration (pfu/l)	Effluent concentration (pfu/l)	Log reduction value
Day 1	1.00E+07	1.0E+02	5
Day 3	1.45E+07	<1.0E+02	>5
Day 6	1.44E+07	<1.0E+02	>5

As can be seen from the results, the influent challenge of the bacteriophages into the filtration system has been maintained in the specified concentrations of approximately 1.0E+07 pfu/l; this is referred to as the 'N_0' value. The effluent concentration, or the concentration of the bacteriophage MS2 detected in the water exiting the filter, is shown to be non detectable (less than about 100 pfu/l, which is the limit of detection using this protocol), up to about 100 pfu/l; these would be referred to as the 'N_s' values. As described previously in this disclosure, since the effluent MS-2 level is too low to be adequately quantified by this method, the log of the influent concentration N_0 can be approximated as the Log Reduction Value (also referred to as the 'LRV') as shown in the above table; this is the direct measure of the viral reduction capability of the filter. According to the calculation detailed earlier in this disclosure, there was a reduction of greater than four logs of the bacteriophage MS-2 in the seeded general test water environment utilizing just the modified filter block. The modifications in the filter block as described in this disclosure have generated a significantly greater viral reduction when compared to an unmodified block.

Example 3 Antimicrobial reduction test with modified filter media wrapped with a 0.2μ nylon membrane

A filter block that was composed of the same ingredients as used in Example 2 except that a pleated 0.2μ nylon membrane was used to wrap around the filter block. The test results are shown in the following table:

Time	Influent concentration (pfu/l)	Effluent concentration (pfu/l)	Log reduction value
Day 1	1.00E+07	1.00E+02	5
Day 3	1.45E+07	4.00E+02	4.6
Day 6	1.44E+07	<1.00E+02	>5

As can be seen from the results, the influent challenge of the bacteriophages into the filtration system has been maintained in the specified concentrations of approximately 1.0E+07 pfu/l; this is referred to as the 'N_0' value. The effluent concentration, or the concentration of the bacteriophage MS2 detected in the water exiting the filter, is shown to be non detectable (less than about 10 pfu/l, which is the limit of detection using this protocol); these would be referred to as the 'N_s' values. As described previously in this disclosure, when the effluent MS-2 level is too low to be adequately quantified by this method, the log of the influent concentration N_0 can be approximated as the Log Reduction Value (also referred to as the 'LRV') as shown in the above table; this is the direct measure of the viral reduction capability of the filter. According to the calculation detailed earlier in this disclosure, there was a reduction of greater than four logs of the bacteriophage MS-2 in the seeded general test water environment utilizing just the modified filter block. The modifications in the filter block as described in this disclosure have generated a significantly greater viral reduction when compared to an unmodified block.

It is further believed that the use of a the use of a pre-filtration membrane stage having a porosity smaller, equal, or slightly greater than the porosity of the carbon block (with or without modifications) can mechanically remove a significant fraction of the colloidal contamination such as test dust and certain types of sparingly soluble humic acids, reduce the contaminant load on the fine pore structures of the carbon block, and generate an overall increase in the available surface area of the carbon block towards viral reduction.

As should be clear to those skilled in the art from the above, the modifications of the representative filter block as described to the present disclosure, results and a significant reduction of microbes from the representative fluid, water. As would most likely be a understood by one skilled in the art, similar results would most likely be expected would removing microbes from gases, such as, for example air. While specific experiments designed to verify removal of microbes from gas such as air have not yet been completed, it is anticipated that microbial reduction achieved utilizing the principals described above would be proven.

While the articles, apparatus and methods for making the articles contained herein constitute preferred embodiments of the disclosure, it is to be understood that the disclosure is not limited to these precise articles, apparatus and methods, and that changes may be made therein without departing from the scope of the disclosure which is defined in the appended claims.

What is claimed is:

1. A separation media for fluids comprising:

a base mixture of organic and inorganic components, the base mixture comprising at least one anti-microbial component; and at least one component of the base mixture comprising a charge-modified group covalently bonded to the surface of the at least one anti-microbial component.

2. The separation media of claim 1 wherein the charge-modified group covalently bonded to at least one component of the base mixture is selected from the group comprising:

charge-carrying monomers, charge-carrying macromolecules, charge-carrying polymers and mixtures thereof.

3. The separation media of claim 2 wherein, the charge-modified group contains a functional group selected from the group comprising:

alkoxy, azeridinium, epoxy, reactive hydrogens, and mixtures thereof.

4. The separation media of claim 2 wherein, the base mixture is selected from the group comprising:

diatomaceous earth, activated carbon, polymers, perlite, porous and non-porous ceramic materials, glass fibers, glass spheres, and combinations thereof.

5. The separation media of claim 1 wherein, the covalently bonded charge-modifying group is permanently associated with at least one component of the base mixture.

6. The separation media of claim 1 wherein, the anti-microbial component has a positive zeta potential at pH from about 5 to about 9.

7. The separation media of claim 2 wherein, the molecular mass of charge-carrying monomers, charge-carrying macromolecules, and charge-carrying polymers is less than about 5,000.

8. The separation media of claim 1 wherein, the base mixture includes a polymer of olefin, or polymer having functional groups of $-NH_2$, -OH, -NH, C=O, -C(=O)-O-, and combinations thereof.

9. The separation media of claim 8 wherein, the polymers are selected from the group comprising:

cellulose, nylon, polyester, polyurethane, modified polyethylene and polypropylene, and combinations thereof.

10. The separation media of claim 2 wherein, the charge-carrying monomer comprises: an organo-silane having alkoxy groups having the following formula:

$A_1A_2A_3SiC_pH_{2p}B^{\oplus}(C_lH_{2l+1})\ (C_mH_{2m+1})\ (C_nH_{2n+1})X^{\ominus}$;

wherein A_1, A_2, and A_3 are independently $C_rH_{2r+1}O$ or OH, where r is in the range of 1 to 5, p is in the range of 1 and 10, B comprises nitrogen or phosphorus, *l*, *m*, and *n* are individually in the range of 1 and 32, and $X^{\ominus}$ is an anion, selected from the group comprising:

Cl, Br, I, NO_3, OH, ClO_3, SO_3, SO_4, MnO_4, PF_6, or BF_4, and combinations thereof.

11. The separation media of claim 2 wherein, the charge-carrying monomer comprises an organo-silane having an alkoxy group according to the following formula:

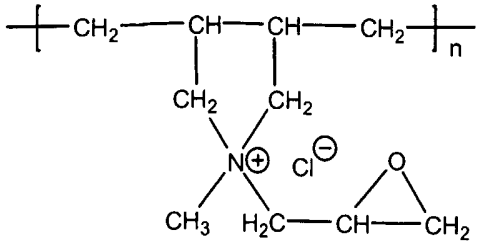
$A_1A_2A_3SiC_pH_{2p}N^{\oplus}(C_5H_5)\ X^{\ominus}$;

wherein A_1, A_2, and A_3 are independently $C_rH_{2r+1}O$ or OH, r is in the range of 1 to 5, p is in the range of 1 to 30, $N^{\oplus}(C_5H_5)$ is a pyridinium group, and X is Cl, Br, I, NO_3, ClO_3, SO_3, SO_4, MnO_4, PF_6, or BF_4 and combinations thereof.

12. The separation media of claim 2 wherein, the at least one charge-carrying macromolecule has branch structure including a plurality of terminals.

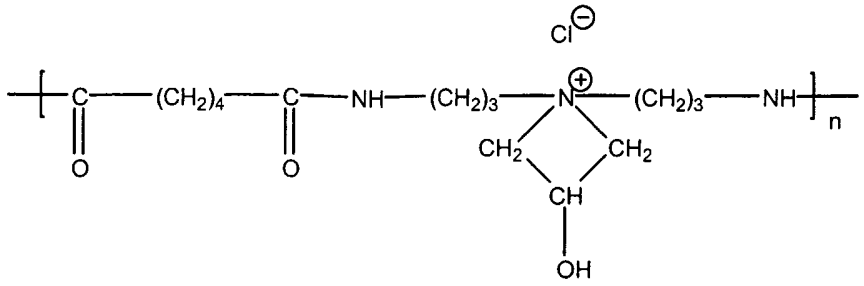
13. The separation media of claim 2 wherein, the at least one of the charge carrying macromolecules includes a quaternary ammonium or phosphonium group operatively connected to one or more of the branch terminals.

14. The separation media of claim 2 wherein, the at least one of the charge carrying macromolecules includes the following repeat unit:



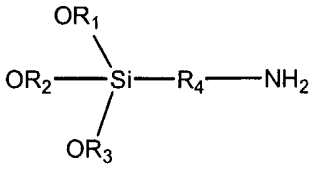
where n is between about 5 and about 24.

15. The separation media of claim 2 wherein, the at least one of the charge carrying macromolecules includes the following repeat unit:



where n is between about 5 and about 16.

16. The separation media of claim 2 wherein, the charge carrying macromolecules includes a linking molecule according to the following structure for covalently bonding to at least one component of the base mixture:



where, R_1, R_2, and R_3 are H's or C_1 to C_5 alkyl groups, R_4 is an aliphatic or aromatic hydrocarbon chain, or the combination of the two, or amino-aliphatic chain, with carbon atoms up to 30.

17. The separation media of claim 1 wherein, the base inorganic component further comprises:

a compound selected from the group comprising:

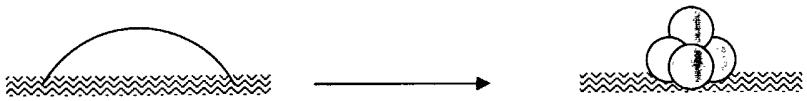
a single transition metal compound or mixtures of transition metal compounds, incorporated therewith by an incipient-wetness impregnation method.

18. The separation media of claim 17 wherein, the transition metal compound includes transition metal oxide, halide, and sulfide.

19. The separation media of claim 17 wherein, the transition metal compound includes:

Ag_2O, AgO, Ag_2S and AgCl.

20. The separation media of claim 17 wherein, at least one of the transition metal compounds is dissolved in a solvent having an equal or a lower surface tension than water.



Prior Art

Figure 1

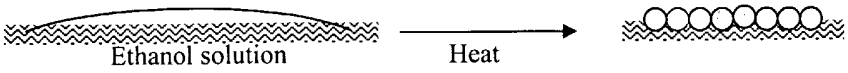
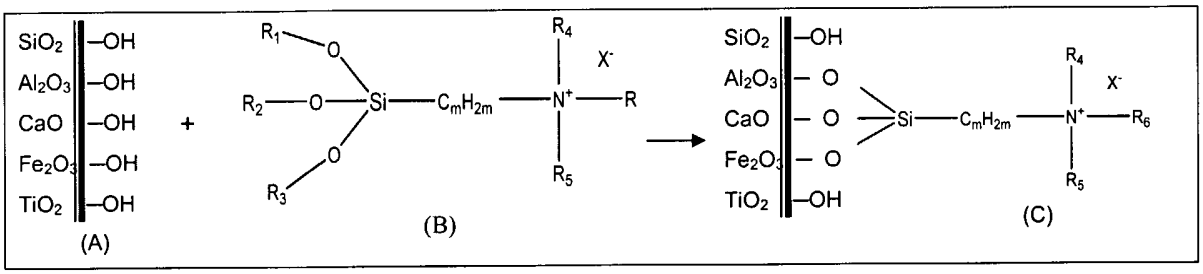


Figure 2



where, m = 1 to 10;
R_1, R_2, R_3 are hydrogen or alkyl groups with 1 to 5 carbon atoms;
R_4, R_5, R_6 are alkyl groups with at least one of them with 5 to 25 carbon atoms;
$X^{\ominus}$ is a counter anion, such as $Cl^{\ominus}$ or $Br^{\ominus}$.

Figure 3

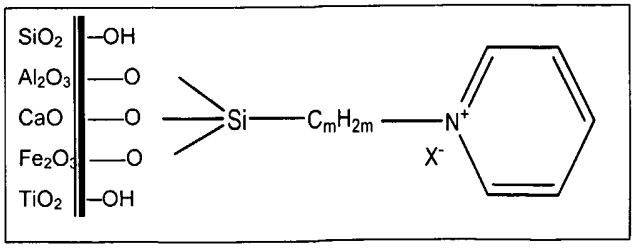


Figure 4

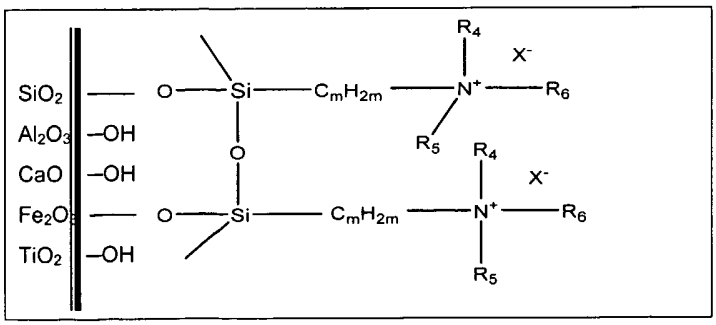


Figure 5

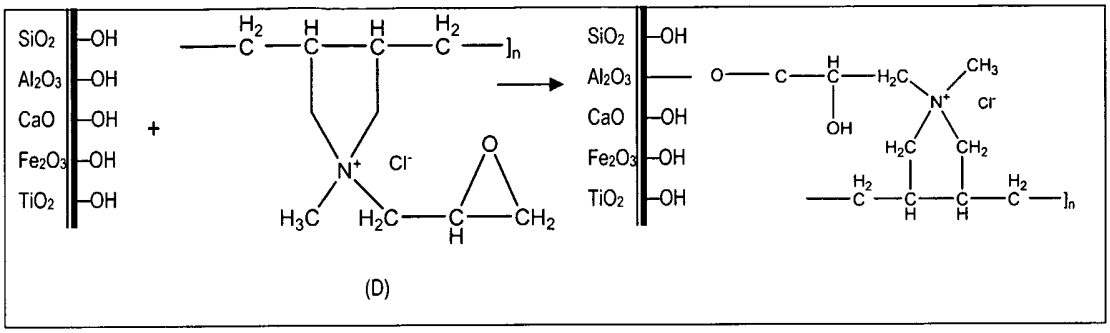
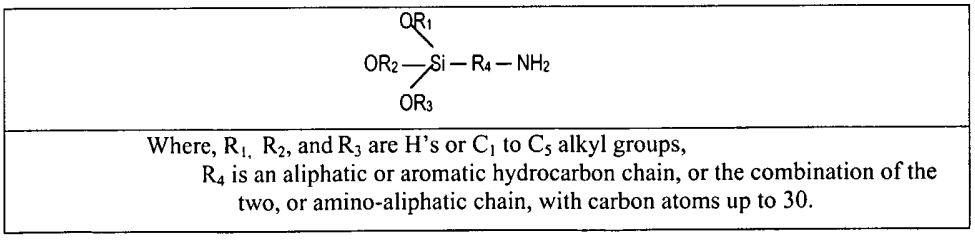


Figure 6



Where, R_1, R_2, and R_3 are H's or C_1 to C_5 alkyl groups,
R_4 is an aliphatic or aromatic hydrocarbon chain, or the combination of the two, or amino-aliphatic chain, with carbon atoms up to 30.

Figure 7

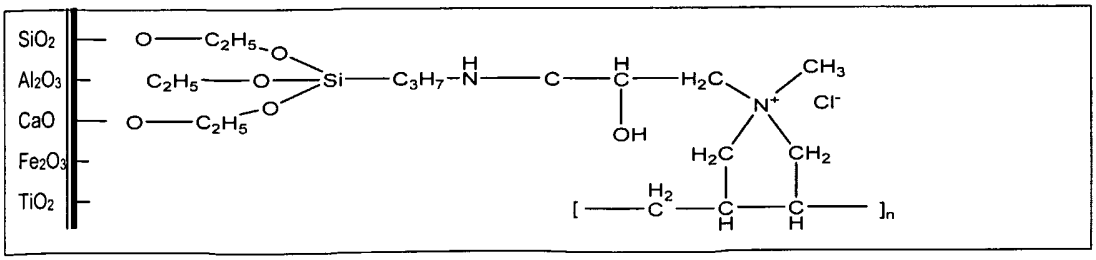


Figure 8

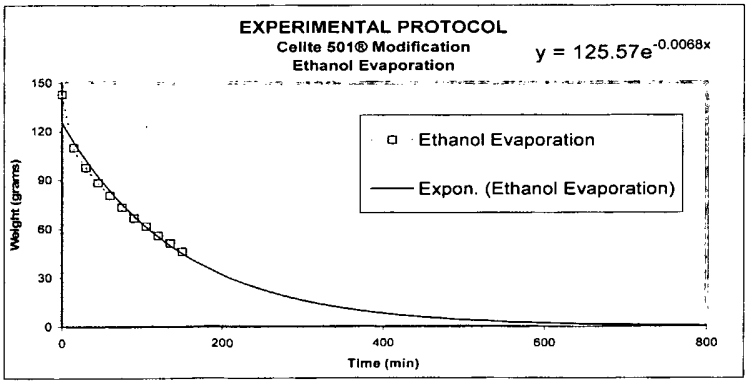

EXPERIMENTAL PROTOCOL
Celite 501® Modification
Ethanol Evaporation
y = 125.57e-0.0068x
Ethanol Evaporation
Expon. (Ethanol Evaporation)
Weight (grams)
Time (min)
150
120
90
60
30
0
0
200
400
600
800

Figure 9

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2005/009812

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C02F1/50 C02F1/28

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)
IPC 7 C02F A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 185 415 A (KAWABATA ET AL) 9 February 1993 (1993-02-09) column 4, line 8 - column 5, line 31	1-20
X	US 5 849 311 A (SAWAN ET AL) 15 December 1998 (1998-12-15) column 2, line 20 - column 13, line 58	1-20

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in 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 document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"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
4 July 2005	12/07/2005

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Liebig, T

Form PCT/ISA/210 (second sheet) (January 2004)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2005/009812

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KANAZAWA A ET AL: "POLYMERIC PHOSPHONIUM SALTS AS A NOVEL CLASS OF CATIONIC BIOCIDES. X. ANTIBACTERIAL ACTIVITY OF FILTERS INCORPORATING PHOSPHONIUM BIOCIDES" JOURNAL OF APPLIED POLYMER SCIENCE, JOHN WILEY AND SONS INC. NEW YORK, US, vol. 54, no. 9, 28 November 1994 (1994-11-28), pages 1305-1310, XP000511828 ISSN: 0021-8995 the whole document	1,13
A	EP 0 296 441 A (HENKEL KOMMANDITGESELLSCHAFT AUF AKTIEN) 28 December 1988 (1988-12-28) the whole document	1-20
A	EP 0 832 561 A (EASTMAN KODAK COMPANY) 1 April 1998 (1998-04-01) the whole document	1-20
A	WORLEY S D ET AL: "Biocidal Polymers" TRENDS IN POLYMER SCIENCE, ELSEVIER SCIENCE PUBLISHERS B.V. AMSTERDAM, NL, vol. 4, no. 11, November 1996 (1996-11), pages 364-370, XP004069690 ISSN: 0966-4793 the whole document	1-20

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US2005/009812

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5185415 A	09-02-1993	JP 2814266 B2	22-10-1998
		JP 3047536 A	28-02-1991
		US RE34740 E	27-09-1994
		DE 69024547 D1	15-02-1996
		DE 69024547 T2	01-08-1996
		EP 0408292 A2	16-01-1991
		ES 2084002 T3	01-05-1996
US 5849311 A	15-12-1998	AU 723898 B2	07-09-2000
		AU 5088898 A	22-05-1998
		CA 2270258 A1	07-05-1998
		EP 0939591 A1	08-09-1999
		JP 2001508041 T	19-06-2001
		TW 381029 B	01-02-2000
		WO 9818330 A1	07-05-1998
		US 6264936 B1	24-07-2001
EP 0296441 A	28-12-1988	DE 3720555 A1	05-01-1989
		EP 0296441 A2	28-12-1988
		JP 1091782 A	11-04-1989
		ZA 8804416 A	22-12-1988
EP 0832561 A	01-04-1998	AU 736967 B2	09-08-2001
		AU 3158697 A	05-02-1998
		CA 2207168 A1	30-01-1998
		DE 69719892 D1	24-04-2003
		DE 69719892 T2	04-12-2003
		DK 832561 T3	12-05-2003
		EP 0832561 A2	01-04-1998
		JP 10087405 A	07-04-1998
		US 5855899 A	05-01-1999