

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
10 July 2008 (10.07.2008)

PCT

(10) International Publication Number  
**WO 2008/083263 A1**

(51) International Patent Classification:  
*C02F 1/76* (2006.01)

(21) International Application Number:  
PCT/US2007/089013

(22) International Filing Date:  
28 December 2007 (28.12.2007)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
11/617,318 28 December 2006 (28.12.2006) US

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(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM,

AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, 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, LV, MC, MT, 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).

**Declarations under Rule 4.17:**

- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
- *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*
- *of inventorship (Rule 4.17(iv))*

**Published:**

- *with international search report*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

(54) Title: ANTIMICROBIAL COMPOSITION

(57) Abstract: An antimicrobial composition prepared by mixing a polymer-ammonium salt formulation comprising one or more polymers and one or more ammonium salts with alkali and a chlorine source in a molar ratio of chlorine (as Cl<sub>2</sub>) to ammonium ion of about 1:10 to about 10:1 and methods of using the composition to control biofouling of aqueous systems.



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## ANTIMICROBIAL COMPOSITION

## TECHNICAL FIELD

5           This invention relates to compositions used in biofouling control in industrial water systems. More specifically, this invention relates to a biocidal composition prepared by mixing a formulation comprising one or more polymers and one or more ammonium salts with alkali and a chlorine source and use of the composition in biofouling control in industrial water systems.

## 10   BACKGROUND OF THE INVENTION

          Chlorine is commonly used in aqueous systems for controlling the growth of microorganisms. For example, in papermaking processes, chlorine is a preferred halogen biocide due to its low cost, broad spectrum and fast biocidal activity, and convenience of monitoring and  
15   control. However, use of chlorine also results in increased corrosion of system components, degradation of felts, destruction of other water treatment additives, and negative impacts on paper-making additives such as dyes and brighteners.

          To improve the biocidal properties of chlorine, particularly against biofilm and filamentous organisms, and to decrease the negative impact of chlorine use, free chlorine can be  
20   stabilized using nitrogenous compounds to form chloramines. Chloramine formation and chloramine's properties as a disinfectant have been known since the early 1900's, and the relative reaction rates of chlorine with amine-containing compounds versus ammonia were studied more than 50 years ago (Weil, I. and J.C. Morris. 1949. "Kinetic Studies on the Chloramines. The Rates of Formation of Monochloramine, N-Chlormethylamine and N-Chlordimethylamine." J. Amer.  
25   Chem. Soc. 71:1664). Chloramines are also approved and widely used for potable water distribution systems (United States Environmental Protection Agency. 1999. Alternative Oxidants and Disinfectants Manual, Chapter 6. EPA publication number 815-R-99-014).

          The use of ammonium salts as practical compositions for stabilizing chlorine has also been known for many years. For example, Beck (J. Beck *et al.*, Aqua I, 25-33, 1986) describes  
30   the use of pre-formed monochloramine for the post-disinfection of drinking water. In this work, chloramines are formed by mixing ammonium sulfate and hypochlorite solution at a concentration of 1000 ppm and adjusting the pH to 7.5 before the point of dosage to avoid carbonate precipitation. This is typical of chloramines applications, in which the usual ammonium ion sources are ammonia, ammonium chloride and ammonium sulfate.

Additional examples of using chloramines to control biofouling include U.S. Patent 4,988,444, which describes the use of chloramines to prevent microbial fouling on reverse osmosis membranes, U. S. Patent 6,773,607 which describes using chloramine formed in ballast water by adding aqueous ammonia or an ammonium salt, and sodium or calcium hypochlorite to the ballast water and U.S. Patents 5,976,386, 6,132,628, 6,478,973 and 7,067,063, and references cited therein which disclose mixing an oxidant, preferably an active chlorine donor and still more preferably sodium hypochlorite and an ammonium salt, preferably chosen among halides, sulfates and nitrates, and adding the biocidal concentrate immediately to the aqueous system to be treated.

## SUMMARY OF THE INVENTION

This invention is an antimicrobial composition prepared by mixing an aqueous polymer-ammonium salt formulation comprising one or more polymers and one or more ammonium salts with a chlorine source in a molar ratio of chlorine (as  $\text{Cl}_2$ ) to ammonium ion of about 1:10 to about 10:1 and sufficient alkali to result in a composition which exhibits effective antimicrobial activity in a system being treated.

In another aspect, this invention is a method of inhibiting the growth of microorganisms in an aqueous system comprising treating the system with an antimicrobial composition prepared by mixing an aqueous polymer-ammonium salt formulation comprising one or more polymers and one or more ammonium salts with a chlorine source in a molar ratio of chlorine (as  $\text{Cl}_2$ ) to ammonium ion of about 1:10 to about 10:1 and sufficient alkali to result in a composition which exhibits effective antimicrobial activity in a system being treated.

The composition of this invention comprises a mixture of polymer, free chlorine and stable chloroamines. This invention, therefore, allows for the selection of polymers in order to obtain a known property or performance in water treatment or papermaking applications derived from the polymers in addition to the biocidal properties of the composition.

## DETAILED DESCRIPTION OF THE INVENTION

As used herein, "anionic monomer" means a monomer as defined herein which possesses a net negative charge. Representative anionic monomers include acrylic acid, and it's salts, including, but not limited to sodium acrylate, and ammonium acrylate, methacrylic acid, and it's salts, including, but not limited to sodium methacrylate, and ammonium methacrylate, 2-acrylamido-2-methylpropanesulfonic acid (AMPS), the sodium salt of AMPS, sodium vinyl sulfonate, styrene sulfonate, maleic acid, and it's salts, including, but not limited to the sodium salt, and ammonium salt, sulfonate itaconate, sulfopropyl acrylate or methacrylate or other water-soluble forms of these or other polymerisable carboxylic or sulphonic acids. Sulfomethylated acrylamide, allyl sulfonate, itaconic acid, acrylamidomethylbutanoic acid, fumaric acid, vinylphosphonic acid, vinylsulfonic acid, allylphosphonic acid, sulfomethylated acrylamide, phosphonomethylated acrylamide, and the like.

"Anionic polymer" means a polymer having an overall negative charge above a certain pH range. The anionic polymer is prepared by vinyl addition polymerization of one or more anionic monomers or by copolymerization of one or more anionic monomers with one or more nonionic, cationic or Zwitterionic monomers. Preferred anionic polymers include polymers and copolymers of acrylic acid, methacrylic acid, acrylamidomethylpropane sulfonic acid, N-vinyl formamide and acrylamide.

"Cationic Monomer" means a monomer as defined herein which possesses a net positive charge. Representative cationic monomers include dialkylaminoalkyl acrylates and methacrylates and their quaternary or acid salts, including, but not limited to, dimethylaminoethyl acrylate methyl chloride quaternary salt (DMAEA-MCQ), dimethylaminoethyl acrylate methyl sulfate quaternary salt, dimethylaminoethyl acrylate benzyl chloride quaternary salt (DMAEA-BCQ), dimethylaminoethyl acrylate sulfuric acid salt, dimethylaminoethyl acrylate hydrochloric acid salt, diethylaminoethyl acrylate, methyl chloride quaternary salt, dimethylaminoethyl methacrylate methyl chloride quaternary salt (DMAEM-MCQ), dimethylaminoethyl methacrylate methyl sulfate quaternary salt, dimethylaminoethyl methacrylate benzyl chloride quaternary salt, dimethylaminoethyl methacrylate sulfuric acid salt, dimethylaminoethyl methacrylate hydrochloric acid salt, diethylaminoethyl methacrylate methyl chloride quaternary salt, dimethylaminoethyl methacryloyl hydrochloric acid salt, dialkylaminoalkylacrylamides or methacrylamides and their quaternary or acid salts such as acrylamidopropyltrimethylammonium chloride, dimethylaminopropyl acrylamide methyl sulfate quaternary salt, dimethylaminopropyl

acrylamide sulfuric acid salt, dimethylaminopropyl acrylamide hydrochloric acid salt, methacrylamidopropyltrimethylammonium chloride, dimethylaminopropyl methacrylamide methyl sulfate quaternary salt, dimethylaminopropyl methacrylamide sulfuric acid salt, dimethylaminopropyl methacrylamide hydrochloric acid salt, and diallyldialkylammonium  
 5 halides such as diallyldiethylammonium chloride and diallyldimethyl ammonium chloride (DADMAC).

“Cationic polymer” means a polymer having an overall positive charge. The cationic polymer is typically prepared by vinyl addition polymerization of one or more cationic monomers, by copolymerization of one or more cationic monomers with one or more nonionic  
 10 monomers, or by polymerization of the cationic monomers with one or more anionic monomers and optionally one or more nonionic monomers or zwitterionic monomers to produce an amphoteric polymer.

While the polymer may be formed initially as a cationic polymer, it is also possible to react certain non-ionic vinyl addition polymers to subsequently produce cationically charged  
 15 polymers. Polymers of this type include those prepared through the reaction of polyacrylamide with dimethylamine and formaldehyde to produce a Mannich derivative.

“Monomer” means a polymerizable allylic, vinylic or acrylic compound. The monomer may be anionic, cationic, nonionic or Zwitterionic. Vinyl monomers are preferred, acrylic monomers are more preferred.

“Nonionic monomer” means a monomer as defined herein which is electrically neutral. Representative non-ionic, water-soluble monomers include acrylamide, methacrylamide, *N*-methylacrylamide, *N,N*-dimethylacrylamide, *N,N*-diethylacrylamide, *N*-isopropylacrylamide, *N*-vinylformamide, *N*-vinylmethylacetamide, *N*-vinylacetamide, *N*-methyl-*N*-vinylacetamide, dimethylhydroxypropyl (meth)acrylate, hydroxyethyl methacrylate, hydroxyethyl acrylate,  
 20 hydroxypropyl acrylate, hydroxypropyl methacrylate, *N*-*t*-butylacrylamide, *N*-methylolacrylamide, vinyl acetate, acrylonitrile, 2-ethylhexyl acrylate, and the like.

“Zwitterionic monomer” means a polymerizable molecule containing cationic and anionic (charged) functionality in equal proportions, so that the molecule is net neutral overall. Representative zwitterionic monomers include *N,N*-dimethyl-*N*-acryloyloxyethyl-*N*-(3-sulfopropyl)-ammonium betaine, *N,N*-dimethyl-*N*-acrylamidopropyl-*N*-(2-carboxymethyl)-  
 30 ammonium betaine, *N,N*-dimethyl-*N*-acrylamidopropyl-*N*-(3-sulfopropyl)-ammonium betaine, *N,N*-dimethyl-*N*-acrylamidopropyl-*N*-(2-carboxymethyl)-ammonium betaine, 2-(methylthio)ethyl methacryloyl-S-(sulfopropyl)-sulfonium betaine, 2-[(2-acryloylethyl)dimethylammonio]ethyl 2-methyl phosphate,

2-(acryloyloxyethyl)-2'-(trimethylammonium)ethyl phosphate, [(2-acryloylethyl)dimethylammonio]methyl phosphonic acid, 2-methacryloyloxyethyl phosphorylcholine (MPC), 2-[(3-acrylamidopropyl)dimethylammonio]ethyl 2'-isopropyl phosphate (AAPI), 1-vinyl-3-(3-sulfopropyl)imidazolium hydroxide, (2-acryloxyethyl) carboxymethyl methylsulfonium chloride, 1-(3-sulfopropyl)-2-vinylpyridinium betaine, *N*-(4-sulfobutyl)-*N*-methyl-*N,N*-diallylamine ammonium betaine (MDABS), *N,N*-diallyl-*N*-methyl-*N*-(2-sulfoethyl) ammonium betaine, and the like.

“Zwitterionic polymer” means a polymer composed from zwitterionic monomers and, possibly, other non-ionic monomer(s), cationic monomers and/or anionic as disclosed in Patent Nos. 6,709,551 and 6,313,246.

“RSV” stands for Reduced Specific Viscosity. Within a series of polymer homologs which are substantially linear and well solvated, “reduced specific viscosity (RSV)” measurements for dilute polymer solutions are an indication of polymer chain length and average molecular weight according to Paul J. Flory, in “*Principles of Polymer Chemistry*”, Cornell University Press, Ithaca, NY, © 1953, Chapter VII, “*Determination of Molecular Weights*”, pp. 266-316. The RSV is measured at a given polymer concentration and temperature and calculated as follows:

$$RSV = \frac{[(\eta/\eta_0)-1]}{c}$$

$\eta$  = viscosity of polymer solution,  $\eta_0$  = viscosity of solvent at the same temperature and  $c$  = concentration of polymer in solution where the units of concentration “ $c$ ” are (grams/100 ml or g/deciliter). Therefore, the units of RSV are dl/g. In this patent application, a 1.0 molar sodium nitrate solution is used for measuring RSV. The polymer concentration in this solvent is measured at about 0.045 g/dL. The RSV is measured at 30°C. The viscosities  $\eta$  and  $\eta_0$  are measured using a Cannon Ubbelohde semimicro dilution viscometer, size 75. The viscometer is mounted in a perfectly vertical position in a constant temperature bath adjusted to  $30 \pm 0.02$  °C. The error inherent in the calculation of RSV is about 2 dl/grams. When two polymer homologs within a series have similar RSV’s that is an indication that they have similar molecular weights.

The antimicrobial composition of this invention is prepared by mixing an aqueous polymer-ammonium salt formulation comprising one or more polymers and one or more ammonium salts with a chlorine source in a molar ratio of chlorine (as  $Cl_2$ ) to ammonium ion of about 1:10 to about 10:1 and sufficient alkali to result in a pH of at least 7.

Suitable chlorine sources include any agent capable of providing free chlorine under the conditions described herein. In an embodiment, the chlorine source is chlorine gas, sodium hypochlorite, calcium hypochlorite, dichloroisocyanurate, trichloroisocyanurate, and the like. In another embodiment, the chlorine source is chlorine gas or sodium hypochlorite. In another  
5 embodiment, the chlorine source is sodium hypochlorite. In another embodiment, the chlorine source is an aqueous sodium hypochlorite solution having about 5 to about 15 percent of chlorine, based on  $\text{Cl}_2$ .

In an embodiment, polymers used in the aqueous polymer-ammonium salt formulation have a weight average molecular weight of at least about 100,000 g/mole.

10 In an embodiment, the aqueous polymer-ammonium salt formulation is an aqueous dispersion of one or more polymers in aqueous ammonium salt solution.

The aqueous dispersion of one or more polymers in aqueous ammonium salt solution may be prepared by polymerizing monomers in an aqueous continuous phase containing one or more ammonium salts. Representative examples of dispersion polymerization of water-soluble  
15 polymers in an aqueous continuous phase can be found in U.S. Patent Nos. 5,605,970; 5,837,776; 5,985,992; 4,929,655; 5,006,590; 5,597,859; and 5,597,858 and in European Patent Nos. 183,466; 657,478; and 630,909.

In a typical synthesis, the polymer dispersion is prepared by combining water, one or more ammonium salts, one or more water-soluble monomers, any polymerization additives such  
20 as chelants, pH buffers or chain transfer agents, and a water-soluble stabilizer polymer. In addition, further processing, structure modifying and/or stabilizing agents may be added to the mixture. All or a portion of this mixture is charged to a reactor equipped with a mixer, thermocouple, nitrogen purging tube, and water condenser. The solution is mixed vigorously, heated to the desired temperature, and then a water-soluble initiator is added. The solution is  
25 purged with nitrogen while maintaining temperature and mixing for several hours. During the course of the reaction, a discontinuous phase containing the water-soluble polymer is formed. A portion of the reaction mixture containing any combination of the starting materials may be added in a semi-batch fashion during the course of the polymerization to improve processing or affect polymer composition or molecular weight. After this time, the products are cooled to  
30 room temperature, and any post-polymerization additives are charged to the reactor. Water continuous dispersions of water-soluble polymers are free flowing liquids with product viscosities of from about 50 to about 10,000 centipoise (cP), as measured at low shear.

Additional inorganic salts may be used in combination with the ammonium salts for preparing the polymer dispersion including inorganic or organic sulfates, phosphates, chlorides,

fluorides, citrates, acetates, tartrates, hydrogenphosphates and mixtures thereof. Representative additional inorganic salts include, sodium sulfate, magnesium sulfate, aluminum sulfate, sodium hydrogen phosphate, potassium hydrogen phosphate, sodium chloride, and the like.

Additional cationic salts may be used in combination with the above inorganic salts for preparing dispersions of anionic polymers. Representative cationic salts include  
5 tetraalkylammonium halides having from 4 to 22 carbon atoms, substituted tetraalkylammonium halides having from 4 to 22 carbon atoms, aryl trialkylammonium halides having from 9 to 22 carbon atoms, and substituted aryl trialkylammonium halides having from 9 to 22 carbon atoms.

Cationic polymer dispersions may also be prepared using a mixture of the inorganic salts  
10 described above with one or more anionic inorganic salts and one or more thiocyanates, perchlorates, chlorates, bromides, iodides or nitrates, including sodium, potassium or ammonium thiocyanate, sodium perchlorate, sodium chlorate, sodium bromide, sodium iodide, sodium nitrate and the like.

Representative anionic salts include metal or ammonium salts of trichloroacetate and  
15 trifluoromethanesulfonate; sulfonates and disulfonates such as methanesulfonate, ethanesulfonate, propanesulfonate, butanesulfonate, butanedisulfonate, pentanesulfonate, hexanesulfonate, hexanedisulfonate, and octanedisulfonate; aryl and substituted aryl sulfonates and disulfonates such as benzenesulfonate, nitrobenzenesulfonate, xylenesulfonate, toluenesulfonate, benzenedisulfonate, naphthalenesulfonate; dialkylsulfosuccinates such as  
20 diisobutylsulfosuccinate, diisooctylsulfosuccinate, dimethylsulfosuccinate, diethylsulfosuccinate, and diisopropylsulfosuccinate; dicycloalkylsulfosuccinates; and diarylsulfosuccinates. Preferred anionic salts include sodium hexanesulfonate, sodium benzenesulfonate, sodium xylenesulfonate, sodium benzenedisulfonate, sodium butanedisulfonate, sodium hexanedisulfonate, sodium octanedisulfonate, and sodium decanedisulfonate. The relatively hydrophobic nature of these  
25 salts facilitate dispersion formation. Such salts may be added in any order with the other reaction components, and the order of addition can be used to effect changes in polymer processing.

Suitable polymeric stabilizing agents for preparing cationic and nonionic polymeric dispersions include water-soluble cationic polymers that are preferably soluble in the aqueous ammonium salt solution. The stabilizer is used in an amount of from about 1 to about 10% by  
30 weight based on the total weight of the polymer dispersion. The polymeric stabilizing agents or stabilizers facilitate discrete particle formation and prevent agglomeration and gel formation.

Suitable cationic stabilizers for preparing cationic and nonionic polymer dispersions include but are not limited to homopolymers of cationic diallyl-*N,N*-disubstituted ammonium monomers, homopolymers of *N,N*-disubstituted-aminoethyl(meth)acrylate monomers and their



quaternary salts, homopolymers of *N,N*-disubstituted-aminopropyl(meth)acrylamide and their quaternary salts, copolymers of diallyl-*N,N*-disubstituted ammonium monomers and *N,N*-disubstituted-aminoethyl(meth)acrylate monomers and their quaternary salts, copolymers of diallyl-*N,N*-disubstituted ammonium monomers and *N,N*-disubstituted-aminopropyl(meth)acrylamide monomers and their quaternary salts and cationic polymers comprising at least 20 mole percent of one or more cationic diallyl-*N,N*-disubstituted ammonium monomers, *N,N*-disubstituted-aminoethyl(meth)acrylate monomers and their quaternary salts or *N,N*-disubstituted-aminopropyl(meth)acrylamide monomers and their quaternary salts and one or more nonionic monomers, preferably (meth)acrylamide, *N*-substituted or *N,N*-disubstituted (meth)acrylamide or styrene, and mixtures thereof. The molecular weight of the stabilizer is preferably in the range of about 10,000 to 10,000,000 g/mol.

Stabilizers used for preparing anionic and nonionic polymer dispersions include anionically charged water soluble polymers having a molecular weight of from about 10,000 to about 10,000,000 and preferably from about 1,000,000 to about 3,000,000. The stabilizer polymer must be soluble or slightly soluble in the salt solution, and must be soluble in water.

Representative anionic stabilizers include but are not limited to polyacrylic acid, poly(meth)acrylic acid, poly(2-acrylamido-2-methyl-1-propanesulfonic acid), copolymers of 2-acrylamido-2-methyl-1-propanesulfonic acid and an anionic comonomer selected from acrylic acid and methacrylic acid, polymers of one or more anionic monomers and one or more nonionic monomers, and the sodium salts of the aforementioned anionic stabilizers.

Nonionic dispersants can also be used alone or in combination with the cationic, anionic and nonionic stabilizers described herein for preparing cationic, anionic, nonionic and Zwitterionic polymer dispersions. Representative nonionic dispersants include, but are not limited to polyvinyl alcohol, polyvinyl pyrrolidinone, polyethylene glycol, polypropylene glycol, polyethylene oxide, polyethylene, soluble starch, epichlorohydrin/dimethylamine, poly(*N*-vinylpyridine), and the like.

A multifunctional alcohol such as glycerin or ethylene glycol may also be included in the polymerization system. The deposition of the fine particles is smoothly carried out in the presence of these alcohols.

The polymerization reaction is initiated by any means that results in generation of a suitable free radical. Initiation may be induced through the use of any number of conventional systems including thermal, photochemical, or redox coupled initiation systems. Thermally derived radicals, in which the radical species results from thermal, homolytic dissociation of a water-soluble azo, peroxide, hydroperoxide and perester compound are preferred. Especially

preferred initiators are azo compounds including 2,2'-azobis(2-amidinopropane) dihydrochloride and 2,2'-azobis(N, N'-dimethyleneisobutylamine) hydrochloride, and the like.

A seed polymer may be added to the reaction mixture before the initiating polymerization of the monomers for the purpose of facilitating a fine dispersion of particles. The seed polymer  
5 is a water-soluble polymer insoluble in the aqueous solution of the polyvalent anionic salt. The monomer composition of the seed polymer need not be identical to that of the water-soluble polymer formed during polymerization. The seed polymer is preferably a polymer prepared by the dispersion polymer process described herein.

In alternative embodiments, the aqueous dispersion of one or more polymers in aqueous  
10 ammonium salt solution may be prepared by dispersing a preformed polymer in aqueous ammonium salt solution. The preformed polymer may be prepared by any of the polymerization methods known in the art including powder, latex or solution polymerization techniques.

Suitable ammonium salts used in preparing the polymer-ammonium salt formulation include any ammonium salt capable of reacting with the chlorine source to form chloramines  
15 under the conditions described herein. In an embodiment, the ammonium salt is selected from ammonium sulfate, ammonium chloride, ammonium bromide, ammonium hydrogen phosphate, ammonium acetate, ammonium formate, ammonium thiocyanate, ammonium persulfate, ammonium hydroxide and mixtures thereof.

In another embodiment, the ammonium salt is selected from ammonium sulfate,  
20 ammonium bromide, ammonium chloride and mixtures thereof.

In another embodiment, the ammonium salt is ammonium sulfate.

The amount of ammonium salts in the polymer dispersion is the amount sufficient to produce a molar ratio of chlorine (as  $\text{Cl}_2$ ) to ammonium ion of about 1:10 to about 10:1.

In an embodiment, the amount of ammonium salts in the polymer dispersion is the  
25 amount sufficient to produce a molar ratio of chlorine (as  $\text{Cl}_2$ ) to ammonium ion of about 1:3 to about 3:1.

In another embodiment, the amount of ammonium salts in the polymer dispersion is the amount sufficient to produce a molar ratio of chlorine (as  $\text{Cl}_2$ ) to ammonium ion of about 1:1.

The level of polymer actives relative to ammonium salts in the polymer-ammonium salt  
30 formulation can be adjusted to optimum levels based on the dosing needs and desired product or process results.

The ammonium salt level in the polymer-ammonium salt formulation can be adjusted up relative to polymer by addition of aqueous ammonium salt solution to the produced polymer at a concentration of ammonium salt higher than that contained in the polymer or polymer-

ammonium salt formulation. The ammonium salt level can be adjusted down relative to polymer by addition of an more dilute aqueous ammonium salt solution, water, polymer or other diluents to result in a concentration of ammonium salt lower than contained in the initial polymer-ammonium salt formulation.

5           In the case of dispersion polymers as described herein, the relative amounts of polymer actives and ammonium salts can be obtained by adjusting the level of the two components at the time of polymer manufacture and/or after polymerization as described above.

          To prepare the antimicrobial composition, the polymer-ammonium salt formulation and chlorine source are mixed with sufficient alkali to result in a composition which exhibits  
10       effective antimicrobial activity in a system being treated, taking into account the pH and other parameters of the particular system.

          In an embodiment, sufficient alkali is used to prepare a composition having a pH of at least about 7. In another embodiment, sufficient alkali is used to prepare a composition having a pH of at least about 10. In another embodiment, sufficient alkali is used to prepare a composition  
15       having a pH of at least about 12.

          In an embodiment, the alkali is aqueous sodium hydroxide.

          To prepare the antimicrobial compositions, the polymer-ammonium salt formulation, the alkali and the chlorine source may be added individually or alternatively, the alkali may be formulated with the chlorine source or the polymer-ammonium salt formulation prior to mixing  
20       of the chlorine source and the polymer-ammonium salt formulation.

          As discussed above, stabilized chlorine compositions are used for inhibiting the growth of microorganisms in aqueous systems. However, biocide addition alone is not always sufficient for deposit/microbial control in industrial process systems. The addition of polymers to improve process efficiencies along with biocides to reduce microbial fouling may improve system  
25       performance to a greater degree than either product alone can achieve.

          Additionally, polymer function in some systems may be compromised in the presence of high microbial activity or biofilm formation. The coordinated application of polymer treatment and biocide helps to ensure proper polymer performance.

          The high ammonium salt concentration found in many polymer product compositions is  
30       potentially wasted in the treatment process unless mixed with a chlorine source. This invention takes advantage of the ammonium salts in polymer products to deliver a dual benefit – polymer dosing and chlorine stabilization using a single product.

          Use of the polymer-ammonium salt formulation described herein can eliminate the need for a separate treatment product to stabilize chlorine. This decreases product inventory, storage

costs and dosing costs.

A wide variety of polymer chemistries, product forms and delivery systems are used in water treatment and papermaking systems. In particular, high molecular weight polyacrylamides are commonly used as process aids and water treatment agents in various industrial and  
5 municipal operations. These water-soluble polymers assist in removing suspended solids and contaminants and in effecting various types of separations.

The present invention is applicable to all industries that can employ polymers as process aids and in water treatment processes. For example, the different types of industrial processes in which the method of the present invention can be applied generally include raw water processes,  
10 waste water processes, industrial water processes, municipal water treatment, food and beverage processes, pharmaceutical processes, electronic manufacturing, utility operations, pulp and paper processes, mining and mineral processes, transportation-related processes, textile processes, plating and metal working processes, laundry and cleaning processes, leather and tanning processes, personal care formulation additives and paint processes.

15 The polymers used to prepare the antimicrobial composition may comprise nonionic, cationic, anionic, amphoteric or Zwitterionic polymers. The polymers and their molecular weight and charge density can be readily selected by one of skill in the art based on the performance desired in the particular system being treated.

In an embodiment, the aqueous system is a papermaking system.

20 The use of dispersion polymers in papermaking processes well documented. For example, the use of high molecular weight cationic polymers including dimethylaminoethylacrylate methyl chloride quaternary salt (DMAEA-MCQ)/acrylamide copolymer and dimethylaminoethylacrylate methyl chloride quaternary salt (DMAEA-BCQ)/acrylamide copolymer in retention and drainage applications is described in Patent Nos.  
25 6,059,930, 6,007,679 and 6,171,505 B1.

High molecular weight anionic and nonionic polymers including polyacrylamide acrylic acid salts/acrylamide copolymer and sodium AMPS/acrylamide copolymer, are often beneficial for the use of increasing retention and drainage in papermaking as described in Patent Nos. 6,331,229 B1 and 6,432,271 B1

30 Moderate molecular weight coagulant type polymers, such as diallyldimethylammonium chloride (DADMAC)/acrylamide copolymers, are useful in paper retention, drainage and process improvement applications as described in Patent Nos. 6,071,379, and 6,238,521 B1.

Combinations of lower and higher molecular weight polymers, modified solubilities and/or cationic and anionic charged polymers are used in papermaking processes. Examples can

be found in Patent No. 6,592,718 B1 and US Patent Application No. 2006/0084771.

High and moderate molecular weight cationic polymers, such as DMAEA-MCQ/acrylamide copolymer and DMAEA-BCQ/acrylamide copolymer are useful in coated broke treatment as described in Patent Nos. 5,891,304 and 5,466,338.

5 High molecular weight cationic polymers such as copolymers of DMAEA-BCQ/acrylamide, or DMAEA-MCQ/acrylamide are useful in clarification and dewatering of paper mill waters and can be used alone or in combination with other additives such as microparticles as described in Patent Nos. 5,938,937, 6,171,505 B1 and 6,413,433 B1.

10 High molecular weight anionic and nonionic polymers such as polyacrylamide or copolymers of acrylic acid salts/acrylamide or sodium AMPS/acrylamide, are often used for clarification and dewatering as discussed in Patent No. 6,217,778 B1.

Moderate molecular weight coagulant type polymers, such as DADMAC/acrylamide copolymers, are useful in clarification of deinking process waters as described in Patent No. 6,019,904. Use of the polymers in color removal of paper mill wastewater is described in Patent  
15 Nos. 5,292,793, 5,435,922 and 6,258,279.

Structurally modified polymers of the type described in Patent No. 6,605,674 B1 are useful in the papermaking process as well as in paper wastewater treatment.

The chlorine source, the aqueous polymer-ammonium salt formulation, and the alkali may all be added to points in the stream of the process system which are the same, or spaced but  
20 typically adjacent to each other. If desired, the chlorine source and the alkali may be premixed and added to the stream of the process system together, and the aqueous polymer-ammonium salt formulation may be separately added to the stream of the process system, either at the same location or at a nearby location. As another option, the aqueous polymer-ammonium salt formulation and the alkali may be premixed and added to the stream of the process system  
25 together, and the chlorine source may be separately added to the stream of the process system, either at the same location or at a nearby location. Alternatively, the chlorine source, the aqueous polymer-ammonium salt formulation, and the alkali may each be separately added to the stream of the processing system, typically at the same or closely spaced points of the stream.

30 In an embodiment, the antimicrobial composition is prepared prior to adding to the system.

The chlorine source, aqueous polymer-ammonium salt formulation, alkali source, or any mixtures thereof may be added to the process system continuously or intermittently. The frequency and timing of addition may be controlled manually or by using control automation linked to timers or sensors that trigger addition based on process system conditions such as

oxidation reduction potential, halogen residual, pH, microbial activity, deposit formation, or other system conditions.

For each addition method, the chlorine source, the aqueous polymer-ammonium salt formulation, and the alkali may be mixed prior to addition to the paper process system. The resulting stabilized product may be stored for a short period of time, and then added to the treated system when desired. Some polymers such as low charge cationic polymers such as acrylamide/DMAEA·MCQ, acrylamide/ DMAEA·BCQ and acrylamide/ DMAEM·MCQ are rapidly degraded at high pH, and require immediate dosing into the process system to retain full advantage of favorable polymer properties. Similarly, some loss of available chlorine occurs over time as the antimicrobial composition is stored. Therefore, immediate application of the mixture into the process system is preferred. As used herein, "immediate" means within one hour, preferably within 10 minutes of formation of the antimicrobial composition.

The frequency and duration of treatment and concentration of active ingredient needed in order to maintain adequate inhibition of microorganisms can be determined by one of skill in the art depending on the characteristics of the system being treated. Typically, a level of about 0.1 to about 100 ppm of chlorine (as  $\text{Cl}_2$ ) is sufficient to exhibit effective control.

The foregoing may be better understood by reference to the following example, which is presented for purposes of illustration and is not intended to limit the scope of the invention.

## EXAMPLE

Three experiments are performed, each with the objective of evaluating the ability of a representative polymer-ammonium salt formulation to stabilize chlorine from sodium hypochlorite. In this example, the polymer-ammonium salt formulation is an DADMAC/acrylamide dispersion copolymer in aqueous ammonium sulfate solution having an RSV of 2.26, available from Nalco Company, Naperville, IL.

Series #1 uses low reactant concentrations of 0.005 molar. Series #2 uses 10-fold higher reactant concentration of 0.05 molar. Series #3 uses the higher reactant concentrations of series #2 along with added sodium hydroxide.

Each series includes two controls: A (chlorine and water); B(chlorine and ammonium sulfate); and a reaction C using chlorine and a representative polymer-ammonium salt formulation.

In each case the concentration of chlorine (as  $\text{Cl}_2$ ) and ammonium sulfate are blended in equimolar ratio. Ammonium sulfate concentrations in the control and polymer-ammonium salt

formulation are equivalent.

After performing each reaction, the product pH is measured. The concentrations of free and stabilized halogen and total reaction yield are determined using *N,N*-diethyl-*p*-phenylenediamine (DPD) reagent. In each set of experiments, 100% yield is determined by measuring the total residual oxidant (TRO) of Reaction "A" in which no halogen stabilizer is present. Residual oxidant values in each product are reported in ppm, and also as a percent yield compared to reactions with no stabilizer. Results are shown in Table 1. Reaction yields are shown in brackets.

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Table 1

Free and Stabilized Chlorine Reaction Products Resulting from Mixtures of a Polymer-Ammonium Salt Formulation and Sodium Hypochlorite.

Series	Reaction Mixture	Reactant Conc.	pH	FRO	3FRO	TRO	3TRO
1A	NaOCl + water	0.005 M Chlorine	9.4	384 [100%]	386 [101%]	384 [100%]	N.D.
1B	NaOCl + ammonium sulfate	0.005 M chlorine and 0.005 M (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	7.5	170 [44%]	388 [101%]	388 [101%]	N.D.
1C	NaOCl + polymer dispersion	0.005 M chlorine and 0.005 M (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	7.2	122 [32%]	388 [101%]	386 [101%]	N.D.
2A	NaOCl + water	0.05 M Chlorine	10.3	3780 [98%]	3800 [98%]	3860 [100%]	3860 [100%]
2B	NaOCl + ammonium sulfate	0.05 M chlorine and 0.05 M (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	8.0	660 [17%]	3680 [95%]	3860 [100%]	3860 [100%]
2C	NaOCl + polymer dispersion	0.05 M chlorine and 0.05 M (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	6.0	360 [9%]	960 [25%]	1460 [38%]	2380 [62%]
3A	NaOCl + NaOH + water	0.05 M chlorine and 0.25% NaOH	12.7	3760 [97%]	3780 [98%]	3840 [99%]	3840 [99%]
3B	NaOCl + NaOH + ammonium sulfate	0.05 M chlorine and 0.25% NaOH and 0.05 M (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	12.6	400 [107%]	2880 [73%]	3940 [101%]	3920 [102%]
3C	NaOCl + NaOH + polymer dispersion	0.05 M chlorine and 0.25% NaOH and 0.05 M (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	12.3	620 [16%]	3540 [92%]	3600 [93%]	3580 [93%]

#### Oxidant Residuals Measured using DPD:

- 15 FRO = ppm Free Residual Oxidant in reaction [% of total oxidant].  
 3FRO = ppm Free Residual Oxidant in reaction [% of total oxidant], with 3-minute DPD reaction time.  
 TRO = ppm Total Residual Oxidant in reaction [% of total oxidant].  
 3TRO = ppm Total Residual Oxidant in reaction [% of total oxidant], with 3-minute DPD  
 20 reaction time.

This example demonstrates that the polymer-ammonium salt formulation reaction with chlorine results in only a small amount of oxidant loss (>90% oxidant recovery), with >80% of the oxidant in a stabilized form expected to have good antimicrobial properties.

- 5        It should be understood that various changes and modifications to the presently preferred embodiments described herein will be apparent to those skilled in the art. Such changes and modifications can be made without departing from the spirit and scope of the present invention and without diminishing its attendant advantages. It is therefore intended that such changes and modifications be covered by the appended claims.

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## CLAIMS

1. An antimicrobial composition prepared by mixing an aqueous polymer-ammonium salt formulation comprising one or more polymers and one or more ammonium salts with a chlorine  
5 source in a molar ratio of chlorine (as  $\text{Cl}_2$ ) to ammonium ion of about 1:10 to about 10:1 and sufficient alkali to result in a composition which exhibits effective antimicrobial activity in a system being treated.
2. The composition of claim 1 wherein said polymers have a weight average molecular  
10 weight greater than about 100,000 g/mole.
3. The composition of claim 2 wherein said chlorine source is selected from chlorine gas and sodium hypochlorite.
- 15 4. The composition of claim 3 wherein said formulation is a dispersion of one or more polymers in an aqueous ammonium salt solution.
5. The composition of claim 4 having a pH of at least about 7.
- 20 6. The composition of claim 5 wherein said ammonium salt is selected from ammonium sulfate, ammonium chloride, ammonium bromide, ammonium acetate, ammonium formate, ammonium thiocyanate, ammonium hydroxide and mixtures thereof.
7. The composition of claim 6 wherein said dispersion of one or more polymers in an  
25 aqueous ammonium salt solution has a reduced specific viscosity in 1 N  $\text{NaNO}_3$  solution of about 0.5 to about 30 dL/g.
8. The composition of claim 7 having a pH greater than about 10.
- 30 9. The composition of claim 8 wherein said ammonium salt is selected from ammonium sulfate, ammonium bromide, ammonium chloride and mixtures thereof.
10. The composition of claim 9 prepared by mixing a dispersion of one or more polymers in an aqueous ammonium salt solution with a chlorine source in a molar ratio of chlorine (as  $\text{Cl}_2$ ) to

ammonium ion of about 1:3 to about 3:1

11. The composition of claim 10 wherein said polymers are selected from the group consisting of cationic polymers and anionic polymers.

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12. The composition of claim 11 wherein said polymers are selected from copolymers of (meth)acrylamide and one or more monomers selected from diallyldimethylammonium chloride, dimethylaminoethyl (meth)acrylate methyl chloride quaternary salt, dimethylaminoethyl (meth)acrylate benzyl chloride quaternary salt, (meth)acrylic acid and its salts and 2-acrylamido-  
10 2-methylpropanesulfonic acid.

13. The composition of claim 12 wherein said polymers have a charge of about 2 to about 30 mole percent.

15 14. The composition of claim 13 wherein said ammonium salt is ammonium sulfate.

15. The composition of claim 14 prepared by mixing a dispersion of one or more polymers in an aqueous ammonium salt solution with a chlorine source in a molar ratio of chlorine (as  $\text{Cl}_2$ ) to ammonium ion of about 1:1.

20

16. The composition of claim 15 having a pH greater than about 12.

17. The composition of claim 1 wherein said polymer-ammonium salt formulation is prepared by polymerizing monomers under free radical forming conditions in an aqueous  
25 ammonium salt solution, wherein said ammonium salt is selected from ammonium sulfate, ammonium bromide, ammonium chloride and mixtures thereof.

18. A method of inhibiting the growth of microorganisms in an aqueous system comprising treating the system with an effective inhibiting amount of an antimicrobial composition  
30 according to claim 1.

19. The method of claim 17 wherein said aqueous system is a papermaking system.

20. The method of claim 18 wherein said antimicrobial composition is prepared prior to adding to the system.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 07/89013

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C02F 1/76 (2008.04)

USPC - 210/755, 764

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)

USPC: 210/755, 764

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

USPC: 210/755, 756, 764; 162/161

(text search)

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

PubWEST(PGPB,USPT,USOC,EPAB,JPAB); Google

Search terms: chlorine, ammonium, chloramines, polymer, dispersion, antimicrobial, biocide, papermaking, wastewater, chlorine gas, sodium hypochlorite

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2003/0121868 A1 (BARAK, A.) 3 July 2003 (03.07.2003) para [0019]-[0020], [0031], [0080], [0087]-[0089], [0176], [0243].	1-20
Y	US 6,059,930 A (WONG SHING, J.B. et al.) 9 May 2000 (09.05.2000) abstract; col 3, ln 46-48; col 4, ln 37-45, 50-52, 60-62; col 5, ln 9-10; col 6, ln 4-6, 12-19.	1-20

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


\* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"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

"&amp;" document member of the same patent family

Date of the actual completion of the international search

16 April 2008 (16.04.2008)

Date of mailing of the international search report

16 MAY 2008

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