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(54) Title: METHOD FOR ENHANCING BIOCIDAL ACTIVITY

(57) **Abstract:** Treatment for enhancing activity of biocidal compounds to control growth of microbes in aqueous systems, which comprises adding to said compounds an effective amount of a dispersant composed of alkyl substituted carboxylated acid or salt thereof and polyoxyethylene-polyoxypropylene block copolymer.

METHOD FOR ENHANCING BIOCIDAL ACTIVITY

BACKGROUND OF THE INVENTION

Bacterial attachments to surfaces in virtually any non-sterile aquatic environment is a well-established phenomenon. Industrial efforts to prevent colonization or to clean fouled surfaces amount to costly expenditures in a number of industrial sectors. Surfactants are regularly employed in water treatment programs as agents believed to play a role in the prevention of organic masses from adhering to surfaces, in the enhancement of biocide efficacy or in the assistance in the water miscibility of various biocidal agents. Surfactants are also regularly used in the agrichemical business, particularly to enhance the action of herbicides. This is accomplished by using the surfactants to alter the surface behavior of the applied droplets, maximizing their interaction with the leaf surface.

There are numerous examples of surfactants which are able to inhibit the colonization of surfaces by inhibiting the overall growth of the organisms in the target environment. Many surfactants, regardless of class, show some inhibition of bacterial growth when used at concentrations high enough to impede surface colonization. In the water treatment industry, the most well known class of surfactants which impart a measure of colonization resistance to submerged surfaces are the cationic quaternary amine surfactants, which also function as biocides. However, even relatively mild nonionic and anionic surfactants can function in an analogous fashion. The concentration of nonionic or anionic surfactants necessary to mediate toxicity is substantially higher than for cationic surfactants, however.

Surfactants have historically been added to biocide packages because they (1) help to maintain some actives in aqueous solution which may otherwise separate (formulation aids) and (2) help relatively hydrophobic biocides to be more miscible in an aqueous environment. Surfactants have also been considered as enhancers of the efficacy of biocides against biofilm-associated organisms by increasing the accessibility of the biocide to its cellular target.

As previously noted, bacteria attach to surfaces, metabolize and grow, resulting in biofilms or microbial slime. This can result in problems in cooling water systems, such as reduced heat exchanger efficiency, blockage of pipes, corrosion of equipment, and harboring of potentially harmful bacteria. Control of slime, including the prevention of formation of slime and/or removal of slime, is important in alleviating these problems.

The present invention refers to a method for enhancing the activity of biocides to control the growth of microbes in an aqueous system. The materials of the present invention have been previously used in areas such as spray, soak tank, in-place pipeline cleaners, and floor scrubbing formulations.

SUMMARY OF THE INVENTION

The present invention relates to methods for enhancing a treatment containing biocidal component to control growth of microbes in an aqueous system. the method comprising adding low foaming, ethoxylated anionic surfactant to the aqueous system, the low foaming, ethoxylated anionic surfactant comprising (a) at least one of alkyl substituted carboxylated acid and alkyl substituted carboxylated acid salt, and (b) polyoxyethylene-polyoxypropylene block copolymer.

The (a) at least one of alkyl substituted carboxylated acid and alkyl substituted carboxylated acid salt, and (b) polyoxyethylene-polyoxypropylene block copolymer can be added in amounts effective to control growth of microbes in the aqueous system at lower levels of biocidal component in the aqueous system than in the absence of the (a) at least one of alkyl substituted carboxylated acid and alkyl substituted carboxylated acid salt, and (b) polyoxyethylene-polyoxypropylene block copolymer.

The (a) at least one of alkyl substituted carboxylated acid and alkyl substituted carboxylated acid salt, and (b) polyoxyethylene-polyoxypropylene block copolymer can be added in amounts effective to obtain at least the same, if not better, control of growth of microbes in the aqueous system as compared to same and/or higher concentrations of biocidal component in the aqueous system in the absence of the (a) at least one of alkyl substituted carboxylated acid and alkyl substituted carboxylated acid salt, and (b) polyoxyethylene-polyoxypropylene block copolymer.

The (a) at least one of alkyl substituted carboxylated acid and alkyl substituted carboxylated acid salt, and (b) polyoxyethylene-polyoxypropylene block copolymer can be added in amounts effective to obtain greater control of growth of microbes in the aqueous system as compared to higher concentrations of biocidal component in the aqueous system in the absence of the (a) at least one of alkyl substituted carboxylated acid and alkyl substituted carboxylated acid salt, and (b) polyoxyethylene-polyoxypropylene block copolymer.

The alkyl substituted carboxylated acid or salt can contain from 6 to 18 carbon atoms, preferably 6 to 12 carbon atoms, and even more preferably 6 to 9 carbon atoms. The alkyl groups can contain from 1 to 6 carbon atoms, preferably 1 to 3 carbon atoms, and even more preferably 1 carbon atom. Preferably, the alkyl substitution is on 3 and 5 carbon atoms of the carboxylic acid. Preferably, the alkyl substituted carboxylated acid or salt comprises at least one of 3,5,5 trimethyl hexanoic acid and salts thereof, 3,5,5 trimethyl octanoic acid and salts thereof, 3,7,7 trimethyl octanoic acid and salts thereof, 3,5,5 trimethyl decanoic acid and salts thereof, and 3,9,9 trimethyl decanoic acid and salts thereof.

Preferably, the alkyl substituted carboxylated acid or salt comprises alkyl substituted carboxylated acid salt, preferably a potassium or sodium salt.

The polyoxyethylene-polyoxypropylene block copolymer preferably has a mole ratio of about 1 to 1.6 moles of polyoxyethylene to 1 mole of polyoxypropylene, more preferably about 1.3 moles of polyoxyethylene to 1 mole of polyoxypropylene. The polyoxyethylene-polyoxypropylene block copolymer preferably has a molecular weight of about 3,000 to 6,600, more preferably about 4,000 to 5,000, and even more preferably about 4,500.

The low foaming, ethoxylated anionic surfactant preferably comprises about 35 to 60 wt% water, based upon total weight of the surfactant, preferably about 25 to 45 wt% of the at least one of alkyl substituted carboxylated acid and alkyl substituted carboxylated acid salt, and more preferably about 28 to 32 wt% of the at least one of alkyl substituted carboxylated acid and alkyl substituted carboxylated acid salt, and about 5 to 25 wt% of the polyoxyethylene-polyoxypropylene block copolymer, more preferably about 11 to 18 wt% of the polyoxyethylene-polyoxypropylene block copolymer.

The biocidal component can comprise at least one of non-oxidizing and oxidizing biocidal compounds. The at least one non-oxidizing biocidal compound can comprise at least of at least one isothiazolone compound and at least one bromonitropropanediol compound. The at least one isothiazolone compound can comprise at least one of 5-chloro-2-methyl-4-isothiazolin-3-one and 2- methyl-4-isothiazolin-3-one, as well as a mixture of 5-chloro-2-methyl-4-isothiazolin-3-one, 2-

methyl-4-isothiazolin-3-one, and 2-bromo-2-nitropropane-1,3-diol. The at least one oxidizing biocidal compound can comprise at least one of hypochlorites, sodium bromide; hydantoins; peracetic acid; chlorine dioxide; ozone; hydrogen peroxide; and halogenated isocyanurates, preferably sodium hypochlorite.

The surfactant can include additional components such as at least one sequestrant, which preferably comprises at least one of polyepoxysuccinic acid and hydroxyethylidene diphosphonic acid.

At least about 5 ppm of the surfactant, more preferably at least about 10 ppm of the surfactant, can be added to the aqueous system, with preferred ranges being about 5 to 200 ppm, more preferably 10 to 50 ppm of the surfactant added to the aqueous system.

The microbes can comprise bacteria, fungi, algae and/or protozoa, including protozoan cysts.

The aqueous system can comprise at least one of cooling water systems (preferably recirculating and/or closed water systems), reverse osmosis systems, pulping and papermaking systems, air washer systems, pasteurizer systems, fire water safety systems, shower water systems, metalworking fluid systems, hydrocarbon storage systems, and aqueous mineral processing systems.

Preferably, the at least one of alkyl substituted carboxylated acid and alkyl substituted carboxylated acid salt comprises potassium or sodium salt of an alkyl substituted carboxylated acid having 6 to 12 carbon atoms and alkyl groups of 1 carbon atom, and the polyoxypropylene-polyoxyethylene block copolymer has a molecular weight of about 4,000 to 5,000 and a mole ratio of about 1 to 1.6 moles of polyoxyethylene to 1 mole of polyoxypropylene. More preferably, the potassium or sodium salt of an alkyl substituted carboxylated acid comprises a potassium or sodium salt of 3,5,5 trimethyl hexanoic acid.

DETAILED DESCRIPTION OF THE INVENTION

The particulars shown herein are by way of example and for purposes of illustrative discussion of embodiments of the present invention only and are presented in the cause of providing what is believed to be the most useful and readily understood description of the principles and conceptual aspects of the present invention. In this regard, no attempt is made to show structural details of the present invention in more detail than is necessary for the fundamental understanding of the present invention, the description making apparent to those skilled in the art how varying forms of the present invention may be embodied in practice.

Unless otherwise stated, all percentages, parts, ratios, etc., are by weight. Also, all percent measurements in this application, unless otherwise stated, are measured by weight based upon 100% of a given sample weight. Thus, for example, 30% represents 30 weight parts out of every 100 weight parts of the sample.

Unless otherwise stated, a reference to a compound or component includes the compound or component by itself, as well as in combination with other compounds or components, such as mixtures of compounds.

Further, when an amount, concentration, or other value or parameter, is given as a list of upper preferable values and lower preferable values, this is to be understood as specifically disclosing all ranges formed from any pair of an upper preferred value and a lower preferred value, regardless whether ranges are separately disclosed.

The dispersant of the present invention enhances biocidal activity as compared to the use of biocides alone. The dispersant according to the present invention includes a combination of an alkyl substituted carboxylated acid salt and a block copolymer that when agitated, such as in cooling towers, will not form excessive amounts of foam, which would be unacceptable for use in various aqueous systems. The method of the present invention allows for a decrease in the amount of biocidal compound added to the system, while maintaining the efficacy of the treatment. Thus, a more environmentally acceptable outcome is achieved, in that less biocidal material may be used while still preferably achieving at least the same level of biofilm kill efficacy. Thus, the dispersant of the present invention is particularly useful in combination with biocides to kill organisms. In addition, it is very effective at removing pre-existing biofilms in aqueous systems. Thus, the dispersant of the present invention is particularly useful in the control of microbes, including the prevention of formation and/or the removal of slime in aqueous systems.

The present invention relates to methods and compositions for enhancing activity of a treatment including a biocidal compound to control growth of microbes, including the prevention of formation and/or the removal of slime, in aqueous systems, which comprises adding to the aqueous system an effective amount of dispersant comprising low foaming, ethoxylated anionic surfactant which is composed of alkyl substituted carboxylated acid and/or salt thereof and ethylene oxide/propylene oxide block copolymer.

The alkyl substituted carboxylated acid or salt thereof can include, but is not limited to, acids and/or salts containing from about 6 to 18 carbon atoms, more preferably from about 6 to 12 carbon atoms, and most preferably from about 6 to 9 carbon atoms. Moreover, the alkyl groups can comprise alkyl groups having from about 1 to 6 carbon atoms, more preferably from about 1 to 3 carbon atoms, and most preferably 1 carbon atom. Preferably, the alkyl substituted carboxylated acid or salt comprises up to about 7 alkyl groups, and preferably contains 3 alkyl groups. Preferably, the acid comprises hexanoic, octanoic and/or decanoic acid, with from 1 to 3 alkyl groups on the various carbons of the acid, which are preferably methyl groups. Moreover, preferably the alkyl substitution is on the 3 and 5 carbons, preferably of hexanoic acid. Particularly preferred alkyl substituted carboxylated acid or salt thereof comprises hexanoic acid, with the alkyl substitution being on the 3 and 5 carbons, preferably one alkyl group on the 3 carbon and two alkyl groups of the 5 carbon, and preferably each of the three alkyl groups are methyl. Thus, a particularly preferred alkyl substituted carboxylated acid or salt thereof comprises 3, 5, 5 hexanoic acid or salt thereof.

Preferably, the alkyl substituted carboxylated acid and/or salt thereof comprises the salt. The salt form can include any cation that helps dissolve the carboxylic acid into solution, and preferably comprises potassium or sodium as the cation. For example, the acid can be formed into the salt by reaction with potassium hydroxide or sodium hydroxide.

Examples of alkyl substituted carboxylated acid and salts according to the present invention include, but are not limited to, 3,5,5 trimethyl hexanoic acid and salts thereof, preferably sodium or potassium salts thereof, 3,5,5 trimethyl octanoic acid and salts thereof, 3,7,7 trimethyl octanoic acid and salts thereof, 3,5,5 trimethyl decanoic acid and salts thereof, and 3,9,9 trimethyl decanoic acid and salts thereof.

The block copolymer comprises polyoxyethylene (EO) - polyoxypropylene (PO), which for the sake of convenience will also be referred to herein as EO/PO block coplymer. The EO/PO block copolymer can comprise any EO/PO block coploymer that maintains low foaming and/or reduces foaming of the alkyl substituted carboxylated acid or salt. The EO/PO mole ratio preferably ranges from about 1 to 1.6 moles EO to l mole PO, with a particularly preferred mole ratio being about 1.3 moles EO to 1 mole PO.

The molecular weight range of the EO/PO block copolymer is preferably about 3,000 to 6,600, most preferably about 4,000 to 5,000, with a particularly preferred value being about 4,500. Thus, a particularly preferred EO/PO block copolymer comprises EO/PO having 1.3 moles EO to 1 mole PO, and a molecular weight of about 4,500.

Examples of EO/PO block copolymers according to the present invention include, but are not limited to, the Plutonic P series available from BASF (Mount Olive, New Jersey), and examples thereof include P65, P68, P84, P85, P104 and P105.

An especially useful material for forming the dispersant of the present invention is Mona NF10, available from Uniqema, Paterson, NJ (formerly Mona Industries, Inc.), which includes therein alkyl substituted carboxylated acid salt and EO/PO block copolymer according to the present invention.

Still further, a particularly preferred low foaming, ethoxylated anionic surfactant according to the present invention is composed of the potassium salt of 3,5,5 trimethyl hexanoic acid and EO/PO block copolymer having a molecular weight of about 4,500, such as P85 available from BASF.

The dispersant preferably comprises about 35 to 70 wt% water, based on the total weight of the dispersant. The amount of the alkyl substituted carboxylated acid or salt in the dispersant is preferably from about 25 to 45 wt%, more preferably from about 28 to 32 wt%, based on the total weight of the dispersant. Moreover, the amount of the EO/PO block copolymer in the dispersant is preferably from about 5 to 25 wt%, more preferably from about 11 to 18 wt%, based on the total weight of the dispersant.

The dispersant according to the present invention can include one or more biocides therein, or biocides can be separately added to the aqueous system. In this regard, the biocide can be added to the aqueous system at the same time as the dispersant, prior to the addition of the dispersant, and/or after the addition of the dispersant. It is preferred that the dispersant be added to the aqueous system prior to addition of the biocide.

As noted above, the present invention allows a decrease in the amount of biocide fed to a system, without decreasing the efficacy of a particular treatment protocol.

Biocides utilizable with the present invention are not limited to any particular biocide or mixture of biocides. Therefore, the following discussion of biocides is not intended to limit the present invention, but is provided to indicate preferred biocides according to the present invention.

Preferably, the biocides according to the present invention include "non-oxidizing" biocides and/or "oxidizing" biocides, and mixtures thereof. For example, non-oxidizing biocides include, but are not limited to, isothiazolones including 5-chloro-2-methyl-4-isothiazolin-3-one, 2- methyl-4-isothiazolin-3-one, and a mixture of 5-chloro-2-methyl-4-isothiazolin-3-one and 2- methyl-4-isothiazolin-3-one sold as Kathon® 886F, available from Rohm and Haas Co.; and 2-bromo-2-nitropropane-1,3-diol (BNPD), available from Angus Chemical Co.

A particularly preferred non-oxidizing biocide comprises a mixture of 5-chloro-2-methyl-4-isothiazolin-3-one, 2- methyl-4-isothiazolin-3-one and 2-bromo-2-nitropropane-1,3-diol, such as disclosed in U.S. Patent No. 4,732,905, which is incorporated by reference herein in its entirety. Preferably, the weight ratio of a combination of the 5-chloro-2-methyl-4-isothiazolin-3-one and 2- methyl-4-isothiazolin-3-one to the 2-bromo-2-nitropropane-1,3-diol is about 1:2.

Oxidizing biocides include, but are not limited to hypochlorites, such as sodium hypochlorite (bleach), potassium hypochlorite and calcium hypochlorite; sodium bromide; hydantoins; peracetic acid; chlorine dioxide; ozone; hydrogen peroxide; and halogenated isocyanurates, preferably sodium hypochlorite.

The organism that is treatable with the dispersant of the present invention can include diverse organisms, including bacteria, fungi, algae and protozoa, including protozoan cysts. In the examples herein *Pseudomonas aeruginosa*, a bacterial species, was utilized in studying the present invention. However, with the guidelines herein, the invention can be utilized to treat various organisms, and is not limited to the specifically disclosed examples.

Materials in addition to the alkyl substituted carboxylated acid salt, the EO/PO block copolymer, and optionally one or more biocides can be included in the dispersant according to the present invention. For example, additives such as sequestrants such as polyepoxysuccinic acid, hydroxyethylidene diphosphonic acid, citric acid and/or ethylenediamine tetraacetic acid (EDTA) can be included in the dispersant according to the present invention.

The dispersant, by itself, or including sequestrants such as polyepoxysuccinic acid or hydroxyethylidene diphosphonic acid, is able to control microbial slime on surfaces. The means of control is by increasing the effectiveness of biocides to kill cells within the slime.

The dispersant according to the present invention is preferably included in the aqueous system at a concentration of at least about 5 parts per million (ppm), more preferably about 10 ppm, with preferred ranges being about 5 to 200 ppm, more preferably about 5 to 50 ppm, more preferably about 10 to 50 ppm.

The concentration of biocide in an aqueous system can be reduced by about 25%, and even more preferably by about 50%, and still maintain at least the same level of effectiveness of biocidal activity by incorporating the effective amounts of dispersion of the present invention in the aqueous system.

The dispersant according to the present invention can be utilized in a variety of aqueous systems, e.g., open recirculating cooling water systems, closed cooling systems, reverse osmosis systems, pulping or papermaking systems, air washer systems, pasteurizer systems, once-through cooling reverse osmosis systems, fire water safety systems, shower water systems, metalworking fluid systems, hydrocarbon storage systems, and aqueous mineral processing systems.

The invention will now be described with respect to certain examples which are merely representative of the invention and should not be construed as limiting thereof.

EXAMPLES

The invention is illustrated in the following non-limiting examples, which are provided for the purpose of representation, and are not to be construed as limiting the scope of the invention. All parts and percentages in the examples are by weight unless indicated otherwise.

Examples 1-8

Bacteria in slime (biofilm) was simulated by incorporating bacteria (*P. aeruginosa*) into alginate, which was then layered onto metal coupons. Layers were exposed to biocide with surfactant and with and without sequestrants. At the end of the treatment (about 24 hours), the alginate was dissolved, releasing bacteria that were monitored by determining viable numbers of bacteria and microbial ATP.

As noted in Table I below, the alkyl carboxylic acid/block copolymer dispersants,

examples are the commercial product, Mona NF-10 (available from Uniqema, formerly Mona Industries, Inc.) with and without sequestrant (polyepoxysuccinic acid, available from BetzDearborn Inc., Trevose, PA) enhanced biocide performance. This was detected by plate counting and ATP measurement. Biocide NX1100 (isothiazolinone/bronopol, available from BetzDearborn Inc., Trevose, PA) with 10 or 50 ppm Mona NF-10 killed 0.4 and 0.6 log more bacteria, respectively, than biocide (NX1100) alone. In other experiments, biocide (NX1100) with 20 ppm Mona NF-10 and sequestrant killed 0.9 log more bacteria and decreased ATP levels 81% greater than with biocide alone. At 100 ppm Mona-NF-10 with sequestrant, biocide efficacy measured as CFU/ml increased 1.2 logs, and as ATP decreased 96% (Table 1). Still further, Dispersant A is prepared by mixing 38 wt% 3,5,5 trimethyl hexanoic acid (obtained from BetzDearborn Inc., Trevose, PA) and 12 wt% P85 (obtained from BASF (Mount Olive, New Jersey) with sufficient KOH to get the 3,5,5 trimethyl hexanoic acid into solution. Increased performance is most likely due to these types of dispersants increasing biocide penetration into the biofilm.

Table 1						
Example No.	**Treatment: product (ppm)**	**CFU/ml (log)**	**Δ log, decrease from biocide**	**Decrease (%)**	**mATP (RLU)**	**Decrease**
1	Biocide (25 ppm)	6.5E (3.8)	-----			
2	Mona NF-10/Biocide (10 ppm/25 ppm)	2.5E3 (3.4)	0.4	62		
3	Mona NF-10/biocide (50 ppm/25 ppm)	1.5E3 (3.2)	0.6	77		
4	Biocide (25 ppm)	1E5(5)	-----	-----	2238	-----
5	MonaNF10/Sequestrant/ Biocide (20 ppm/40 ppm/25 ppm)	1.3E4 (4.1)	0.9	85	427	81
6	Mona NF10 /Sequestrant/Biocide (100 ppm/40 ppm/25 ppm)	5.8E3 (3.8)	1.2	94	93	96
7	Biocide (25 ppm)	9.5E4 (4.98)	-----	-----	-----	-----
8	Dispersant A /biocide (50 ppm/25 ppm)	1.8E4 (4.26)	0.72	81	-----	-----

Examples 9-18

Bacteria were suspended in phosphate/saline water to which was added NX1100, obtained from BetzDearborn Inc., Trevose, PA, (representative of non-oxidizer biocide) or sodium hypochlorite, obtained from BetzDearborn Inc., Trevose, PA (representative of oxidizer biocide), and Mona NF-10, obtained from Uniqema. Paterson, NJ (representative of alkyl carboxylic acid/block copolymer dispersant material), with and without sequestrant (polyepoxysuccinic acid, obtained from BetzDearborn Inc., Trevose, PA). Initial concentration of bacteria was about 10^7 - 10^8 CFU/ml. Treatment was for 3 hours at 24 ± 2°C. Samples were removed and plated, with results shown in Table 2, below. The dispersant increases the efficacy of the non-oxidizer and oxidizer biocide above the biocide alone. As found in Table 2, the biocide efficacy increase for the non-oxidizer was 98%, and for the oxidizer was 78%.

Table 2

Example No.	Treatment: product (ppm)	% Decrease From Biocide	% Decrease From Control
9	A (10)	----	51
10	A/B (10/10)	98.1	99.1
11	A/B (10/20)	98.6	99.3
12	A/B (10/50)	99.3	99.7
13	A/B/C (10/10/40)	98.3	99.1
14	A/B/C (10/50/40)	99.5	99.8
15	D (0.75)	-----	34.5
16	D/B/C (0.75/10/40)	78	85.5
17	D/B/C (0.75/50/40)	90	93.3
18	D/B/C (0.75/100/40)	99	99.1

A = NX1100 (Isothiazolinone/Bronopol)

B = Mona NF-10 (alkyl carboxylic acid/block copolymer)

C = Polyepoxysuccinic Acid

D = Hypochlorite

While this invention has been described with respect to particular embodiments thereof, it is apparent that numerous other forms and modifications of this invention will be obvious to those skilled in the art. The appended claims and this invention generally should be construed to cover all such obvious forms and modifications which are within the true spirit and scope of the present invention.

We claim:

1. A method for enhancing a treatment containing biocidal component to control growth of microbes in an aqueous system, said method comprising adding to said aqueous system low foaming, ethoxylated anionic surfactant, said low foaming, ethoxylated anionic surfactant comprising (a) at least one of alkyl substituted carboxylated acid and alkyl substituted carboxylated acid salt, and (b) polyoxyethylene-polyoxypropylene block copolymer.

2. The method according to claim 1, wherein the (a) at least one of alkyl substituted carboxylated acid and alkyl substituted carboxylated acid salt, and (b) polyoxyethylene-polyoxypropylene block copolymer are added in amounts effective to control growth of microbes in said aqueous system at lower levels of biocidal component in said aqueous system than in the absence of the (a) at least one of alkyl substituted carboxylated acid and alkyl substituted carboxylated acid salt, and (b) polyoxyethylene-polyoxypropylene block copolymer.

3. The method according to claim 1, wherein said alkyl substituted carboxylated acid or salt contains from 6 to 18 carbon atoms.

4. The method according to claim 3, wherein said alkyl substituted carboxylated acid or salt comprises alkyl groups having from 1 to 6 carbon atoms.

5. The method according to claim 4, wherein said alkyl substituted carboxylated acid or salt comprises alkyl groups having 1 carbon atom.

6. The method according to claim 5, wherein alkyl substitution is on 3 and 5 carbon atoms of the carboxylic acid.

7. The method according to claim 1, wherein the alkyl substituted carboxylated acid or salt comprises alkyl substituted carboxylated acid salt.

8. The method according to claim 7, wherein the alkyl substituted carboxylated acid salt comprises potassium or sodium salt.

9. The method according to claim 1, wherein the alkyl substituted carboxylated acid or salt comprises at least one of 3,5,5 trimethyl hexanoic acid and salts thereof, 3,5,5 trimethyl octanoic acid and salts thereof, 3,7,7 trimethyl octanoic acid and salts thereof, 3,5,5 trimethyl decanoic acid and salts thereof, and 3,9,9 trimethyl decanoic acid and salts thereof.

10. The method according to claim 1, wherein the polyoxyethylene-polyoxypropylene block copolymer has a mole ratio of about 1 to 1.6 moles of polyoxyethylene to 1 mole of polyoxypropylene.

11. The method according to claim 10, wherein the polyoxyethylene-polyoxypropylene block copolymer has a molecular weight of about 3,000 to 6,600.

12. The method according to claim 1, wherein the low foaming, ethoxylated anionic surfactant comprises water about 35 to 60 wt% water, based upon total weight of the surfactant.

13. The method according to claim 12, wherein the low foaming, ethoxylated anionic surfactant comprises about 25 to 45 wt% of the at least one of alkyl substituted carboxylated acid and alkyl substituted carboxylated acid salt, based upon total weight of the surfactant.

14. The method according to claim 13, wherein the low foaming, ethoxylated anionic surfactant comprises about 5 to 25 wt% of the polyoxyethylene-polyoxypropylene block copolymer, based upon total weight of the surfactant.

15. The method according to claim 1, wherein the biocidal component comprises at least one of non-oxidizing and oxidizing biocidal compounds.

16. The method according to claim 15, wherein the biocidal component comprises at least one non-oxidizing biocidal compound.

17. The method according to claim 16, wherein the at least one non-oxidizing biocidal compound comprises at least of at least one compound isothiazolone compound and at least one bromonitropropanediol compound.

18. The method according to claim 17, wherein the non-oxidizing biocidal compound comprises isothiazolones, and the isothiazolone comprise at least one of 5-chloro-2-methyl-4-isothiazolin-3-one and 2- methyl-4-isothiazolin-3-one.

19. The method according to claim 17, wherein the at least one non-oxidizing compound comprises a mixture of 5-chloro-2-methyl-4-isothiazolin-3-one, 2- methyl-4-isothiazolin-3-one, and 2-bromo-2-nitropropane-1,3-diol.

20. The method according to claim 16, wherein the biocidal component comprises at least one oxidizing biocidal compound.

21. The method according to claim 20, wherein the at least one oxidizing biocidal compound comprises at least one of hypochlorites, sodium bromide;

hydantoins; peracetic acid; chlorine dioxide; ozone; hydrogen peroxide; and halogenated isocyanurates.

22. The method according to claim 21, wherein the at least one oxidizing biocidal compound comprises sodium hypochlorite.

23. The method according to claim 1, wherein the surfactant additionally includes at least one sequestrant.

24. The method according to claim 23, where the at least one sequestrant comprises at least one of polyepoxysuccinic acid and hydroxyethylidene diphosphonic acid.

25. The method according to claim 1, wherein about 5 to 200 ppm of the surfactant is added to the aqueous system.

26. The method according to claim 1, wherein said microbes comprise bacteria.

27. The method according to claim 1, wherein said microbes comprise at least one of fungi, algae and protozoa.

28. The method according to claim 1, wherein said aqueous system comprises at least one of cooling water systems, reverse osmosis systems, pulping and papermaking systems, air washer systems, pasteurizer systems, fire water safety systems, shower water systems, metalworking fluid systems, hydrocarbon storage systems, and aqueous mineral processing systems.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 01/03975

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 A01N59/00 A01N43/80 A01N25/30 C02F1/50 //(A01N59/00, 37:02),(A01N43/80,37:02,33:20)

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 A01N C02F D21H

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)

WPI Data, PAJ, EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 1 560 327 A (NALCO CHEMICAL CO) 6 February 1980 (1980-02-06) page 1, line 7 - line 37; claims 1-4; examples IV,,V	1-28
A	EP 0 741 109 A (BETZ LABORATORIES) 6 November 1996 (1996-11-06) the whole document	1-28
A	US 5 942 219 A (HENDRIKS WILLIAM A) 24 August 1999 (1999-08-24) the whole document	1-28
A	US 5 935 920 A (GEKE JUERGEN ET AL) 10 August 1999 (1999-08-10) column 2, line 50 -column 3, line 37 column 4, line 19 - line 32 column 4, line 37 - line 50; table 1	1-28

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

[X] Patent family members are listed in annex.

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"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
10 July 2001	18/07/2001

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	Muellners, W

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Form PCT/ISA/210 (second sheet) (July 1992)

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 670 055 A (YU F PHILIP ET AL) 23 September 1997 (1997-09-23) column 1 -column 2, line 34; claims	1-28

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