[0005] This reduced efficacy is evidenced by the typically much higher concentrations of chemical biocides required for biofilm removal and control relative to control of planktonic organisms. This can increase both the cost of treatment and may also add an additional concern of corrosion due to extraordinarily high concentrations of corrosive chemical biocides.

[0006] In this regard, several biocides are used for MIC control in oil field gathering lines. Commonly used biocides are non-oxidizing chemicals such as glutaraldehyde or bis[tetrakis(hydroxymethyl)phosphonium] sulfate (THPS). Some concern has arisen that these biocides may be inherently corrosive at high end use concentrations and could cause general corrosion in the assets they are protecting from MIC.

[0007] Another group of biocides used in industry are quaternary amines. However, quaternary amines used alone at reasonable and affordable treatment concentrations are generally not as effective as other biocides in controlling microorganisms attached to metal surfaces and bulk fluids.

[0008] In view of the above, a need exists for an improved composition for preventing and inhibiting biofilm growth in industrial systems, particularly in oil field applications.

SUMMARY

[0009] In general, the present disclosure is directed to a method for preventing and eradicating biofilm growth in industrial systems, such as in oil field applications. The present disclosure is also directed to a composition for preventing or inhibiting biofilm growth. The composition can be used in aqueous systems to control pitting, corrosion, and the like in various tubes, pipes and tiles, especially those made from metals.

[00010] In one embodiment, the composition comprises a first non-oxidizing biocide combined with a second non-oxidizing biocide. The first biocide may comprise a phosphonium sulphate salt such as bis[tetrakis(hydroxymethyl)phosphonium] sulphate. The second biocide, on the other hand, may comprise a quaternary ammonium salt, such as one having the following formula:

$$(R^1R^2R^3R^4N^+)_n\ X^{n-} \quad (I)$$

[0014] Other features and aspects of the present disclosure are discussed in greater detail below.

DETAILED DESCRIPTION

[0015] It is to be understood by one of the ordinary skill in the art that the present discussion is a description of exemplary embodiments only, and is not intended as limiting the broader aspects of the present disclosure.

[0016] The extent and nature of MIC vary with the context of the problem. The diverse nature of physico-chemical conditions in oil field applications, as well as diverse microbiology and environments in which biofilms grow call for a variety of tactics and strategies for MIC control that might include corrosion inhibitors, microbiological control, biofilm control and prevention, pipe cleaning, pigging, and mixtures thereof.

[0017] The present disclosure is directed to an improved composition and process for preventing the growth of biofilms in aqueous systems, such as those related to oil field applications. In accordance with the present disclosure, a first biocide is combined with a second biocide. The combination of biocides can provide various advantages and benefits. For instance, using a combination of biocides can provide greater efficacy over a larger range of microorganisms. In addition, biocides can be selected that are complementary to each other. For instance, in one embodiment, a non-oxidizing biocide, such as a phosphonium sulphate salt, may be combined with a second biocide comprising a quaternary ammonium compound.

[0018] Unfortunately, however, many biocides are incompatible when mixed together. For instance, a phosphonium sulphate salt is generally incompatible in a solution with a quaternary ammonium compound, and particularly a dialkyl dimethyl ammonium compound, especially at higher concentrations. Consequently, the two biocides have a tendency to separate from each other making application of the biocides to an aqueous system problematic.

[0019] In accordance with the present disclosure, however, a stabilizing agent is added to the blend of biocides. The stabilizing agent, in one embodiment, produces a single phase solution, even when the biocides are present at a relatively high concentration.

[0020] In one embodiment, the stabilizing agent may comprise a hydrotrope that stabilizes the blends of biocides providing a product that can be more readily

shipped and diluted. A single phase solution can be produced without having to add additional co-solvents or without having to use expensive polymers.

[0021] In one embodiment, the stabilizing agent may comprise an alkyl trimethyl ammonium compound, such as an alkyl trimethyl ammonium salt. When added to an aqueous composition containing a phosphonium sulphate salt and a dialkyl dimethyl ammonium compound, the stabilizing agent can produce a clear concentrate, even at total active concentrations of greater than about 15% by weight, such as greater than about 20% by weight, such as even greater than about 25% by weight.

[0022] As described above, the composition in the present disclosure contains a first non-oxidizing biocide, at least a second non-oxidizing biocide, and a stabilizing agent. The first non-oxidizing biocide may include, for instance, glutaraldehyde, isothiazolin, 2,2-dibromo-3-nitrilopropionamide, 2-bromo-2-nitropropane-1,3 diol, 1-bromo-1-(bromomethyl)-1,3-propanedicarbonitrile, tetrachloroisophthalonitrile, Poly(oxyethylene(dimethyliminio)ethylene(dimethyliminio)ethylene dichloride, methylene bisthiocyanate, 2-decylthioethanamine, dithiocarbamate, cyanodithioimidocarbonate, 2-methyl-5-nitroimidazole-1-ethanol, 2-(2-bromo-2-nitroethenyl)furan, beta-bromo-beta-nitrostyrene, beta-nitrostyrene, beta-nitrovinyl furan, 2-bromo-2-bromomethyl glutaronitrile, bis(trichloromethyl) sulfone, S-(2-hydroxypropyl)thiomethanesulfonate, tetrahydro-3,5-dimethyl-2H-1,3,5-hydrazine-2-thione, 2-(thiocyanomethylthio)benzothiazole, 2-bromo-4'-hydroxyacetophenone, 1,4-bis(bromoacetoxy)-2-butene, bis(tributyltin)oxide, 2-(tert-butylamino)-4-chloro-6-(ethylamino)-s-triazine, dodecylguanidine acetate, dodecylguanidine hydrochloride, coco alkyldimethylamine oxide, n-coco alkyltrimethylenediamine, tetra-alkyl phosphonium chloride, 7-oxabicyclo[2.2.1]heptane-2,3-dicarboxylic acid, 4,5-dichloro-2-n-octyl-4-isothiazoline-3-one, 5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one. In one embodiment, the first biocide may comprise a phosphorous compound, such as a phosphonium compound.

[0023] The phosphorus compound may contain one phosphorus atom and may be of the formula $[HORPR'\text{-}_n0_m]_yX_x$ wherein n is 2 or 3; m is 0 or 1 such that (n+m)=2 or 3; x is 0 or 1 such that (n+x)=2 or 4; y is equal to the valency of X; R is an alkylene group of 1 to 4, preferably 1, carbon atoms with the hydroxy group attached to the 1, 2, 3 or 4 numbered carbon atom; each R' may be the same or

[0029] In one embodiment, the second biocide may comprise a quaternary ammonium salt, such as a dialkyl dimethyl ammonium compound, such as a dialkyl dimethyl ammonium salt.

[0030] In one embodiment, the salt comprises a halide, such as a chloride. Each alkyl group in the dialkyl dimethyl ammonium compound can have a carbon chain length of from about 4 carbon atoms to about 48 carbon atoms, such as from about 6 carbon atoms to about 28 carbon atoms. In one particular embodiment, the carbon chain length is from about 8 carbon atoms to about 20 carbon atoms. In one particular embodiment, for instance, a didecyl dimethyl ammonium salt is used.

[0031] In addition to a first biocide and a second biocide, the composition may include further biocides. For instance, a mixture of quaternary ammonium compounds, such as a mixture of dialkyl dimethyl ammonium compounds, may be present in the composition in conjunction with the first biocide, which may comprise a phosphonium sulfate salt.

[0032] The relative amounts of each biocide present in the composition can vary depending upon numerous factors and the end use application. In one particular embodiment, when combining a phosphonium sulfate salt with a dialkyl dimethyl ammonium compound, the first biocide and the second biocide may be present in the composition at a weight ratio of generally less than about 10:1. For instance, the weight ratio may be from about 10:1 to about 1:1.

[0033] The concentration of the first biocide, such as a phosphonium salt, can be in the range of 50 – 2000 ppm, preferably in the range of 75 – 1000 ppm, and most preferably in the range of 125 – 500 ppm and the concentration of the second biocide, such as a quaternary ammonium salt, is in the range of 25 – 1000 ppm, preferably in the range of 37 – 500 ppm, and most preferably in the range of 63 – 250 ppm.

[0034] In accordance with the present disclosure, the composition further contains a stabilizing agent that increases the compatibility of the first biocide and the second biocide. In one embodiment, a stabilizing agent is present in an amount sufficient such that the resulting composition comprises a single phase solution. In one embodiment, the stabilizing agent may comprise a quaternary ammonium compound that is different from the second biocide present in the composition. In one particular embodiment, for instance, the stabilizing agent may

WHAT IS CLAIMED:

1. A composition for preventing or inhibiting biofilm growth comprising:

a first non-oxidizing biocide blended with a second non-oxidizing biocide, the second biocide comprising a quaternary ammonium compound, the first biocide and the second biocide being blended with a stabilizing agent, the stabilizing agent comprising alkyltrimethylammonium compound that is different from the second biocide,

wherein the first biocide and the second biocide are present in the composition at concentrations such that the biocides are immiscible,

wherein the composition has a total active concentration of greater than 15% by weight, and

wherein the stabilizing agent is present in an amount sufficient to produce a single phase solution.

2. The composition of claim 1, wherein the first biocide comprises a phosphonium sulfate salt.

3. The composition of claims 1 to 2, wherein the first biocide comprises bis[tetrakis(hydroxymethyl)phosphonium] sulfate.

4. The composition of claims 1 to 3, wherein the second biocide comprises a dialkyl dimethyl ammonium compound.

5. The composition of claims 1 to 4, wherein the first biocide and the second biocide are present in the composition at a ratio of from 10:1 to 1:1.

6. The composition of claims 1 to 5, wherein the composition is polymer-free.

7. The composition of claims 1 to 6, wherein the second biocide comprises a monomeric dialkyl dimethyl ammonium compound.

8. The composition of claim 1 to 7, wherein the second biocide comprises a quaternary ammonium compound of the formula

$$(R^1R^2R^3R^4N^+)_n\ X^{n-} \quad (I)$$

wherein R^1 through R^4 are independently selected from the group consisting of C_{1-20} aliphatic hydrocarbyl groups and C_{7-11} aromatic hydrocarbyl groups, and X^{n-} is a counter-anion selected from the group consisting of carbonate, bicarbonate, halides, phosphates,

ethosulfates, citrates, borates, nitrate, C_{1-20} carboxylates, and mixtures thereof, wherein *n* designates the number of negative charges of the counter-anion.

9. The composition of claim 1 to 8, wherein the alkyl group in the alkyl trimethyl ammonium compound has a carbon chain length of 4 to 48 carbon atoms.

10. The composition of claim 8, wherein X^{n-} comprises a halide.

11. A water treatment composition for oil field applications comprising the composition of claim 1 to 10 further comprising a corrosion inhibitor.

12. The water treatment composition of claim 11, further comprising an anti-foaming agent, a chelating agent, an anti-static agent, a surfactant, a dispersing agent, a scale inhibitor or mixtures thereof.

13. A process for producing a water treatment composition for oil field applications comprising diluting the composition defined in any one of claims 1 to 10 with a carrier comprising water and adding the diluted composition to a water source.

14. The process of claim 13, further comprising the step of adding to the diluted composition a corrosion inhibitor, a scale inhibitor, an anti-foaming agent, a chelating agent, an anti-static agent, a surfactant, a dispersing agent, or mixtures thereof.

15. A method of controlling biofilm in an industrial system comprising adding to an aqueous medium in the industrial system a composition comprising a first non-oxidizing biocide blended with a second non-oxidizing biocide, the second biocide comprising a quaternary ammonium compound, the first biocide and the second biocide being blended with a stabilizing agent, the stabilizing agent comprising an alkyltrimethylammonium compound that is different from the second biocide,

wherein the first biocide and the second biocide are present in the composition at concentrations such that the biocides are immiscible,

wherein the composition has a total active concentration of greater than 15% by weight, and

wherein the stabilizing agent is present in an amount sufficient to produce a single phase solution.

16. The process of claim 15, further comprising the step of diluting the composition prior to adding the composition to the aqueous medium.

17. The process of claim 15 or 16, wherein the composition is combined with a corrosion inhibitor, a scale inhibitor, an anti-foaming agent, a chelating agent, an anti-static agent, a surfactant, a dispersing agent, or mixtures thereof.

18. The process of claims 15 to 17, wherein the first biocide comprises a phosphonium sulfate salt and the second biocide comprises a dialkyl dimethyl ammonium compound and wherein the first biocide and the second biocide are contained in the composition at a weight ratio of from 10:1 to 1:1.