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(54) **Title:** METHOD FOR FORMATION OF AN AQUEOUS WELL TREATMENT FLUID WITH BIOCIDAL ACTIVITY

(57) **Abstract:** The present invention relates to a method of formation of an aqueous well treatment fluid composition with biocidal activity. The method has use on oil and gas field operations. A method of formation of an aqueous well treatment composition with antimicrobial activity comprising adding to an aqueous composition, a source of hydrogen peroxide, selected from the group consisting of percarbonates and peroxides; and an N-acetylated ethylene diamine; such that an effective antimicrobial amount of peracetic acid is formed.

Method for Formation of an Aqueous Well Treatment Fluid with Biocidal Activity

Field of Invention

The present invention relates to a method of formation of an aqueous well treatment fluid composition with biocidal activity. The method has use in oil and gas field operations.

Background to the Invention

Microbiological control is important in oil and gas field operations. Bacteria in oil fields can pose several costly problems, including erosion that can lead to pipeline and vessel failures and the production of hydrogen sulphide gas, which can be lethal even in relatively low doses. Fracturing fluids, for instance, often contain polymers which encourage growth of microorganisms. The proliferation of microorganisms can result in the formation of slime or biofilm, which can be deleterious to the fracturing fluid and pose risks to the environment.

Biocides are used in fracking to prevent biofilm formation downhole. Biofilms may lead to clogging and hinder gas extraction. Biocides inhibit growth of two key bacterial classes found in wells; Sulphate Reducing Bacteria (SRB) and Acid Producing Bacteria (APB), both of which can cause Microbially Induced Corrosion (MIC). MIC can cause corrosion of production casing and tubing, leading to potential failure and environmental contamination. The SRB produce sulphides as part of their respiratory process which leads to “souring” of the well, causing the produced gas to be foul smelling, potentially toxic and highly corrosive to steel.

Several biocides have been used in oil and gas field operations, for example glutaraldehyde and tetrakis hydroxymethyl phosphonium sulphate. However, since the water used in such operations is often discharged into the environment, caution is advised since these biocides can have environmental consequences.

A commonly used biocide for fracking is glutaraldehyde. Other biocides used in fracking include 2,2-Dibromo-3-Nitrilopropionamide (DBNPA), tetrakis-hydroxymethylphosphoniumsulfate (THPS), 2-bromo-2-nitropropane-1,3-diol

(Bronopol), 3,5-Dimethyl-1,3,5-thiadiazinane-2-thione (Dazomet), tributyltetradecylphosphoniumchloride (TTPC), halogenated oxidisers and peracetic acid (PAA). Most of these biocides are potent aquatic toxins at low concentrations and some may present hazards to humans such as carcinogenicity, mutagenicity and other developmental toxicities. Hence, they pose an environmental risk in case of spillage or build-up of residues in the environment. In addition to the risk presented by the biocide itself, many degrade into hazardous substances. For instance, DBPNA degrades to give DBA, a carcinogen, Bronopol produces nitrosamines and chlorinated biocides give a range of disinfectant by-products. Some of these by-products are more persistent in the environment than the parent biocide. In contrast, PAA has environmental advantage over other biocides used in fracking due to its short half-life in solution and low hazard degradation products, acetic acid and water.

Peracetic acid (PAA) has strong oxidising potential and aqueous solutions of this chemical have antimicrobial and biocidal properties. It quickly degrades in the environment into relatively innocuous by-products, acetic acid and water and thus addresses some of the environmental concerns above. PAA solutions can be used in fracking. Such solutions typically have high hydrogen peroxide concentration. Although they have excellent biocidal activity, they often lead to corrosion of hardware used in the fracking process, such as steel, and have deleterious effects on other chemicals used in the fracking process, such as polymer additives.

Attempts have been made to overcome these disadvantages associated with PAA. GB 2477257, for instance, describes an aqueous well treatment fluid composition with biocidal activity comprising a polymer or copolymer for modifying fluid viscosity, an organic monocarboxylic peracid and hydrogen peroxide, the hydrogen peroxide concentration being less than the peracid concentration. The level of hydrogen peroxide concentration is kept low, such that it does not adversely affect the viscosity modifying polymer.

US 2013/0259743 also describes peracid compositions having low hydrogen peroxide content, for use in fracturing fluids. Catalase enzymes are used to

reduce the hydrogen peroxide content. The treated water reduces corrosion caused by hydrogen peroxide and reduces microbial-induced corrosion. The antimicrobial composition is said to not interfere with friction reducers, viscosity enhancers and other functional ingredients found in the water source. Preferred ratios for H_2O_2:peracid are said to be in the range 0:100 to 1:10.

WO 2011/159859 also describes microbiological control in oil and gas field operations. This publication describes a method for inhibiting bacterial growth in a fracturing fluid that includes adding an effective bacterial inhibiting amount of peracetic acid into a fracturing fluid comprising water, at least one polymeric viscosifier, and at least one proppant. Methods of inhibiting bacterial contamination in ballast water of an offshore oil rig are also provided. An effective bacterial inhibiting amount of peracetic acid is added into the ballast water.

A process suitable for creating and feeding a dispersion of chemical additives into a hydrocarbon process stream is described in WO2014/055339A1.

Given the expansion of the fracking industry, there remains a need to provide improved compositions for use in fracking, and methods for generating them.

Summary of the Invention

In a first aspect of the invention, there is provided a method for formation of an aqueous well treatment composition with antimicrobial activity comprising adding to an aqueous composition:

(i) a source of hydrogen peroxide, selected from the group consisting of percarbonates and peroxides; and
(ii) an N-acetylated ethylene diamine

such that an effective antimicrobial amount of peracetic acid is formed.

The aqueous well treatment fluid of the invention is antimicrobial, i.e. inhibits and/or controls microorganisms. The aqueous well treatment fluid of the invention may be biocidal, i.e. kills microorganisms.

A second aspect of the invention provides a method according to the first aspect of the invention which further comprises directing the aqueous well treatment composition into a subterranean environment.

A third aspect of the invention provides an aqueous well treatment composition obtainable by the method of the first aspect of the invention.

The present invention provides a means for providing aqueous well treatment compositions with biocidal activity in an environmentally-friendly manner. The organic monocarboxylic peracid produced, e.g. peracetic acid, degrades to harmless by-products in the environment in a relatively short period of time. Furthermore, the N-acetylated ethylene diamine can be provided in solid form and released in a steady manner, which allows a steady and constant concentration of antimicrobial to be produced. The source of hydrogen peroxide can also be provided in solid form, and this will not react with the N-acetylated ethylene diamine until the two are mixed together in aqueous solution. The use of solid starting materials results in easier handling and less transportation volume to sites which are frequently remote and have poor access. The transportation of the TAED and peroxide source as separate components gives safety advantages compared to transportation of peracetic acid in solution. PAA in solution is an acidic, corrosive, highly irritant liquid which can intensify fires through oxygen release. Additionally, lower corrosion in the well, especially of metallic components such as steel components, is expected from the invention. This may be due to lower amounts of H_2O_2 compared to preformed PAA solutions.

Tetra-acetylethylene diamine (TAED) is a well-known activator for peroxide-based bleaches, for instance used in laundry detergents. The peroxide is formed from a persalt such as a perborate, a percarbonate or a persulphate, which can be formulated as a solid material in a detergent composition. The persalt dissolves in the water and decomposes to form a hydroperoxyl ion, which reacts with TAED to give peracetic acid. Peracetic acid is known to be an efficient bleach, in particular for textiles, and has good low temperature efficacy.

TAED has been used to generate peracetic acid to destroy microorganisms in waste in a water holding tank. US 7,291,276 describes a method in which TAED is added in a controlled time release manner to peroxygen resulting in the production of peracetic acid.

Peracetic acid is normally supplied as an aqueous formulation comprising the following equilibrium:

$CH_3C(=O)OOH + H_2O \leftrightarrow CH_3COOH + H_2O_2$

The amount of peroxide can be calculated using measurements from titration against potassium permanganate. 2 moles of permanganate reacts with 5 moles of peroxide. The permanganate only oxidises the hydrogen peroxide and cannot oxidise any peracetic acid present, as it is already in its highest oxidation state. In this manner, the relative amounts of peracetic acid and hydrogen peroxide can be determined without affecting the balance of equilibrium.

Commercial peracetic acid solutions normally contain a concentration of hydrogen peroxide in excess of the peracetic acid concentration. Some products developed for oilfield applications are offered with lower concentrations of hydrogen peroxide, for instance VigorOx® Oil and Gas supplied by PeroxyChem which contains 15-17% PAA and 9-11% hydrogen peroxide. However, the present inventors have found that using an N-acetylated ethylene diamine in accordance with the invention can result in a much higher ratio of peracetic acid to hydrogen peroxide. Lower concentrations of hydrogen peroxide are beneficial as hydrogen peroxide is a strong oxidant and can degrade polymer additives present in the aqueous well treatment compositions, as well as damage equipment through corrosion.

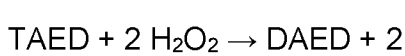
Detailed Description of the Invention

The hydrogen peroxide or precursor is formed, for instance, by adding to water an organic persalt, preferably a peroxide or a percarbonate. The persalt and the N-acetylated ethylene diamine material can be added together as part of the same solid composition. Sources of hydrogen peroxide include hydrogen peroxide

solution, calcium peroxide and sodium percarbonate. The hydrogen peroxide source is preferably sodium percarbonate.

In the process, the N-acetylated ethylene diamine material and peroxygen bleach precursor may be present in amounts such that the peroxygen bleach precursor is present in a small stoichiometric excess as compared to the activator.

A typical N-acetylated ethylene diamine material, TAED, reacts with hydrogen peroxide according to the following reaction to generate peracetic acid:



$$TAED + 2\ H_2O_2 \rightarrow DAED + 2\ H_3CC(=O)OOH$$

DAED is a harmless by-product of the reaction.

An “effective antimicrobial amount”, in this invention, means a quantity of biocide giving at least a 6-log reduction in the relevant bacterial populations. Biocidal treatment with a biocide giving 6-log reductions in the relevant bacterial populations may lead to long term well protection for periods of months or longer and may also reduce the risk of souring or Microbially Induced Corrosion (MIC).

The aqueous well treatment composition may have a peracetic acid : hydrogen peroxide ratio by mass of at least 1:1:, preferably at least 2:1, more preferably at least 10:1, most preferably at least 20:1.

Preferably, the peracetic acid (PAA) formed is present in an amount of at least 2 ppm and no greater than 700 ppm. Too little PAA may have insufficient biocidal activity, or even no biocidal activity at all.

A concentration of 2 ppm PAA could be achieved by reacting 0.0037 grams per litre of sodium percarbonate (PCS) with 0.0036 grams per litre of a granular product containing about 92 wt% TAED. The yield may be 91.5% of the theoretical maximum PAA release.

A concentration of 700 ppm PAA could be achieved by reacting 1.281 grams per litre of sodium percarbonate (PCS) with 1.248 grams per litre of a granular product containing about 92 wt% TAED. The yield may be 91.5% of the theoretical maximum PAA release.

The aqueous well treatment composition of the invention has biocidal activity against a range of microorganisms, including at least one of plankton, phytoplankton, zooplankton, microbial organisms, nekton organisms, or benthic organisms in the aqueous well treatment composition. In particular, the composition of the invention may inhibit growth of two key bacterial classes found in wells; Sulphate Reducing Bacteria (SRB) and Acid Producing Bacteria (APB), both of which can cause MIC. MIC may damage production casing and tubing, leading to potential failure and environmental contamination. The SRB produce sulphides as part of their respiratory process which leads to “souring” of the well, causing the produced gas to be foul smelling, potentially toxic and highly corrosive to steel.

Inorganic sulphide removal is important in oil and gas production environments due to the hazardous and corrosive nature of H_2S. Peracetic acid can oxidise sulphides and thereby reduce corrosivity of the fracking fluid by biocidal and chemical means.

The aqueous well treatment composition of the invention is intended for use with aqueous treatment fluids that are conventionally used in subterranean oil and gas field well operations, such as well drilling, formation fracturing, productivity enhancement, secondary recovery and the like.

The fluid may be pumped at high pressure into the well during fracturing. Suitable pressures are from 2000 to 20000 psi, preferably from 4000 to 15000 psi. Such fluids are generally referred to as fracturing fluids and may comprise the aqueous well treatment composition of the invention, additional water, a polymeric viscosifier, a proppant, corrosion inhibitors, scale inhibitors and other additives. Other additives may for instance include biocides, breakers, cross-linkers and gels, clay and shale stabilizers, iron chelators, non-emulsifiers, and surfactants.

Reduction of peroxide levels in accordance with the invention may reduce deleterious reactions with any of the constituents of the fracking fluid.

Suitable polymeric viscosifiers include polymers selected from the group consisting of polysaccharides, polyacrylamides, polyglycosans, and carboxyalkyl ethers, and combinations thereof. They are generally used in the amount 0.01 to 1 wt%, based on the weight of the composition. Preferably the polymeric viscosifier is a friction reducer.

Suitable corrosion and scale inhibitors include those described in US 2013/0259743.

Generally fracking fluids are acidifed and therefore compositions used in this invention may further comprise pH adjusters and buffers. The compositions may additionally comprise other components such as lubricant, enzymes, pigments, dyes and sequestrants, for instance sequestrants for heavy metals, which may provide desirable stabilisation of the peracetic acid formed in the reaction process.

Examples

Examples 1a, b, c and d

Examples 1a-d demonstrate the biocidal efficacy of the invention (example 2) compared to two commercially available biocide products: pre-formed PAA solution (example 3) and glutaraldehyde solution (example 4). A control test with no biocide was also conducted for comparison (example 1).

Biocidal performance was tested using the industry standard “Time to Kill Test”, detailed by the National Association of Corrosion Engineers (Standard Test Method, TM0-194-94, *Field Monitoring of Bacterial Growth in Oilfield Systems,* NACE International, Houston, Texas, 1994).

Biocidal efficacy of PAA generated *in-situ* from TAED and PCS was tested against two bacterial types. “Total viable bacteria count” (TVC) is a general heterotrophic bacteria mixed culture. TVC is important to control because it gives rise to fouling

and plugging of filters, components and reservoirs. “Sulphate-reducing bacteria” (SRB) was also tested against. SRB must be controlled in an oilfield because they produce hydrogen sulphide, which is toxic to humans, and are involved in microbial-influenced corrosion of various metals, including steel.

Bacterial samples were prepared by introducing sterilised carbon steel coupons under anaerobic conditions to cultures of SRB and of mixed heterotrophic bacteria (used to represent TVB), in a single water sample type, both obtained from a UK oilfield produced water of low salinity. Three weeks incubation at 30°C were allowed for formation of a sessile biofilm.

The incubated coupons, coated with a sessile biofilm, were exposed to the biocides of examples 1a-d for periods of 0.5, 1, 2 and 4 hours at 30°C. Following exposure, the remaining sessile bacterial population was determined by sonication to remove the surface deposit into sterile medium, followed by serial dilution in accordance with NACE TM0194.

The single water sample used included salts in the amounts given in Table 1.

Salt	**Concentration (g/litre)**
$CaCl_2.6H_2O$	0.148
$MgSO_4.7H_2O$	0.071
KCl	0.006
Na_2SO_4	0.018
$NaHCO_3$	0.139

Table 1: test water composition

The bacterial samples were exposed to the test solutions of examples 1a-d at 30°C and average number of colony-forming units of total viable bacteria and sulphate reducing bacteria per cm^2 of steel surface were measured at time zero, 0.5 hours, 1 hour, 2 hours and 4 hours.

Example 1a (control)

The bacterial sample coupons were exposed to the test water composition in the absence of any biocide to generate control results for average bacterial amounts. The control results are as follows:

	Time zero	0.5 hours	1 hour	2 hours	4 hours
Sulphate-reducing bacteria (SRB)	$5.0*10^5$	$5.0*10^5$	10^5	10^5	$5.0*10^5$
Total viable bacteria (TVB)	$>10^6$	$>10^6$	$>10^6$	$>10^6$	$>10^6$

Table 2: control results for the average number of colony-forming units per cm^2 of steel surface on the test coupons for SRB and TVB in the absence of biocide.

Example 1b (invention)

An aqueous solution was prepared by mixing 27.50 g TAED (tetra acetylethylene diamine) with 28.34 g activator PCS (sodium percarbonate) under alkaline conditions (10 g NaOH). PAA (peracetic acid) was released; theoretical maximum for these reagent amounts is 15000ppm. At maximum PAA release, the solution was stabilised by adjusting the pH to 4.5 with acetic acid.

Maximum PAA release was determined by iodometric titration. The amount of PAA released at any time interval can be determined by taking an aliquot of the aqueous solution, quenching with glacial acetic acid, ice and potassium iodide solution and then titrating the quenched solution with sodium thiosulphate. The glacial acetic acid and ice quench any further peracetic acid formation and the potassium iodide is oxidised by the PAA that has already formed to liberate iodine. The liberated iodine reacts with the sodium thiosulphate in the titration step.

The stabilised PAA solution was diluted in water to give samples with PAA concentration of 42.5 ppm, 85 ppm and 170 ppm. This corresponds to concentrations of the commercial product of example 1c of 250 ppmv, 500ppmv and 1000 ppmv, respectively.

The stabilised PAA solution was added to aliquots of the test water composition to give test solution having PAA concentrations of 42.5 ppm, 85 ppm and 170 ppm.

	Time zero	0.5 hours	1 hour	2 hours	4 hours
Sulphate-reducing bacteria (SRB) colony-forming units per cm^2 on steel surface					
42.5 ppm PAA	$5.0*10^5$	None detected	None detected	None detected	None detected
85 ppm PAA	$5.0*10^5$	None detected	None detected	None detected	None detected
170 ppm PAA	$5.0*10^5$	None detected	None detected	None detected	None detected
Total viable bacteria (TVB) colony-forming units per cm^2 on steel surface					
42.5 ppm PAA	$>10^6$	None detected	None detected	None detected	None detected
85 ppm PAA	$>10^6$	None detected	None detected	None detected	None detected
170 ppm PAA	$>10^6$	None detected	None detected	None detected	None detected

Table 3: average number of colony-forming units per cm^2 of steel surface on the test coupons for SRB and TVB with the biocide of the invention in three different concentrations of *in situ* generated PAA.

Example 1c (comparative)

Commercial product "VigorOx® Oil and Gas" PAA solution was added to the test water composition at concentrations of 250 ppmv, 500 ppmv and 1000 ppmv. This resulted in three test solutions having PAA concentrations of 42.5 ppm, 85 ppm and 170 ppm, respectively.

The VigorOx® comprises 33-38 wt% acetic acid; 9-11 wt% hydrogen peroxide, 30-44 wt% water, 15-17 wt% peracetic acid and <0.2 wt% sulphuric acid.

	Time zero	0.5 hours	1 hour	2 hours	4 hours
Sulphate-reducing bacteria (SRB) colony-forming units per cm^2 on steel surface					
42.5 ppm PAA	$5.0*10^5$	None detected	None detected	None detected	None detected
85 ppm PAA	$5.0*10^5$	None detected	None detected	None detected	None detected
170 ppm PAA	$5.0*10^5$	None detected	None detected	None detected	None detected
Total viable bacteria (TVB) colony-forming units per cm^2 on steel surface					
42.5 ppm PAA	$>10^6$	None detected	None detected	None detected	None detected
85 ppm PAA	$>10^6$	None detected	None detected	None detected	None detected
170 ppm PAA	$>10^6$	None detected	None detected	None detected	None detected

Table 4: average number of colony-forming units per cm^2 of steel surface on the test coupons for SRB and TVB with a commercially available preformed PAA biocide at three different concentrations of PAA.

Example 1d (comparative)

Commercially available biocide 50% glutaraldehyde solution was added to the test water composition in amounts of 250 ppmv, 500 ppmv and 1000 ppmv. The resulting test solutions had active ingredient (glutaraldehyde) concentrations of 125 ppm, 250 ppm and 500 ppm, respectively.

	Time zero	0.5 hours	1 hour	2 hours	4 hours
Sulphate-reducing bacteria (SRB) colony-forming units per cm^2 on steel surface					
125 ppm glutaraldehyde	$5.0*10^5$	$5.0*10^3$	10^3	10^2	$5.0*10^1$
250 ppm glutaraldehyde	$5.0*10^5$	$5.0*10^3$	10^1	None detected	None detected
500 ppm glutaraldehyde	$5.0*10^5$	None detected	None detected	None detected	None detected

Total viable bacteria (TVB) colony-forming units per cm^2 on steel surface					
125 ppm glutaraldehyde	$>10^6$	$5.0*10^4$	$5*10^3$	10^2	10^1
250 ppm glutaraldehyde	$>10^6$	$5.0*10^3$	10^1	$5*10^2$	None detected
500 ppm glutaraldehyde	$>10^6$	10^1	None detected	None detected	None detected

Table 5: average number of colony-forming units per cm^2 of steel surface on the test coupons for SRB and TVB with a commercially available 50% glutaraldehyde biocide at three different concentrations of glutaraldehyde.

Analysis, examples 1a-d

Example 1b, of the invention, at all three concentrations performed equally as well as known commercial preformed PAA solutions (Example 1c) in terms of biocidal performance against both total viable bacteria and sulphate-reducing bacteria cultures. The example of the invention performed better in these tests compared to known commercially-used glutaraldehyde solution (Example 1d).

Example 2

Biocidal performance of *in-situ* generated PAA from TAED/PCS was compared against three commercially available biocide products.

Each biocide product was diluted in a bacteria-contaminated water sample consisting of 10 vol% produced water from an oil field and 90 vol% Houston tap water. Concentrations of biocide ingredients are given in table 6.

Prior to contact with the contaminated water sample, PAA generated *in-situ* from TAED and PCS was allowed 5 minutes for the amount of PAA released to reach 150 ppm. Peracetic acid release can be measured by iodometric titration.

After 5 minutes contact time at 30°C, the amount of bacteria in the solution was calculated from light transmission measurements using a bioluminescence enzyme assay method, for example by using a LuminUltra® kit in accordance with ASTM D7687 and/or ASTM E2694. A control measurement of the bacteria count

in a contaminated water sample in the absence of any biocide product was made for comparison.

Sample	Bacteria count per mL
Control – no biocide	$1*10^5$
150 ppm *in-situ* generated PAA from TAED/PCS	$1*10^4$
150 ppm DBNPA (BioClear® 2000)	$2*10^4$
189 ppm glutaraldehyde (BioClear® 225)	$9*10^4$
149 ppm glutaraldehyde/quaternary component* (BioClear® 242D)	$8*10^3$

Table 6: biocide efficacy comparison

*Quaternary component is alkyl (C14 50%, C12 40%, C16 10%) dimethyl benzyl ammonium chloride

Analysis, example 2

The biocide efficacy test of example 2 shows that a PCS/TAED based system delivering 150 ppm of PAA can offer comparable biocidal performance to similar active ingredient concentrations of DBNPA and of glutaraldehyde/quat and improved biocidal performance against similar concentrations of glutaraldehyde.

Example 3

The aqueous well treatment composition used in the present invention may reduce corrosion compared to preformed PAA solutions.

Formulation 3a, of the invention, was prepared by combining 997.02 g deionised water, 1.0440 g of a granular product containing 92 wt% TAED, 1.0761 g PCS and 0.864 g sodium hydroxide.

Formulation 3b, a comparative example utilising a preformed PAA solution, was prepared by combining 998.62 g deionised water and 1.282 g preformed PAA solution containing a PAA concentration of at least 30% and less than 50% PAA.

The amounts of PAA and H_2O_2 were measured using iodometric titration and potassium permanganate titration, respectively, over the course of 7 days.

	Formulation 3a	Formulation 3b
Theoretical maximum PAA	640 ppm	385 to 641 ppm
Maximum PAA generated	586 ppm	515 ppm
PAA: H_2O_2 (initial)	34.5	8.7
PAA: H_2O_2 (after 7 days)	481	5.8

Table 7: peracid and peroxide ratio comparison between the composition of the invention and commercially available preformed PAA solutions

Analysis: Example 3

These results show that, under identical conditions, a dosage of a TAED/PCS system to 20% above that required to deliver a target PAA concentration delivers a peracid concentration greater than or similar to that of a preformed peracid solution at the initial target PAA concentration for the entire duration of the study.

Moreover, a dosage of a TAED/PCS system to 20% above that required to deliver a target PAA concentration maintains the peroxide concentration at a level significantly lower than that of a preformed peracid solution at the initial target PAA concentration for the entire duration of the study. Additionally, this shows that, even if the PAA solution is made up in advance from TAED and PCS in aqueous solution and not immediately used in a well, the amount of PAA in solution is maintained at a level sufficient to deliver the biocidal effect.

Example 3 demonstrates one of the key advantages of the method and product of the invention compared to preformed PAA solutions. In the invention, it is possible to control the equilibrium between peroxide and peracid such that it is weighted heavily towards peracid. This control is not possible with commercially available preformed PAA solutions, meaning that higher amounts of H_2O_2 will be present in solution for the same amount of PAA, with potentially negative consequences for corrosion in use.

Example 4

The corrosivity of the invention to carbon steel was compared to a commercially available, preformed PAA solution (VigorOx®, composition as described previously). Triplicate carbon steel coupons of grade C1018 were suspended within two test cells, one containing 1000 ml of test water (table 1) which was treated with 1000 ppm of VigorOx and a second cell containing 1000 ml of test water (table 1) treated with a peracetic acid equivalent concentration of activated TAED (an *in situ* generated PAA solution made from the reaction between sodium percarbonate and TAED), based on titrimetric analysis of the peracetic acid levels in the VigorOx product. The cells were heated to 30°C and maintained at that temperature. The test cells were sparged with oxygen-free nitrogen gas for the entire 168 hours exposure period to eliminate oxygen corrosion.

After the 168 hour exposure period, the carbon steel coupons were removed from the test cells. The coupons were then cleaned and dried in accordance with ASTM G31-72 so that the corrosion rates could be calculated. The corrosion rates given by calculation are average rates for the exposure period, based on the mass loss of each coupon and its surface area. Corrosion rate was calculated according to the following formula:

Corrosion rate = $[(8.76*10^4)*(\text{mass loss})]/[(\text{surface area})*(\text{time of exposure})*(7.85)]$

Mass loss was measured in g, to the nearest g; surface area was measured in cm^2, to the nearest cm^2; time of exposure was measured in hours, to the nearest 0.01 hours. $8.76*10^4$ is a constant to convert mass loss to depth of penetration. 7.85 g/cm^3 is the density of the carbon steel coupons.

Source of PAA	Pre-test mass, g	Post-test mass, g	Mass loss, g	Surface area, cm^2	Exposure time, hours	Corrosion rate, mm/year	Mean corrosion rate, mm/year
VigorOx	14.7326	14.5984	0.1342	27.25	168	0.33	0.26
VigorOx	14.8465	14.8465	0.1037	27.25	168	0.25	
VigorOx	14.7606	14.6796	0.0810	27.25	168	0.20	
TAED/PCS	14.7847	14.6940	0.0907	27.25	168	0.22	0.26
TAED/PCS	14.8829	14.7670	0.1159	27.25	168	0.28	
TAED/PCS	14.7531	14.6396	0.1135	27.25	168	0.28	

Table 8: Mass loss corrosion test results

Analysis, Example 4

These results show that the biocide of the invention – in the absence of any corrosion inhibitors - is no more corrosive than a commercially available biocide, for the same concentration of PAA.

What is claimed is:

1. A method of formation of an aqueous well treatment composition with antimicrobial activity comprising adding to an aqueous composition:

(i) a source of hydrogen peroxide, selected from the group consisting of percarbonates and peroxides; and

(ii) an N-acetylated ethylene diamine;

such that an effective antimicrobial amount of peracetic acid is formed.

2. The method according to claim 1 wherein the N-acetylated ethylene diamine material comprises N,N,N',N'-tetraacetylethylene diamine (TAED).

3. The method according to claim 1 or claim 2 wherein the effective antimicrobial amount is 1-1000ppm.

4. The method of any preceding claim wherein the well treatment composition has biocidal activity.

5. The method according to any preceding claim wherein the hydrogen peroxide is added in stoichiometric excess to the N-acetylated ethylene diamine.

6. The method according to any preceding claim wherein the hydrogen peroxide concentration in the resultant composition is less than the resultant organic monocarboxylic peracid concentration, preferably wherein the ratio by mass of organic monocarboxylic peracid to hydrogen peroxide is more than 2:1, preferably more than 10:1.

7. The method according to any preceding claim, wherein the source of hydrogen peroxide is added in an amount of from 0.0037 to 1.281 g per litre of aqueous well treatment composition.

8. The method according to any preceding claim, wherein the N-acetylated ethylene diamine is added in an amount of from 0.0036 to 1.248 g per litre of aqueous well treatment composition.

9. The method according to any preceding claim wherein the organic monocarboxylic peracid is peracetic acid.

10. The method according to any preceding claim wherein the source of hydrogen peroxide is a peroxygen compound selected from the group consisting of sodium percarbonate and calcium peroxide, preferably sodium percarbonate.

11. The method according to any preceding claim wherein the aqueous well treatment composition further comprises one or more additives selected from polymeric viscosifiers, proppants, corrosion inhibitors, scale inhibitors, biocides, breakers, cross-linkers and gels, clay and shale stabilizers, iron chelators, non-emulsifiers, surfactants, pH adjusters and enzymes.

12. The method according to any preceding claim wherein the organic monocarboxylic peracid inhibits the growth of at least one of plankton, phytoplankton, zooplankton, microbial organisms, nekton organisms, or benthic organisms in the aqueous well treatment composition.

13. The method according to any of preceding claim which further comprises directing the aqueous well treatment composition into a subterranean environment.

14. The method according to any preceding claim for use in an oil or gas well.

15. The method according to claim 11 or 12 which comprises injecting the aqueous well treatment composition into a wellbore through a formation at sufficiently high pressure to fracture the formation.

16. An aqueous well treatment composition obtainable by the method of any of claims 1 to 12, wherein the ratio by mass of organic monocarboxylic peracid to hydrogen peroxide is more than 1:1.

17. The aqueous well treatment composition of claim 16, wherein the ratio by mass of organic monocarboxylic peracid to hydrogen peroxide is more than 2:1, preferably more than 10:1.

18. A method of creating an antimicrobial or biocidal environment in an oil or gas well, said method comprising forming an aqueous well treatment composition according to claim 1 and directing the aqueous well treatment composition into the oil or gas well.

19. The method of claim 18, further comprising contacting the aqueous well treatment composition with a metal surface, preferably a steel surface.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2017/030361

A. CLASSIFICATION OF SUBJECT MATTER
INV. A01N37/16 A01N59/00 A01P1/00
ADD.

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)
A01N

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	paragraph [0021] example 1 claim 17	1-19

X	US 2010/092574 A1 (SWEENY PHILIP GERDON [US]) 15 April 2010 (2010-04-15)	1,2,4,9, 11-14, 18,19
Y	paragraphs [0002], [0022] claims 1-4	1-19

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Y	paragraph [0079] claims 1, 2, 25, 26	1-19

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

[X] See patent family annex.

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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
13 June 2017	22/06/2017

Name and mailing address of the ISA/	Authorized officer
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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