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(71) **Applicant** *(for all designated States except US)*: **MEDENTECH LIMITED** [IE/IE]; Clonard Road, Wexford (IE).

(72) **Inventors; and**
(75) **Inventors/Applicants** *(for US only)*: **STAFFORD, Ulick** [IE/IE]; Newtown, Adamstown, Enniscorthy, County Wexford (IE). **STARKEY, Ronald, Joe** [US/US]; 39321 Bay Drive, Ponchatoula, LA 70454 (US).

(74) **Agents**: **O'BRIEN, John, A.** et al.; c/o John A. O'Brien & Associates, Third Floor, Duncairn House, 14 Carysfort Avenue, Blackrock, County Dublin (IE).

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(54) **Title**: INHIBITION OF BACTERIAL GROWTH IN OIL FIELD FLUIDS

(57) **Abstract**: A method for inhibiting bacterial growth in oil field fluids comprises the step of adding to the fluid a tablet composition comprising sodium dichloro-isocyanurate in an amount to achieve an effective biocidal action, and an effervescent base. The tablet provides a sanitising solution having a pH in the range of from 5.5 to 7.5.

"Inhibition of bacterial growth in oil field fluids"

Introduction

Fracturing (also referred to as fracting) is a treatment that is commonly performed to stimulate the flow of oil and gas in oil and gas wells. Fracturing fluids are pumped at high pressure into the oil or gas reservoir to cause a fracture in the reservoir through which oil can flow from the reservoir.

Fracturing fluids contain a range of different agents, depending on the characteristics of the reservoir. The fluids are generally prepared at or close to the well site. Large volumes of water are required. The water is drawn from a wide range of sources and stored in large storage tanks. The water and, consequently the fracturing fluid prepared using it, is often contaminated with micro-organisms which can cause major problems in use. Such organisms proliferate in the anaerobic environment in oil wells causing blockage or corrosion and can chemically degrade some of the agents used in the fracturing fluid. Fracting and well stimulation utilises long chain polyacrylamide polymers or guar gums as friction reducers (materials used to increase viscosity). It is necessary to treat water used in the fracting/stimulation process to prevent microbiological degradation of the friction reducers.

Liquid biocides are often added to the water and/or fracturing fluid in an effort to alleviate these problems. However, handling of liquid biocides on site creates problems for workers. Biocides in particulate form can be used but these present problems because they are often hygroscopic and form clumps in storage. Further, there are major difficulties in dispersing such particulate biocide formulations in the storage tanks. The tanks have little to no circulation and dispersing the biocide throughout the tank is difficult. Biocides in particulate form are preferred for safety of handling and ease of application. In recent years, fracting/stimulation is being performed above aquifers and the safety of the biocide to drinking water is a concern.

Statements of Invention

According to the invention sodium dichloro-isocyanurate (NaDCC) that contains effervescent material is added in a tableted form to fracturing tanks. The effervescent material aids in the dissolution and dispersion of the NaDCC in the stagnant fracturing tank. NaDCC has a high

solubility and produces hypochlorous acid at a neutral pH. The neutral pH hypochlorous solution is less corrosive than other forms of hypochlorous - generating materials such as bleach or TCCA. Further advantages of NaDCC in fracting/stimulation applications consist of well defined demand testing procedures that can be performed on site to minimise use of the biocide. In addition, NaDCC is currently used in treating potable water and there is a large body of empirical data showing its safety, should aquifer contamination take place.

According to the invention there is provided the use of a water soluble sanitising tablet composition comprising sodium dichloro-isocyanurate and an effervescent base. The effervescent tablet format has the advantages of being in a unit dose format, which self-dissolves in water, to produce sanitizer solutions of known and accurate strength, without having to weigh out powders, measure out liquids and to compute the required dosage and solution strength. Tablets are easier and safer to handle and store, and they do not spill.

The effervescent base may comprise an alkali buffering agent, an aliphatic carboxylic acid and an alkali metal bicarbonate to provide a sanitising solution having a weakly acid to neutral pH. (5.5 to 7.5)

Sodium dichloro-isocyanurate is readily soluble in water, producing solutions that are effective sanitisers and, more particularly in relation to this invention, remain active over a wide range of pH.

In one embodiment the alkali buffering agent is sodium carbonate. Sodium carbonate is readily soluble in water, is available in pharmaceutical or food grades and is strongly alkaline.

In one embodiment the alkali metal bicarbonate is sodium bicarbonate. Sodium bicarbonate readily dissolves in water and causes effervescence releasing carbon dioxide gas. Potassium bicarbonate may also be used.

In one embodiment the aliphatic carboxylic acid is adipic acid. Adipic acid has the advantage of being non hygroscopic, which helps to preserve the integrity and stability of the finished tablet formulation. Adipic acid also has lubricating properties that aid the tabletting process. Malic

acid, succinic acid, citric acid, ascorbic acid, fumaric acid, tartaric acid, citric anhydride, succinic anhydride, sodium dihydrogen phosphate, disodium dihydrogen pyrophosphate, or acid citrate salts may also be used.

The tablet composition used in the invention preferably delivers up to 40 ppm of available chlorine to the fracting water. 40 ppm available chlorine solution has the wide-spectrum activity necessary for effective sanitation, being effective against cysts, viruses, mycobacteria, bacteria and fungi and is within WHO organisation recommendation for drinking water. In a preferred embodiment the invention delivers approximately 5 ppm of available chlorine to the fracting water. 5 ppm available chlorine solution has the wide-spectrum activity necessary for effective sanitation, being effective against cysts, viruses, mycobacteria, bacteria and fungi and is close to the maximum amount of chlorine recommended by US EPA for drinking water. Use of this amount of chlorine will not pollute ground water if fracting water leaks into water aquifers.

The water soluble disinfecting tablet may consist essentially of:-

from 35% to 65% by weight of sodium dichloro-isocyanurate;
from 15-50% alkali metal bicarbonate;
from 15-35% aliphatic carboxylic acid;
from 3-25% alkali metal carbonate.

The water soluble disinfecting tablet may consist essentially of:-

from 40% to 50% by weight of sodium dichloro-isocyanurate;
from 18-30% alkali metal bicarbonate;
from 18-25% aliphatic carboxylic acid;
from 4-21% alkali metal carbonate.

In one case the water soluble disinfecting tablet consists essentially of:-

from 40% to 45% by weight of sodium dichloro-isocyanurate;
from 18-22% alkali metal bicarbonate;
from 18-22% aliphatic carboxylic acid;
from 15-21% alkali metal carbonate.

In one embodiment the tablet comprises approximately sodium dichloro-isocyanurate 42%, sodium bicarbonate 19%, adipic acid 19% and sodium carbonate 20%.

In another case the water soluble disinfecting tablet may consist essentially of:-

from 48% to 52% by weight of sodium dichloro-isocyanurate;

from 21-25% alkali metal bicarbonate;

from 21-25% aliphatic carboxylic acid;

from 5-7% alkali metal carbonate.

In one embodiment the tablet comprises approximately sodium dichloro-isocyanurate 50%, sodium bicarbonate 23%, adipic acid 22% and sodium carbonate 5%.

The invention also provides a water soluble sanitising composition for use in fracting tanks comprising a chlorinated isocyanurate and an effervescent base, the effervescent base comprising sodium carbonate, adipic acid and sodium bicarbonate in an approximate weight ratio of 1:1:1.

The invention further provides a water soluble sanitising composition for use in fracting tanks comprising a chlorinated isocyanurate and an effervescent base, the effervescent base comprising sodium carbonate, adipic acid and sodium bicarbonate in an approximate weight ratio of 1:5:5.

The tablet compositions used in the invention may be formed by a direct compression technique, which enables the manufacture of the alkali effervescent tablets without pre-processing by granulation and drying of the ingredients or addition of tabletting aids.

The invention provides a method to sanitise water used for fracting prior to the dissolution of biodegradable friction reducers by adding an effervescent tablet containing sodium dichloro-isocyanurate. The effervescent action of the tablet dissolution mixes the disinfectant chlorine in the stagnant water in the tank.

In some cases several tablets may be added in a bag. The bag may be opened prior to the addition of the tablets or the bag may be of a water soluble material. The number of tablets in

the bag will be calculated to add the appropriate concentration of chlorine to the water in the tank to disinfect the water.

Detailed Description

The present invention provides a method of treating a fracturing liquid water soluble composition comprising sodium dichloro-isocyanurate and an alkali buffering effervescent base, which provides a non-toxic solution having a weakly acidic to neutral pH from between 5.5 and 7.5. This is a pH range that will not cause corrosion of the fracting tanks. The composition is very stable in solution and simple to use.

The composition of the invention is produced in a solid tablet form. A solid tablet form eliminates the necessity to weigh out a quantity of powder or granules each time a sanitiser solution is required and avoids storage problems with such particulates. Using a single solid tablet form also ensures that a sanitising solution having an accurate and known disinfectant concentration is produced in a one step process. The handling of a solid tablet form is also easier and safer than handling chlorinated powders or granules or hypochlorite solutions.

Effervescent tablets are preferred because they disperse quickly in solution and dissolve the active ingredient. There is no need to crush the tablets and/or stir the solutions to achieve a clear sanitising solution within a reasonable time period.

Example 1

Tablets are prepared having the following formulation by weight. The formulation given is for a single tablet.

Sodium dichloro-isocyanurate	42%
Sodium bicarbonate	19%
Adipic acid	19%
Sodium carbonate	20%

8.15g sodium dichloro-isocyanurate, 3.75g sodium bicarbonate, 3.59g adipic acid and 3.76g of sodium carbonate are weighed out and dry blended together. The dry blend is then compressed by direct compression (on chrome plated tooling) into tablets. pH 7.01 in solution of deionised water. This pH is ideal for drinking water (allowed range by EPA 6.5-8.0). This pH balanced formula would be very safe if water is lost to the ground water and would be ideal water for preparing the fracting solution.

50 of these tablets (962 g) added to a 40,000 L of water in a fracting tank produces a disinfection solution of 6 ppm of chlorine which is sufficient to disinfect water.

Example 2

Tablets are prepared having the following formulation by weight. The formulation given is for a single tablet.

Sodium dichloro-isocyanurate	50%
Sodium bicarbonate	23%
Adipic acid	22%
Sodium carbonate	5%

8.68g sodium dichloroisocyanurate, 3.99g sodium bicarbonate, 3.82g adipic acid and 0.87g of sodium carbonate are weighed out and dry blended together. The dry blend is then compressed by direct compression (on chrome plated tooling) into tablets. pH 5.8 in deionised water This formulation lowers the pH when compared to other disinfectants. Chlorine is a more effective disinfectant at lower pH.

52 of these tablets (902 g) added to a 40,000 L of water in a fracting tank produces a disinfection solution of 6.5 ppm of chlorine which is sufficient to disinfect water.

The chlorine demand of the water may be measured prior to addition of the tablets using a suitable test kit. Additional tablets will be dosed to be consumed by the chlorine demand. Testing the chlorine demand will allow the correct tablet dose to be made to disinfect the water

without overdosing. Overdosing may leave additional material that will attack the friction reducing agents when they are added.

The invention is not limited to the embodiments hereinbefore described which may be varied in detail.

Claims

1. A method for inhibiting bacterial growth in oil field fluids comprising the step of adding to the fluid a tablet composition comprising sodium dichloro-isocyanurate in an amount to achieve an effective biocidal action, and an effervescent base.

2. A method as claimed in claim 1 wherein the tablet provides a sanitising solution having a pH in the range of from 5.5 to 7.5.

3. A method as claimed in claim 1 or 2 wherein the tablet provides a sanitising solution having a pH of approximately 7.

4. A method as claimed in claim 1 or 2 wherein the tablet provides a sanitising solution having a pH of approximately 5.8.

5. A method as claimed in any of claims 1 to 4 wherein the tablet contains an amount of from 35% to 65% by weight of sodium dichloro-isocyanurate.

6. A method as claimed in any of claims 1 to 5 wherein the tablet contains an amount of from 40% to 50% by weight of sodium dichloro-isocyanurate.

7. A method as claimed in any of claims 1 to 6 wherein the tablet contains an amount of from 40% to 45% by weight of sodium dichloro-isocyanurate.

8. A method as claimed in any of claims 1 to 7 wherein the tablet contains approximately 42% by weight of sodium dichloro-isocyanurate.

9. A method as claimed in any of claims 1 to 5 wherein the tablet contains an amount of from 48% to 52% by weight of sodium dichloro-isocyanurate

10. A method as claimed in claim 9 wherein the tablet contains approximately 50% by weight of sodium dichloro-isocyanurate.

11. A method as claimed in any of claims 1 to 10 wherein the effervescent base comprises an alkali buffering agent, an aliphatic carboxylic acid, and an alkali metal bicarbonate.

12. A method as claimed in claim 11 wherein the alkali buffering agent is sodium carbonate.

13. A method as claimed in claim 12 wherein the sodium carbonate comprises from 3% to 25% by weight of the tablet composition.

14. A method as claimed in claim 12 or 13 wherein the sodium carbonate comprises from 4% to 21% by weight of the tablet composition.

15. A method as claimed in claim 14 wherein the sodium carbonate comprises from 15% to 21% by weight of the tablet composition.

16. A method as claimed in claim 15 wherein the sodium carbonate comprises approximately 20% by weight of the tablet composition.

17. A method as claimed in claim 12 or 13 wherein the sodium carbonate comprises from 5% to 7% by weight of the tablet composition.

18. A method as claimed in claim 17 wherein the sodium carbonate comprises approximately 5% by weight of the tablet composition.

19. A method as claimed in any of claims 11 to 18 wherein the aliphatic carboxylic acid is adipic acid.

20. A method as claimed in claim 19 wherein the adipic acid comprises from 15% to 35% by weight of the tablet composition.

21. A method as claimed in claim 20 wherein the adipic acid comprises from 18% to 25% by weight of the tablet composition.

22. A method as claimed in claim 21 wherein the adipic acid comprises from 18% to 22% by weight of the tablet composition.

23. A method as claimed in claim 21 wherein the adipic acid comprises approximately 19% by weight of the tablet composition.

24. A method as claimed in claim 22 wherein the adipic acid comprises approximately 22% by weight of the tablet composition.

25. A method as claimed in any of claims 11 to 24 wherein the alkali metal bicarbonate is sodium bicarbonate.

26. A method as claimed in claim 25 wherein the sodium bicarbonate comprises from 15% to 50% by weight of the tablet composition.

27. A method as claimed in claim 26 wherein the sodium bicarbonate comprises from 18% to 30% by weight of the tablet composition.

28. A method as claimed in claim 27 wherein the sodium bicarbonate comprises from 18% to 22% by weight of the tablet composition.

29. A method as claimed in claim 28 wherein the sodium bicarbonate comprises approximately 19% by weight of the tablet composition.

30. A method as claimed in claim 27 wherein the sodium bicarbonate comprises approximately 23% by weight of the tablet composition.

31. A method as claimed in any of claims 1 to 11 wherein the tablet comprises sodium dichloro-isocyanurate in an amount of approximately 42%, sodium bicarbonate in an

amount of approximately 19%; adipic acid in an amount of approximately 19%; and sodium carbonate in an amount of approximately 20% to provide a sanitising solution having a pH of approximately 7.

32. A method as claimed in any of claims 1 to 11 wherein the tablet comprises sodium dichloro-isocyanurate in an amount of approximately 50%, sodium bicarbonate in an amount of approximately 23%, adipic acid in an amount of approximately 22% and sodium carbonate in an amount of approximately 5% to provide a sanitising solution having a pH of approximately 5.8..

33. A method as claimed in any of claims 1 to 32 comprising adding a receptacle containing a plurality of the tablets to a fracting tank.

34. A method as claimed in claim 33 wherein the receptacle is of a material that is soluble in water.

35. A method as claimed in claim 33 or 34 wherein the receptacle comprises a bag.

INTERNATIONAL SEARCH REPORT

International application No
PCT/IE2012/000005

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K8/60 C09K8/68 A01N25/34 A01N59/00 C02F1/76
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)
C09K A01N C02F

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2010/113144 A2 (MEDENTECH LTD [IE]; STAFFORD ULICK [IE]) 7 October 2010 (2010-10-07)	1-35
Y	page 2, line 19 - page 3, line 9; claims 38,39 the whole document	1-35
Y	US 2010/307757 A1 (BLOW KRISTEL A [US] ET AL) 9 December 2010 (2010-12-09) paragraphs [0042], [0043], [0049] - [0060] the whole document	1-35
A	US 2010/311623 A1 (REY PAUL [US] ET AL) 9 December 2010 (2010-12-09) paragraphs [0107], [0108]	1-35

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

[X] See patent family annex.

* Special categories of cited documents :

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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
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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, Fax: (+31-70) 340-3016	Straub, Thomas

INTERNATIONAL SEARCH REPORT

International application No
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	US 2011/287984 A1 (MIRAKYAN ANDREY [US] ET AL) 24 November 2011 (2011-11-24) the whole document	1-35

Form PCT/ISA/210 (continuation of second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/IE2012/000005

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