AO 120 (Rev. 08/10)

TO:	REPORT ON THE FILING OR DETERMINATION OF AN ACTION REGARDING A PATENT OR TRADEMARK
Mail Stop 8 **Director of the U.S. Patent and Trademark Office** **P.O. Box 1450** **Alexandria, VA 22313-1450**	

In Compliance with 35 U.S.C. § 290 and/or 15 U.S.C. § 1116 you are hereby advised that a court action has been filed in the U.S. District Court Western District of Oklahoma on the following

☐ Trademarks or ☑ Patents. (☐ the patent action involves 35 U.S.C. § 292.):

DOCKET NO.	DATE FILED	U.S. DISTRICT COURT
CIV-23-316-JD	4/13/2023	Western District of Oklahoma

PLAINTIFF	DEFENDANT
Flex-Chem Holding Company Llc	Pharaoh Energy Services Llc

	PATENT OR TRADEMARK NO.	DATE OF PATENT OR TRADEMARK	HOLDER OF PATENT OR TRADEMARK
1	US 10,697,282 B2	6/30/2020	Flex - Chem Holding Company, LLC
2	US 10,633,575 B2	4/28/2020	Flex - Chem Holding Company , LLC
3	US 9,944,843 B2	4/17/2018	Flex - Chem Holding Company, LLC
4			
5			

In the above—entitled case, the following patent(s)/ trademark(s) have been included:

DATE INCLUDED	INCLUDED BY ☐ Amendment ☐ Answer ☐ Cross Bill ☐ Other Pleading	
PATENT OR TRADEMARK NO.	DATE OF PATENT OR TRADEMARK	HOLDER OF PATENT OR TRADEMARK
1		
2		
3		
4		
5		

In the above—entitled case, the following decision has been rendered or judgement issued:

DECISION/JUDGEMENT

CLERK	(BY) DEPUTY CLERK	DATE
	R. Rosson	4/13/2023

Copy 1—Upon initiation of action, mail this copy to Director Copy 3—Upon termination of action, mail this copy to Director
Copy 2—Upon filing document adding patent(s), mail this copy to Director Copy 4—Case file copy

PHARAOH, EX. 1002

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	ISSUE DATE	PATENT NO.	ATTORNEY DOCKET NO.	CONFIRMATION NO.
14/686,237	04/17/2018	9944843	04697.0001USU1	2601

23552 7590 03/28/2018

MERCHANT & GOULD P.C.
P.O. BOX 2903
MINNEAPOLIS, MN 55402-0903

ISSUE NOTIFICATION

The projected patent number and issue date are specified above.

Determination of Patent Term Adjustment under 35 U.S.C. 154 (b)
(application filed on or after May 29, 2000)

The Patent Term Adjustment is 252 day(s). Any patent to issue from the above-identified application will include an indication of the adjustment on the front page.

If a Continued Prosecution Application (CPA) was filed in the above-identified application, the filing date that determines Patent Term Adjustment is the filing date of the most recent CPA.

Applicant will be able to obtain more detailed information by accessing the Patent Application Information Retrieval (PAIR) WEB site (http://pair.uspto.gov).

Any questions regarding the Patent Term Extension or Adjustment determination should be directed to the Office of Patent Legal Administration at (571)-272-7702. Questions relating to issue and publication fee payments should be directed to the Application Assistance Unit (AAU) of the Office of Data Management (ODM) at (571)-272-4200.

APPLICANT(s) (Please see PAIR WEB site http://pair.uspto.gov for additional applicants):

Andrew Bryce Conway, Weatherford, OK;
Flex-Chem Holding Company, LLC, Weatherford, OK;

The United States represents the largest, most dynamic marketplace in the world and is an unparalleled location for business investment, innovation, and commercialization of new technologies. The USA offers tremendous resources and advantages for those who invest and manufacture goods here. Through SelectUSA, our nation works to encourage and facilitate business investment. To learn more about why the USA is the best country in the world to develop technology, manufacture products, and grow your business, visit SelectUSA.gov.

Electronic Acknowledgement Receipt

EFS ID:	31833069
Application Number:	14686237
International Application Number:	
Confirmation Number:	2601
Title of Invention:	STIMULATION OF WELLS IN NANO-DARCY SHALE FORMATIONS
First Named Inventor/Applicant Name:	Andrew Bryce Conway
Customer Number:	23552
Filer:	Brian Peter McCall
Filer Authorized By:	
Attorney Docket Number:	04697.0001USU1
Receipt Date:	20-FEB-2018
Filing Date:	14-APR-2015
Time Stamp:	15:02:26
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	CARD
Payment was successfully received in RAM	$720
RAM confirmation Number	022118INTEFSW15022200
Deposit Account	132725
Authorized User	Brian McCall
The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows: 37 CFR 1.16 (National application filing, search, and examination fees) 37 CFR 1.17 (Patent application and reexamination processing fees)	

Electronic Patent Application Fee Transmittal

Application Number:	14686237
Filing Date:	14-Apr-2015
Title of Invention:	STIMULATION OF WELLS IN NANO-DARCY SHALE FORMATIONS
First Named Inventor/Applicant Name:	Andrew Bryce Conway
Filer:	Brian Peter McCall
Attorney Docket Number:	04697.0001USU1

Filed as Small Entity

Filing Fees for Utility under 35 USC 111(a)

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
PETITION FEE-37CFR 1.17(H) (GROUP II)	2464	1	70	70
RCE- 1st Request	2801	1	650	650
Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				

Adjustment date: 03/27/2018 SDIRETA1
02/21/2018 INTEFGU 00001586 14686237
02 FC:2801 -650.00 DP
Refund Ref: 0030211014
03/27/2018
Credit Card Refund Total: $650.00
Master C: XXXXXXXXXXXX4404

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	14/686,237	Conway, Andrew Bryce
	Examiner	Art Unit
	CATHERINE A LOIKITH	3674

CPC - Searched*		
Symbol	Date	Examiner
E21B 43/16, 43/25	7/21/2017	CAL
E21B 43/16, 43/25	11/28/2017	CAL
updated search above	01/08/2018	CAL

CPC Combination Sets - Searched*		
Symbol	Date	Examiner

US Classification - Searched*			
Class	Subclass	Date	Examiner

* See search history printout included with this form or the SEARCH NOTES box below to determine the scope of the search.

Search Notes		
Search Notes	Date	Examiner
text searches in EAST	7/21/2017	CAL
text searches in EAST	12/13/2017	CAL

Interference Search			
US Class/CPC Symbol	US Subclass/CPC Group	Date	Examiner
see EAST search history		12/14/2017	CAL

PHARAOH, EX. 1002
P. 5

Bibliographic Data

Application No: 14686237

Foreign Priority claimed: ○ Yes ◉ No

35 USC 119 (a-d) conditions met: ☐ Yes ☑ No ☐ Met After Allowance

Verified and Acknowledged: /Catherine Loikith/ (Examiner's Signature) | (Initials)

Title: STIMULATION OF WELLS IN NANO-DARCY SHALE FORMATIONS

FILING or 371(c) DATE	CLASS	GROUP ART UNIT	ATTORNEY DOCKET NO.
04/14/2015	166	3674	04697.0001USU1
RULE			

APPLICANTS

Flex-Chem Holding Company, LLC, Weatherford, OK,

INVENTORS

Andrew Bryce Conway, Weatherford, OK, UNITED STATES

CONTINUING DATA

This application has PRO of 62087899 12/05/2014

This application has PRO of 61979210 04/14/2014

FOREIGN APPLICATIONS

IF REQUIRED, FOREIGN LICENSE GRANTED**

04/24/2015

STATE OR COUNTRY

UNITED STATES

ADDRESS

MERCHANT & GOULD P.C.
P.O. BOX 2903
MINNEAPOLIS, MN 55402-0903
UNITED STATES

FILING FEE RECEIVED

$800

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
14/686,237	04/14/2015	Andrew Bryce Conway	04697.0001USU1	2601

23552 7590 03/14/2018

MERCHANT & GOULD P.C.
P.O. BOX 2903
MINNEAPOLIS, MINNESOTA 55402-0903

EXAMINER	
LOIKITH, CATHERINE A	

ART UNIT	PAPER NUMBER
3674	

NOTIFICATION DATE	DELIVERY MODE
03/14/2018	ELECTRONIC

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Notice of the Office communication was sent electronically on above-indicated "Notification Date" to the following e-mail address(es):

USPTO23552@merchantgould.com

Notice of Allowability	Application No. 14/686,237	Applicant(s) Conway, Andrew Bryce	
	Examiner CATHERINE A LOIKITH	Art Unit 3674	AIA Status Yes

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address--

All claims being allowable, PROSECUTION ON THE MERITS IS (OR REMAINS) CLOSED in this application. If not included herewith (or previously mailed), a Notice of Allowance (PTOL-85) or other appropriate communication will be mailed in due course. **THIS NOTICE OF ALLOWABILITY IS NOT A GRANT OF PATENT RIGHTS.** This application is subject to withdrawal from issue at the initiative of the Office or upon petition by the applicant. See 37 CFR 1.313 and MPEP 1308.

1. ☑ This communication is responsive to the IDS filed 20 February 2018.
   ☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on _____.

2. ☐ An election was made by the applicant in response to a restriction requirement set forth during the interview on _____; the restriction requirement and election have been incorporated into this action.

3. ☑ The allowed claim(s) is/are 1-13 . As a result of the allowed claim(s), you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information, please see **http://www.uspto.gov/patents/init_events/pph/index.jsp** or send an inquiry to **PPHfeedback@uspto.gov.**

4. ☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

   Certified copies:

   a) ☐ All b) ☐ Some *c) ☐ None of the:

   1. ☐ Certified copies of the priority documents have been received.
   2. ☐ Certified copies of the priority documents have been received in Application No. _____ .
   3. ☐ Copies of the certified copies of the priority documents have been received in this national stage application from the International Bureau (PCT Rule 17.2(a)).

   * Certified copies not received: _____ .

Applicant has THREE MONTHS FROM THE "MAILING DATE" of this communication to file areply complying with the requirements noted below. Failure to timely comply will result in ABANDONMENT of this application.
THIS THREE-MONTH PERIOD IS NOT EXTENDABLE.

5. ☐ CORRECTED DRAWINGS (as "replacement sheets") must be submitted.
   ☐ including changes required by the attached Examiner's Amendment / Comment or in the Office action of Paper No./Mail Date _____ .

   Identifying indicia such as the application number (see 37 CFR 1.84(c)) should be written on the drawings in the front (not the back) of each sheet. Replacement sheet(s) should be labeled as such in the header according to 37 CFR 1.121(d).

6. ☐ DEPOSIT OF and/or INFORMATION about the deposit of BIOLOGICAL MATERIAL must be submitted. Note the attached Examiner's comment regarding REQUIREMENT FOR THE DEPOSIT OF BIOLOGICAL MATERIAL.

Attachment(s)

1. ☐ Notice of References Cited (PTO-892)
2. ☑ Information Disclosure Statements (PTO/SB/08), Paper No./Mail Date _____.
3. ☐ Examiner's Comment Regarding Requirement for Deposit of Biological Material _____.
4. ☐ Interview Summary (PTO-413), Paper No./Mail Date. _____.
5. ☐ Examiner's Amendment/Comment
6. ☐ Examiner's Statement of Reasons for Allowance
7. ☐ Other _____.

/Catherine Loikith/
Primary Examiner, Art Unit 3674

Doc code: IDS
Doc description: Information Disclosure Statement (IDS) Filed

PTO/SB/08a (03-15)
Approved for use through 07/31/2016. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	14686237
Filing Date	2015-04-14
First Named Inventor	Andrew Bryce Conway
Art Unit	3674
Examiner Name	Catherine A. Loikith
Attorney Docket Number	04697.0001USU1

U.S.PATENTS Remove

Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1					

If you wish to add additional U.S. Patent citation information please click the Add button. Add

U.S.PATENT APPLICATION PUBLICATIONS Remove

Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1					

If you wish to add additional U.S. Published Application citation information please click the Add button. Add

FOREIGN PATENT DOCUMENTS Remove

Examiner Initial*	Cite No	Foreign Document Number[3]	Country Code[2] i	Kind Code[4]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear	T[5]
	1							

If you wish to add additional Foreign Patent Document citation information please click the Add button Add

NON-PATENT LITERATURE DOCUMENTS Remove

Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /CAL/

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	14686237
	Filing Date	2015-04-14
	First Named Inventor	Andrew Bryce Conway
	Art Unit	3674
	Examiner Name	Catherine A. Loikith
	Attorney Docket Number	04697.0001USU1

	1	Australian Examination Report, Application No. 2015247994, dated February 8, 2018, 3pgs.

If you wish to add additional non-patent literature document citation information please click the Add button Add

EXAMINER SIGNATURE

Examiner Signature	/Catherine Loikith/	Date Considered	03/06/2018

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /CAL/

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	14686237
Filing Date	2015-04-14
First Named Inventor	Andrew Bryce Conway
Art Unit	3674
Examiner Name	Catherine A. Loikith
Attorney Docket Number	04697.0001USU1

CERTIFICATION STATEMENT

Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

☒ That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

See attached certification statement.

☒ The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

A certification statement is not submitted herewith.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/Brian P. McCall/	Date (YYYY-MM-DD)	2018-02-20
Name/Print	Brian P. McCall	Registration Number	68734

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1 hour to complete, including gathering, preparing and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /CAL/

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C. 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether the Freedom of Information Act requires disclosure of these record s.

2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.

3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.

4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).

5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.

6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.

9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /CAL/

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	14/686,237	Conway, Andrew Bryce
	Examiner	**Art Unit**
	CATHERINE A LOIKITH	3674

CPC						
Symbol					**Type**	**Version**
C09K	/	8	/	605	F	2013-01-01
C09K	/	8	/	528	I	2013-01-01
C09K	/	8	/	602	I	2013-01-01
E21B	/	43	/	267	I	2013-01-01
C09K	/	8	/	62	I	2013-01-01
C09K	/	2208	/	32	A	2013-01-01
C09K	/	8	/	72	A	2013-01-01

CPC Combination Sets							
Symbol					**Type**	**Set**	**Ranking**	**Version**
	/		/					

NONE		Total Claims Allowed:	
(Assistant Examiner)	(Date)	13	
/Catherine Loikith/ Primary Examiner, Art Unit 3674	06 March 2018	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	1	1

U.S. Patent and Trademark Office

Part of Paper No.: 20180306

PHARAOH, EX. 1002
P. 13

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	14/686,237	Conway, Andrew Bryce
	Examiner	**Art Unit**
	CATHERINE A LOIKITH	3674

INTERNATIONAL CLASSIFICATION				
CLAIMED				
E21B	/	43	/	16
E21B	/	43	/	25

NON-CLAIMED				
	/		/	

US ORIGINAL CLASSIFICATION	
CLASS	**SUBCLASS**

CROSS REFERENCES(S)						
CLASS	**SUBCLASS (ONE SUBCLASS PER BLOCK)**					

NONE		**Total Claims Allowed:**	
(Assistant Examiner)	(Date)	13	
/Catherine Loikith/ Primary Examiner, Art Unit 3674	06 March 2018	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	1	1

U.S. Patent and Trademark Office

Part of Paper No.: 20180306

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	14/686,237	Conway, Andrew Bryce
	Examiner	**Art Unit**
	CATHERINE A LOIKITH	3674

☐ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

CLAIMS

Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original
1	1	10	10												
2	2	11	11												
3	3	12	12												
4	4	13	13												
5	5		14												
6	6		15												
7	7		16												
8	8		17												
9	9														

NONE		**Total Claims Allowed:**	
(Assistant Examiner)	(Date)	13	
/Catherine Loikith/ Primary Examiner, Art Unit 3674	06 March 2018	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	1	1

U.S. Patent and Trademark Office Part of Paper No.: 20180306

PHARAOH, EX. 1002
P. 15

EAST Search History

EAST Search History (Prior Art)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
S76	15	(("0599474") or ("3700280") or ("2012171857")).PN.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2018/03/06 14:09

EAST Search History (Interference)

< This search history is empty>

3/ 6/ 2018 5:42:09 PM
C:\ Users\ cloikith\ Documents\ EAST\ Workspaces\ 14686237.wsp

Doc code: RCEX
Doc description: Request for Continued Examination (RCE)

PTO/SB/30EFS (07-14)
Approved for use through 07/31/2016. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

REQUEST FOR CONTINUED EXAMINATION(RCE)TRANSMITTAL
(Submitted Only via EFS-Web)

Application Number	14686237	Filing Date	2015-04-14	Docket Number (if applicable)	04697.0001USU1	Art Unit	3674
First Named Inventor	Andrew Bryce Conway			Examiner Name	Catherine A. Loikith		

This is a Request for Continued Examination (RCE) under 37 CFR 1.114 of the above-identified application.
Request for Continued Examination (RCE) practice under 37 CFR 1.114 does not apply to any utility or plant application filed prior to June 8, 1995, to any international application that does not comply with the requirements of 35 U.S.C. 371, or to any design application. The Instruction Sheet for this form is located at WWW.USPTO.GOV.

SUBMISSION REQUIRED UNDER 37 CFR 1.114

Note: If the RCE is proper, any previously filed unentered amendments and amendments enclosed with the RCE will be entered in the order in which they were filed unless applicant instructs otherwise. If applicant does not wish to have any previously filed unentered amendment(s) entered, applicant must request non-entry of such amendment(s).

☐ Previously submitted. If a final Office action is outstanding, any amendments filed after the final Office action may be considered as a submission even if this box is not checked.

- ☐ Consider the arguments in the Appeal Brief or Reply Brief previously filed on _____
- ☐ Other _____

☒ Enclosed

- ☐ Amendment/Reply
- ☒ Information Disclosure Statement (IDS)
- ☐ Affidavit(s)/ Declaration(s)
- ☒ Other Petition to Withdraw an Application from Issuance After Payment of the Issue Fee (Web-based ePetition); QPIDS Request

MISCELLANEOUS

☐ Suspension of action on the above-identified application is requested under 37 CFR 1.103(c) for a period of months _____ (Period of suspension shall not exceed 3 months; Fee under 37 CFR 1.17(i) required)

☐ Other _____

FEES

The RCE fee under 37 CFR 1.17(e) is required by 37 CFR 1.114 when the RCE is filed.

☒ The Director is hereby authorized to charge any underpayment of fees, or credit any overpayments, to Deposit Account No 132725

SIGNATURE OF APPLICANT, ATTORNEY, OR AGENT REQUIRED

☒ Patent Practitioner Signature

Applicant Signature

PTO/SB/30EFS (07-14)
Approved for use through 07/31/2016. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
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Signature of Registered U.S. Patent Practitioner			
Signature	/Brian P. McCall/	Date (YYYY-MM-DD)	2018-02-20
Name	Brian P. McCall	Registration Number	68734

This collection of information is required by 37 CFR 1.114. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450.

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

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The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C. 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether the Freedom of Information Act requires disclosure of these records.

2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.

3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.

4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).

5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.

6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.

9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

PTO/SB/08a (03-15)
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INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	14686237
Filing Date	2015-04-14
First Named Inventor	Andrew Bryce Conway
Art Unit	3674
Examiner Name	Catherine A. Loikith
Attorney Docket Number	04697.0001USU1

U.S.PATENTS Remove

Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
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Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
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FOREIGN PATENT DOCUMENTS Remove

Examiner Initial*	Cite No	Foreign Document Number[3]	Country Code[2] i	Kind Code[4]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear	T[5]
	1							

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NON-PATENT LITERATURE DOCUMENTS Remove

Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	14686237
	Filing Date	2015-04-14
	First Named Inventor	Andrew Bryce Conway
	Art Unit	3674
	Examiner Name	Catherine A. Loikith
	Attorney Docket Number	04697.0001USU1

	1	Australian Examination Report, Application No. 2015247994, dated February 8, 2018, 3pgs.

If you wish to add additional non-patent literature document citation information please click the Add button Add

EXAMINER SIGNATURE

Examiner Signature		Date Considered	

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	14686237
	Filing Date	2015-04-14
	First Named Inventor	Andrew Bryce Conway
	Art Unit	3674
	Examiner Name	Catherine A. Loikith
	Attorney Docket Number	04697.0001USU1

CERTIFICATION STATEMENT

Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

☒ That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

See attached certification statement.

☒ The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

A certification statement is not submitted herewith.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/Brian P. McCall/	Date (YYYY-MM-DD)	2018-02-20
Name/Print	Brian P. McCall	Registration Number	68734

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1 hour to complete, including gathering, preparing and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).

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7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

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9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

Doc Code: PET.AUTO Document Description: Petition automatically granted by EFS-Web	PTO/SB/140 U.S. Patent and Trademark Office Department of Commerce

Electronic Petition Request	**PETITION TO WITHDRAW AN APPLICATION FROM ISSUE AFTER PAYMENT OF THE ISSUE FEE UNDER 37 CFR 1.313(c)**
Application Number	14686237
Filing Date	14-Apr-2015
First Named Inventor	Andrew Conway
Art Unit	3674
Examiner Name	CATHERINE LOIKITH
Attorney Docket Number	04697.0001USU1
Title	STIMULATION OF WELLS IN NANO-DARCY SHALE FORMATIONS

An application may be withdrawn from issue for further action upon petition by the applicant. To request that the Office withdraw an application from issue, applicant must file a petition under this section including the fee set forth in § 1.17(h) and a showing of good and sufficient reasons why withdrawal of the application from issue is necessary.

APPLICANT HEREBY PETITIONS TO WITHDRAW THIS APPLICATION FROM ISSUE UNDER 37 CFR 1.313(c).

A grantable petition requires the following items:
(1) Petition fee; and
(2) One of the following reasons:
(a) Unpatentability of one or more claims, which must be accompanied by an unequivocal statement that one or more claims are unpatentable, an amendment to such claim or claims, and an explanation as to how the amendment causes such claim or claims to be patentable;
(b) Consideration of a request for continued examination in compliance with § 1.114 (for a utility or plant application only); or
(c) Express abandonment of the application. Such express abandonment may be in favor of a continuing application, but not a CPA under 37 CFR 1.53(d).

Petition Fee

◉	Small Entity
○	Micro Entity
○	Regular Undiscounted

Reason for withdrawal from issue

◯ One or more claims are unpatentable ◉ Consideration of a request for continued examination (RCE) (List of Required Documents and Fees) ◯ Applicant hereby expressly abandons the instant application (any attorney/agent signing for this reason must have power of attorney pursuant to 37 CFR 1.32(b)).
RCE request,submission, and fee. ☐ I certify, in accordance with 37 CFR 1.4(d)(4) that : The RCE request ,submission, and fee have already been filed in the above-identified application on ☒ Are attached.
THIS PORTION MUST BE COMPLETED BY THE SIGNATORY OR SIGNATORIES I certify, in accordance with 37 CFR 1.4(d)(4) that I am: ◉ An attorney or agent registered to practice before the Patent and Trademark Office who has been given power of attorney in this application. ◯ An attorney or agent registered to practice before the Patent and Trademark Office, acting in a representative capacity. ◯ A sole inventor ◯ A joint inventor; I certify that I am authorized to sign this submission on behalf of all of the inventors as evidenced by the power of attorney in the application ◯ A joint inventor; all of whom are signing this e-petition

Signature	/Brian P. McCall/
Name	Brian P. McCall
Registration Number	68734

Electronic Patent Application Fee Transmittal

Application Number:	14686237
Filing Date:	14-Apr-2015
Title of Invention:	STIMULATION OF WELLS IN NANO-DARCY SHALE FORMATIONS
First Named Inventor/Applicant Name:	Andrew Bryce Conway
Filer:	Brian Peter McCall
Attorney Docket Number:	04697.0001USU1

Filed as Small Entity

Filing Fees for Utility under 35 USC 111(a)

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
PETITION FEE-37CFR 1.17(H) (GROUP II)	2464	1	70	70
RCE- 1st Request	2801	1	650	650
Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Post-Allowance-and-Post-Issuance:				
Extension-of-Time:				
Miscellaneous:				
			Total in USD ($)	**720**

UNITED STATES PATENT AND TRADEMARK OFFICE

Commissioner for Patents
United States Patent and Trademark Office
P.O. Box 1450
Alexandria, VA 22313-1450
www.uspto.gov

Decision Date : February 20, 2018

In re Application of :

Andrew Conway

DECISION ON PETITION

UNDER CFR 1.313(c)(2)

Application No : 14686237

Filed : 14-Apr-2015

Attorney Docket No : 04697.0001USU1

This is an electronic decision on the petition under 37 CFR 1.313(c)(2), filed February 20, 2018 , to withdraw the above-identified application from issue after payment of the issue fee.

The petition is **GRANTED.**

The above-identified application is withdrawn from issue for consideration of a submission under 37 CFR 1.114 (request for continued examination). See 37 CFR 1.313(c)(2).

Petitioner is advised that the issue fee paid in this application cannot be refunded. If, however, this application is again allowed, petitioner may request that it be applied towards the issue fee required by the new Notice of Allowance.

Telephone inquiries concerning this decision should be directed to the Patent Electronic Business Center (EBC) at 866-217-9197.

This application file is being referred to Technology Center AU 3674 for processing of the request for continuing examination under 37 CFR 1.114 .

Office of Petitions

Electronic Acknowledgement Receipt

EFS ID:	31833069
Application Number:	14686237
International Application Number:	
Confirmation Number:	2601
Title of Invention:	STIMULATION OF WELLS IN NANO-DARCY SHALE FORMATIONS
First Named Inventor/Applicant Name:	Andrew Bryce Conway
Customer Number:	23552
Filer:	Brian Peter McCall
Filer Authorized By:	
Attorney Docket Number:	04697.0001USU1
Receipt Date:	20-FEB-2018
Filing Date:	14-APR-2015
Time Stamp:	15:02:26
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	CARD
Payment was successfully received in RAM	$720
RAM confirmation Number	022118INTEFSW15022200
Deposit Account	132725
Authorized User	Brian McCall

The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows:

37 CFR 1.16 (National application filing, search, and examination fees)

37 CFR 1.17 (Patent application and reexamination processing fees)

37 CFR 1.19 (Document supply fees)

37 CFR 1.20 (Post Issuance fees)

37 CFR 1.21 (Miscellaneous fees and charges)

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Quick Path Information Disclosure Statement	2018-02-20--QPIDS--04697-0001USU1.PDF	359317 b06490c591e469ad30d6d274ce484eba188bed0c	no	2
Warnings:					
Information:					
2	Other Reference-Patent/App/Search documents	Australian-Examination-Report--04697-0001USU1.PDF	102693 c5a2572334844eb8c4367133d69ccf053a2ba9bd	no	3
Warnings:					
Information:					
3	Request for Continued Examination (RCE)	2018-02-20--RCE--04697-0001USU1.PDF	1349960 9b0a0b59dd91cb55c95e233144aa6c8048a86937	no	3
Warnings:					
Information:					
4	Quick Path Information Disclosure Statement	2018-02-20--SIDS-8--04697-0001USU1.pdf	71520 32e6ecd7c5dffa586a22da11113585eb49da711e	no	4
Warnings:					
Information:					
5	Petition automatically granted by EFS	petition-request.pdf	31509 0af95851ff0a01751db830e622c131db03ac3f39	no	2
Warnings:					
Information:					
6	Fee Worksheet (SB06)	fee-info.pdf	32277 725be05c3d6edefc8962155c5bb8d592ad33d1da	no	2
Warnings:					
Information:					

Total Files Size (in bytes):	1947276

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

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ABN: 38 113 072 755

8 February 2018

Examination report No. 1 for standard patent application

Phillips Ormonde Fitzpatrick
PO Box 323
Collins Street West VIC 8007
Australia

Your reference	1069413
Application number	2015247994
Applicant name	Flex-Chem Holding Company, LLC
Earliest priority date	14 April 2014

Final date for acceptance:	**8 February 2019**
Date of this report:	8 February 2018
Examination request date:	31 October 2017

Dear Phillips Ormonde Fitzpatrick,

Your request for accelerated examination under the Patent Prosecution Highway has been received by the office and this application has been examined under *section 45 of the Patents Act 1990*. I consider that this application does not meet the requirements of the Act because there are issues with the application that are explained in the report details.

You have **12 months** from the date of this report to overcome all my objection(s) otherwise this application will lapse.

You will also need to pay any annual continuation fees that apply. Your next continuation fee is due on **10 April 2019**.

NOTE: There is a current postponement of acceptance in place. If you overcome all other objections before the expiration of that postponement, the Commissioner will only accept the application at that time if you have filed a clear and unambiguous statement requesting the withdrawal of that postponement. Otherwise, a further adverse report will be issued.

Details of this patent application can be viewed on AusPat, our Australian patent search database.

Yours sincerely,

Serinel Samuel
Section: MECH 2 – CONSTRUCTION & MINING
Phone: (612) 6283 2382

PHARAOH, EX. 1002
P. 32

Report details

Basis of the report

In examining this application I have considered:

- the PCT pamphlet as originally filed
- allowed and/or proposed amendment/s under S104 up to and including amendment item number 2, filed on 23 January 2018.

Summary of novelty, inventive step and patentable subject matter

	Satisfy requirements?	*Claim numbers*
Novelty/inventive step	**Yes**	NONE
	No	1-13
Patentable subject matter	**Yes**	1-13
	No	NONE

Detailed objections on issues that have been identified

Documents cited or considered relevant

D1 : EP 0599474 A2 (HALLIBURTON COMPANY et al.) 01 June 1994 *
Category: **X** Claims: 1-13

D2 : US 3700280 A (MICHAEL N. PAPADOPOULOS et al.) 24 October 1972 *
Category: **X** Claims: 1-13

D3 : WO 2012171857 A1 (AKZO NOBEL CHEMICALS INTERNATIONAL B.V et al.) 20 December 2012 *
Category: **X** Claims: 1-13

* Cited in the EP examination report dated 23 August 2017 for Application No. 15780712.

Special categories of cited documents:

X: The claimed invention cannot be considered novel under *subsection 7(1)* in light of the document and/or cannot be considered to involve an inventive step under *subsection 7(2)* of the Act in light of the common general knowledge considered together with the document.

PHARAOH, EX. 1002
P. 33

Novelty and inventive step

1 Claims 1-3, 5-7 and 10-13, substantially having the similar scope as EP claims 1-4, 6 and 9-12 are not novel and lack an inventive step in light of the prior art documents discussed in the EP examination report of the application No. 15780712 dated 23 August 2017

While the objection regarding these documents was not made under Australian law, I agree with the reasons given in that report and consider that they support a corresponding objection against the Australian claims. It is noted that the claims are amended slightly. however the disclosures of the cited documents are applicable for the existing well also. Also, I agree with the inherent features such as nano-darcy shale and the contact time as explained in the EP examination report. The EP examination report comprehensively points out the treatment mixtures used to adjust the fracturing fluid to the desired pH from the cited documents.

Furthermore, I have considered each of the appended claims 4, 6, 8 and 9. Each of these claims is not considered to make any patentable contribution over the teachings of any of D1-D3. The relevant features of these claims are either disclosed in any of the above cited documents D1-D3 or are common general knowledge in the art and which therefore cannot contribute to providing novelty or an inventive step. For example, document D3 discloses key features relating to dependent claim 4 at abstract and page 2, line 17. Please also see item 3 of the EP examination report regarding these claims.

END OF REPORT

PHARAOH, EX. 1002
P. 34

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
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APPLICATION NO.	ISSUE DATE	PATENT NO.	ATTORNEY DOCKET NO.	CONFIRMATION NO.
14/686,237	03/06/2018	9909054	04697.0001USU1	2601

23552 7590 02/14/2018

MERCHANT & GOULD P.C.
P.O. BOX 2903
MINNEAPOLIS, MN 55402-0903

ISSUE NOTIFICATION

The projected patent number and issue date are specified above.

Determination of Patent Term Adjustment under 35 U.S.C. 154 (b)
(application filed on or after May 29, 2000)

The Patent Term Adjustment is 272 day(s). Any patent to issue from the above-identified application will include an indication of the adjustment on the front page.

If a Continued Prosecution Application (CPA) was filed in the above-identified application, the filing date that determines Patent Term Adjustment is the filing date of the most recent CPA.

Applicant will be able to obtain more detailed information by accessing the Patent Application Information Retrieval (PAIR) WEB site (http://pair.uspto.gov).

Any questions regarding the Patent Term Extension or Adjustment determination should be directed to the Office of Patent Legal Administration at (571)-272-7702. Questions relating to issue and publication fee payments should be directed to the Application Assistance Unit (AAU) of the Office of Data Management (ODM) at (571)-272-4200.

APPLICANT(s) (Please see PAIR WEB site http://pair.uspto.gov for additional applicants):

Andrew Bryce Conway, Weatherford, OK;
Flex-Chem Holding Company, LLC, Weatherford, OK;

The United States represents the largest, most dynamic marketplace in the world and is an unparalleled location for business investment, innovation, and commercialization of new technologies. The USA offers tremendous resources and advantages for those who invest and manufacture goods here. Through SelectUSA, our nation works to encourage and facilitate business investment. To learn more about why the USA is the best country in the world to develop technology, manufacture products, and grow your business, visit SelectUSA.gov.

PART B - FEE(S) TRANSMITTAL

Complete and send this form, together with applicable fee(s), to: Mail Mail Stop ISSUE FEE
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450
or Fax (571)-273-2885

INSTRUCTIONS: This form should be used for transmitting the ISSUE FEE and PUBLICATION FEE (if required). Blocks 1 through 5 should be completed where appropriate. All further correspondence including the Patent, advance orders and notification of maintenance fees will be mailed to the current correspondence address as indicated unless corrected below or directed otherwise in Block 1, by (a) specifying a new correspondence address; and/or (b) indicating a separate "FEE ADDRESS" for maintenance fee notifications.

CURRENT CORRESPONDENCE ADDRESS (Note: Use Block 1 for any change of address)

23552 7590 12/27/2017
MERCHANT & GOULD P.C.
P.O. BOX 2903
MINNEAPOLIS, MINNESOTA 55402-0903

Note: A certificate of mailing can only be used for domestic mailings of the Fee(s) Transmittal. This certificate cannot be used for any other accompanying papers. Each additional paper, such as an assignment or formal drawing, must have its own certificate of mailing or transmission.

Certificate of Mailing or Transmission
I hereby certify that this Fee(s) Transmittal is being deposited with the United States Postal Service with sufficient postage for first class mail in an envelope addressed to the Mail Stop ISSUE FEE address above, or being facsimile transmitted to the USPTO (571) 273-2885, on the date indicated below.

(Depositor's name)
(Signature)
(Date)

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
14/686,237	04/14/2015	Andrew Bryce Conway	04697.0001USU1	2601

TITLE OF INVENTION: STIMULATION OF WELLS IN NANO-DARCY SHALE FORMATIONS

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
REGULAR	SMALL	$480	$0.00	$0.00	$480	03/27/2018

EXAMINER	ART UNIT	CLASS-SUBCLASS
LOIKITH, CATHERINE A	3674	166-250010

1. Change of correspondence address or indication of "Fee Address" (37 CFR 1.363).

☐ Change of correspondence address (or Change of Correspondence Address form PTO/SB/122) attached.

☐ "Fee Address" indication (or "Fee Address" Indication form PTO/SB/47; Rev 03-02 or more recent) attached. **Use of a Customer Number is required.**

2. For printing on the patent front page, list
(1) The names of up to 3 registered patent attorneys or agents OR, alternatively,
(2) The name of a single firm (having as a member a registered attorney or agent) and the names of up to 2 registered patent attorneys or agents. If no name is listed, no name will be printed.

1 Merchant & Gould P.C.
2
3

3. ASSIGNEE NAME AND RESIDENCE DATA TO BE PRINTED ON THE PATENT (print or type)

PLEASE NOTE: Unless an assignee is identified below, no assignee data will appear on the patent. If an assignee is identified below, the document has been filed for recordation as set forth in 37 CFR 3.11. Completion of this form is NOT a substitute for filing an assignment.

(A) NAME OF ASSIGNEE: Flex-Chem Holding Company, LLC

(B) RESIDENCE: (CITY and STATE OR COUNTRY): Weatherford, OK

Please check the appropriate assignee category or categories (will not be printed on the patent) : ☐ Individual ☒ Corporation or other private group entity ☐ Government

4a. The following fee(s) are submitted:

☒ Issue Fee

☐ Publication Fee (No small entity discount permitted)

☐ Advance Order - # of Copies _____

4b. Payment of Fee(s): **(Please first reapply any previously paid issue fee shown above)**

☐ A check is enclosed.

☒ Payment by credit card. Form PTO-2038 is attached.

☒ The director is hereby authorized to charge the required fee(s), any deficiency, or credits any overpayment, to Deposit Account Number 13-2725 (enclose an extra copy of this form).

5. **Change in Entity Status** (from status indicated above)

☐ Applicant certifying micro entity status. See 37 CFR 1.29

☐ Applicant asserting small entity status. See 37 CFR 1.27

☐ Applicant changing to regular undiscounted fee status.

NOTE: Absent a valid certification of Micro Entity Status (see forms PTO/SB/15A and 15B), issue fee payment in the micro entity amount will not be accepted at the risk of application abandonment.
NOTE: If the application was previously under micro entity status, checking this box will be taken to be a notification of loss of entitlement to micro entity status.
NOTE: Checking this box will be taken to be a notification of loss of entitlement to small or micro entity status, as applicable.

NOTE: This form must be signed in accordance with 37 CFR 1.31 and 1.33. See 37 CFR 1.4 for signature requirements and certifications.

Authorized Signature /Brian P. McCall/ Date January 19, 2018

Typed or printed name Brian P. McCall Registration No. 68,734

Electronic Patent Application Fee Transmittal

Application Number:	14686237
Filing Date:	14-Apr-2015
Title of Invention:	STIMULATION OF WELLS IN NANO-DARCY SHALE FORMATIONS
First Named Inventor/Applicant Name:	Andrew Bryce Conway
Filer:	Brian Peter McCall/Amy Miller
Attorney Docket Number:	04697.0001USU1

Filed as Small Entity

Filing Fees for Utility under 35 USC 111(a)

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				
UTILITY APPL ISSUE FEE	2501	1	480	480

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Extension-of-Time:				
Miscellaneous:				
			Total in USD ($)	**480**

Electronic Acknowledgement Receipt

EFS ID:	31548395
Application Number:	14686237
International Application Number:	
Confirmation Number:	2601
Title of Invention:	STIMULATION OF WELLS IN NANO-DARCY SHALE FORMATIONS
First Named Inventor/Applicant Name:	Andrew Bryce Conway
Customer Number:	23552
Filer:	Brian Peter McCall
Filer Authorized By:	
Attorney Docket Number:	04697.0001USU1
Receipt Date:	19-JAN-2018
Filing Date:	14-APR-2015
Time Stamp:	14:06:03
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	CARD
Payment was successfully received in RAM	$480
RAM confirmation Number	012218INTEFSW14064800
Deposit Account	132725
Authorized User	Brian McCall

The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows:

37 CFR 1.16 (National application filing, search, and examination fees)

37 CFR 1.17 (Patent application and reexamination processing fees)

37 CFR 1.19 (Document supply fees)

37 CFR 1.20 (Post Issuance fees)

37 CFR 1.21 (Miscellaneous fees and charges)

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Issue Fee Payment (PTO-85B)	2018-01-19--PTOL-85B--04697-0001USU1.PDF	124877 d9a22a5a70d85b31448337a6c6e9e2731a49a17d	no	1
Warnings:					
Information:					
2	Fee Worksheet (SB06)	fee-info.pdf	30561 6aaf8cd41b7cc52d0e3439202d4dc7f4a3d4e5f3	no	2
Warnings:					
Information:					
		Total Files Size (in bytes):	155438		

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

EAST Search History

EAST Search History (Prior Art)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
L1	1	("5678632").PN.	US-PGPUB; USPAT	OR	OFF	2018/01/08 15:28
L2	10155	(E21B43/16 OR E21B43/25).CPC.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2018/01/08 15:30

EAST Search History (Interference)

<This search history is empty>

1/8/2018 3:33:13 PM
C:\Users\cloikith\Documents\EAST\Workspaces\14686237.wsp

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United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
14/686,237	04/14/2015	Andrew Bryce Conway	04697.0001USU1	2601

23552 7590 01/17/2018

MERCHANT & GOULD P.C.
P.O. BOX 2903
MINNEAPOLIS, MINNESOTA 55402-0903

EXAMINER	
LOIKITH, CATHERINE A	

ART UNIT	PAPER NUMBER
3674	

NOTIFICATION DATE	DELIVERY MODE
01/17/2018	ELECTRONIC

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Notice of the Office communication was sent electronically on above-indicated "Notification Date" to the following e-mail address(es):

USPTO23552@merchantgould.com

Notice of Allowability	Application No. 14/686,237	Applicant(s) Conway, Andrew Bryce	
	Examiner CATHERINE A LOIKITH	Art Unit 3674	AIA Status Yes

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address--

All claims being allowable, PROSECUTION ON THE MERITS IS (OR REMAINS) CLOSED in this application. If not included herewith (or previously mailed), a Notice of Allowance (PTOL-85) or other appropriate communication will be mailed in due course. **THIS NOTICE OF ALLOWABILITY IS NOT A GRANT OF PATENT RIGHTS.** This application is subject to withdrawal from issue at the initiative of the Office or upon petition by the applicant. See 37 CFR 1.313 and MPEP 1308.

1. ☑ This communication is responsive to the IDS filed 19 December 2017 .
   ☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on _____ .

2. ☑ An election was made by the applicant in response to a restriction requirement set forth during the interview on 06 July 2017; the restriction requirement and election have been incorporated into this action.

3. ☑ The allowed claim(s) is/are 1-13 . As a result of the allowed claim(s), you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information, please see **http://www.uspto.gov/patents/init_events/pph/index.jsp** or send an inquiry to **PPHfeedback@uspto.gov.**

4. ☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

   Certified copies:

   a) ☐ All b) ☐ Some *c) ☐ None of the:

   1. ☐ Certified copies of the priority documents have been received.
   2. ☐ Certified copies of the priority documents have been received in Application No. _____ .
   3. ☐ Copies of the certified copies of the priority documents have been received in this national stage application from the International Bureau (PCT Rule 17.2(a)).

   * Certified copies not received: _____ .

Applicant has THREE MONTHS FROM THE "MAILING DATE" of this communication to file areply complying with the requirements noted below. Failure to timely comply will result in ABANDONMENT of this application.
THIS THREE-MONTH PERIOD IS NOT EXTENDABLE.

5. ☐ CORRECTED DRAWINGS (as "replacement sheets") must be submitted.
   ☐ including changes required by the attached Examiner's Amendment / Comment or in the Office action of Paper No./Mail Date _____ .

   Identifying indicia such as the application number (see 37 CFR 1.84(c)) should be written on the drawings in the front (not the back) of each sheet. Replacement sheet(s) should be labeled as such in the header according to 37 CFR 1.121(d).

6. ☐ DEPOSIT OF and/or INFORMATION about the deposit of BIOLOGICAL MATERIAL must be submitted. Note the attached Examiner's comment regarding REQUIREMENT FOR THE DEPOSIT OF BIOLOGICAL MATERIAL.

Attachment(s)

1. ☐ Notice of References Cited (PTO-892)
2. ☑ Information Disclosure Statements (PTO/SB/08), Paper No./Mail Date _____
3. ☐ Examiner's Comment Regarding Requirement for Deposit of Biological Material _____
4. ☐ Interview Summary (PTO-413), Paper No./Mail Date. _____ .
5. ☐ Examiner's Amendment/Comment
6. ☐ Examiner's Statement of Reasons for Allowance
7. ☐ Other _____ .

/Catherine Loikith/
Primary Examiner, Art Unit 3674

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	14/686,237	Conway, Andrew Bryce
	Examiner	Art Unit
	CATHERINE A LOIKITH	3674

CPC - Searched*		
Symbol	Date	Examiner
E21B 43/16, 43/25	7/21/2017	CAL
E21B 43/16, 43/25	11/28/2017	CAL
updated search above	01/08/2018	CAL

CPC Combination Sets - Searched*		
Symbol	Date	Examiner

US Classification - Searched*			
Class	Subclass	Date	Examiner

* See search history printout included with this form or the SEARCH NOTES box below to determine the scope of the search.

Search Notes		
Search Notes	Date	Examiner
text searches in EAST	7/21/2017	CAL
text searches in EAST	12/13/2017	CAL

Interference Search			
US Class/CPC Symbol	US Subclass/CPC Group	Date	Examiner
see EAST search history		12/14/2017	CAL

PHARAOH, EX. 1002
P. 44

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	14/686,237	Conway, Andrew Bryce
	Examiner	Art Unit
	CATHERINE A LOIKITH	3674

CPC						
Symbol					Type	Version
C09K	/	8	/	605	F	2013-01-01
E21B	/	43	/	267	I	2013-01-01
C09K	/	8	/	62	I	2013-01-01
C09K	/	8	/	528	I	2013-01-01
C09K	/	8	/	602	I	2013-01-01
C09K	/	8	/	72	A	2013-01-01
C09K	/	2208	/	32	A	2013-01-01

CPC Combination Sets								
Symbol					Type	Set	Ranking	Version
	/		/					

NONE		Total Claims Allowed:	
(Assistant Examiner)	(Date)	13	
/Catherine Loikith/ Primary Examiner, Art Unit 3674	08 January 2018	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	1	1

U.S. Patent and Trademark Office

Part of Paper No.: 20180108

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	14/686,237	Conway, Andrew Bryce
	Examiner	Art Unit
	CATHERINE A LOIKITH	3674

INTERNATIONAL CLASSIFICATION					
CLAIMED					
E21B	/	43	/	16	
E21B	/	43	/	25	

NON-CLAIMED				
	/		/	

US ORIGINAL CLASSIFICATION	
CLASS	SUBCLASS

CROSS REFERENCES(S)						
CLASS	SUBCLASS (ONE SUBCLASS PER BLOCK)					

NONE		Total Claims Allowed:	
(Assistant Examiner)	(Date)	13	
/Catherine Loikith/ Primary Examiner, Art Unit 3674	08 January 2018	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	1	1

U.S. Patent and Trademark Office

Part of Paper No.: 20180108

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	14/686,237	Conway, Andrew Bryce
	Examiner	Art Unit
	CATHERINE A LOIKITH	3674

☐ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

CLAIMS

Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original
1	1	10	10												
2	2	11	11												
3	3	12	12												
4	4	13	13												
5	5		14												
6	6		15												
7	7		16												
8	8		17												
9	9														

NONE		Total Claims Allowed:	
(Assistant Examiner)	(Date)	13	
/Catherine Loikith/ Primary Examiner, Art Unit 3674	08 January 2018	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	1	1

U.S. Patent and Trademark Office

Part of Paper No.: 20180108

Doc code: IDS
Doc description: Information Disclosure Statement (IDS) Filed

PTO/SB/08a (03-15)
Approved for use through 07/31/2016. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	14686237
Filing Date	2015-04-14
First Named Inventor	Andrew Bryce Conway
Art Unit	3674
Examiner Name	Catherine A. Loikith
Attorney Docket Number	04697.0001USU1

U.S.PATENTS Remove

Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	5678632		1997-10-21	Moses et al.	

If you wish to add additional U.S. Patent citation information please click the Add button. Add

U.S.PATENT APPLICATION PUBLICATIONS Remove

Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1					

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FOREIGN PATENT DOCUMENTS Remove

Examiner Initial*	Cite No	Foreign Document Number[3]	Country Code[2] i	Kind Code[4]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear	T[5]
	1							

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NON-PATENT LITERATURE DOCUMENTS Remove

Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /CAL/

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	14686237
Filing Date	2015-04-14
First Named Inventor	Andrew Bryce Conway
Art Unit	3674
Examiner Name	Catherine A. Loikith
Attorney Docket Number	04697.0001USU1

	1	

If you wish to add additional non-patent literature document citation information please click the Add button Add

EXAMINER SIGNATURE

Examiner Signature	/Catherine Loikith/	Date Considered	01/08/2018

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /CAL/

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	14686237
Filing Date	2015-04-14
First Named Inventor	Andrew Bryce Conway
Art Unit	3674
Examiner Name	Catherine A. Loikith
Attorney Docket Number	04697.0001USU1

CERTIFICATION STATEMENT

Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

See attached certification statement.

☒ The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

☒ A certification statement is not submitted herewith.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/Brian P. McCall/	Date (YYYY-MM-DD)	2017-12-19
Name/Print	Brian P. McCall	Registration Number	68734

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1 hour to complete, including gathering, preparing and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /CAL/

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The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C. 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether the Freedom of Information Act requires disclosure of these record s.

2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.

3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.

4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).

5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.

6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.

9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /CAL/

Doc code: IDS
Doc description: Information Disclosure Statement (IDS) Filed

PTO/SB/08a (03-15)
Approved for use through 07/31/2016. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
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First Named Inventor	Andrew Bryce Conway
Art Unit	3674
Examiner Name	Catherine A. Loikith
Attorney Docket Number	04697.0001USU1

U.S.PATENTS Remove

Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	8236734		2012-08-07	Shen et al.	
	2	6527051	B1	2003-03-04	Reddy et al.	
	3	6225262	B1	2002-05-01	Irwin	
	4	6162766	A	2000-12-19	Muir	
	5	5497830	A	1996-03-12	Boles	

If you wish to add additional U.S. Patent citation information please click the Add button. Add

U.S.PATENT APPLICATION PUBLICATIONS Remove

Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	20160067845	A1	2016-03-10	Conway	

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /CAL/

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	14686237
	Filing Date	2015-04-14
	First Named Inventor	Andrew Bryce Conway
	Art Unit	3674
	Examiner Name	Catherine A. Loikith
	Attorney Docket Number	04697.0001USU1

	2	20020160920	A1	2002-10-31	Dawson et al.	
	3	20090298721	A1	2009-12-03	Robb et al.	
	4	20110214862	A1	2011-09-08	Horton	

If you wish to add additional U.S. Published Application citation information please click the Add button. Add

FOREIGN PATENT DOCUMENTS Remove

Examiner Initial*	Cite No	Foreign Document Number[3]	Country Code[2] i	Kind Code[4]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear	T[5]
	1	0326720	EP	A1	1989-08-09	AGIP S.p.A.		
	2	0505169	EP	A1	1992-09-23	Smith et al.		
	3	2009091652	WO	A2	2009-07-23	Horton et al.		
	4	2013019188	WO		2013-02-07	Dismuke et al.		

If you wish to add additional Foreign Patent Document citation information please click the Add button Add

NON-PATENT LITERATURE DOCUMENTS Remove

Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /CAL/

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	14686237
Filing Date	2015-04-14
First Named Inventor	Andrew Bryce Conway
Art Unit	3674
Examiner Name	Catherine A. Loikith
Attorney Docket Number	04697.0001USU1

	1	European Search Report for European Patent Application No. 14856530.2 - 1354, June 23, 2017, 8pgs.
	2	Written Opinion, PCT/US2015/048634 mailed December 7, 2015, 5pgs.
	3	International Search Report, PCT/US2015/048634 mailed December 7, 2015, 2pgs.
	4	Geiver, The Slickwater Story, The Bakken magazine, http://thebakken.com/articles/711/the-slickwater-story, July 14, 2014, 2pgs.
	5	Huang R.Y.M.; Jarvis, N.R. 1973. Ionically crosslinked hydrophilic polymer membranes: Synthesis and measurement of transport properties, J Polym Sci 41: 117-127, 11 pgs.
	6	Ahmed, E.M. 2015. Hydrogel: Preparation, characterization, and applications: A review, J Adv Res 6: 105-121, 17pgs.
	7	Akin, H.; Hasirci, V.N.; Hasirci, N. 1990. Permeability properties of charged hydrogel-carrying membranes, Polymer 31 (2): 270-275, 6pgs.
	8	RICK MCCURDY, High Rate Hydraulic Fracturing Additives in Non-Marcellus Unconventional Shales, May 2011, pages 17-21, Proceedings of the Technical Workshops for the Hydraulic Fracturing Study: Chemical & Analytical Methods http://water.epa.gov/type/groundwater/uic/class2/hydraulicfracturing/upload/proceedingsofhfchemanalmethodsfinalmay2011.pdf

If you wish to add additional non-patent literature document citation information please click the Add button Add

EXAMINER SIGNATURE

Examiner Signature	/Catherine Loikith/	Date Considered	12/13/2017

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /CAL/

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	14686237
Filing Date	2015-04-14
First Named Inventor	Andrew Bryce Conway
Art Unit	3674
Examiner Name	Catherine A. Loikith
Attorney Docket Number	04697.0001USU1

CERTIFICATION STATEMENT

Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

See attached certification statement.

☒ The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

☒ A certification statement is not submitted herewith.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/Brian P. McCall/	Date (YYYY-MM-DD)	2017-10-24
Name/Print	Brian P. McCall	Registration Number	68734

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1 hour to complete, including gathering, preparing and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /CAL/

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C. 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether the Freedom of Information Act requires disclosure of these record s.

2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.

3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.

4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).

5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.

6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.

9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /CAL/

EAST Search History

EAST Search History (Prior Art)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
S59	9871	(E21B43/16 OR E21B43/25).CPC.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/11/28 16:52
S60	1	("3700280").PN.	US-PGPUB; USPAT	OR	ON	2017/12/13 11:38
S61	9	("20020160920" | "20090298721" | "20110214862" | "20160067845" | "5497830" | "6162766" | "6225262" | "6527051" | "8236734").PN.	US-PGPUB; USPAT	OR	ON	2017/12/13 11:38
S62	9	(S60 S61) AND (metal WITH complex$4 citric WITH acid edta ethylenediaminetetraacetic acetic WITH acid)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/12/13 11:40
S63	1	(S60 S61) AND metal WITH complex$4	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/12/13 11:43
S64	5	("0599474").PN.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2017/12/13 11:51
S65	0	S61 AND shale	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/12/13 11:52
S66	1	S62 AND shale	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/12/13 11:52
S67	1	S66 AND fractur$3 WITH pressure	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/12/13 11:53
S68	35539	metal WITH complexing	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/12/14 15:45
S69	430	metal WITH complexing AND (oilfield wellbore downhole subterranean)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO;	OR	ON	2017/12/14 15:46

			DERWENT; IBM_TDB			

EAST Search History (Interference)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
S70	123	(complex$3 shale).clm.	US-PGPUB; USPAT	AND	ON	2017/12/14 15:30
S71	52	(complex$3 shale metal).clm.	US-PGPUB; USPAT	AND	ON	2017/12/14 15:30
S72	1	(complex$3 shale metal nano$1darcy).clm.	US-PGPUB; USPAT	AND	ON	2017/12/14 15:31

12/14/2017 3:48:15 PM
C:\Users\cloikith\Documents\EAST\Workspaces\14686237.wsp

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

NOTICE OF ALLOWANCE AND FEE(S) DUE

23552 7590 12/27/2017

MERCHANT & GOULD P.C.
P.O. BOX 2903
MINNEAPOLIS, MINNESOTA 55402-0903

EXAMINER	
LOIKITH, CATHERINE A	
ART UNIT	PAPER NUMBER
3674	

DATE MAILED: 12/27/2017

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
14/686,237	04/14/2015	Andrew Bryce Conway	04697.0001USU1	2601

TITLE OF INVENTION: STIMULATION OF WELLS IN NANO-DARCY SHALE FORMATIONS

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
REGULAR	SMALL	$480	$0.00	$0.00	$480	03/27/2018

THE APPLICATION IDENTIFIED ABOVE HAS BEEN EXAMINED AND IS ALLOWED FOR ISSUANCE AS A PATENT. PROSECUTION ON THE MERITS IS CLOSED. THIS NOTICE OF ALLOWANCE IS NOT A GRANT OF PATENT RIGHTS. THIS APPLICATION IS SUBJECT TO WITHDRAWAL FROM ISSUE AT THE INITIATIVE OF THE OFFICE OR UPON PETITION BY THE APPLICANT. SEE 37 CFR 1.313 AND MPEP 1308.

THE ISSUE FEE AND PUBLICATION FEE (IF REQUIRED) MUST BE PAID WITHIN THREE MONTHS FROM THE MAILING DATE OF THIS NOTICE OR THIS APPLICATION SHALL BE REGARDED AS ABANDONED. THIS STATUTORY PERIOD CANNOT BE EXTENDED. SEE 35 U.S.C. 151. THE ISSUE FEE DUE INDICATED ABOVE DOES NOT REFLECT A CREDIT FOR ANY PREVIOUSLY PAID ISSUE FEE IN THIS APPLICATION. IF AN ISSUE FEE HAS PREVIOUSLY BEEN PAID IN THIS APPLICATION (AS SHOWN ABOVE), THE RETURN OF PART B OF THIS FORM WILL BE CONSIDERED A REQUEST TO REAPPLY THE PREVIOUSLY PAID ISSUE FEE TOWARD THE ISSUE FEE NOW DUE.

HOW TO REPLY TO THIS NOTICE:

I. Review the ENTITY STATUS shown above. If the ENTITY STATUS is shown as SMALL or MICRO, verify whether entitlement to that entity status still applies.

If the ENTITY STATUS is the same as shown above, pay the TOTAL FEE(S) DUE shown above.

If the ENTITY STATUS is changed from that shown above, on PART B - FEE(S) TRANSMITTAL, complete section number 5 titled "Change in Entity Status (from status indicated above)".

For purposes of this notice, small entity fees are 1/2 the amount of undiscounted fees, and micro entity fees are 1/2 the amount of small entity fees.

II. PART B - FEE(S) TRANSMITTAL, or its equivalent, must be completed and returned to the United States Patent and Trademark Office (USPTO) with your ISSUE FEE and PUBLICATION FEE (if required). If you are charging the fee(s) to your deposit account, section "4b" of Part B - Fee(s) Transmittal should be completed and an extra copy of the form should be submitted. If an equivalent of Part B is filed, a request to reapply a previously paid issue fee must be clearly made, and delays in processing may occur due to the difficulty in recognizing the paper as an equivalent of Part B.

III. All communications regarding this application must give the application number. Please direct all communications prior to issuance to Mail Stop ISSUE FEE unless advised to the contrary.

IMPORTANT REMINDER: Utility patents issuing on applications filed on or after Dec. 12, 1980 may require payment of maintenance fees. It is patentee's responsibility to ensure timely payment of maintenance fees when due.

PART B - FEE(S) TRANSMITTAL

Complete and send this form, together with applicable fee(s), to: Mail **Mail Stop ISSUE FEE**
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450
or Fax (571)-273-2885

INSTRUCTIONS: This form should be used for transmitting the ISSUE FEE and PUBLICATION FEE (if required). Blocks 1 through 5 should be completed where appropriate. All further correspondence including the Patent, advance orders and notification of maintenance fees will be mailed to the current correspondence address as indicated unless corrected below or directed otherwise in Block 1, by (a) specifying a new correspondence address; and/or (b) indicating a separate "FEE ADDRESS" for maintenance fee notifications.

CURRENT CORRESPONDENCE ADDRESS (Note: Use Block 1 for any change of address)

23552 7590 12/27/2017
MERCHANT & GOULD P.C.
P.O. BOX 2903
MINNEAPOLIS, MINNESOTA 55402-0903

Note: A certificate of mailing can only be used for domestic mailings of the Fee(s) Transmittal. This certificate cannot be used for any other accompanying papers. Each additional paper, such as an assignment or formal drawing, must have its own certificate of mailing or transmission.

Certificate of Mailing or Transmission
I hereby certify that this Fee(s) Transmittal is being deposited with the United States Postal Service with sufficient postage for first class mail in an envelope addressed to the Mail Stop ISSUE FEE address above, or being facsimile transmitted to the USPTO (571) 273-2885, on the date indicated below.

(Depositor's name)
(Signature)
(Date)

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
14/686,237	04/14/2015	Andrew Bryce Conway	04697.0001USU1	2601

TITLE OF INVENTION: STIMULATION OF WELLS IN NANO-DARCY SHALE FORMATIONS

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
REGULAR	SMALL	$480	$0.00	$0.00	$480	03/27/2018

EXAMINER	ART UNIT	CLASS-SUBCLASS
LOIKITH, CATHERINE A	3674	166-250010

1. Change of correspondence address or indication of "Fee Address" (37 CFR 1.363).

❑ Change of correspondence address (or Change of Correspondence Address form PTO/SB/122) attached.

❑ "Fee Address" indication (or "Fee Address" Indication form PTO/SB/47; Rev 03-02 or more recent) attached. **Use of a Customer Number is required.**

2. For printing on the patent front page, list
(1) The names of up to 3 registered patent attorneys or agents OR, alternatively,
(2) The name of a single firm (having as a member a registered attorney or agent) and the names of up to 2 registered patent attorneys or agents. If no name is listed, no name will be printed.

1 _____
2 _____
3 _____

3. ASSIGNEE NAME AND RESIDENCE DATA TO BE PRINTED ON THE PATENT (print or type)

PLEASE NOTE: Unless an assignee is identified below, no assignee data will appear on the patent. If an assignee is identified below, the document has been filed for recordation as set forth in 37 CFR 3.11. Completion of this form is NOT a substitute for filing an assignment.

(A) NAME OF ASSIGNEE (B) RESIDENCE: (CITY and STATE OR COUNTRY)

Please check the appropriate assignee category or categories (will not be printed on the patent) : ❑ Individual ❑ Corporation or other private group entity ❑ Government

4a. The following fee(s) are submitted:

❑ Issue Fee

❑ Publication Fee (No small entity discount permitted)

❑ Advance Order - # of Copies _____

4b. Payment of Fee(s): **(Please first reapply any previously paid issue fee shown above)**

❑ A check is enclosed.

❑ Payment by credit card. Form PTO-2038 is attached.

❑ The director is hereby authorized to charge the required fee(s), any deficiency, or credits any overpayment, to Deposit Account Number _____ (enclose an extra copy of this form).

5. **Change in Entity Status** (from status indicated above)

❑ Applicant certifying micro entity status. See 37 CFR 1.29

❑ Applicant asserting small entity status. See 37 CFR 1.27

❑ Applicant changing to regular undiscounted fee status.

NOTE: Absent a valid certification of Micro Entity Status (see forms PTO/SB/15A and 15B), issue fee payment in the micro entity amount will not be accepted at the risk of application abandonment.
NOTE: If the application was previously under micro entity status, checking this box will be taken to be a notification of loss of entitlement to micro entity status.
NOTE: Checking this box will be taken to be a notification of loss of entitlement to small or micro entity status, as applicable.

NOTE: This form must be signed in accordance with 37 CFR 1.31 and 1.33. See 37 CFR 1.4 for signature requirements and certifications.

Authorized Signature _____ Date _____

Typed or printed name _____ Registration No. _____

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
14/686,237	04/14/2015	Andrew Bryce Conway	04697.0001USU1	2601

23552 7590 12/27/2017

MERCHANT & GOULD P.C.
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MINNEAPOLIS, MINNESOTA 55402-0903

EXAMINER	
LOIKITH, CATHERINE A	
ART UNIT	**PAPER NUMBER**
3674	

DATE MAILED: 12/27/2017

OMB Clearance and PRA Burden Statement for PTOL-85 Part B

The Paperwork Reduction Act (PRA) of 1995 requires Federal agencies to obtain Office of Management and Budget approval before requesting most types of information from the public. When OMB approves an agency request to collect information from the public, OMB (i) provides a valid OMB Control Number and expiration date for the agency to display on the instrument that will be used to collect the information and (ii) requires the agency to inform the public about the OMB Control Number's legal significance in accordance with 5 CFR 1320.5(b).

The information collected by PTOL-85 Part B is required by 37 CFR 1.311. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, Virginia 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, Virginia 22313-1450. Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

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The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether disclosure of these records is required by the Freedom of Information Act.
2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspection or an issued patent.
9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

Notice of Allowability	Application No. 14/686,237	Applicant(s) Conway, Andrew Bryce	
	Examiner CATHERINE A LOIKITH	Art Unit 3674	AIA Status Yes

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address--

All claims being allowable, PROSECUTION ON THE MERITS IS (OR REMAINS) CLOSED in this application. If not included herewith (or previously mailed), a Notice of Allowance (PTOL-85) or other appropriate communication will be mailed in due course. **THIS NOTICE OF ALLOWABILITY IS NOT A GRANT OF PATENT RIGHTS.** This application is subject to withdrawal from issue at the initiative of the Office or upon petition by the applicant. See 37 CFR 1.313 and MPEP 1308.

1. ☑ This communication is responsive to the amendment filed 24 October 2017 and the Examiner's Amendment attached herewith .
   ☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on _____ .

2. ☑ An election was made by the applicant in response to a restriction requirement set forth during the interview on 06 July 2017; the restriction requirement and election have been incorporated into this action.

3. ☑ The allowed claim(s) is/are 1-13 . As a result of the allowed claim(s), you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information, please see **http://www.uspto.gov/patents/init_events/pph/index.jsp** or send an inquiry to **PPHfeedback@uspto.gov.**

4. ☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

   Certified copies:

   a) ☐ All b) ☐ Some *c) ☐ None of the:

   1. ☐ Certified copies of the priority documents have been received.
   2. ☐ Certified copies of the priority documents have been received in Application No. _____ .
   3. ☐ Copies of the certified copies of the priority documents have been received in this national stage application from the International Bureau (PCT Rule 17.2(a)).

   * Certified copies not received: _____ .

Applicant has THREE MONTHS FROM THE "MAILING DATE" of this communication to file areply complying with the requirements noted below. Failure to timely comply will result in ABANDONMENT of this application.
THIS THREE-MONTH PERIOD IS NOT EXTENDABLE.

5. ☐ CORRECTED DRAWINGS (as "replacement sheets") must be submitted.
   ☐ including changes required by the attached Examiner's Amendment / Comment or in the Office action of Paper No./Mail Date _____ .

   Identifying indicia such as the application number (see 37 CFR 1.84(c)) should be written on the drawings in the front (not the back) of each sheet. Replacement sheet(s) should be labeled as such in the header according to 37 CFR 1.121(d).

6. ☐ DEPOSIT OF and/or INFORMATION about the deposit of BIOLOGICAL MATERIAL must be submitted. Note the attached Examiner's comment regarding REQUIREMENT FOR THE DEPOSIT OF BIOLOGICAL MATERIAL.

Attachment(s)

1. ☐ Notice of References Cited (PTO-892)
2. ☑ Information Disclosure Statements (PTO/SB/08), Paper No./Mail Date _____
3. ☐ Examiner's Comment Regarding Requirement for Deposit of Biological Material _____
4. ☐ Interview Summary (PTO-413), Paper No./Mail Date. _____ .
5. ☑ Examiner's Amendment/Comment
6. ☐ Examiner's Statement of Reasons for Allowance
7. ☐ Other _____ .

/Catherine Loikith/
Primary Examiner, Art Unit 3674

Notice of Pre-AIA or AIA Status

The present application, filed on or after March 16, 2013, is being examined under the first inventor to file provisions of the AIA.

EXAMINER'S AMENDMENT

An examiner's amendment to the record appears below. Should the changes and/or additions be unacceptable to applicant, an amendment may be filed as provided by 37 CFR 1.312. To ensure consideration of such an amendment, it MUST be submitted no later than the payment of the issue fee.

The application has been amended as follows:

In the Specification:

In the Abstract filed October 24, 2017 on line 2 "are disclosed" has been deleted.

In the Claims:

This application is in condition for allowance except for the presence of claims 14-17 directed to a Species non-elected without traverse. Accordingly, claims 14-17 have been cancelled.

Conclusion

Any inquiry concerning this communication or earlier communications from the examiner should be directed to CATHERINE A LOIKITH whose telephone number is (571)270-7822. The examiner can normally be reached on M-F 9am-5:30pm.

Examiner interviews are available via telephone, in-person, and video conferencing using a USPTO supplied web-based collaboration tool. To schedule an interview, applicant is encouraged to use the USPTO Automated Interview Request (AIR) at http://www.uspto.gov/interviewpractice.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Doug Hutton can be reached on 571-272-4137. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see http://pair-direct.uspto.gov. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a USPTO Customer Service Representative or access to the automated information system, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.

/Catherine Loikith/
Primary Examiner, Art Unit 3674

12/14/17

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	14/686,237	Conway, Andrew Bryce
	Examiner	Art Unit
	CATHERINE A LOIKITH	3674

CPC						
Symbol					Type	Version
C09K	/	8	/	605	F	2013-01-01
E21B	/	43	/	267	I	2013-01-01
C09K	/	8	/	62	I	2013-01-01
C09K	/	8	/	528	I	2013-01-01
C09K	/	8	/	602	I	2013-01-01
C09K	/	8	/	72	A	2013-01-01
C09K	/	2208	/	32	A	2013-01-01

CPC Combination Sets								
Symbol					Type	Set	Ranking	Version
	/		/					

NONE		Total Claims Allowed:	
(Assistant Examiner)	(Date)	13	
/Catherine Loikith/ Primary Examiner, Art Unit 3674	14 December 2017	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	1	1

U.S. Patent and Trademark Office

Part of Paper No.: 20171214

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	14/686,237	Conway, Andrew Bryce
	Examiner	Art Unit
	CATHERINE A LOIKITH	3674

INTERNATIONAL CLASSIFICATION					
CLAIMED					
E21B	/	43	/	16	
E21B	/	43	/	25	

NON-CLAIMED				
	/		/	

US ORIGINAL CLASSIFICATION	
CLASS	SUBCLASS

CROSS REFERENCES(S)						
CLASS	SUBCLASS (ONE SUBCLASS PER BLOCK)					

NONE		Total Claims Allowed:	
(Assistant Examiner)	(Date)	13	
/Catherine Loikith/ Primary Examiner, Art Unit 3674	14 December 2017	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	1	1

U.S. Patent and Trademark Office

Part of Paper No.: 20171214

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	14/686,237	Conway, Andrew Bryce
	Examiner	Art Unit
	CATHERINE A LOIKITH	3674

☐ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

CLAIMS

Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original
1	1	10	10												
2	2	11	11												
3	3	12	12												
4	4	13	13												
5	5		14												
6	6		15												
7	7		16												
8	8		17												
9	9														

NONE		**Total Claims Allowed:**	
(Assistant Examiner)	(Date)	13	
/Catherine Loikith/ Primary Examiner, Art Unit 3674	14 December 2017	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	1	1

U.S. Patent and Trademark Office

Part of Paper No.: 20171214

Doc code: IDS
Doc description: Information Disclosure Statement (IDS) Filed

PTO/SB/08a (03-15)
Approved for use through 07/31/2016. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	14686237
Filing Date	2015-04-14
First Named Inventor	Andrew Bryce Conway
Art Unit	3676
Examiner Name	Waseem Moorad
Attorney Docket Number	04697.0001USU1

U.S.PATENTS Remove

Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	3700280	A	1972-10-24	Papadopolous et al.	

If you wish to add additional U.S. Patent citation information please click the Add button. Add

U.S.PATENT APPLICATION PUBLICATIONS Remove

Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1					

If you wish to add additional U.S. Published Application citation information please click the Add button. Add

FOREIGN PATENT DOCUMENTS Remove

Examiner Initial*	Cite No	Foreign Document Number[3]	Country Code[2] i	Kind Code[4]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear	T[5]
	1	0599474	EP	A2	1994-06-01	Halliburton Co.		
	2	2012171857	WO	A1	2012-12-20	Nasr-El-Din et al.		

If you wish to add additional Foreign Patent Document citation information please click the Add button Add

NON-PATENT LITERATURE DOCUMENTS Remove

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /CAL/

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	14686237
Filing Date	2015-04-14
First Named Inventor	Andrew Bryce Conway
Art Unit	3676
Examiner Name	Waseem Moorad
Attorney Docket Number	04697.0001USU1

Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]
	1	European Search Report dated August 31, 2017, Application No. EP15780712.4, 7pgs.	

If you wish to add additional non-patent literature document citation information please click the Add button Add

EXAMINER SIGNATURE

Examiner Signature	/Catherine Loikith/	Date Considered	12/13/2017

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /CAL/

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	14686237
Filing Date	2015-04-14
First Named Inventor	Andrew Bryce Conway
Art Unit	3676
Examiner Name	Waseem Moorad
Attorney Docket Number	04697.0001USU1

CERTIFICATION STATEMENT

Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

☒ That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

See attached certification statement.

The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

A certification statement is not submitted herewith.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/Brian P. McCall/	Date (YYYY-MM-DD)	2017-09-29
Name/Print	Brian P. McCall	Registration Number	68734

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1 hour to complete, including gathering, preparing and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /CAL/

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C. 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether the Freedom of Information Act requires disclosure of these record s.

2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.

3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.

4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).

5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.

6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.

9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /CAL/

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United States Patent and Trademark Office
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www.uspto.gov

BIB DATA SHEET

CONFIRMATION NO. 2601

SERIAL NUMBER	FILING or 371(c) DATE RULE	CLASS	GROUP ART UNIT	ATTORNEY DOCKET NO.
14/686,237	04/14/2015	166	3674	04697.0001USU1

APPLICANTS
Flex-Chem Holding Company, LLC, Weatherford, OK;

INVENTORS
Andrew Bryce Conway, Weatherford, OK;

**** CONTINUING DATA ***************************
This appln claims benefit of 61/979,210 04/14/2014
and claims benefit of 62/087,899 12/05/2014

**** FOREIGN APPLICATIONS ***************************

**** IF REQUIRED, FOREIGN FILING LICENSE GRANTED **** ** SMALL ENTITY **
04/24/2015

Foreign Priority claimed ☐ Yes ☑ No 35 USC 119(a-d) conditions met ☐ Yes ☐ No Verified and Acknowledged /CATHERINE A LOIKITH/ Examiner's Signature	☐ Met after Allowance Initials	STATE OR COUNTRY	SHEETS DRAWINGS	TOTAL CLAIMS	INDEPENDENT CLAIMS
		OK	5	17	2

ADDRESS

MERCHANT & GOULD P.C.
P.O. BOX 2903
MINNEAPOLIS, MN 55402-0903
UNITED STATES

TITLE

STIMULATION OF WELLS IN NANO-DARCY SHALE FORMATIONS

FILING FEE RECEIVED		
800	FEES: Authority has been given in Paper No._____ to charge/credit DEPOSIT ACCOUNT No._____ for following:	☐ All Fees ☐ 1.16 Fees (Filing) ☐ 1.17 Fees (Processing Ext. of time) ☐ 1.18 Fees (Issue) ☐ Other _____ ☐ Credit

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	14/686,237	Conway, Andrew Bryce
	Examiner	Art Unit
	CATHERINE A LOIKITH	3674

CPC - Searched*		
Symbol	Date	Examiner
E21B 43/16, 43/25	7/21/2017	CAL
E21B 43/16, 43/25	11/28/2017	CAL

CPC Combination Sets - Searched*		
Symbol	Date	Examiner

US Classification - Searched*			
Class	Subclass	Date	Examiner

* See search history printout included with this form or the SEARCH NOTES box below to determine the scope of the search.

Search Notes		
Search Notes	Date	Examiner
text searches in EAST	7/21/2017	CAL
text searches in EAST	12/13/2017	CAL

Interference Search			
US Class/CPC Symbol	US Subclass/CPC Group	Date	Examiner
see EAST search history		12/14/2017	CAL

PHARAOH, EX. 1002
P. 74

PTO/SB/08a (03-15)
Approved for use through 07/31/2016. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
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INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	14686237
Filing Date	2015-04-14
First Named Inventor	Andrew Bryce Conway
Art Unit	3674
Examiner Name	Catherine A. Loikith
Attorney Docket Number	04697.0001USU1

U.S.PATENTS Remove

Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	5678632		1997-10-21	Moses et al.	

If you wish to add additional U.S. Patent citation information please click the Add button. Add

U.S.PATENT APPLICATION PUBLICATIONS Remove

Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
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Examiner Initial*	Cite No	Foreign Document Number[3]	Country Code[2] i	Kind Code[4]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear	T[5]
	1							

If you wish to add additional Foreign Patent Document citation information please click the Add button Add

NON-PATENT LITERATURE DOCUMENTS Remove

Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	14686237
	Filing Date	2015-04-14
	First Named Inventor	Andrew Bryce Conway
	Art Unit	3674
	Examiner Name	Catherine A. Loikith
	Attorney Docket Number	04697.0001USU1

	1	

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EXAMINER SIGNATURE

Examiner Signature		Date Considered	

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	14686237
Filing Date	2015-04-14
First Named Inventor	Andrew Bryce Conway
Art Unit	3674
Examiner Name	Catherine A. Loikith
Attorney Docket Number	04697.0001USU1

CERTIFICATION STATEMENT

Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

See attached certification statement.

☒ The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

☒ A certification statement is not submitted herewith.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/Brian P. McCall/	Date (YYYY-MM-DD)	2017-12-19
Name/Print	Brian P. McCall	Registration Number	68734

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1 hour to complete, including gathering, preparing and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

Privacy Act Statement

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The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C. 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether the Freedom of Information Act requires disclosure of these record s.

2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.

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6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

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Electronic Patent Application Fee Transmittal

Application Number:	14686237
Filing Date:	14-Apr-2015
Title of Invention:	STIMULATION OF WELLS IN NANO-DARCY SHALE FORMATIONS
First Named Inventor/Applicant Name:	Andrew Bryce Conway
Filer:	Brian Peter McCall/Amy Miller
Attorney Docket Number:	04697.0001USU1

Filed as Small Entity

Filing Fees for Utility under 35 USC 111(a)

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				
Extension-of-Time:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Miscellaneous:				
SUBMISSION- INFORMATION DISCLOSURE STMT	2806	1	90	90
		Total in USD ($)		**90**

Electronic Acknowledgement Receipt

EFS ID:	31266872
Application Number:	14686237
International Application Number:	
Confirmation Number:	2601
Title of Invention:	STIMULATION OF WELLS IN NANO-DARCY SHALE FORMATIONS
First Named Inventor/Applicant Name:	Andrew Bryce Conway
Customer Number:	23552
Filer:	Brian Peter McCall
Filer Authorized By:	
Attorney Docket Number:	04697.0001USU1
Receipt Date:	19-DEC-2017
Filing Date:	14-APR-2015
Time Stamp:	10:15:15
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	CARD
Payment was successfully received in RAM	$90
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Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Information Disclosure Statement (IDS) Form (SB08)	2017-12-19--SIDS-7--04697-0001USU1.PDF	1034946 6ebaea9f186a4815b80d5b02277a9f854cc3fa2e	no	4
Warnings:					
Information:					
2	Fee Worksheet (SB06)	fee-info.pdf	30481 c9cf8436ca9a3b0095a997745a3400dacc048dab	no	2
Warnings:					
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New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant:	Andrew Bryce Conway	Examiner:	Catherine A Loikith
Serial No.:	14/686,237	Group Art Unit:	3674
Filed:	April 14, 2015	Docket No.:	04697.0001USU1
Customer No.:	23552	Confirmation No.:	2601
Title:	Stimulation of Wells in Nano-Darcy Shale Formations		

AMENDMENT & RESPONSE

Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

Attention Commissioner:

Please consider and enter the following amendments and/or remarks in response to the recent action for this patent application.

An **interview summary** is included with this paper.

Amendments to the **drawings** are included with this paper.

Amendments to the **specification** are included with this paper.

Amendments to the **claims** are included with this paper.

Remarks are included with this paper.

Interview Summary

Applicant thanks Examiner Loikith for her time during the recent telephonic interview on September 26, 2017 with Brian McCall (Reg. No. 68,734). Although no agreement was reached, the Examiner's discussions regarding the scope of the prior art relative to the current language of the claims was helpful in the preparation of this Amendment.

PHARAOH, EX. 1002
P. 84

In the Drawings

A set of replacement drawings sheets is filed herewith. Each of Figures 1-5 have been formalized for improved clarity.

In the specification

Please amend the Abstract as indicated below.

~~This disclosure describes formulations~~ Formulations and methods for stimulating the production from wells in nano-darcy shale formations are disclosed. In one embodiment, the method includes injecting a treatment mixture containing a metal complexing agent into a nano-darcy shale formation adjacent to a well at a pressure below the fracture pressure of the formation. A sufficient contact time is allowed and then the treatment mixture is pumped from the subsurface. This has been shown to stimulate well production in shale formations. Without being held to a particular theory it appears that the metal complexing agent is binding with naturally occurring metals in the shale formation, and particularly divalent metal ions, which are then extracted with the spent fluid. This removal of naturally occurring metals may be increasing the permeability of the formation in the contact region adjacent to the well, thereby causing the observed increased production.

Listing of Claims:

This listing of claims will replace all prior versions and listings of claims in the application.

1. (Currently Amended) A method for stimulating an existing well in a nano-darcy shale formation comprising:

providing a treatment mixture containing between about 0.1% and 95% by weight metal complexing agent at a pH of between about 0 and 10;

injecting the treatment mixture into the well at a pressure less than a fracture pressure of the nano-darcy shale formation until at least some of the treatment mixture exits the well and contacts the nano-darcy shale formation;

maintaining the treatment mixture in contact with the nano-darcy shale formation for a contact time of between about 1 minute to 100 days, thereby allowing the metal complexing agent to bind with at least some naturally-occurring metals contained within the nano-darcy shale formation; and

removing the treatment mixture from the well after the contact time, thereby removing the bound naturally-occurring metals from the non-darcy shale formation and thereby improving the hydrocarbon production of the well relative to the hydrocarbon production immediately prior to performance of the method.

2. (Original) The method of claim 1 wherein the metal complexing agent is citric acid.

3. (Original) The method of claim 1 wherein the metal complexing agent is ethylenediaminetetraacetic acid (EDTA).

4. (Original) The method of claim 1 wherein the metal complexing agent is acetic acid.

5. (Original) The method of claim 1 wherein the metal complexing agent includes at least one of ethylenediaminetetraacetic acid (EDTA), propylenediaminetetraacetic acid (PDTA), nitrilotriacetic acid (NTA), N-(2- hydroxyethyl)ethylenediaminetriacetic acid (HEDTA),

diethylenetriaminepentaacetic acid (DTPA), hydroxyethyliminodiacetic acid (HEIDA), cyclohexylenediaminetetraacetic acid (CDTA), diphenylaminesulfonic acid (DPAS), ethylenediaminedi(o-hydroxyphenylacetic) acid (EDDHA), glucoheptonic acid, gluconic acid, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, phthalic acid, terephthalic acid, aconitic acid, carballylic acid, trimesic acid, isocitric acid, citric acid, or any salt or derivative of any of the previously listed compounds.

6. (Original) The method of claim 1 wherein the treatment mixture comprises:
between about 0.1% and 95% by weight metal complexing agent;
between 1 and 10,000 parts per million (ppm) of a corrosion inhibitor;
between 1 and 10,000 ppm of a biocide;
between 1 and 10,000 ppm of a colloidal silica deposition inhibitor;
between 1 and 500 gallons per thousand gallons (gpt) of a mutual solvent; and
between 1 and 2000 parts per million of a surfactant.

7. (Original) The method of claim 1 wherein the treatment mixture further comprises between 0.1 and 95% of acid(s) as pH modifier.

8. (Original) The method of claim 1 wherein the injecting operation further comprises:
alternately injecting a first amount of treatment mixture and a second amount of a diverting mixture into the well.

9. (Original) The method of claim 1 wherein the injecting operation further comprises:
injecting the treatment mixture until the pressure within the well reaches a predetermined target pressure calculated based on the fracture pressure of the nano-darcy shale formation; and
upon reaching the target pressure, shutting in the well.

10. (Currently Amended) The method of claim 1, ~~wherein the injecting operation~~ further comprising ~~comprises~~:

injecting the treatment mixture containing a metal complexing agent ~~such as citric acid or EDTA~~ in combination with hydraulic fracturing and injecting into the formation in conjunction with propagation of ~~the~~ induced fractures, the metal complexing agent including citric acid or EDTA.

11. (Original) The method of claim 1 further comprising:
monitoring at least one of pH and well pressure during the maintaining operation; and
initiating the removing operation based on results of the monitoring operation.

12. (Original) The method of claim 1 further wherein the metal complexing agent is selected from glutamic acid diacetic acid (GLDA), methylglycine diacetic acid (MGDA), β-alanine diacetic acid (β-ADA), ethylenediaminedisuccinic acid, S,S- ethylenediaminedisuccinic acid (EDDS), iminodisuccinic acid (IDS), hydroxyiminodisuccinic acid (HIDS), polyamino disuccinic acids, N-bis[2-(l,2- dicarboxyethoxy)ethyl]glycine (BCA6), N-bis[2-(l,2-dicarboxyethoxy)ethyl]aspartic acid (BCA5), N-bis[2-(l,2- dicarboxyethoxy)ethyl]methylglycine (MCBA5), N-tris[(l,2- dicarboxyethoxy)ethyl]amine (TCA6), N-methyliminodiacetic acid (MIDA), iminodiacetic acid (IDA), N-(2-acetamido)iminodiacetic acid (ADA), hydroxymethyl-iminodiacetic acid, 2-(2-carboxyethylamino) succinic acid (CEAA), 2-(2-carboxymethylamino) succinic acid (CMAA), diethylenetriamine- N,N"-disuccinic acid, triethylenetetramine-N,N"'-disuccinic acid, 1,6- hexamethylenediamine-N,N'-disuccinic acid, tetraethylenepentamine-N,N""- disuccinic acid, 2-hydroxypropylene-l,3-diamine-N,N'-disuccinic acid, 1,2-propylenediamine-N,N'-disuccinic acid, l,3-propylenediamine-N,N'-disuccinic acid, cis-cyclohexanediamine-N,N'-disuccinic acid, trans-cyclohexanediamine- N,N'-disuccinic acid, ethylenebis(oxyethylenenitrilo)-N,N'-disuccinic acid, glucoheptanoic acid, cysteic acid-N,N-diacetic acid, cysteic acid-N-monoacetic acid, alanine-N-monoacetic acid, N-(3-hydroxysuccinyl) aspartic acid, N-[2-(3- hydroxysuccinyl)]-L-serine, aspartic acid-N,N-diacetic acid, aspartic acid-N- monoacetic acid, any salt thereof, any derivative thereof, or any combination thereof.

13. (Original) The method of claim 1 further wherein the metal complexing agent is selected from acetic acid, acrylates, dihydroxymaleic acid, salts of dihydroxymaleic acid, EDTA

(ethylenediamine tetraacetic acid), salts of EDTA, erythorbic acid, erythroboric acid, formic acid, gluconodeltalactone, GLDA (glutamic acid N,N-diacetic acid), salts of GLDA, HEDTA (hydroxyethylenediamine triacetic acid), salts of HEDTA, HEIDA (disodium ethanoldiglycine), salts of HEIDA, MGDA (methylglycine N,N-diacetic acid), salts of MGDA, NTA (nitriolotriacetic acid), organic metal complexers, ligands, porphyrins, pigments, peptides, saccharides, nucleic acids, phosphonic acid, polyacrylic acid and citric acid in an amount sufficient to sequester at least a portion of a metal compound.

14. (Withdrawn) A method for fracturing and stimulating a well in a nano-darcy shale formation comprising:

providing a treatment mixture containing between about 0.1% and 95% by weight metal complexing agent at a pH of between about 0 and 10;

injecting the treatment mixture into the well at a pressure greater than a fracture pressure of the nano-darcy shale formation until at least some of the treatment mixture enters fractures in the nano-darcy shale formation, thereby allowing the metal complexing agent to bind with at least some naturally-occurring metals contained within the nano-darcy shale formation; and

removing spent treatment mixture and fracturing fluids from the well after the fractures are created, thereby removing the bound naturally-occurring metals from the non-darcy shale formation.

15. (Withdrawn) The method of claim 14 wherein the injecting operation is part of a fracturing operation that causes the fractures to occur in the nano-darcy shale formation.

16. (Withdrawn) The method of claim 14 further comprising:

fracturing the nano-darcy shale formation; and

wherein the injecting operation occurs after the fracturing operation causes the fractures to occur in the nano-darcy shale formation.

17. (Withdrawn) The method of claim 16 wherein the injecting operation includes injecting proppant into the fractures to occur in the nano-darcy shale formation.

REMARKS

This is in response to the Office Action issued July 28, 2017. Claims 1 and 10 are amended. No new matter is added. Claims 14-17 are withdrawn. Claims 1-13 are pending. Applicants respectfully submit that all pending claims are in condition for allowance. Favorable reconsideration is requested for at least the following reasons.

I. Drawings

The Office Action objected to the drawings "because Figures 2-4 are very grainy and unclear." *Office Action*, p. 2. Applicant submits new versions of Figures 2-4 herewith. Accordingly, Applicant respectfully requests withdrawal of the objection.

II. Specification

The Office Action objected to the abstract of the disclosure "because it contains the implied phrase 'This disclosure describes.'" *Office Action*, p. 3. Applicant has amended the abstract to remove "This disclosure describes." Accordingly, Applicant respectfully requests withdrawal of the objection.

III. Claim Rejections – 35 U.S.C. § 112

The Office Action rejected claim 10 under 35 U.S.C. § 112(b), as purportedly being indefinite. *Office Action*, p. 3. The Office Action takes issue with three aspects of claim 10. First, the Office Action asserts that "the phrase 'such as' renders the claim indefinite." *Id.*, p. 4. Without acceding to the correctness of the rejection, and solely to advance prosecution, Applicant has amended claim 10 to recite "the metal complexing agent including citric acid or EDTA."

Second, the Office Action asserts that "the limitation 'the induced fractures' in the last line" has insufficient antecedent basis. *Id.* Again, without acceding to the correctness of the rejection and solely to advance prosecution, Applicant has amended claim 10 to remove "the" from "the induced factures."

Third, the Office Action asserts that claim 10 is "indefinite since it requires 'hydraulic fracturing' and 'propagation of the induced fractures.' It is unclear how this is possible as the pressure range in claim 1 (as elected in the response filed July 6, 2017) is less than the fracture

pressure. Therefore, claim 10 is not within the pressure range defined in claim 1 and is indefinite." *Office Action*, p. 4. Although Applicant disagrees with the Office Action's assertions, claim 10 is amended to recite "The method of claim 1, further comprising . . ." to indicate that the recited limitations are an operation in addition to the injecting operation recited in claim 1.

In sum, Applicant has amended claim 10 to overcome the issues asserted in the Office Action. Accordingly, Applicant respectfully requests withdrawal of the rejection.

IV. Claim Rejections – 35 U.S.C. § 103

A. Claims 1-7 and 10-13

The Office Action rejected claims 1-7 and 10-13 under 35 U.S.C. § 103, as purportedly being unpatentable over Horton et al. (US 2011/0053811). Applicant respectfully traverses the rejection and the characterization of the claims and cited reference.

Claim 1 is directed to a method for stimulating an existing well in a nano-darcy shale formation. As amended, claim 1 recites, in part:

- providing a treatment mixture containing between about 0.1% and 95% by weight metal complexing agent at a pH of between about 0 and 10;
- injecting the treatment mixture into the well at a pressure less than a fracture pressure of the nano-darcy shale formation until at least some of the treatment mixture exits the well and contacts the nano-darcy shale formation; and
- removing the treatment mixture from the well after the contact time, thereby removing the bound naturally-occurring metals from the non-darcy shale formation and thereby improving the hydrocarbon production of the well relative to the hydrocarbon production immediately prior to performance of the method.

In a non-limiting example consistent with the claim limitations, the instant specification describes injecting a treatment mixture containing a metal complexing agent such as citric acid or EDTA into a nano-darcy shale formation adjacent to a well and at a pressure below the fracture pressure of the formation. *Applicant's Specification*, ¶ [0019]. The treatment mixture is allowed sufficient contact time to bind with naturally occurring metals in the formation. *Id.* After the contact time, the treatment mixture is pumped from the subsurface. *Id.* The removal of

naturally occurring metals increases "the permeability of the formation in the contact region adjacent to the well, thereby causing the increased production." *Id.*

The Office Action asserts that Horton teaches injecting the treatment mixture into the well at a pressure less than a fracture pressure of the formation until at least some of the treatment mixture contacts the formation. *Office Action*, p. 5. In support, the Office Action cites to paragraph [0022] and reasons that Horton teaches these limitations "since Horton does not explicitly teach injecting at a pressure above a fracture pressure." Applicant respectfully disagrees.

Horton does not tech injecting a treatment mixture until at least some of the treatment mixture exits the well and contacts the nano-darcy shale formation, as recited in claim 1. In fact, Horton teaches exactly the opposite: Horton does not want any remediation mixture to leave the well and contact the formation. Horton teaches a drilling fluid containing additives that prevent the drilling fluid from leaving the wellbore and entering the formation during the drilling operation while minimizing the effect on the post-drilling characteristics of the formation. Thus, Horton teaches the opposite of the claimed method, where treatment is injected into a shale formation adjacent to the wellbore to change characteristics of the formation.

To expand on that point, Horton is directed to remediating xanthan deposition by contacting xanthan deposits with a remediation fluid containing at least one chelating agent in wellbore fluids. *Horton*, Abstract. In addition, Horton distinguishes its "wellbore fluids" from fluids that enter surrounding or adjacent rock formations. *E.g., Horton*, ¶ [0004]. For instance, Horton describes that common uses of wellbore fluids is "minimizing fluid loss into and stabilizing the formation through which the well is being drilled, minimizing fluid loss into the formation after the well has been drilled and during completion operations". *Horton*, ¶ [0004].

Moreover, Horton's wellbore fluid contains one or more additives for the purpose of preventing the wellbore fluid from entering the rock formation, which is the opposite of the operations recited in claim 1. That is, Horton teaches that iron "cations are dissolved from iron-containing minerals and solids in the downhole environment, and then they may crosslink with xanthan gum to form scale" and, "[a]s a result, xanthan gum crosslinked with Fe(II)/Fe(III) cations may form an insoluble solid deposition or scale on the formation and/or oilfield equipment." *Horton*, ¶ [0027]. Thus, Horton does not teach a well stimulation treatment

mixture as recited in claim 1 that improves the hydrocarbon production of the well relative to the production prior to performance of the method.

In sum, Horton fails to teach multiple limitations of claim 1. Accordingly, claim 1 is allowable over Horton. Therefore, Applicant respectfully requests withdrawal of the rejection of claim 1 and the claims that depend therefrom.

B. Claims 8 and 9

The Office Action rejected claims 1-7 and 10-13 under 35 U.S.C. § 103, as purportedly being unpatentable over Horton et al. (US 2011/0053811) in view of Conway (US 2015/0114653). Applicant respectfully traverses the rejection and the characterization of the claims and cited reference.

As an initial matter, Applicant asserts that Conway does not qualify as prior art to the instant application. Conway published on April 30, 2015. The instant application was filed April 14, 2015 and claims priority back to April 14, 2014 and December 5, 2014. Thus, the instant application has an effective filing date more than one year prior to the publication of Conway. Additionally, Conway and the instant application have a common inventor, Bryce Conway, and a common assignee, Flex-Chem. Applicant respectfully requests identification of the specific provision that qualifies Conway as prior art under 35 U.S.C. § 102(a).

Claims 8 and 9 depend from claim 1. As discussed above, claim 1 is allowable over Horton. Conway cannot cure the deficiencies of Horton. Therefore, claims 8 and 9 are allowable over the combination of Horton and Conway and Applicant respectfully requests withdrawal of the rejection.

V. Conclusion

Applicants believe that the pending claims are in condition for allowance. If it would be helpful to obtain favorable consideration of this case, the Examiner is encouraged to call and discuss this case with the undersigned.

This paper constitutes a request for any needed extension of time and an authorization to charge all fees therefore to deposit account No. 13-2725, if not otherwise specifically requested. The undersigned hereby authorizes the charge of any fees created by the filing of this document or any deficiency of fees submitted herewith to be charged to deposit account No. 13-2725.

Respectfully submitted,
MERCHANT & GOULD P.C.
P.O. Box 2903
Minneapolis, Minnesota 55402-0903
(608) 280-6762

Date: October 24, 2017

/Brian P. McCall/
Name: Brian P. McCall
Reg. No.: 68,734

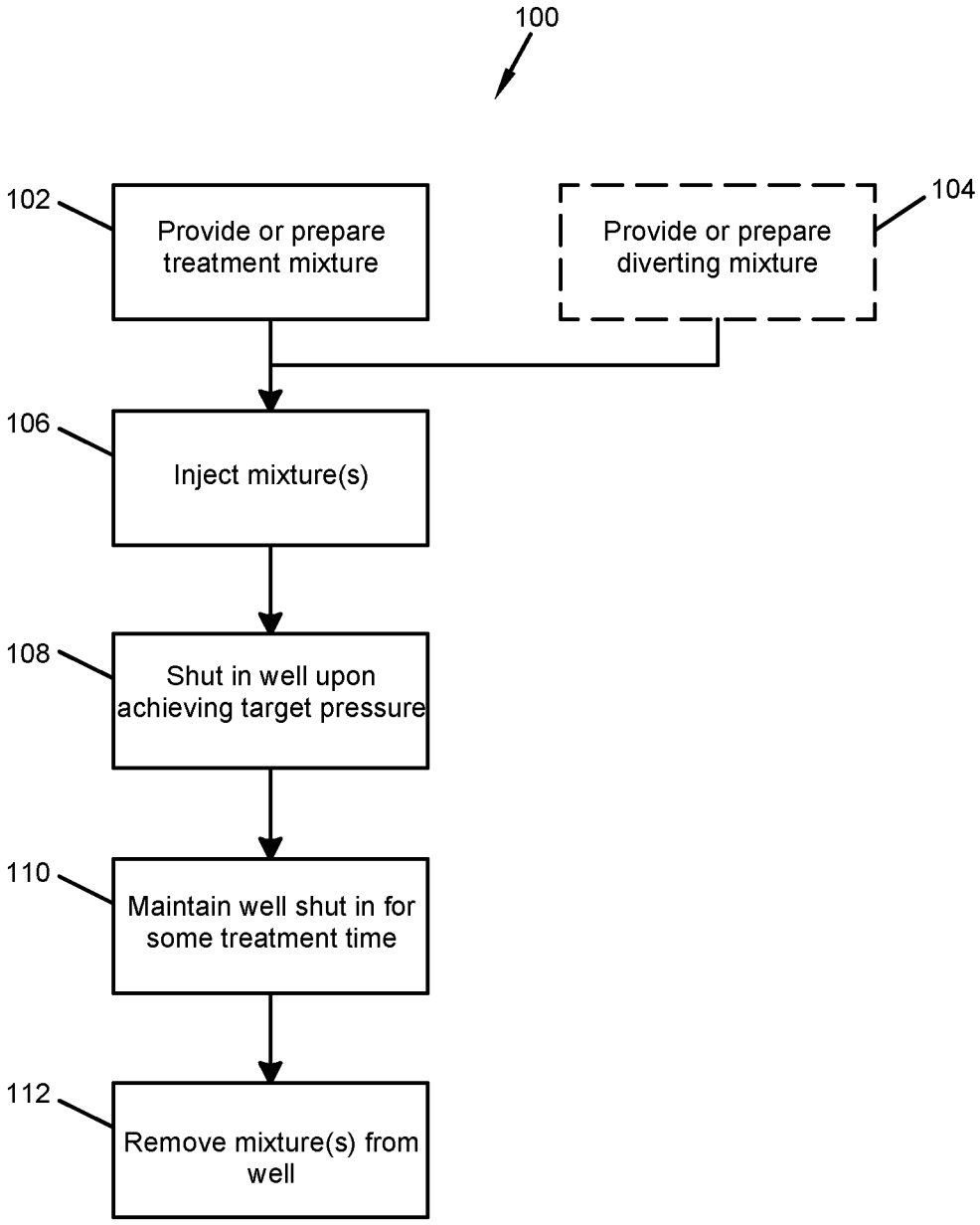

100
102
Provide or prepare treatment mixture
104
Provide or prepare diverting mixture
106
Inject mixture(s)
108
Shut in well upon achieving target pressure
110
Maintain well shut in for some treatment time
112
Remove mixture(s) from well

FIG. 1

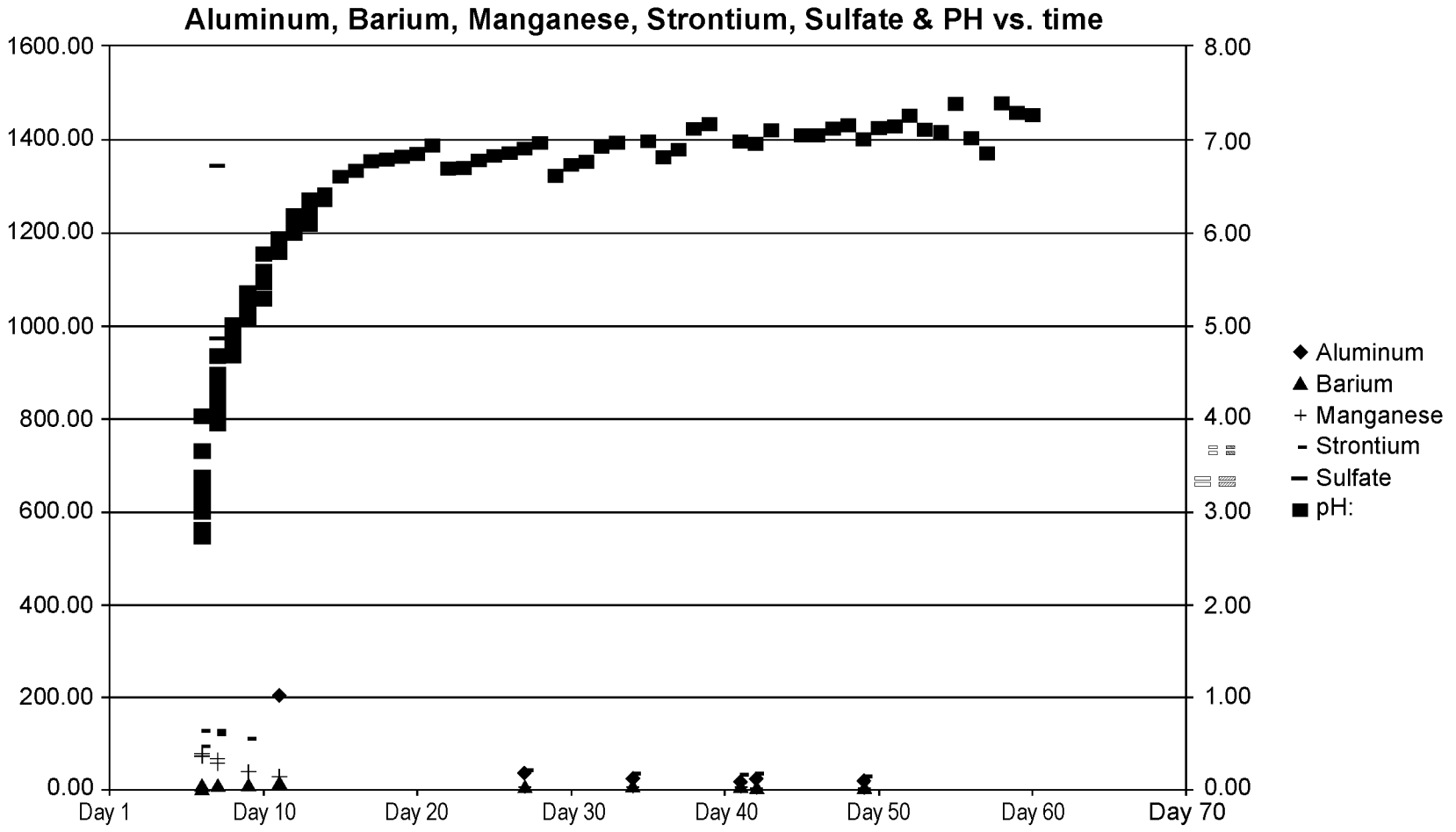

Aluminum, Barium, Manganese, Strontium, Sulfate & PH vs. time
1600.00
1400.00
1200.00
1000.00
800.00
600.00
400.00
200.00
0.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
Day 1
Day 10
Day 20
Day 30
Day 40
Day 50
Day 60
Day 70
Aluminum
Barium
Manganese
Strontium
Sulfate
pH:

FIG. 2

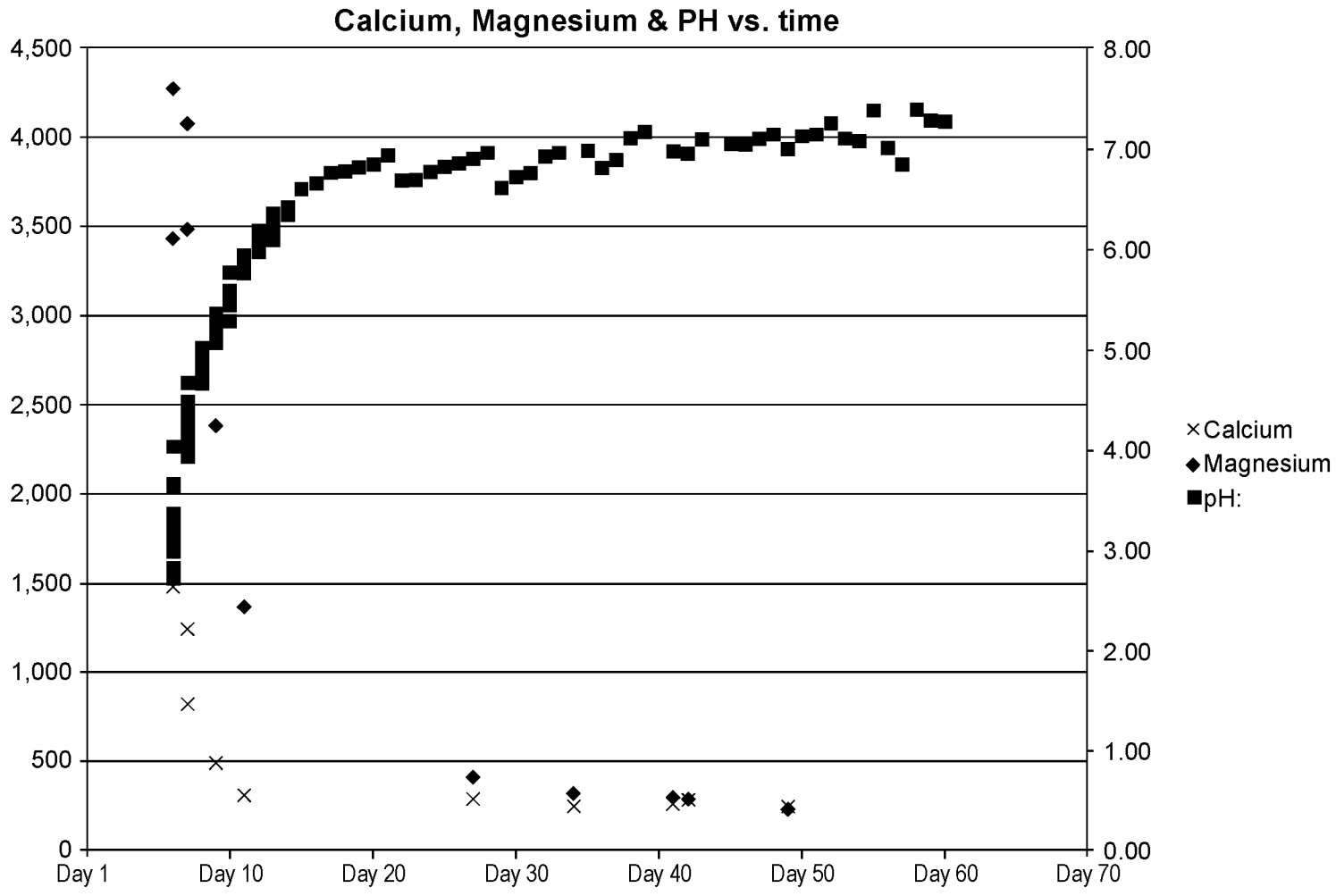


FIG. 3

REPLACEMENT SHEET
14/686,237

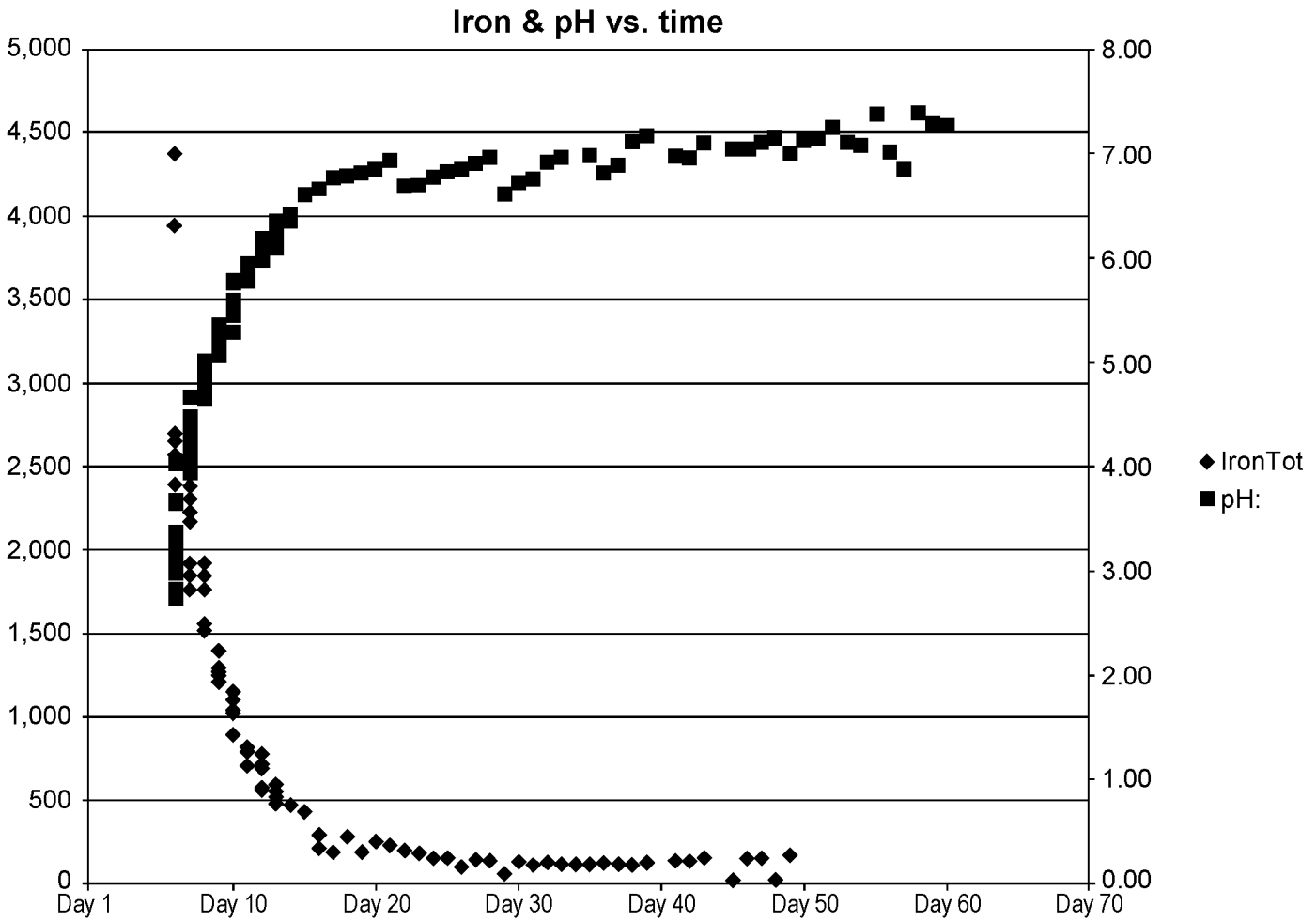

Iron & pH vs. time
5,000
4,500
4,000
3,500
3,000
2,500
2,000
1,500
1,000
500
0
8.00
7.00
6.00
5.00
4.00
3.00
2.00
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Day 1
Day 10
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Day 30
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Day 60
Day 70
IronTot
pH:

FIG. 4

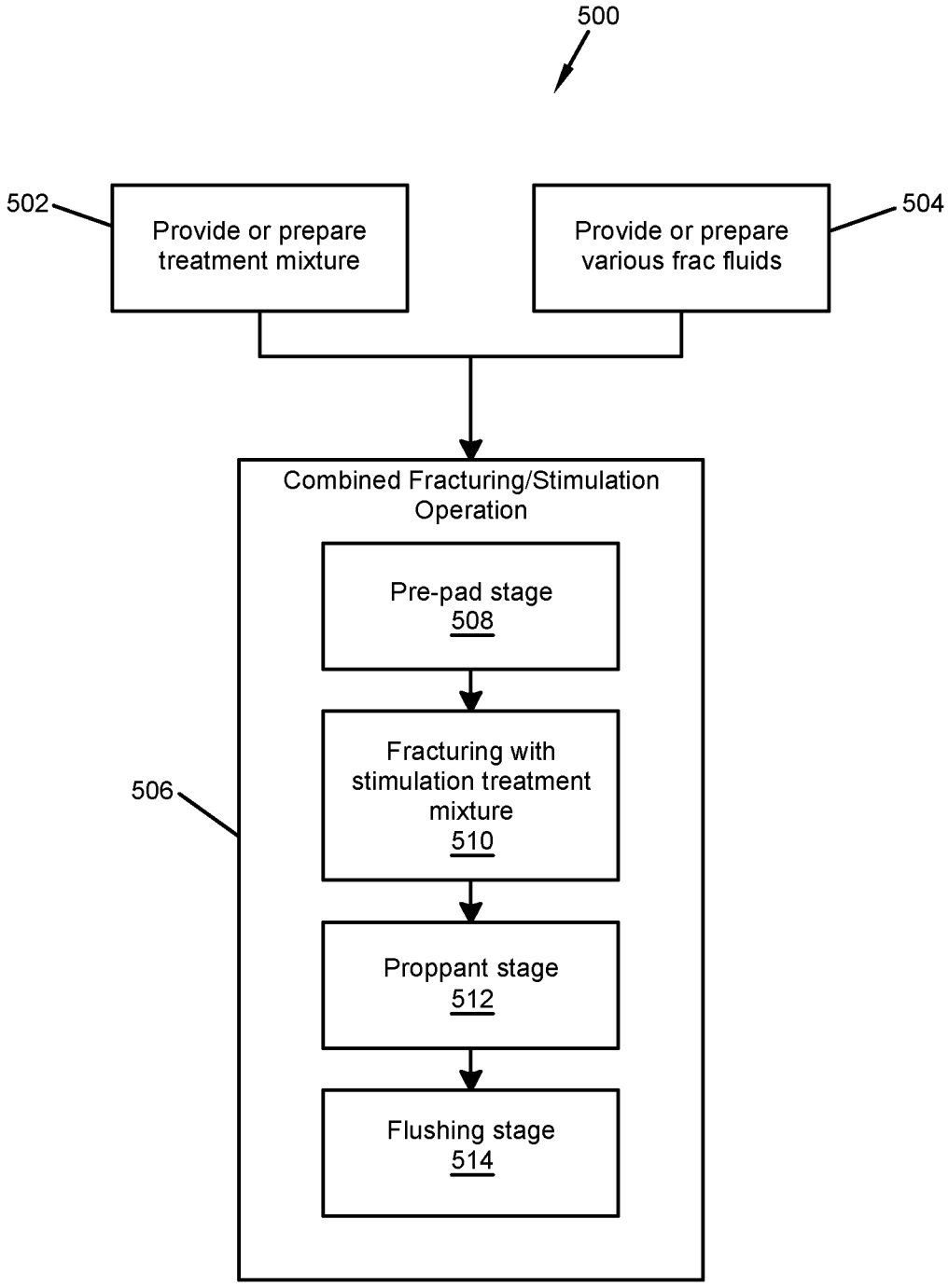

500
502
Provide or prepare treatment mixture
504
Provide or prepare various frac fluids
Combined Fracturing/Stimulation Operation
506
Pre-pad stage
508
Fracturing with stimulation treatment mixture
510
Proppant stage
512
Flushing stage
514

FIG. 5

PTO/SB/08a (03-15)
Approved for use through 07/31/2016. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
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INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	14686237
Filing Date	2015-04-14
First Named Inventor	Andrew Bryce Conway
Art Unit	3674
Examiner Name	Catherine A. Loikith
Attorney Docket Number	04697.0001USU1

U.S.PATENTS Remove

Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	8236734		2012-08-07	Shen et al.	
	2	6527051	B1	2003-03-04	Reddy et al.	
	3	6225262	B1	2002-05-01	Irwin	
	4	6162766	A	2000-12-19	Muir	
	5	5497830	A	1996-03-12	Boles	

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Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	20160067845	A1	2016-03-10	Conway	

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	14686237
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	First Named Inventor	Andrew Bryce Conway
	Art Unit	3674
	Examiner Name	Catherine A. Loikith
	Attorney Docket Number	04697.0001USU1

	2	20020160920	A1	2002-10-31	Dawson et al.	
	3	20090298721	A1	2009-12-03	Robb et al.	
	4	20110214862	A1	2011-09-08	Horton	

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Examiner Initial*	Cite No	Foreign Document Number[3]	Country Code[2] i	Kind Code[4]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear	T[5]
	1	0326720	EP	A1	1989-08-09	AGIP S.p.A.		
	2	0505169	EP	A1	1992-09-23	Smith et al.		
	3	2009091652	WO	A2	2009-07-23	Horton et al.		
	4	2013019188	WO		2013-02-07	Dismuke et al.		

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Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	14686237
	Filing Date	2015-04-14
	First Named Inventor	Andrew Bryce Conway
	Art Unit	3674
	Examiner Name	Catherine A. Loikith
	Attorney Docket Number	04697.0001USU1

	1	European Search Report for European Patent Application No. 14856530.2 - 1354, June 23, 2017, 8pgs.
	2	Written Opinion, PCT/US2015/048634 mailed December 7, 2015, 5pgs.
	3	International Search Report, PCT/US2015/048634 mailed December 7, 2015, 2pgs.
	4	Geiver, The Slickwater Story, The Bakken magazine, http://thebakken.com/articles/711/the-slickwater-story, July 14, 2014, 2pgs.
	5	Huang R.Y.M.; Jarvis, N.R. 1973. Ionically crosslinked hydrophilic polymer membranes: Synthesis and measurement of transport properties, J Polym Sci 41: 117-127, 11 pgs.
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	7	Akin, H.; Hasirci, V.N.; Hasirci, N. 1990. Permeability properties of charged hydrogel-carrying membranes, Polymer 31 (2): 270-275, 6pgs.
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Application Number	14686237
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CERTIFICATION STATEMENT

Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

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(71) Applicant: **ENIRICERCHE S.p.A.**
Corso Venezia 16
I-20121 Milan(IT)

Applicant: **AGIP S.p.A.**
Corso Venezia 16
I-20121 Milano(IT)

(72) Inventor: **Lockhart, Thomas Paul**
Via Europa 30
I-20097 San Donato Milanese, Milan(IT)
Inventor: **Burrafato, Giovanni**
Via Fratelli Cervi, 13/c
I-20080 Tavazzano, Milan(IT)

(74) Representative: **Roggero, Sergio et al**
Ing. Barzanò & Zanardo Milano S.p.A. Via Borgonuovo 10
I-20121 Milano(IT)

(54) Method of removing polymer gels from a petroleum reservoir.

(57) When used as occlusion agents or to cause fractures in a petroleum reservoir, polymer gels crosslinked with polyvalent metal ions can be removed by the use of special complexing agents.

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METHOD OF REMOVING POLYMER GELS FROM A PETROLEUM RESERVOIR

This invention relates to a method of removing polymer gels in a petroleum reservoir.

The normal primary recovery method for petroleum makes use of its natural tendency to escape from a reservoir owing to the pressure of the reservoir, but allows only partial extraction of the crude contained therein. To increase the quantity of petroleum extractable from an oil reservoir it is usual to employ assisted recovery techniques, which consist most frequently of introducing into the reservoir a fluid which passes through the pores in the rock and transports the crude contained therein to the production wells.

Water flooding is the most frequently used assisted recovery method because of its low cost and ease of implementation. The main problem connected with the water flooding method is that the reservoir rock is often comprised of zones of different permeability and thus the water tends to pass preferentially through those zones of higher permeability, leaving substantially unrecovered the petroleum resident in the zones of lesser permeability, which are bypassed and remain unswept by the water flood.

A solution to this problem is to partially or completely occlude the higher permeability zones after their petroleum has been extracted by a water flood so that the water injected subsequently will be caused to flow to the less permeable zones bypassed previously. Obviously, such occlusions would serve also for the enhanced recovery of petroleum from a reservoir employing other well-known techniques, such as polymer or surfactant flooding, based on the use of an injected fluid to sweep crude oil from a reservoir.

This occlusion can be carried out by various methods, most of which are based on the use of polymer gels. The gels most widely used are those obtained from water-soluble polymers crosslinkable with polyvalent metal ions. Commonly used polymers of this type are, for example, polyacrylamides, partially hydrolyzed polyacrylamides, and copolymers of acrylamide with vinyl comonomers such as acrylamide-N-vinylpyrrolidone and sodium acrylamido-2-methylpropanesulphonate. Other polymers frequently used are polysaccharides, in particular xanthan and scleroglucan, and cellulose-based polymers such as hydroxyethylcellulose, carboxymethylcellulose and carboxymethylhydroxyethylcellulose. Examples of polyvalent metal ions generally used in crosslinking polymers are Cr^{+3}, Al^{+3}, Ti^{+4}, Zn^{+2}, Fe^{+2}, Fe^{+3}, Sn^{+4}.

There are generally two methods of introducing the gel into the reservoir. The first is to inject a polymer solution which is already surface-gelled, while the second is based on in-situ gel formation. Although surface-gelled polymer solution can be more selectively positioned in the higher permeability zones of a reservoir, in - situ gelling is generally preferred to the surface-gelled polymer because the ungelled solution can penetrate more deeply into the reservoir.

There are various in-situ gelling methods. In the case, for examples, of polymers crosslinkable with Al^{+3}, the gel is formed by injecting into the reservoir in two successive steps an aqueous polymer solution and an aqueous solution of Al^{+3}, generally as aluminum citrate; gelation occurs when the two solutions mix within the reservoir. In the case of polymers crosslinked with Cr^{+3}, it is usual to feed the polymer together with chromium in a higher oxidation state unreactive toward crosslinking the polymer (for example, bichromate) and then to introduce a solution of a suitable reducing agent such as thiourea or thiosulphite. Reduction of the chromium to Cr^{+3}, leads to gelation.

Polymer gels crosslinked with polyvalent metal ions are also used in some instances, when fed into the well under pressure as aqueous high-viscosity solutions, to form fractures in the reservoir rock in order to facilitate the recovery of petroleum. Other uses of gels in the petroleum field include well completion, sealing abandoned wells, and sand consolidation.

A problem connected with the use of polymer gels in a petroleum reservoir which has still not been solved satisfactorily is that of removing the gelled polymers when they have performed their task, or at other times if this appears desireable. For example, if using such gels as occlusion agents for permeability modification purposes, various situations can arise which would make it desirable to remove the gel from the area occupied by it, such situations can be, for example:

a) incorrect positioning of the gel in the reservoir;
b) occlusion of zones which still contain petroleum;
c) the need to replace a deteriorated gel with fresh gel;
d) change of petroleum recovery strategy for the reservoir;
e) inadvertant, undesireable formation of the gel within the well itself.

A convenient method of removing a gelled solution would also be of use for cleanup of the above-ground well site and equipment during or after the injection of gellable compositions into a reservoir.

It is known in the art to remove gelled polymers from the occupied area by methods based on the use of oxidizing agents and strong acids or bases. For example, US patent 4,569,393 describes the use of sodium hypochlorite, GB 1,337,651 describes the use of other oxidizing agents including potassium

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permanganate, and GB 2,165,567 describes the use of organic peroxide oxidizing agents. However, the use of said known agents is not completely satisfactory because they can damage the reservoir and alter the crude it contains, and because they present a health risk to the personnel using them. These agents act by degrading the polymer and, because part of the polymer treated with said agents can remain in the reservoir in the form of an insoluble residue, they can prevent the complete reopening of the occluded zone.

It has now been found possible to overcome the drawbacks of the known art and to remove (in the sense of degelling) polymer gels in a petroleum reservoir which have been crosslinked with polyvalent metal ions, by the use of particular complexing agents. More particularly, according to the present invention, said gels can be degelled by a process consisting of bringing the gel in the well into contact with an aqueous solution of a complexing agent able to form with the polyvalent metal ion a coordination complex which is thermodynamically more stable than that which the ion forms with the polymer. Said complexing agents can be either organic or inorganic in nature.

In particular, as organic complexing agents, compounds can be used having at least two identical or different functional groups containing O, N, or S, and preferably chosen from the carboxyl, amino, pyridine, imidazole, hydroxyl, and sulphydryl groups. The carboxyl groups can be present either in acid or neutralized form, and the amino groups can be primary, secondary, or tertiary. In a preferred form of the invention, the organic complexing agents are carboxylic acids with from 2 to 4 carboxyl groups, either as such or as alkaline metal salts, or are amino acids or hydroxyacids, or are alkyleneamines, or polyalkyleneamines.

Examples of complexing agents useful for the purposes of the present invention are:
trisodium citrate (Na_3 citrate)
disodium oxalate (Na_2 oxalate)
disodium ethylenediaminetetraacetate (Na_2 EDTA)
tartaric acid
malonic acid
maleic acid
citric acid
oxalic acid
salicylic acid
glycine
glutamic acid
aspartic acid
alpha-amino-n-butyric acid
methionine
serine
threonine
ethylenediamine
triethylenetetramine
diethylenetriamine
tris(2-aminoethyl)amine

Inorganic complexing agents suitable for the purpose can be chosen from phosphorous compounds such as phosphoric and organophosphonic acids and their alkaline salts such as, for example sodium pyrophosphate, alkaline tripolyphosphate, inorganic bases such as ammonium hydroxide, and fluorides of the alkaline metals, for example potassium fluoride.

Some of said complexing agents are used in the art (US 3,926,258 US 4,488,601, US 3,762,476) to delay the formation of the gel and allow it to take a deeper position in the reservoir. In contrast, according to the objects of the present invention, the complexing agents act on the already gelled polymer within the well to cause its complete and irreversible degelation.

The method of the present invention can be generally used to remove all gels which have been formed from natural or synthetic water-soluble polymers by crosslinking with a polyvalent metal ion.

In particular the method of the present invention is preferably used to remove gels deriving from acrylamide polymers or copolymers, or from polysaccharides, crosslinked by means of Cr^{+3}. Said gels are generally obtained from polymers having a molecular weight of between 200,000 and 40,000,000 g/mol and are characterized by a polymer concentration of between 500 and 20,000 ppm and a Cr^{+3} concentration of between 10 and 3000 ppm.

The degelling of crosslinked polymers is implemented in practice by bringing into contact, either in one portion or gradually with time, an aqueous solution of the complexing agent containing a quantity of

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complexing agent such that the molar ratio of complexing agent to crosslinking metal ion is at least 1:50 and prefereably varies from 1:1 to 50:1.

If the reservoir is particularly rich in metal ions which, as is the case with Ca^{+2}, could cause precipitation of certain complexing agents from their aqueous solutions,it is convenient to use a larger quantity of the complexing agent, in order to ensure that the quantity necessary for degelling the polymer remains in solution.

The concentration of the aqueous solution of the complexing agent is not critical for the present invention. One can, for example, use solutions having a concentration of complexing agent from 100 to 100,000 ppm, and preferably from 1000-10,000 ppm. Said solutions act conveniently at the typical reservoir temperatures (between 20 and 200 °C) and, when operating under the preferred conditions, the gel is completely and irreversibly degelled within a time period varying from less than 1 to 15 days. The polymer degelled in this manner is in the form of a flowable liquid which can be easily removed from the previously occluded zone.

The method of the present invention therefore enables complete reopening of the occluded zone to be obtained in a simple and inexpensive manner. In addition, in contrast to the methods used in the art, it does not degrade the polymer and in no way damages the reservoir. The examples given hereinafter are for illustrative purposes only, and are in no way intended to be taken as limitative of the invention itself.

EXAMPLE 1

The gel preparation and subsequent treatments described in this and the other examples were carried out in suitable closed containers, as commonly accepted for the study of the behaviour of gels in the assisted recovery of petroleum.

An aqueous solution of 10,000 ppm (by weight) of commercial polyacrylamide (Aldrich, average molecular weight 5,000,000 -6,000,000, approximately 1% hydrolyzed) was left under slight stirring overnight to ensure maximum dispersion of the polymer molecules. It was then filtered through a 5 micron Millipore filter to remove any polymer microgel particles which may have been present. An aqueous solution of $CrCl_3$ containing 1000 ppm of Cr^{+3} was prepared separately and left at ambient temperature until the blue coloration characteristic of the $Cr(H_2O)_6^{+3}$ ion had appeared. Three test-tubes fitted with screw-top enclosures were each filled with 8 ml of polyacrylamide solution, with 0,5ml of $CrCl_3$ solution and with 1,5 ml of distilled water in order to obtain three gelling solutions each containing 8000 ppm of polyacrylamide and 50 ppm of Cr^{+3}. The solutions were then left to gel at ambient temperature for 16 hours.

One of the gels obtained was left as such to serve as the first control. Water in a quantity equal to 10% of the gel volume was added to another gel to serve as a second control. An aqueous solution containing 10,000 ppm of Na_2EDTA was added to the third gel in quantity equal to 10% of the gel volume, to yield a final concentration, after diffusion of the degelling agent throughout the gel, of 1000 ppm of Na_2EDTA (calculated for the total sample volume gel + solution).

The gel to which water and that to which Na_2EDTA were added were than left at ambient temperature and monitored by gently inverting the test-tubes twice a day so as not to mechanically damage the gel. After 7 days, the gel to which the Na_2EDTA solution had been added became a flowable liquid containing no residual gel structure, and was characterized by a violet color typical of the $Cr(EDTA)^{-3}$ complex. UV analysis of this degelled solution in fact showed 2 absorption peaks at 393 and 548 nm, corresponding to the known spectrum of the $Cr(EDTA)^{-3}$ complex. In contrast, the control gels were still unchanged and stable after 80 days.

EXAMPLE 2

Aqueous solution of the complexing agents Na_3citrate Na_2oxalate and Na_2EDTA of concentration 10,000 ppm were added to 3 gel samples prepared as described in Example 1. The volume of solution of the complexing agent added was 10% of the gel volume so that, after allowing for diffusion through the gel, a complexing agent concentration of 1,000 ppm was obtained. To reference sample were prepared as described in Example 1, together with a comparison sample consisting of gel with 10% by volume of a 10,000 ppm solution of Na acetate added. The gels thus treated were left at ambient temperature (20 °C) and examined twice a day as described in the previous example.

In order to evaluate the effect of temperature on the degelation process, additional samples were

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prepared and stored at 60° C after treating with solutions of degelling agents. Additional reference samples as described in Example 1 were also prepared for this series of degelation samples. The effect of gel age on the degelation process (that is, age of the gel prior to treatment with the degelling solution) was evaluated for other gel samples which were left to age for 5 days prior to treating them with degelling solutions.

The results of these degelation experiments are shown in Table 1.

The reference gels all proved to be stable under the test con-ditions, while the gels treated with the complexing agents Na_2EDTA, Na_3citrate, and Na_2oxalate underwent complete degelation under all conditions evaluated. The time to degel was shorter at 60° than at 20° C. The gels aged for 5 days prior to degelling treatment required somewhat longer times to degel. The gel treated with Na acetate, an organic compound with only one functional group, remained completely unaltered both at 20° and at 60° C.

EXAMPLE 3

A gel sample prepared as described in Example 1 was left to age for 30 days. It was then treated with 10% by volume of a 10,000 ppm solution of Na_3citrate. After 4 days at 60° C, the gel was completely degelled. On comparing this result with those of the preceding example it can be deduced that the degelling time remains short even if the gel has been left to age for a long period.

EXAMPLE 4

A series of gels prepared as described in Example 1 and left to age for 4 days were treated with aqueous solutions (in quantities equal to 10% of the gel volume) of the complexing agents Na_2EDTA, Na_3 citrate, and Na_2oxalate at concentrations of 1000 ppm and 100 ppm so as to obtain concentration of 100 and 10 ppm respectively after the solution had diffused through the gel. For comparison purposes, a test with Na acetate was also carried out. The results are shown in Table 2.

Starting with solutions degelling agent of 1000 ppm concentration, fluid solutions showing only slight retention of gel structure were obtained in 10-14 days, whereas starting with solutions of 100 ppm concentration there was a reduction in viscosity after 50 days, but with partial preservation of the gelled structure. These tests indicate that, even at low proportions of complexing agent to Cr^{+3} in the gel, the gels are rendered substantially fluid in a reasonable period of time. Such fluid gels, although they may be more difficult to mobilize than a perfectly degelled, fluid solution, should be mobile under pressure within the reservoir, and thus it should be possible to remove them from the zones in which they have been formed.

EXAMPLE 5

Three gel samples prepared as described in Example 1 and left to age for 30 DAYS were treated with aqueous solutions of the complexing agents oxalic acid, citric acid and ethylenediamine of 10,000 ppm concentration as described in the preceding examples. The results obtained are shown in Table 3. The results demonstrate that neutral complexing agents (ethylenediamine) and the acid forms of carboxylate degelling agents are also effective agents for the scope of the invention.

EXAMPLE 6

To three gel samples prepared as described in Example 1 were added solutions (in a quantity equal to 10% of the gel volume) of the inorganic degelling agents sodium pyrophosphate ($Na_4P_2O_7$), potassium fluoride (KF), and ammonia (NH_3) at concentration reported in table 4. Whereas pyrophosphate produced a rapid degellation, the weaker complexing agents fluoride and ammonia produced slower or partial degelation.

EXAMPLE 7

To demonstrate that the degellation method of the present invention functions with polyacrilamides of a

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higher degree of hydrolysis a sample of polyacrylamide 10% hydrolyzed was prepared by base hydrolysis from the commercial polyacrylamide employed in the previous examples. Aqueous gels comprised of 8000 ppm of this hydrolyzed polymer and 100 ppm Cr^{+3} were prepared as described in example 1 and treated with solutions of the following degelling agents: Na_2EDTA, ethylenediamine, Na_2malonate, Na_2oxalate, Na_3citrate, and sodium pyrophosphate. The results show that comparable degellation times are obtained with this polyacrylamide polymer.

TABLE 1

Complexing agent (10,000 ppm solution)	Molar ratio compl.agent:Cr^{+3}	Gel ageing[a] (days)	Degelling time (days)	
			20 °C	60 °C
Na_2EDTA	3:1	1	7	2
"	"	5	16	4
Na_3 citrate	3.5:1	1	8	2
"	"	5	10	3
Na_2 oxalate	8:1	1	7	2
"	"	5	10	3
Na acetate	13:1	1	>80[b]	>80[b]
"	"	5	"	"

a) the gel used is polyacrylamide (8000 ppm)/Cr^{+3} (50 ppm)
b) no change is observed in the gel structure

TABLE 2

Complexing agent	Complexing agent solution conc. (ppm)	Molar ratio compl.agent:Cr^{+3}	Degelling time[a] at 60 °C (days)
Na_2EDTA	1000	0.3:1	15
"	100	0.03:1	>30
Na_3 citrate	1000	0.35:1	10
"	100	0.035:1	>30[b]
Na_2 oxalate	1000	0.8:1	10
"	100	0.08:1	>30[b]
Na acetate	1000	1.3:1	>50[c]
"	100	0.13:1	"

a) the gel used is polyacrylamide (8000 ppm)/Cr^{+3} (50 ppm), aged 4 days
b) a viscosity reduction is observed, with partial rentention of the gel structure
c) no change in gel structure is observed.

TABLE 3

Complexing agent	Molar ratio complexing agent:Cr^{+3}	Degelling time [a] at 60 °C (days)
citric acid	4.5:1	4
oxalic acid	12:1	6
ethylenediamine	17:1	6

a) the gel used is polyacrylamide (8000 ppm)/Cr^{+3} (50 ppm), aged 30 days

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TABLE 4

Complexing agent	Complexing agent solution concentration (ppm)	Degelling time[a] at 60° C (days)
$Na_4P_2O_7$	10000	2
KF	100000	26[b]
NH_3	50000	g[b]

(a) The gel used was polyacrylamide (8000 ppm)/Cr^{+3}(50 ppm) aged 25 days prior to treatment with the complexing agent solution
(b) These solutions were highly fluid, but retained a slight gel structure.

TABLE 5

Complexing agent	Molar ratio Complexing agent:Cr^{+3}	Degelling time[a] at 60° C (days)
Na_2EDTA	3:1	15
Ethylenediamine	9:1	25
Na_2malonate	9:1	12
Na_2oxalate	9:1	4
Na_3citrate	3:1	5
$Na_4P_2O_7$	9:1	1

(a) The gel used was 10% hydrolyzed polyacrylamide (8000 ppm)/Cr^{+3} (100 ppm)

Claims

1. A method for removing from a petroleum reservoir natural or synthetic water-soluble polymer gels crosslinked with a polyvalent metal ion, characterised by bringing the gel into contact with an aqueous solution of an organic or inorganic complexing agent able to form with the polyvalent metal ion a coordination complex which is thermodynamically more stable than that which the metal ion forms with the polymer.

2. A method as claimed in claim 1, characterised in that the polymer is an acrylamide polymer or copolymer or a polysaccharide of molecular weight between 200,000 and 40,000,000, and the polyvalent metal ion is Cr^{+3}.

3. A method as claimed in claim 2, characterised in that the polymer concentration in the gel varies from 500 to 20,000 ppm and the Cr^{+3} concentration varies from 10 to 3000 ppm.

4. A method as claimed in claim 1, characterised in that the complexing agent is an organic compound with at least two identical or different functional groups containing O, N or S.

5. A method as claimed in claim 4, characterised in that the functional groups are chosen from the groups: carboxyl, either in the acid or neutralized form, primary amino, secondary amino, tertiary amino, pyridine, imidazole, hydroxyl, sulphydryl.

6. A method as claimed in claim 5, characterised in that the complexing agent is chosen from carboxylic acids having from 2 to 4 carboxyl groups, either as such or as alkaline metal salts, amino acids, hydroxyacids, alkyleneamines and polyalkyleneamines.

7. A method as claimed in claim 6, characterised in that the complexing agent is chosen from:
trisodium citrate
disodium ethylenediaminetetraacetate
disodium oxalate

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tartaric acid
malonic acid
maleic acid
citric acid
oxalic acid
salicylic acid
glycine
glutamic acid
aspartic acid
alpha-amino-n-butyric acid
methionine
serine
threonine
triethylenetetramine
diethylenetriamine
tris(2-aminoethyl)amine
ethylenediamine

8. A method as claimed in claim 1, characterised in that the inorganic complexing agent is chosen from phosphorus acids either as such or as their alkaline salts, alkaline tripolyphosphates, and ammonium hydroxide.

9. A method as claimed in claim 8, characterised in that the inorganic complexing agent is sodium pyrophosphate.

10. A method as claimed in claim 1, characterised in that the molar ratio of complexing agent to polyvalent metal ion is at least 1:50.

11. A method as claimed in claim 10, characterised in that the molar ratio of complexing agent to polyvalent metal ion varies from 1:1 to 50:1.

12. A method as claimed in claim 1, characterised in that the aqueous solution of the complexing agent has a concentration of between 100 and 100000 ppm.

aqueous solution of the complexing agent has a concentration of between 100 and 100000 ppm.

13. A method as claimed in claim 12, characterised in that the aqueous solution of the complexing agent has a concentration of between 1000 and 10000 ppm.

14. A method as claimed in claim 1, characterised in that the aqueous solution of the complexing agent is fed either in a single portion or gradually with time.

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European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 88 20 2875

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X Y	US-A-4 604 218 (J.C. DAWSON) * Claim 1; column 6, lines 1-51; column 7, line 64 - column 8, line 19 *	1,4-14 2,3	E 21 B 43/25 E 21 B 43/26 E 21 B 37/06
D,Y	US-A-3 926 258 (J.E. HESSERT) * Claims 1,2,5,9 *	1-14	
D,Y	US-A-3 762 476 (J.W. GALL) * Claims 1,2 *	1-14	
P,X	EP-A-0 275 624 (PETROLITE) * Claims 1-4,11; column 4, line 35 - column 6, line 16 *	1-14	

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

E 21 B

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	28-04-1989	ROTSAERT L.D.C.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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(71) Applicant : **HALLIBURTON COMPANY**
P.O. Drawer 1431
Duncan Oklahoma 73536 (US)

(72) Inventor : **Smith, William H.**
Box 212
Walters, Oklahoma 73572 (US)
Inventor : **Weaver, Jim D.**
Route 4, Box 231B1
Duncan, Oklahoma 73533 (US)

(74) Representative : **Wain, Christopher Paul et al**
A.A. THORNTON & CO. Northumberland
House 303-306 High Holborn
London WC1V 7LE (GB)

(54) **Metal-crosslinked polymer gels and breakage thereof.**

(57) Metal-crosslinked polymer gels, useful in oil and gas well treating operations, contain an esterified chelating agent for the metal ion, which hydrolyses over a period of time, eg. at elevated downhole temperatures, to form the chelating agent which then removes the metal ion from the polymer and breaks the gel. Thus, the cross-linked viscous gel is used as such downhole and thereafter broken for removal.

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This invention relates generally to metal-crosslinked polymer gels and their breakage, and is particularly but not exclusively concerned with the use of such gels for treating subterranean formations penetrated by a wellbore.

Viscous treating fluids are commonly utilized in the drilling, completion and treatment of subterranean formations penetrated by wellbores. Upon completion of the treatment, it is ordinarily desirable to remove the treating fluid from the well. To effectively remove the fluid, the viscosity of the fluid must be reduced. The reduction of fluid viscosity is referred to as "breaking" or "breakage" of the gel.

A viscous treating fluid used in the treatment of subterranean formations is normally comprised of a polysaccharide or synthetic polymer in an aqueous solution which is crosslinked with an organometailic compound. Examples of well treatments in which metal-crosslinked polymers are used are hydraulic fracturing, gravel packing operations, water blocking, and other well completion operations.

In hydraulic fracturing applications, a viscous treating fluid is used to transport propping materials to the formation. The treating fluid is introduced at a rate and pressure sufficient to produce a fracture or fractures in the subterranean formation and to extend the produced fracture or fractures from the wellbore into the formation. Upon the creation of the fracture or fractures, additional treatment fluid containing the propping materials can be introduced into the fracture or fractures in order to prevent complete closure. The propped fracture creates a conductive channel extending from the wellbore into the formation to facilitate the flow of oil and gas from the formation to the wellbore.

Upon completion of a treatment, it is desirable to reduce the viscosity of the treating fluid so that it can be recovered from the formation. Various materials known as "breakers" have been used to reduce the viscosity of the treating fluids. Acids, enzymes, and oxidizers are commonly used to reduce the viscosity of metal-crosslinked polymer fluids. These known breakers are somewhat effective to reduce viscosity by degrading polymer chains of the treating fluid; however, they are relatively ineffective against the metal-crosslinked portion of the polymer.

We have now devised an improved method of breaking a cross-linked gel.

According to the present invention, there is provided a method of reducing the viscosity of a gel comprised of a polymer in a fluid crosslinked with a metal ion, said method comprising contacting said gel with a compound which is initially inactive as a chelating agent for said metal ion but which is capable after a period of time of producing a chelating agent for said metal ion; maintaining said contact for said period of time whereby thereafter said chelating agent is formed which complexes said metal ion to remove metal ion from said gel thereby to reduce the viscosity of said gel.

The invention also provides a composition useful for treating a subterranean formation, said composition comprising a fluid, a polymer which is crosslinked with a metal ion, and an ester of a chelating agent for said metal ion; wherein the chemical association between the metal ion and the ester is less than the chemical association between the metal ion and the polymer, and the chemical association between the metal ion and the chelating agent is greater than the chemical association between the metal ion and the polymer.

The method of the invention provides improved degradation of viscous treating fluids such as those used in well completion practices. The invention involves the use of a compound which is not per se a breaker for the crosslinked polymer, but which with passage of time, converts to an active breaker for the crosslinked polymer. During the period of breaker inactivity, the polymer while in a high viscosity condition can be employed as a treating fluid for such purposes as fracturing, gravel packing and the like. After the passage of a period of time sufficient to enable the high viscosity polymer to perform as desired, the compound converts to a breaker which then acts to reduce the viscosity of the treating fluid to a value sufficiently low to enable convenient removal of the fluid from a well.

The specific active breaker employed herein is a chelating agent which removes from the crosslinked polymer the metal ion used to crosslink the polymer. By chelating and thus removing the metal ion from the polymer, the viscosity of the polymer is reduced. Accordingly, the chemical association between the active breaker and metal ion must be greater than the chemical association between polymer and ion, but the association between the compound and the metal ion must be less than the association between the polymer and the metal ion.

Among the preferred compounds are esters of carboxylic acid chelating agents which are not active per se as chelators but, depending upon such factors as pH, temperature, and specific ester substituent, with time convert to active chelating agents.

The method of the invention is particularly useful in the treatment of subterranean formations. Thus, a polymer gel is mixed with the compound and pumped into a subterranean formation during the inactive period of the compound.

The preferred carboxylic acids useful herein are those having multi dentate sites. Thus, the preferred chelating agents are polycarboxylic acids of which the most preferred are aminopolycarboxylic acids.

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Examples of esters of carboxylic acids include esters of ethylenediaminetetraacetic acid (EDTA), esters of nitrilotriacetic acid (NTA), esters of citric acid and esters of hydroxyacetic acid. The esterified carboxylated chelator is relatively inactive initially, but undergoes hydrolysis to produce an acid and an active ligand. The rate of conversion of the ester depends among other things, upon the temperature, pH and ester substituents. The produced acid initiates degradation of the polymer chain and the active ligand removes the metal ion from the polymer to allow further degradation of the polymer, which in turn reduces the viscosity.

The present invention provides a method for improved degradation of metal-crosslinked polymers. The method of the invention is effective to at least partially remove concentrated gels, skins, or plugs which may be formed as the result of using viscous fluids during the performance of a variety of well completion practices, such as hydraulic fracturing or temporary wellbore plugging.

In performing various well stimulation practices, an aqueous treating fluid is prepared which comprises a polymer, a crosslinking agent, and various other treating fluid additives such as pH buffers, biocides, stabilizers, and other additives. The aqueous fluid can also contain salt, but the presence of salt is not essential for the practice of this invention. Typical salts which are used in well stimulation treating fluids include potassium chloride, magnesium chloride, sodium chloride, calcium chloride, other such salts, and mixtures of salts. The aqueous fluid can also be a salt water-alcohol solution having in the range of from about 0 to about 80 percent alcohol by volume. Typically the alcohols used for treating fluids have from 1 to 5 carbon atoms. The aqueous fluid can also contain liquid or gaseous carbon dioxide, nitrogen gas or the like.

The aqueous fluid is used to solvate or hydrate the polymer. The polymers useful in the present invention must be capable of reacting with various metal ion crosslinkers. Examples of these polymers include solvatable polysaccharides which include the galactomannan polymers, glucomannan polymers, and their derivatives. Typical examples include guar and its derivatives; and modified cellulose such as hydroxyethyl cellulose derivatives, carboxymethyl cellulose, and other modified celluloses. Synthetic polymers which are capable of forming a crosslink with metal ions are also useful in the present invention. Examples of crosslinkable synthetic polymers include polyacrylamides, poly 2-amino-2-methyl propane sulfonic acid, and various other synthetic polymers and copolymers. In this instance, the method of the present invention removes the metal ion from the crosslinked complex thereby reducing the viscosity of the solution to a value near that of water.

The polymer is present in the aqueous fluid in an amount in the range of from about 0.2 to about 2.0 parts by weight polymer per 100 parts by weight aqueous fluid. The selection of a polymer concentration depends upon the actual well conditions and the type of well treatment which is to be effected.

The pH of the aqueous fluid which contains the polymer can be adjusted if necessary to render the fluid compatible with a crosslinking agent which is used to increase the viscosity of the polymer solution. The pH adjusting material can be added to the aqueous fluid before, during or after the addition of the polymer to the aqueous fluid. Typical materials for adjusting the pH are commonly used acids, acid buffers and mixture of acids and bases. For example, hydrochloric acid, fumaric acid, sodium bicarbonate, sodium diacetate and sodium carbonate are typical pH adjusting agents. The pH range for the fluid and method of the present invention is from about 4 to about 12.

Crosslinking compounds suitable for the present invention include the variety of well-known organometailic chelates. Organic chelates of titanium, zirconium, aluminum, as well as other metals are well known to those skilled in the art. The selection of an appropriate crosslinking agent depends upon the type of treatment to be performed and the polymer to be used. The amount of the crosslinking agent used also depends upon the well conditions and the type of treatment to be effected, but is generally in the range of from about 0.01 to about 0.6 parts by weight crosslinking agent per 100 parts by weight of the aqueous fluid. In some applications the aqueous polymer solution is crosslinked immediately upon addition of the crosslinking agent to form a highly viscous gel. In another application, the reaction of the crosslinking compound can be retarded so that viscous gel formation does not occur until the desired time.

After the treating fluid is formed as discussed above, and has been pumped into a subterranean formation, it is generally desirable to convert the highly viscous gel to a low viscosity fluid. This allows the fluid to be easily and effectively removed from the formation and to allow desired material such as oil or gas, to flow into the wellbore. This reduction in viscosity of the treating fluid is commonly referred to as "breaking".

There are various methods available for breaking treating fluid. Fluids typically break after the passage of time and/or prolonged exposure to high temperatures. However, it is highly desirable to be able to predict and control the breaking within relatively narrow limits. Mild oxidizing agents are useful as breakers when a fluid is used in a relatively high temperature formation, although formation temperatures of 300°F (149°C) or greater will generally break the fluid relatively quickly without the aid of an oxidizing agent. One suitable oxidizing agent is ammonium persulfate. Enzymes are used as breakers for treating fluids which are used at formation temperatures below 140°F (60°C). Suitable enzymes for use are alpha and beta amylases, amyloglucosidase, oligoglucosidase, cellulase, and hemicellulase.

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Often times addition of these typical breakers to the treating fluid results in insufficient breaking of the treating fluid. Insufficient breaking means that highly concentrated gels, skins, or plugs are detected visually or experimentally in the broken fluid. In other words, although the overall viscosity of the fluid has been reduced, localized areas of crosslinked polymer are still present. In treating subterranean formations the polymer fluid may become highly concentrated as aqueous fluid is lost to the formation. Such highly concentrated polymer gels resist further breaking and may cause plugging or at the very least impair the ability of fluids to flow from the formation.

In accordance with the present invention, a method has been discovered which provides improved degradation of metal ion-crosslinked polymer fluids. The addition of particular esterified carboxylated chelators to the metal-crosslinked polymer fluid results in substantially complete degradation of the fluid in a predictable time. It has been discovered that esterified carboxylated chelators produce - but are not themselves - highly effective breakers for metal-crosslinked polymer fluids and are particularly suitable for well completion practices.

In the ester form, a carboxylic acid molecule is rendered relatively inactive as a chelator. However, at elevated temperatures or various pH values, the ester undergoes hydrolysis to form a free, active ligand or chelator. It is believed that the method and fluid of the present invention utilizes both the acid production from hydrolysis and the liberation of an active and highly effective chelator for metal ions to achieve improved degradation of the treating fluid. The produced acid lowers the viscosity of the polymer chain of natural polymers, while the active chelator removes the metal ion which crosslinks the polymer chains, i.e., the chelator uncrosslinks the polymer.

Some esterified carboxylated chelators that are suitable for use in this invention include esterified forms of ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), citric acid and hydroxyacetic acid, among others.

It is believed that the association constant of the carboxylated chelator/metal ion complex is preferably at least one order of magnitude greater than the association constant of the polymer/metal ion complex. However, as long as the association constant of the carboxylated chelator/metal ion complex is greater, the esterified carboxylated chelator is suitable for use in the present invention.

While total esterification of the acid function is preferred, it is to be understood that total substitution is not required and that a partially esterified compound may perform satisfactorily in the method of the present invention. It is only required that the degree of substitution be sufficient to render the carboxylic acid ineffective as a metal ion complexor.

Esterified forms of the carboxylated chelators that are suitable for this method include alkyl and substituted alkyl esters having in the range of from about 1 to 20 carbon atoms per ester group. Such compounds would therefore include methyl ester, ethyl ester, propyl ester, and other homologs. Some specific compounds useful herein include the esters of tetracyclohexyl EDTA, tetra-1-octyl EDTA, tetra-n-butyl EDTA, tetrabenzyl EDTA and tetramethyl EDTA. The number of derivatives of the carboxylated chelators which may be used in the present invention is great and the numerous derivatives are known to those skilled in the art. The preferred esterified carboxylated chelators for practice of this invention are the esters of citric acid and the esters of EDTA, in particular, the tetramethyl ester, the tetracyclohexyl ester and the tetrabenzyl ester of EDTA.

The selection of a particular esterified carboxylated chelator depends upon the rate of breaking of the crosslinked polymer that is desired. The breaking rate of the treating fluid of this invention is affected by the formation temperature, pH of the treating fluid, and rate of hydrolysis of the ester among other factors. The concentration of the esterified carboxylated chelator in the treating fluid is generally an amount stoichiometrically equal to the amount of metal ion present in the treating fluid. However, to insure complete breaking, the preferred practice is to add slightly more than an equal molar amount. In practicing the present invention, conventional breakers, i.e. oxidizers or enzymes, may also be used and the amount of esterified carboxylated chelator to be added again depends upon the rate at which breaking is desired.

As previously stated, the esterified carboxylated chelator remains relatively inactive at low temperatures, but undergoes hydrolysis at elevated temperatures. The rate of hydrolysis with respect to temperature generally depends upon the ester substituents.

In one preferred process for carrying out this invention a viscous treating fluid containing an ester of a polycarboxylic acid is injected down a wellbore and into a subterranean formation at a pressure sufficient to fracture the formation. The treating fluid comprises an aqueous fluid which is prepared by adding from about 30 pounds to about 70 pounds of polymer to each 1,000 gallons of aqueous fluid. The typical polymers used in fracturing are polysaccharide polymers, but synthetic polymers may also be used. The pH of the aqueous fluid is adjusted to enable hydration of the polymer, as well as to achieve a pH compatible with the selected metal ion crosslinking agent.

In normal fracturing operations, a polymer fluid is first introduced into the wellbore which is then followed

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by the crosslinked polymer. The metal ion crosslinking agent is introduced into the polymer fluid as it is injected into the wellbore. The delayed breaker of the present invention can be introduced while the polymer is being solvated or can be introduced as the fluid is being injected into the wellbore.

After the aqueous fluid has been injected into the subterranean formation, the highly viscous fluid is heated as it travels through the formation. When the aqueous fluid is sufficiently heated to initiate hydrolysis of the ester, the carboxylate chelator is released. The free carboxylate chelator is then able to react with metal-ion of the crosslinked polymer. As the polymer degrades and becomes uncrosslinked by the carboxylate chelator, the fluid begins to convert to a low viscosity fluid. Over time the viscosity is so reduced that the fluid is easily removed from the well without substamtial impairment of the formation.

The following examples are provided to illustrate the present invention but do not limit the invention in any way.

Example 1

Samples of an aqueous crosslinked polymer containing an esterified chelating agent were prepared and subjected to a constant temperature of 180°F (82°C) and observed until the samples broke. The break time was recorded.

Recipe:

Brine, Calcium Bromide/Calcium Chloride 15.2 lb/gal (1.70g/cm^3)

Polymer(1) 100 lb/1000 gal (12kg/m^3) Brine pH adjusted w/HCl to 3.3 Crosslinking agents(2) 3.2 vol/1000 vol Brine

Ester varies(3)

(1) The polymer was dihydroxypropyl-hydroxyethyl cellulose preconditioned in a solvent consisting of 70 percent by volume isopropyl alcohol and 30 percent by volume ethylene glycol at the rate of 3 ml solvent per gram of polymer.

(2) The crosslinking agent was a complex of zirconium in tetraethylamine.

(3) The ester was the tetramethyl ester of EDTA (20% active).

TABLE 1

Results

Sample No.	Ester X vol/1000 vol Brine	Break Time, Hours
1	3	79 - 94
2	10	54 - 69

Example 1 shows that a given crosslinked gel can be broken by addition thereto of an ester of EDTA and further that the length of time required to achieve the break can be increased by reducing the quantity of ester employed.

Example 1 also shows that the gel will crosslink in the presence of EDTA which has been esterified.

Example 2

A quantity of hydrated polymer was prepared by admixing the ingredients identified in the following recipe and permitting the mixture to stand for a time sufficient to form a gel.

Water solution containing 2% KCl by weight of solution

Polymer: hydroxpropyl guar	40 lb//1000 gal (4.79 kg/m^3) water
fumaric acid	2.5 lb/1000 gal (0.30 kg/m^3) water
sodium bicarborate	2.5 lb/1000 gel (0.30 kg/m^3) water

The gel was then mixed with 0.8 vol crosslinking agent per 1000 vol of gel to thereby form a crosslinking agent was an organic complex of titanium.

Filter cake was prepared by passing the crosslinked gel at a temperature of 180°F (82°C) and 1000 psig

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(6.89 M Pa g) through an Ohio Sandstone core having a permeability of 0.1 milldarcy. The filter cake was removed from the core and divided into samples of equal size.

A filter cake sample was then placed in a bottle containing 50 ml of 2% KCl solution. A quantity of tetramethyl ester of EDTA (20% active), as set out below, was then placed in each bottle containing a filter cake. The bottle was then placed in an oven maintained at 180°F (82°C) and observed. The time required to break the filter cake was recorded.

TABLE 2

Results

Sample No.	X vol /1000 vol 2% KCL Solution	Break Time, Hours
1	0	did not break, no change in sample
2	0.4	some complex after 93 hours
3	0.8	30 hours - break starts
4	1.2	30 hours
5	1.6	6 - 21 hours

Example 2 shows that a filter cake produced by a crosslinked gel can be broken by contacting the cake with an ester of EDTA. The example also shows that the length of time required to break can be increased by reducing the quantity of ester employed.

Example 3

A quantity of hydrated polymer was prepared in accordance with the following procedure.

Recipe

Tap Water	1000 ml
KCl	20 gm
gelling agent (dihydroxypropyl-hydroxyethyl-cellulose)	12 gm

The above ingredients were permitted to stand for two hours to form a gel and then an equimolar mixture of formic acid and sodium formate was added to the gel at the rate of 3 ml per liter of gel. The gelling agent was preconditioned by first mixing it with a solvent consisting of 70 percent by volume isopropyl alcohol and 30 percent by volume ethylene glycol at the rate of 3 ml solvent per gram of polymer.

The gel was then further treated as follows:

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TABLE 3

Sample No.	Gel, ml	EDTA, gm	Crosslinker*, ml	Time to Form Complex, Minutes
1	150	0	0.48	25
2	150	0.36	0.48	did not complex

*Complex of zirconium in tetraethylamine

Example 3 shows that a given gel, similar to the one used in Example 1, will not form a crosslink in the presence of EDTA which is not esterified. The example also shows that a crosslink is formed in the absence of EDTA. Compare the results in Example 1 with the results in Example 3 and note that the esterified EDTA does not prevent crosslinking but will, after a delay, produce a break in the gel.

Example 4

The rate of conversion of an ester of a polycarboxylic acid to the acid itself is a function of a number of factors including pH, temperature and ester substituent. Accordingly, for example, a crosslinked gel of known pH used to treat a subterranean formation of known temperature can be broken in a predicted time by appropriate selection of ester substituent for the particular polycarboxylic acid being employed as the breaker.

Since the rate at which an ester converts to the acid form does vary depending on the structure, a user, knowing temperature and pH conditions, may engage in limited laboratory work to aid in ester selection. The information contained in Table 4, which is a list of calculated hydrolysis rates of esters relative to the methyl ester substituent, may be used in conjunction with laboratory work to help calculate specific break times for specific esters.

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TABLE 4

PREDICTED RELATIVE RATES OF HYDROLYSIS* OF ESTERIFIED CHELATING AGENTS

Alcohol Group	Acid Group	Relative Hydrolysis Rate**
Methyl-	EDTA	1.00
n-Butyl-	EDTA	1.34
iso-Butyl	EDTA	0.87
2-Butyl-	EDTA	1.05
t-Butyl-	EDTA	0.65
Benzyl-	EDTA	1.50
p-Methoxybenzyl-	EDTA	1.13
m-Methoxybenzyl-	EDTA	1.16
m-Chlorobezyl-	EDTA	1.14
p-Chlorobenzyl-	EDTA	1.17
Phenyl-	EDTA	1.23
Methyl-	Citric	5.54
Methyl-	NTA	0.74
Methyl-	Glycolic	1.47

* These rates were calculated using Quanta Software after the method described by D. F. DeTar, S. Binzet and P. Darba, J. Org Chem. 1987, 52, 2074-2082

** First Ester Group

EXAMPLE 5

Samples of an aqueous crosslinked polymer containing an esterified chelating agent were prepared and subjected to a constant temperature of 150°F (66°C) and observed until the samples broke. The break time was recorded.

Recipe:

Brine, Calcium chloride 9.0 lb/gal (1.08 g/cm^3)

Polymer(1) 120 lb/1000 gal (14.4 kg/m^3) Brine pH adjusted with an equimolar mixture of formic acid and sodium formate at the rate of 3 ml per liter of gel. Crosslinking agents(2) 3.84 vol/1000 vol Brine

Ester varies(3)

(1) The polymer was dihydroxypropyl-hydroxyethyl cellulose preconditioned in a solvent consisting of 70 percent by volume isopropyl alcohol and 30 percent by volume ethylene glycol at the rate of 3 ml solvent per gram of polymer.

(2) The crosslinking agent was a complex of zirconium in tetraethylamine.

(3) Various different esters of EDTA.

Example 5 shows that a given crosslinked gel can be broken by addition thereto of an ester of EDTA and further that the length of time required to achieve the break can be increased by reducing the quantity of ester employed.

Example 5 also shows that the gel will crosslink in the presence of EDTA which has been esterified.

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TABLE 5

EDTA Ester	Break Time 15 vol / 1000 vol	20 vol / 1000 vol	25 vol / 1000 vol	50 vol / 1000 vol
* tetra cyclohexanol	~30 day	~12 day	--	45 hr/200°F (93°C)
** tetra Benzyl	~19 hr.	--	~16 hr.	--
*** tetra Isoamyl	~24-27 hr.	--	~17 hr.	--

Note: 1 day = 24 hr.
* 26% active
** 45% active
*** 63% active

Claims

1. A method of reducing the viscosity of a gel comprised of a polymer in a fluid crosslinked with a metal ion, said method comprising contacting said gel with a compound which is initially inactive as a chelating agent for said metal ion but which is capable after a period of time of producing a chelating agent for said metal ion; maintaining said contact for said period of time whereby thereafter said chelating agent is formed which complexes said metal ion to remove metal ion from said gel thereby to reduce the viscosity of said gel.

2. A method according to claim 1, wherein said compound is an ester of a carboxylated chelating agent, and said fluid is an aqueous fluid.

3. A method according to claim 2, wherein said carboxylated chelating agent is ethylenediaminetetraacetic acid, nitrilotriacetic acid, citric acid or hydroxyacetic acid.

4. A method according to claim 3, wherein the pH of the gel is 4 to 7, the temperature of the gel is from 175°F (79°C) to 200°F (93°C), and said compound is the tetramethyl ester of ethylenediaminetetraacetic acid.

5. A method according to any of claims 1 to 4 wherein, after contacting the gel with the compound, the gel is pumped downhole to treat a subterranean formation during said period of time, and thereafter removing the reduced viscosity gel.

6. A composition useful for treating a subterranean formation, said composition comprising a fluid, a polymer which is crosslinked with a metal ion, and an ester of a chelating agent for said metal ion; wherein the chemical association between the metal ion and the ester is less than the chemical association between the metal ion and the polymer, and the chemical association between the metal ion and the chelating agent is greater than the chemical association between the metal ion and the polymer.

7. A composition according to claim 6, wherein the ester is an alkyl or substituted alkyl ester having from 1 to 6 carbon atoms per ester group on the chelating agent.

8. A composition according to claim 6 or 7, wherein said chelating agent is a polycarboxylic acid.

9. A composition according to claim 6 or 7, wherein the ester is an alkyl or substituted alkyl ester of ethylenediaminetetraacetic acid, nitrilotriacetic acid, citric acid or hydroxyacetic acid.

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10. A composition according to claim 9, wherein the ester is the tetramethyl or tetracyclohexyl ester of ethylenediaminetetraacetic acid.

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European Patent Office

EUROPEAN SEARCH REPORT

Application Number EP 92302338.6

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	EP - A - 0 326 720 (ENI) * Abstract * --	1	E 21 B 43/25 E 21 B 43/26 E 21 B 43/27
A	GB - A - 2 158 487 (DOW) * Abstract * --	1,3	
A	US - A - 4 968 442 (FALK) * Abstract * --	1,3	
A	US - A - 3 926 258 (HESSERT) * Abstract * ----	1	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

E 21 B 33/00
E 21 B 43/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	29-05-1992	BRUNHUBER

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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(71) Applicant *(for all designated States except US)*: **M-I L.L.C.** [US/US]; 5950 North Course Drive, Houston, TX 77072 (US).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **HORTON, Robert, L.** [US/US]; 1103 Springdale Ct., Sugar Land, TX 77479 (US). **DARRING, Michael, T.** [US/US]; 516 Pelican Avenue, New Orleans, LA 70114 (US). **MOLINA, Hiram** [US/US]; 536 Longview Dr., Destrehan, LA 70047 (US).

(74) Agent: **LORD, Robert, P.**; Osha * Liang LLP, 909 Fannin Street, Suite 3500, Houston, TX 77010 (US).

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(54) Title: METHODS FOR PREVENTING OR REMEDIATING XANTHAN DEPOSITION

(57) Abstract: Methods for remediation and/or prevention of polymer deposition on surfaces, in particular, on surfaces of drilling machinery and earth formations in the petroleum industry are described herein. Embodiments disclosed herein relate to a method of remediating xanthan deposition, the method including the steps of contacting xanthan deposition, including xanthan complexed with polyvalent metal ions, with a remediation fluid containing at least one chelating agent; and allowing the fluid to dissolve the xanthan deposition. Also disclosed is a method of preventing polymer deposition, including emplacing a wellbore fluid including a crosslinkable polymer and at least one chelating agent in a wellbore; wherein the at least one chelating agent complexes with polyvalent metal ions present in the wellbore. Also disclosed is an improved wellbore fluid including a base fluid; a polymer comprising chemical groups reactive to polyvalent metal ions found downhole; and at least one chelating agent; wherein the least one chelating agent complexes with polyvalent metal ions downhole.

METHODS FOR PREVENTING OR REMEDIATING XANTHAN DEPOSITION

BACKGROUND OF INVENTION

Field of the Invention

[0001] Embodiments disclosed herein relate generally to methods for remediation and/or prevention of polymer deposition on surfaces, in particular, on surfaces of drilling machinery and earth formations in the petroleum industry. Even more particularly, embodiments disclosed herein relate to methods for the remediation and/or prevention of the deposition of xanthan on surfaces of drilling machinery and earth formations in the petroleum industry.

Background Art

[0002] When drilling or completing wells in earth formations, various fluids typically are used in the well for a variety of reasons. For the purposes herein, these fluids will be generically referred to as "wellbore fluids." Common uses for wellbore fluids include: lubrication and cooling of drill bit cutting surfaces while drilling generally or drilling-in (*i.e.*, drilling in a targeted petroliferous formation), transportation of "cuttings" (pieces of formation dislodged by the cutting action of the teeth on a drill bit) to the surface, controlling formation fluid pressure to prevent blowouts, maintaining well stability, suspending solids in the well, minimizing fluid loss into and stabilizing the formation through which the well is being drilled, minimizing fluid loss into the formation after the well has been drilled and during completion operations such as, for example, perforating the well, replacing a tool, attaching a screen to the end of the production tubulars, gravel-packing the well, or fracturing the formation in the vicinity of the well, displacing the fluid within the well with another fluid, cleaning the well, testing the well, emplacing a packer and packer fluid, abandoning the well or preparing the well for abandonment, and otherwise treating the well or the formation.

[0003] Depending on the particular application or well to be drilled, a drilling operator typically chooses between a water-based wellbore fluid and an oil-based or synthetic wellbore fluid. Each of the water-based fluid and oil-based fluid typically

include a variety of additives to create a fluid having the rheological profile suitable for a particular drilling application. For example, a variety of compounds are typically added to water- or brine-based wellbore fluids, including viscosifiers, corrosion inhibitors, lubricants, pH control additives, surfactants, solvents, thinning agents, and/or weighting agents, among other additives.

[0004] Viscosifiers are used to enhance viscosity, thereby providing wellbore fluids with the rheological profiles that enable wells to be drilled more easily. Viscosifiers are typically clays, polymers and oligomers, and may be either synthetic or natural. Some typical water- or brine-based wellbore fluid viscosifying additives include clays, synthetic polymers, natural polymers and derivatives thereof. Similarly, a variety of compounds are also typically added to a oil-based fluid including weighting agents, wetting agents, organophilic clays, viscosifiers, fluid loss control agents, surfactants, dispersants, interfacial tension reducers, pH buffers, mutual solvents, thinners, thinning agents and cleaning agents.

[0005] Examples of synthetic polymers and oligomers that can be used as viscosifiers include poly(ethylene glycol) [PEG], poly(diallyl amine), poly(acrylamide), poly(aminomethylpropylsulfonate) [AMPS polymer], poly(acrylonitrile), poly(vinyl acetate) [PVA], poly(vinyl alcohol) [PVOH], poly(vinyl amine), poly(vinyl sulfonate), poly(styryl sulfonate), poly(acrylate), poly(methyl acrylate), poly(methacrylate), poly(methyl methacrylate), poly(vinylpyrrolidone), poly(vinyl lactam), and co-, ter-, and quater-polymers of the following co-monomers: ethylene, butadiene, isoprene, styrene, divinylbenzene, divinyl amine, 1,4-pentadiene-3-one (divinyl ketone), 1,6-heptadiene-4-one (diallyl ketone), diallyl amine, ethylene glycol, acrylamide, AMPS, acrylonitrile, vinyl acetate, vinyl alcohol, vinyl amine, vinyl sulfonate, styryl sulfonate, acrylate, methyl acrylate, methacrylate, methyl methacrylate, vinylpyrrolidone, and vinyl lactams.

[0006] Natural polymers and derivatives thereof such as xanthan gum, guar gum, and hydroxyethyl cellulose (HEC) may also be used as wellbore fluid viscosifying additives. In addition, a wide variety of polysaccharides and polysaccharide derivatives may be used, as is well known in the art. These polysaccharides are typically used to enhance viscosity in fresh water, seawater, brines, saturated brines, lignosulfate, or heavy mud systems.

[0007] Synthetic polymers, for example, polyacrylamides, have been found to suffer such deficiencies as viscosity loss in brines and severe shear sensitivity. Because, as has been well documented in the prior art, xanthan is relatively insensitive to salts (does not precipitate or lose viscosity under normal conditions), is shear stable, thermostable and viscosity stable over a wide pH range, xanthan is a good choice of a viscosifying additive. Moreover, xanthan is not adsorbed on the elements of the porous rock formations to the extent of causing permanent productivity reduction, and it gives viscosities (5 to 100 centipoise units at 7.3 $sec.^{-1}$ shear rate) at low concentrations (100 to 3000 ppm) useful for wellbore fluids and in enhanced oil recovery. The use of solutions of xanthan or derivatives of xanthan in wellbore fluids is described in U.S. Patent Nos. 3,243,000; 3,198,268; 3,532,166; 3,305,016; 3,251,417; 3,319,606; 3,319,715; 3,373,810; 3,434,542; 3,729,460 and 4,119,546.

[0008] Accordingly, there exists a continuing need for development related to wellbore fluids containing xanthan therein.

SUMMARY OF INVENTION

[0009] In one aspect, embodiments disclosed herein relate to a method of remediating xanthan deposition, the method including the steps of contacting xanthan deposition, including xanthan complexed with polyvalent metal ions, with a remediation fluid containing at least one chelating agent; and allowing the fluid to dissolve the xanthan deposition.

[0010] In another aspect, embodiments disclosed herein relate to a method of preventing polymer deposition, including emplacing a wellbore fluid including a crosslinkable polymer and at least one chelating agent in a wellbore; wherein the at least one chelating agent complexes with polyvalent metal ions present in the wellbore.

[0011] In yet another aspect, embodiments disclosed herein relate to an improved wellbore fluid including a base fluid; a polymer comprising chemical groups reactive to polyvalent metal ions found downhole; and at least one chelating agent; wherein the least one chelating agent complexes with polyvalent metal ions downhole.

[0012] Other aspects and advantages of the invention will be apparent from the following description and the appended claims.

DETAILED DESCRIPTION

[0013] Generally, embodiments disclosed herein relate to methods of remediating or preventing xanthan deposition. More specifically, embodiments disclosed herein relate to dissolving and/or preventing the formation of deposited xanthan scale on oilfield equipment, in a wellbore, and on the earthen formation. More specifically still, embodiments disclosed herein relate to methods of dissolving xanthan scale in which the active chelating agent may be reclaimed for further use.

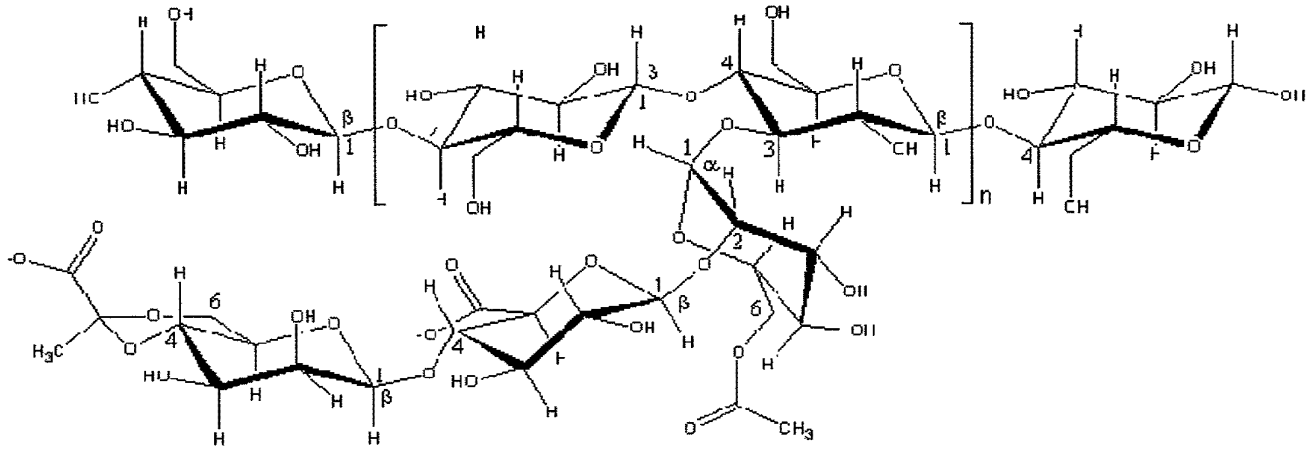
[0014] The inventors have advantageously found that the addition of a chelating agent to a wellbore fluid prevents the buildup of polymer scale in the wellbore, on the earthen formation and on downhole equipment. The inventors have further advantageously found that the use of a remediation fluid comprising a chelating agent removes polymer scale from the wellbore, on the downhole equipment and earthen formation. As used herein, "chelating agent" is a compound whose molecular structure can envelop and/or sequester a certain type of ion in a stable and soluble complex. When sequestered inside the complex, the cations have a limited ability to react with other ions, clays or polymers, for example.

[0015] Frequently, a wellbore fluid may contain a polymer capable of complexing with polyvalent metal ions found in the wellbore and in earthen formation, and which has been observed to form polymer scale when drilling through formations of that type. In some embodiments, it has been found that the addition of particular chelating agents to a wellbore fluid may prevent the buildup of polymer scale in the wellbore, on downhole equipment, or on or within the formation itself. For example, chelating agents may be added to a wellbore fluid used in the normal course of drilling or oil recovery. The improved wellbore fluid may then be used in drilling or in oil recovery operations. Improved wellbore fluids of the present disclosure containing chelating agents may prevent the buildup of polymer scale in the wellbore, on the downhole equipment and on the earthen formation. The present disclosure addresses any scale that is or may be induced by the interaction of polyvalent metal ions and xanthan or other polymers regardless of the source of the polyvalent metal ions.

[0016] In other embodiments, it has been found that the use of a remediation fluid comprising a chelating agent can remove polymer scale from the wellbore, on downhole equipment, or on the formation itself. For example, after polymer scale has been observed on the equipment, or thought to exist on the formation, a remediation fluid of the present disclosure may be introduced downhole. The remediation fluid may then remove the polyvalent ions from the crosslinked polymer, allowing the polymer to return to its fluid, un-crosslinked state. The polymer may then be recycled into the wellbore fluid for circulation or other use in the wellbore. Alternatively, the remediation fluid may be used to remove polymer scale from equipment in need of repair.

[0017] Polymers used as components of wellbore fluids in downhole applications, as mentioned above, include both synthetic and natural polymers. Included among those polymers used in the wellbore are some polymers which possess reactive groups capable of interacting with polyvalent ions found downhole, causing crosslinking or some type of gelation of the polymer.

[0018] For example, xanthan is a polymer frequently used in well fluids. Xanthan is a high molecular weight biopolymer that may be produced by the bacterium *Xanthomonas campestris*, and precipitated from the fermentation broth, usually by an alcohol. Structurally, xanthan is a heteropolysaccharide, the backbone consisting of D-glucose repeating units that are bonded together by 1,4-β-glucosidic linkages. The glucan backbone is protected by trisaccharide side chains attached by β-1,3-glycosidic or mannosidic linkages. The trisaccharide side chains consist of mannose and glucuronic acid moieties. This structure is represented as below:



[0019] Each molecule consists of about 7000 pentamers. The trisaccharide mannose and glucuronic acid side chains lend rigidity to the xanthan molecule, and allow it to form a right-handed helix. Its natural state has been proposed to be bimolecular antiparallel double helices. The helicity of the xanthan molecule facilitates its interaction with itself and with other long chain molecules to form thick mixtures and gels in water.

[0020] Xanthan may be used in a variety of industrial applications, for example, as described in U.S. Patent No. 4,119,546. Typical well applications include, but are not limited to, those mentioned above, most typically as a brine thickener in drilling muds and workover fluids, as a viscosifier in hydraulic fracturing, cementing, and other well completion operations, as a proppant carrier or gel blocking agent in gravel packing and frac packing operations, in secondary and tertiary recovery operations, and in non-petroleum-producing applications such as a clarifier for use in refining processes. Although the application uses xanthan as an example throughout, one of skill in the art would recognize that the wellbore fluids and remediation fluids of the present disclosure may be used with any polymer capable of interacting with polyvalent ions to result in crosslinking or gelation.

[0021] In applications where xanthan is used as a viscosifier in wellbore fluids, the wellbore fluid may be prepared in a large variety of formulations. Specific formulations may depend on the state of drilling a well at a particular time, for example, depending on the depth and/or the composition of the formation. The amount of xanthan gum in the wellbore fluid may be varied to provide the desired viscosity. In one embodiment, the xanthan gum may range from about 0.1 to about 7.0 wt % of the total weight of the wellbore fluid. In another embodiment, xanthan gum in addition to other any other included polymers, may range from about 0.2 to 2.0 wt % of the total weight of the wellbore fluid, and from 0.3 to 1.0 wt % in yet another embodiment.

[0022] The wellbore fluid composition described above may be adapted to provide improved wellbore fluids under conditions of high temperature and pressure, such as those encountered in deep wells. Further, one skilled in the art would recognize that, in addition to xanthan gum, other additives may be included in the wellbore fluid disclosed herein, for instance, wetting agents, organophilic clays, corrosion inhibitors,

oxygen scavengers, anti-oxidants and free radical scavengers, biocides, weighting agents, other viscosifiers, surfactants, dispersants, interfacial tension reducers, pH buffers, mutual solvents and thinning agents.

[0023] However, some of these polymer viscosifiers are believed to form scale in the wellbore, on the surfaces of downhole equipment and on the formation because they may be easily be precipitated by crosslinking with metal ions, which exist in may circumstances plentifully in the downhole environment. For instance, xanthan biopolymer has carboxylic groups which can serve as cross-linking sites for polyvalent metal ions such as iron, magnesium and calcium. These metal ions are commonly found in oil-bearing formation waters.

[0024] Xanthan-containing fluids are known to cause damage to the permeability of the near wellbore area due to mud or scale buildup on the formation faces and on the surfaces of any downhole equipment. When the wellbore fluid is supplied downhole during drilling operations, at least part of xanthan gum contained in the wellbore fluid may crosslink with polyvalent metal cations in the downhole environment.

[0025] Polyvalent metal cations which crosslink xanthan gum may stem from minerals naturally present in the subterranean formations, from metallic substances in oilfield equipment, or from base fluids used in formulating wellbore fluids (e.g., from brines). Nonlimiting examples of such metal cations include aluminum, iron, zirconium, calcium, and chromium. For instance, Fe(II)/Fe(III) cations are dissolved from iron-containing minerals and solids in the downhole environment, and then they may crosslink with xanthan gum to form scale. As a result, xanthan gum crosslinked with Fe(II)/Fe(III) cations may form an insoluble solid deposition or scale on the formation and/or oilfield equipment.

[0026] The result of this crosslinking is biopolymer immobilization and formation plugging due to a gelation mechanism. Heavy metal ions such as Cr^{3+}, Al^{3+}, Fe^{2+}, Ca^{2+} and Fe^{3+} are well known to cause gelation of xanthan. There are also other ions which may complex with xanthan in certain pH intervals. Xanthan gelation is thought to occur via the carboxylic groups, and the mechanism of gelation does not appear to selectively favor any polyvalent ion over others. The crosslinking reaction is thought to be a ligand exchange reaction where water molecules coordinated to the heavy metal ion are exchanged for the carboxylic groups of the xanthan polymer. The

polyvalent heavy metal ion may complex to several carboxylic groups of the xanthan backbone causing the xanthan polymer chain to crosslink with itself, or with other polymer chains forming an insoluble scale or gel.

[0027] When used in polymer flooding, oil production is thus reduced because the xanthan cannot readily migrate through the rock formation. Similarly, scale deposits can also result in plugging of well bores, well casing perforations and tubing strings, as well as sticking of downhole safety valves, downhole pumps and other downhole and surface equipment and lines.

[0028] In general, it is undesirable that such scale is formed downhole because the encrustation must be removed in a time- and cost-efficient manner. For example, plugged tubing and equipment has to be removed and replaced. Alternatively, scale is removed from contaminated tubing and equipment through equipment decontamination processes. This results in significant costs in terms of equipment costs, man-hours, and downtime.

[0029] On the surface, typical equipment decontamination processes include both mechanical and chemical efforts, such as milling, high pressure water jetting, sand blasting, cryogenic immersion, and chemical solvents. For instance, water jetting using pressures in excess of 140MPa (with and without abrasives) can be effective for scale removal. However, use of mechanical methods such as high pressure water jetting generally requires that each pipe or piece of equipment be treated individually with significant levels of manual intervention, which is both time consuming and expensive, and sometimes also fails to thoroughly treat the contaminated area. Alternatively, chemical processes may include contacting scale with a chemical solvent such that the chemical solvent can dissolve the scale. However these techniques are limited to the surface and do not solve problems associated with deposition formed in the wellbore.

[0030] A common prior art approach to removing xanthan scale has been to apply acid or strong oxidative breaker systems to dissolve the xanthan gum. A typical wellbore treatment to remove such damage consists of hydrochloric acid solutions, solutions of lithium or sodium hypochlorite, or highly concentrated solutions of conventional oxidizers like sodium or ammonium persulfate or perborate. Although acids and oxidative solution washes appear to perform reasonably well in a laboratory

environment where contact of scale with a reactive solution is easily achieved, application of these solutions may not be so effective for removing the damage in horizontal intervals. Additional concerns regarding the use of acidic or oxidative cleanup treatments include the reactivity with tubulars which may result and elevated iron concentrations being injected into the reservoir in a manner which may promote sludging problems and exacerbate the scale issue. As such, conventional acid and oxidizer treatments are typically ineffective to remove or mitigate xanthan scale due to the resistance of xanthan towards oxidizers and acids. Further, conventional chemical processes require the disposal of solvents once saturated, and the large amount of fairly expensive solvents necessary for decontamination may be associated with increased costs and environmental and safety concerns.

[0031] Well treatments using xanthan-specific enzymes have been proposed to treat xanthan polymer buildup. However, these treatments employ enzymes that are typically not effective at temperatures greater than about 150°F. Because many wells have downhole temperatures exceeding 150°F, proposed enzyme treatments for removing xanthan scale would be ineffective in many wells having temperatures exceeding this level.

[0032] Further, the glucan backbone of the xanthan biopolymer is protected by the trisaccharide side chains which lie alongside, making it relatively stable to acids, alkalis and enzymes. This presents an on-going challenge to remediate or prevent xanthan deposition. Accordingly, there exists a continuing need for a more effective means for removing scale that results from crosslinking of polysaccharides and polysaccharide derivatives with polyvalent metal ions.

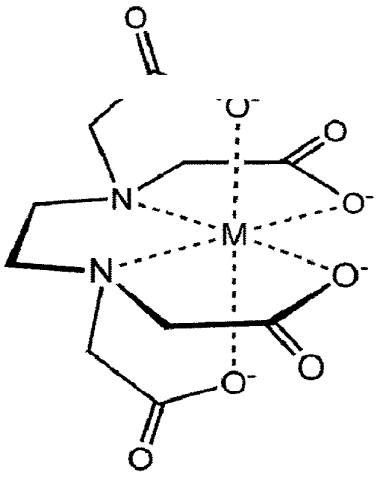
[0033] Scale that may be effectively removed from oilfield equipment in embodiments disclosed herein includes oilfield scales containing xanthan gum, for example, scale containing xanthan gum crosslinked with polyvalent metal cations.

[0034] As mentioned above, the inventors have advantageously found that the addition of a chelating agent to the wellbore fluid prevents the formation of polymer scale or removes polymer scale in the downhole environment. Chelating agents useful in the embodiments disclosed herein sequester polyvalent metal ions through bonds to two or more atoms of the chelating agent. Useful chelating agents may include organic ligands such as ethylenediamine, diaminopropane, diaminobutane,

diethylenetriamine, triethylenetetraamine, tetraethylenepentamine, pentaethylenehexamine, tris(aminoethyl)amine, triaminopropane, diaminoaminoethylpropane, diaminomethylpropane, diaminodimethylbutane, bipyridine, dipyridylamine, phenanthroline , aminoethylpyridine, terpyridine, biguanide and pyridine aldazine.

[0035] In some embodiments, the chelating agent that may be used in the solution to dissolve the metal scale may be a polydentate chelator such that multiple bonds are formed with the complexed metal ion. Polydentate chelators suitable may include, for example, ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), nitrilotriacetic acid (NTA), ethyleneglycoltetraacetic acid (EGTA), 1,2-bis(o-aminophenoxy)ethane-N,N,N',N'-tetraaceticacid (BAPTA), cyclohexanediaminetetraacetic acid (CDTA), triethylenetetraaminehexaacetic acid (TTHA), glutamic-N,N-diacetic acid (GLDA), salts thereof, and mixtures thereof. However, this list is not intended to have any limitation on the chelating agents suitable for use in the embodiments disclosed herein. One of ordinary skill in the art would recognize that selection of the chelating agent may depend on the metal scale to be dissolved. In particular, the selection of the chelating agent may be related to the specificity of the chelating agent to the particular scaling cation, the logK value, the optimum pH for sequestering and the commercial availability of the chelating agent, as well as downhole conditions, *etc.*

[0036] In a particular embodiment, the chelating agent used to dissolve metal scale is EDTA or salts thereof. Salts of EDTA may include, for example, alkali metal salts such as a tetrapotassium salt or tetrasodium salt. However, as the pH of the dissolving solution is altered in the processes disclosed herein, a dipotassium or disodium salt or the acid may be present in the solution. EDTA is an amino acid, as shown below, with four carboxylate and two amine groups. This polydentate chelator is typically used to sequester di- and trivalent metal ions, for example Mn(II), Cu(II), Fe(III), and Co(III).



[0037] Wellbore fluids of embodiments of this disclosure containing chelating agents may be emplaced in the wellbore using conventional techniques known in the art. If used as a preventative additive, the chelating agent may be added to the drilling, completion, or workover fluid. If, however, remediation of a particular interval of the wellbore is needed, a remediation fluid including a chelating agent may be injected to such interval, in addition to other intervals. The wellbore fluid may contain an amount of chelating agent sufficient to prevent polymer crosslinking, or alternatively to remediate polymer crosslinking. The wellbore fluids may be used in conjunction with any drilling, completion, or production operation.

[0038] As the wellbore fluid encounters polyvalent ions, the chelating agent may complex with the polyvalent ion to form a chelated complex. The bonds between the sequestered polyvalent ion and the chelating agent may be any combination of coordination or ionic bonds. The resultant chelated complex has enhanced stability through the chelant effect, relative to crosslinking with the reactive groups of the polymer, for example the carboxylic groups of the xanthan biopolymer.

[0039] In embodiments where the chelating agent is part of the wellbore fluid, in which xanthan is included, the polyvalent ions may preferably react with the chelating agent to form a stable chelated complex. The stable chelated complex may be thermodynamically and/or kinetically favored to the crosslinked polymer. As such, the deposition of polymer scale in the wellbore may be significantly decreased, thereby promoting well stability and productivity.

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[0040] In embodiments where the chelating agent is part of a remediation fluid, the polyvalent ions crosslinked to the polymer may release on favorable interaction and complexation with the chelating agent. As the remediation fluid containing the chelating agent encounters polymer-bound polyvalent ions, the ions may preferentially dissociate from the polymer and complex with the chelating agent. As the polymer releases the bound polyvalent ions to the remediation fluid, the polymer scale dissolves, and the polymer then may return to its fluid, pseudoplastic state.

[0041] Following use in preventing/remediating polymer deposition, the wellbore fluids may be collected and subjected to reclamation techniques typically used with wellbore fluids. Additionally, it may be desirable to remove the chelating agent from a collected aqueous portion of a fluid. Once the chelating agent becomes saturated with the metal cations, the wellbore fluid or remediation fluid may then be removed and recycled. One suitable method for recycling used chelating agents is described in U.S. Patent Application Serial No. 11/690,660, which is assigned to the assignee of the present disclosure. That application is incorporated by reference in its entirety.

[0042] In some embodiments disclosed herein, the remediation solution may possess a dissolution capacity of at least 70 grams of scale per liter of remediation solution. In other embodiments, the remediation solution may possess a dissolution capacity of at least 80 grams of scale per liter of remediation solution.

[0043] Exemplary Embodiment

[0044] In one embodiment, an aqueous solution of 5000 ppm of $FeCl_2$ and an aqueous xanthan gum solution at 2 ppb with a pH ranging from 9 to 10 are prepared. 50 ml of the xanthan gum solution is taken, and is added in the $FeCl_2$ solution drop by drop until precipitants can be observed. The precipitants include iron-crosslinked xanthan, iron hydroxide, and/or mixed iron oxide-hydroxide compounds. 1 ppb of disodium EDTA is added to the xanthan solution. After the EDTA solution has substantially dissolved the precipitants, the solution may be acidified with hydrochloric acid to a pH between 0 and 1 to further break up the viscosity of the solution.

[0045] Upon isolation of the precipitated solids, a fresh solution of potassium carbonate may be added to the solids to achieve a final pH of about 6, whereby the dipotassium salt of EDTA will be formed and will be soluble at a level of about 10 %

by weight. After filtering the still-precipitated iron-crosslinked xanthan out of the solution, additional potassium carbonate may be added to the filtrate to bring the amount of potassium carbonate in the solution to about 15 % by weight.

[0046] Advantageously, embodiments disclosed herein may provide for a process where the formation of mineral scale downhole may be prevented and where the dissolving solution may be reclaimed without loss of performance. By sequestering metal ions which may otherwise react with well fluid polymer to form polymer scale, the inactive salts remaining in the dissolving solution may be removed from the system to avoid buildup of impurities in the dissolving solution which could otherwise lead to a reduction in the rate and/or efficiency of scale prevention performance. If small quantities of chelating agent are lost in the process, small amounts may be added for subsequent reaction cycles so that recycling of the chelating agent and dissolving solution may be achieved without performance losses in dissolution rate or sequestering capacity in successive cycles.

[0047] Also, embodiments disclosed herein may provide for a process by which existing mineral scale can be removed from oilfield equipment and the wellbore. By precipitating the polymer scale and the chelating agent as an insoluble acid, the inactive salts remaining in the dissolving solution may be removed from the system to avoid buildup of impurities in the dissolving solution which could otherwise lead to a reduction in the rate and/or efficiency of scale dissolution performance.

[0048] While the invention has been described with respect to a limited number of embodiments, those skilled in the art, having benefit of this disclosure, will appreciate that other embodiments can be devised which do not depart from the scope of the invention as disclosed herein. Accordingly, the scope of the invention should be limited only by the attached claims.

CLAIMS

What is claimed:

1. A method of remediating xanthan deposition, the method comprising the steps of:
   contacting xanthan deposition comprising xanthan complexed with polyvalent metal ions with a remediation fluid comprising at least one chelating agent; and
   allowing the fluid to dissolve the xanthan deposition.

2. The method of claim 1, wherein the polyvalent metal ions are derived from at least one of a downhole formation and downhole equipment.

3. The method of claim 1, wherein the polyvalent metal ions comprise at least one of Fe(II), Fe(III), Al^{3+}, Zr^{4+}, Ca^{2+} and Cr^{2+}.

4. The method of claim 1, wherein the xanthan deposition contains xanthan crosslinked with at least one of Fe(II) and Fe(III) ions.

5. The method of claim 1, wherein the chelating agent comprises at least one of EDTA, DTPA, GLDA, NTA and salts thereof.

6. A method of preventing polymer deposition, comprising:
   emplacing a wellbore fluid comprising a crosslinkable polymer and at least one chelating agent in a wellbore;
   wherein the at least one chelating agent complexes with polyvalent metal ions present in the wellbore.

7. The method of claim 6, wherein the polymer comprises chemical groups reactive to polyvalent ions.

8. The method of claim 6, wherein the crosslinkable polymer comprises xanthan polymer.

9. The method of claim 6, wherein the chelating agent comprises at least one of EDTA, DTPA, GLDA, NTA, and salts thereof.

10. The method of claim 6, wherein the polyvalent metal ions are derived from at least one of a downhole formation, downhole equipment, and a base fluid from which the wellbore fluid was formulated.

11. The method of claim 6, wherein the polyvalent metal ions comprise at least one of Fe(II), Fe(III), Al^{3+}, Zr^{4+}, Ca^{2+} and Cr^{2+}.

12. An improved wellbore fluid comprising:

a base fluid;

a polymer comprising chemical groups reactive to polyvalent metal ions found downhole; and

at least one chelating agent;

wherein the least one chelating agent complexes with polyvalent metal ions downhole.

13. The wellbore fluid of claim 12, wherein the polymer is xanthan polymer.

14. The wellbore fluid of claim 12, wherein the chelating agent comprises at least one of EDTA, DTPA, GLDA, NTA, and salts thereof.

15. The wellbore fluid of claim 12, wherein the polyvalent metal ions are derived from at least one of a downhole formation, downhole equipment, and the base fluid from which the wellbore fluid was formulated.

16. The wellbore fluid of claim 12, wherein the polyvalent metal ions comprise at least one of Fe(II), Fe(III), Al^{3+}, Zr^{4+}, Ca^{2+} and Cr^{2+}.

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(71) **Applicant** *(for all designated States except US)*: **CESI CHEMICAL, INC.** [US/US]; 1004 S. Plainsman Road, Marlow, OK 73055 (US).

(72) **Inventors; and**

(75) **Inventors/Applicants** *(for US only)*: **DISMUKE, Keith** [US/US]; 2230 Long Cove Circle, Katy, TX 77450 (US). **KAUFMAN, Phillip, B.** [US/US]; 15435 Dobbin Drive, Conroe, TX 77384 (US). **JUPPE, Herbert** [US/US]; 5210 Mariners Harbor, Houston, TX 77041 (US). **PENNY, Glenn, S.** [US/US]; 8701 New Trails, Suite 110, The Woodlands, TX 77381 (US). **FOX, Richard, Nelson** [US/US]; 24811 North Pointe Place, Katy, TX 77494 (US). **ZHOU, Bill** [US/US]; 30 Powers Bend Way, The Woodlands, TX 77382 (US).

(74) **Agent**: **SULLIVAN, David, M.**; Crowe & Dunlevy, 20 North Broadway, Suite 1800, Oklahoma City, OK 73102 (US).

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(54) **Title**: GAS GENERATING SYSTEM FOR STIMULATION AND DELIQUIFICATION

(57) **Abstract**: A gas generating system for use in stimulation or in deliquification/dewatering includes a foam generating agent, a foam enhancing agent and a gas generating additive. The foam generating agent is absorbed or adsorbed on a first plurality of substrates and the foam boosting agent is absorbed or adsorbed on a second plurality of substrates. The gas generating additive preferably includes an acidic component contained within a releasing mechanism container and a carbonate or bicarbonate contained within a releasing mechanism container. The use of encapsulated substrate permits the staged and targeted delivery of treatment chemicals in fractures extending from the wellbore or in the wellbore itself.

GAS GENERATING SYSTEM FOR STIMULATION AND DELIQUIFICATION

FIELD OF THE INVENTION

[001] The present invention generally relates to the production of petroleum and more particularly to compositions and processes for improving the recovery of hydrocarbons, that is, gas or oil (petroleum), from a subterranean geological formation using stimulation techniques such as conventional hydraulic fracturing, slickwater fracturing, or acidizing, or for well deliquification of water and/or condensate to allow reservoirs to more efficiently produce.

BACKGROUND OF THE INVENTION

[002] Well stimulation treatments are commonly used to initiate, enhance or restore the productivity of a well. Hydraulic fracturing is a particularly common well stimulation technique that involves the high-pressure injection of specially engineered treatment fluids into the reservoir. The high-pressure treatment fluid, which often includes polymers or gellants to viscosify, thicken, or gel the treatment fluid, causes a fracture to extend away from the wellbore into the formation (reservoir) according to the natural stresses of the formation. The polymers or gellants include natural products such as polysaccharide polymers like guar gum, guar derivatives, biopolymers, cellulose and its derivatives or synthetic polymers like polyacrylamides. Viscoelastic surfactants are also widely used instead of polymers in frac fluids. Propping agents, usually called proppants,

such as grains of sand of a particular size are often mixed with the treatment fluid to keep the fracture open after the high-pressure subsides when treatment is complete. The increased permeability resulting from the stimulation operation enhances the flow of hydrocarbons into the wellbore. Proppants can include sand, glass beads, ceramic proppants, resin coated sands, resin coated ceramic proppants, on the fly coated proppants, and the like.

[003] In many recently developed reservoirs, hydraulic fracturing is used to unlock oil and gas reserves during the completion of the well. In this way, hydraulic fracturing is no longer used only in remedial stimulation efforts. Many newly completed wells are candidates for hydraulic fracturing to optimize the initial recovery of hydrocarbons.

[004] Slickwater fracturing involves using low viscosity fluids that have friction (drag) reducing polymers instead for this stimulation technique. Proppants are again used for this high pressure pumping technique. The stimulation technique of acidizing can be either fracture acidizing or matrix acidizing. In the first case, high pressure is used while in the second case the acid dissolves the formation matrix.

[005] Well deliquification is another term for well dewatering that occurs in oilfield wells that have build-ups of water, hydrocarbons or condensates that need to be removed to allow hydrocarbon liquid and gas production. Basically, the velocity of the gas is not high enough to remove the water or condensate so the well will not produce (it shuts-down or dies). Another term for this build up is liquid loading. Like stimulation, well deliquification restores well productivity.

[006] Various methods are used for deliquification including pumps, gas lift, and chemicals such as surfactants in the form of soap sticks or liquids injected downhole. These last chemical methods cause the water or condensate to foam which thereby reduces the hydrostatic head (pressure on the formation) and allows the gas to be produced.

[007] The deliquification can occur in vertical, inclined, or horizontal wells or in parts of wells that have various inclination angles in different parts of the wellbore. Therefore, this idea could be applied more effectively than current cylindrical soap sticks which would not have a tendency to move/roll down the wellbore into the horizontal part of the well from the vertical and inclined sections of the well.

[008] In some cases, however, conventional stimulation techniques fail to yield a significant improvement in production over an extended period. Water and condensate accumulate in gas wells and restrict production. In horizontal wells that have been hydraulically fractured, water and condensate tend to accumulate in vertical fractures, especially in horizontal sections of the wellbore. The accumulation of water and condensate in vertical fractures blocks the flow of gas or oil or condensate into the wellbore. Accordingly, there is a need for an enhanced stimulation technique that overcomes these and other deficiencies in the prior art.

SUMMARY OF THE INVENTION

[009] In preferred embodiments, the present invention includes a gas generating system for use in stimulation or gas well deliquification. The gas generating system preferably includes a gas generating additive, a foam generating agent and a foam enhancing

agent. The gas generating additive preferably includes an acidic component contained within a releasing mechanism container alone or with a carbonate or bicarbonate contained within the same or a different releasing container. The foam generating agent is absorbed or adsorbed on a first plurality of substrates and the foam boosting agent is absorbed or adsorbed on a second plurality of substrates. If any of the above components are solids rather than liquids, they do not need to be absorbed or adsorbed first but can be directly encapsulated as solids.

[010] In another aspect, preferred embodiments include gas generating system for use in a stimulation operation, wherein the composition includes a first plurality of substrates, wherein on each of the first plurality of substrates a foam generating chemical has been absorbed or adsorbed with and wherein each of the first plurality of substrates is encapsulated with an exterior coating. The composition further includes a second plurality of substrates, wherein on each of the second plurality of substrates a foam enhancing chemical has been absorbed or adsorbed and wherein each of the second plurality of substrates is encapsulated with an exterior coating. The foam generating chemical and the foam enhancing chemical can be encapsulated separately as noted above or mixed together before encapsulation individually.

[011] The gas generating system optionally includes a first plurality of gas generating capsules, wherein each of the first plurality of gas generating capsules includes an acidic component encapsulated within an exterior coating and a second plurality of gas generating capsules, wherein each of the second plurality of gas generating capsules

includes a carbonate or bicarbonate component encapsulated within an exterior coating.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[012] The present invention discloses a gas generating system that includes a plurality of components that are intended to be pumped downhole during a stimulation operation or a gas well deliquification process. As used herein, the term "gas generating system" refers to the prescribed group of substrates and additives that collectively work to overcome the deficiencies of the prior art. Although the present invention is not so limited, in preferred embodiments, the gas generating system can include up to three primary components: (1) pelletized or encapsulated independent gas generators; (2) a first plurality of substrates that have been treated with foam generating chemicals; and (3) a second plurality of substrates that have been treated with foam enhancing chemicals.

[013] For the purposes of this patent application, absorption generally refers to when atoms, molecules, or ions enter as a solid or liquid into a bulk phase - gas, liquid or solid material. As an example, a sponge (a porous media) will absorb water when the sponge is dry. Adsorption is similar, but refers to a surface rather than a volume: adsorption is a process that occurs when a gas or liquid solute accumulates on (or onto) the surface of a solid or, more rarely, a liquid (adsorbent), forming a molecular or atomic film (the adsorbate). It is different from absorption in which a substance diffuses into a liquid or solid to form a solution. The capsules, canisters or other terms used to describe the

encapsulated material can release their chemicals due to crushing, melting, leaching, dissolving, defusing etc. and combinations thereof. The term "release" will refer to any or all of these delivery mechanisms.

[014] The gas generators preferably can include an acidic component and a carbonate or bicarbonate. The carbonates and bicarbonates of the gas generating capsules include alkali metal, alkaline earth metal, and ammonium carbonates and bicarbonates. In an exemplar of the particularly preferred embodiments, the carbonate component is sodium bicarbonate. In a presently preferred embodiment, the gas generators include a first plurality of gas generating capsules that each includes an acidic component encapsulated within an exterior coating and a second plurality of gas generating capsules that each includes a carbonate or bicarbonate encapsulated within an exterior coating. During use, the encapsulation layer surrounding the acidic and carbonate or bicarbonates deteriorates, which allows the mixing of the acidic component and carbonate or bicarbonate. On mixing, the acidic component and carbonate or bicarbonate release gas, which enhances (stimulates) the creation of foam within the proppant pack and geologic fractures.

[015] In particularly preferred embodiments, the acidic component of the gas generating capsules is selected from the group consisting of organic acids, including, but not limited to, lactic acid, acetic acid, formic acid, citric acid, oxalic acid and uric acid and also inorganic acids (mineral acids), including but not limited to hydrochloric acid, sulfuric acid, hydrofluoric acid, nitric acid, phosphoric acid, and hydrobromic acid and

combinations thereof of the inorganic and organic acids, individually or together. In an exemplar of the particularly preferred embodiments, the acidic component is citric acid. The carbonate or bicarbonate of the gas generating capsules is preferably sodium carbonates or sodium bicarbonate. If the acidic component or carbonate or bicarbonate is presented in liquid form, it is necessary to separately encapsulate the acidic component and carbonate or bicarbonate to prevent the premature reaction of the gas generators. If the gas generators are provided in solid form, it may be acceptable to encapsulate the gas generators within the same coating. Suitable coatings further include not only lipids but also waxes and polymers identified below that do not deteriorate in the presence of encapsulated acids and bases, such as carbonates and bicarbonates.

[016] An acid alone can also be used downhole in the reservoir to react with the formation. Any ester that generates acid can be used. Solid acid precursors such as lactic acid and polylactic acid may be combined with accelerators to increase the reaction and production of gas. The resulting acid dissolves carbonate formations such a limestone and dolomite to generate gas *in situ*.

[017] Other gas generating chemicals include, but are not limited to, compounds containing hydrazine or azo groups, for example, hydrazine, azodicarbonamide, azobis (isobutyronitrile), p-toluene sulfonyl hydrazide, p-toluene sulfonyl semicarbazide, carbohydrazide, p-p' oxybis (benzenesulfonylhydrazide) and mixtures thereof. Additional examples of nitrogen gas generating chemicals which do not contain

hydrazine or azo groups and which are also useful in the present invention include, but are not limited to, ammonium salts of organic or inorganic acids, hydroxylamine sulfate, carbamide and mixtures thereof. Of these, azodicarbonamide or carbohydrazide are preferred. The gas generating chemical or chemicals utilized are combined with the well treating fluid in a general amount, depending on the amount of gas desired under downhole conditions, in the range of up to about 10% by weight of the treating fluid, more preferably in an amount in the range of from about 0.3% to about 8% and most preferably about 4%.

[018] Gas generating chemicals containing hydrazide groups in which the two nitrogen atoms are connected by a single bond as well as connected to one or two hydrogens produce gas upon reaction with an oxidizing agent. It is believed that the oxidizing agent oxidizes the hydrazide group to azo structure. Therefore, hydrazide materials containing two mutually single bonded nitrogens which in turn are also bonded to one or more hydrogens need oxidizing agents for activation. To enhance the water solubility of such materials, alkaline pH is generally required. Occasionally, additional chemicals may be needed to increase the rate of gas production.

[019] The gas generating system optionally includes a first plurality of substrates absorbed or adsorbed with foam generating (foamer) chemicals. The foam generating substrates are preferably manufactured by absorbing or adsorbing a substrate as the material with a foam generating chemical. The foam generating chemical, if it is a solid, does not need a substrate and can be encapsulated directly. The foam generating chemical is

preferably a "foamer" or “soap,” which includes a surfactant component that reduces the surface tension and fluid density of the well fluid mixture (water and/or condensate) in the wellbore. Upon mixing with water and gas, foamers produce gas bubbles which lift the water or condensate from the well, thereby permitting increased production. In preferred embodiments, the foam generating chemicals include nonionic, anionic, cationic, and amphoteric/zwitterionic foaming surfactants and mixtures thereof.

[020] Typical nonionic foaming surfactants include polyalkoxylated alcohols or phenols, in particular ethoxylated and propoxylated alcohols and phenols; ethers or esters of sugar derivatives, such as alkylpolyglucosides and alkylpolysaccharides; polyalkoxylated fatty acid esters and amides; polyalkoxylated amines; block copolymers of polyethylene oxide and polypropylene oxide; sorbitan esters; polysorbates; and polyglycerol esters of fatty acids. Typical anionic foaming surfactants include alkyl carboxylates; alkyl sulfonates; alkyl sulfates and alkyl ether sulfates; alkylbenzene sulfonates and sulfates; alkyl ether sulfonates; α-olefin sulfonates; N-acyl amino acids, such as N-acyl sarcosinates and N-acyl glutamates; N-acyl amino sulfonates, such as N-acyl taurates; acyl hydroxycarbonates; acyl hydroxysulfonates, such as acyl isethionates; mono- and dialkyl sulfocuccinates; alkyl ether sulfosuccinates; glyceryl ether solfonates; alkyl ether phosphates; and alkyl aryl ether phosphates. Cationic foaming surfactants are generally quaternary ammonium salts from alkylamines or alkanolamines with formula $R^1R^2R^3R^4N^+X^-$, in which R^1, R^2, R^3, and R^4 are the same or different and represent an alkyl, aryl, benzyl or polyalkoxylate alkyl group. In particular, the polyalkoxylated alky group

represents alkyl polyethylene oxides or alkyl polypropylene oxides. Some examples of cationic foaming surfactants include cocotrimonium chloride, stearalkonium chloride, cetyltrimonium chloride, and the like. Typical amphoteric/zwitterionic foaming surfactants include amine oxides; alkyl betaines and sulfobetaines; alkylamido betaines and sulfobetaines, such as cocamidopropyl betaine; hydroxysultaines, such as cocamidopropyl hydroxysultaine; imidazolinium betaines and sulfobetaines; amphoacetates; and amphopropionates.

[021] Suitable foamers are available from CESI Chemical, Inc. of Marlow, Oklahoma under the CAP-FOAM brand and include others more fully disclosed in United States Patent No. 7,122,509, entitled High Temperature Foamer Formulations for Downhole Injection, the disclosure of which is herein incorporated by reference. Other suitable foamers include OFI-4880, an ammonium C6 – 10 alcohol ether sulfate from Specialty Intermediates, Inc. and Harcros Foamer 846-64, polyethylene glycol mono-C6-10 alkyl ether sulfate ammonium salt available from Harcros Chemicals, Inc. of Kansas City, Kansas. Alkyl ether sulfonates (AESs) are available from Oil Chem Technologies, Sugar Land, TX, as AES-128, AES-205, AES-506, and 7-58. Sulfonates such as alpha-olefin sulfonates (AOS) with amines such as triethanaolamine (TEA) may also provide suitable foam generating components. The foam generating chemical can be a liquid, a solid, or in another composition, such as a microemulsion. Suitable microemulsions that may be used as the foam generating chemical are disclosed in United States Patent No. 7,380,606, the disclosure of which is herein incorporated by reference.

[022] The gas generating system optionally includes a second plurality of substrates absorbed or adsorbed with foam enhancing (foam booster) chemicals. In a preferred embodiment, the foam enhancer is selected from the group of anionic surfactants such as carboxylated alkyl polyglycosides, amphoteric/zwitterionic surfactants such as amine oxides, betaines, sulfobetaines, amphopropionates, hydroxysultaines, nonionic surfactants such as fatty alcohols, fatty alcohol ethoxylates, alkanolamides, and polyalkoxylated amines and cationic surfactants including quaternary amine salts. Alternatively, the foam enhancers include solvents such as mutual solvents including ethyleneglycol monobutyl ether (EGMBE) and water-soluble polymers such as hydroxypropyl guar and polyacrylamides. Examples of alkanolamides include lauric mono- and diethanolamide, myristic mono- and diethanolamide, and coconut mono- and diethanolamide. A commercially available alkanomide is Ninol CMP, coconut monoethanolamine, from Stepan Company. Examples of amine oxides include cocoamine oxide, laurylamine oxide, and cocamidopropylamine oxide. A commercially available amine oxide is Mackamine CAO, cocamidopropylamine oxide, from Rhodia.

[023] The foam generating chemicals can often be interchanged with the foam enhancing chemicals. That is, the same chemistries can be used for both foam generation and foam enhancement. As noted above, the foam generating and foam enhancing chemicals are preferably absorbed or adsorbed on a selected substrate. Suitable substrates include proppants having a matrix which is capable of absorbing the foam generating chemical. Particularly suitable substrates include porous ceramic proppants.

[024] Alternatively, the proppant may constitute any suitable substrate that is capable of adsorbing the foam generating chemical. Suitable adsorption substrates include finely divided minerals, fibers, ground almond shells, ground walnut shells, glass beads, and ground coconut shells. Further suitable water-insoluble adsorbents include activated carbon and/or coals, silica particulates, precipitated silicas, silica (quartz sand), alumina, silica-alumina such as silica gel, mica, silicate, e.g., orthosilicates or metasilicates, calcium silicate, sand (e.g., 20-40 mesh), bauxite, kaolin, talc, zirconia, boron and glass, including glass microspheres or beads, fly ash, zeolites, diatomaceous earth, ground walnut shells, fuller's earth and organic synthetic high molecular weight water-insoluble adsorbents. In a particularly preferred embodiment, the proppant is an ultra-lightweight proppant (ULWP) manufactured from a porous ceramic having a mesh size of 20/40. Suitable proppants are available from Carbo Ceramics of Houston, Texas, and BJ Services of Houston, Texas (now part of Baker Hughes of Houston, TX) under the LiteProp™ brand name.

[025] The lower specific gravity proppants or other substrates will allow a variety of final gas generating systems to be used that can rise into the top (upper) part of vertical factures in the horizontal section of the wellbore. Higher specific gravity gas generating systems could also be used to fall/sink into the bottom of the vertical fractures in the horizontal part of the wellbore. In a particularly preferred embodiment, mixtures of various specific gravity gas generating systems could be used to more effectively cover the entire fracture volume.

[026] The process for absorbing or adsorbing the substrates with the foam generating chemicals or foam enhancing chemicals includes placing the substrates into the treatment chemicals and allowing the substrates to absorb or adsorb the treatment chemical, with or without pressure or vacuum. Due to the viscous nature of some of the treatment chemicals, it may be necessary to heat the treatment chemicals to permit increased absorption and adsorption into the substrate. Following processing, the substrates are preferably dried.

[027] In particularly preferred embodiments, each of the absorbed or adsorbed substrates is encapsulated with an exterior coating to prevent the premature release or reaction of the foam generating chemical from the substrate. Delaying the release of the treatment chemicals allows for a more targeted delivery of the foam generating and foam enhancing chemicals in the hydraulic fracture. Preferred coatings include lipid coatings, hydrogenated vegetable oils, including triglycerides such as hydrogenated cottonseed, corn, peanut, soybean, palm, palm kernel, babassu, sunflower, safflower oils. Preferred hydrogenated vegetable oils include hydrogenated palm oil, cottonseed oil, and soybean oil. The most preferred hydrogenated vegetable oil is hydrogenated soybean oil. Suitable encapsulating products are available, for example but not necessarily limited to those, from Balchem Corporation of New Hampton, New York.

[028] Alternatively, the absorbed or adsorbed substrate can be encapsulated with a suitable wax. The wax can be paraffin wax; a petroleum wax; a mineral wax such as ozokerite, ceresin, Utah wax or montan wax; a vegetable wax such as, for example, carnuba wax,

Japan wax, bayberry wax or flax wax; an animal wax such as, for example, spermaceti; or an insect wax such as beeswax, Chinese wax or shellac wax. Suitable encapsulating products are available from Balchem Corporation of New Hampton, New York, and others.

[029] In yet alternative preferred embodiments, the encapsulating layer may be formed with a water-soluble polymer. Suitable water-soluble polymers include polysaccharide, polylactide, polyglycolide, polyorthoester, polyaminoacid, polyactoacid, polyglycolacid, polyacrylamide, a chitosan and a mixture of these polymers. The encapsulating layer may also be formed from an oil-soluble polymer. Suitable oil-soluble polymers include polyester, polyolefins, polyethylene and mixtures thereof.

[030] As an alternative to impregnating the foam generating and foam enhancing chemicals on a substrate, the foam generating and foam enhancing chemicals may be used in an isolated form. For example, it may be desirable to employ solid foam generating and foam enhancing chemicals with an encapsulated boundary structure to provide for a selectively delayed release of the treatment chemicals. Alternatively, it may be desirable to use an unencapsulated solid foam generating and/or foam enhancing chemical. Such solid form foam generating and enhancing products may be provided in pellets or stick forms.

[031] The ratios of the various components within the inventive gas generating system are preferably selected based on the needs of a particular application. For example, it may be desirable to include only the foam generating substrate and foam enhancing

substrate, while excluding the gas generating capsules. In other applications, it may be desirable to exclude the foam enhancing substrates while relying solely on the benefits provided by the foam generating substrates and gas generating capsules. In yet other applications, it may be desirable to employ only the foam generating substrate or only the gas generating capsules.

[032] In a particularly preferred embodiment, the gas generating system includes between about 0 and 99% by weight of foam generating substrate, about 0 and 99% by weight of foam enhancing substrate and about 0 and 99% by weight of portions of acidic and carbonate or bicarbonate gas generating capsules. In an alternate preferred embodiment, the gas generating system includes between about 10 and 80% by weight of foam generating substrate, about 10 and 80 % by weight of foam enhancing substrate and about 10 and 90% by weight of equal portions of acidic and carbonate or bicarbonate gas generating capsules. Often the ratios of the acidic and carbonate or bicarbonate gas generating capsules are about one to one, but they may vary considerably as desired for the situation.

[033] In yet another alternate preferred embodiment, the gas generating system includes between about 15 and 80% by weight of foam generating substrate, about 20% and 80% by weight of foam enhancing substrate and about 20 and 80% by weight of portions of acidic and carbonate or bicarbonate gas generating capsules. During use, the selected gas generating system is mixed with a carrier fluid having a suitable viscosity. The carrier fluid and suspended substrates are then injected downhole, where the fracturing

fluid flows into the reservoir adjacent the well. The suspended gas generating system forms within a proppant pack that prevents the expanded fractures from closing. A viscosity breaker can then be used to reduce the viscosity of the carrier fluid to facilitate removal. The gas generating system remains captured in the fractures extending from the wellbore.

[034] Over time, exposure to the downhole environment causes the encapsulation layers covering the foam generating substrates, foam enhancer substrates and/or gas generating capsules to deteriorate. The deterioration of the exterior coatings allows the time-lapsed release of the treatment chemicals from the substrates and gas generating capsules. In a preferred embodiment, the foam generating substrates, foam enhancing substrates and gas generating capsules are configured to provide a staged release of the respective chemicals.

[035] For example, it may be desirable to increase the thickness of the gas generating capsules to delay the mixing of the citric acid and sodium bicarbonate until after the foam generating chemicals and foam enhancing chemicals have been released and allowed to mix with the fluids in the fractured reservoir. Similarly, it may be desirable to stage the release of the foam enhancing chemicals until after the foam generating chemicals have been released. Alternatively, it may be desirable to use different encapsulation products to provide for a staged release of the various treatment chemicals. For example, it may be desirable to use a lipid coating on the foam generating substrates and foam enhancing substrates while using a more durable

polymer coating on the gas generating capsules. It will be appreciated that further refinement of the staged delivery of the treatment chemicals can be accomplished by varying both the thickness and chemical composition of the encapsulation layers. Various melting point waxes, different thicknesses, different materials, and other methods can be used to vary the release time and order.

[036] It may further be desirable to manufacture different encapsulation layers within each of the various components of the gas generating system. For example, it may be desirable to encapsulate a first portion of the foam generating substrates with a quick release coating and a second portion of the foam generating substrates with a delayed release coating. In this way, the release of foam generating chemicals from the substrate can be distributed over an extended period. Similarly, it may be desirable to distribute the release of foam enhancer chemicals and gas generating chemicals over extended periods by varying the thickness and/or chemical composition and number of the encapsulation layers of the respective foam enhancing substrates and gas generating capsules.

EXAMPLES

EXAMPLE 1

[037] In a blender test, 200 ml of tap water and 0.4 ml of liquid foamer (0.4 g for solid foamer) were added to a one quart Waring blender cup. After all the foamer is dissolved in the water, the foamer solution was mixed at 1600 rpm for 30 seconds. Immediately after mixing, a timer was started to establish the half-life of the foam. The foam was poured

from the blender into a 1000 ml graduated cylinder quickly and foam height was measured. Half-life was recorded when 100 ml of water was seen in the bottom of the graduated cylinder. The results of this study are presented in TABLE 1 below:

TABLE 1

FOAM HEIGHT AND HALF-LIFE

Foamer	Foamer type	Foam height (ml)	Foam half-life (seconds)
Nacconol® 90G	Anionic	970	398
Steposol® CA-207/Nacconol® 90G (10:1, w/w)	Anionic	820	332
Foamer LLF	Anionic	780	277
Mackadet® EZ-154	Anionic + amphoteric	760	352
Steposol® CA-207	Anionic	640	214
Mackam® OK-50	Amphoteric	650	184
Mackam® LSB-50	Amphoteric	530	158
Pluronic® F98	Nonionic	440	130
Tetronic® 908	Nonionic	430	140

Foamers used:

[01] Nacconol® 90G, Stepan Company: Sodium dodecylbenzene sulfonate, solid, 90% active

[02] Steposol® CA-207, Stepan Company: alkyl ether sulfate, liquid, 60% active

[03] Foamer LLF, Harcros Chemicals: alkyl ether sulfate, liquid, 97% active

[04] Mackadet® EZ-154, Rhodia: Mixture of disodium lauryl sulfosuccinate, sodium C14-16 olefin sulfonate, and lauramidopropyl betaine, solid, 100% active

[05] Mackam® OK-50, Rhodia: cocamidopropyl betaine, liquid, 39% active

[06] Mackam® LSB-50, Rhodia: lauramidopropyl hydroxysultaine, liquid, 43% active

[07] Pluronic® F98, BASF: difunctional block copolymer surfactant, solid, 100% active

[08] Tetronic® 908, BASF: tetrafunctional block copolymer surfactant, solid, 100% active

EXAMPLE 2

[038] In a sand column test, a 6" column (0.98" diameter) was packed with a slurry of 20/40 mesh Ottawa sand, and encapsulated gas generator with/without encapsulated foamer (Foamer LLF [003] from Table 1 above) in tap water or tap water with 20% (v/v) of condensate with a 50.5 degree API Gravity. The packed sand column was immersed vertically in a water bath with a temperature of about 135 °F. Water and or water condensate mixture recovered from the sand column was weighed to calculate percent fluid recovery.

[039] The results below in Tables 2 and 3 demonstrate that encapsulated foamer helps recover more fluid in both tap water and tap water with 20% (v/v) condensate.

TABLE 2

PERCENT FLUID RECOVERY WITHOUT CONDENSATE

Time (min)	Percent fluid recovery (%)	
	Pack column with: encap. gas generator (1.0 g) and sand (100 g)	
	Without encapsulated foamer	With encapsulated foamer (2.0 g)
4	0	1.7
10	2.9	9.6
15	7.9	30.8
20	14.4	65.7
30	24.1	85.8
40	32.1	88.7
50	35.6	88.8

60	39.1	89.0
100	48.5	
120	49.2	

TABLE 3

PERCENT FLUID RECOVERY WITH 20% (V/V) CONDENSATE

Time (min)	Percent fluid recovery (%)	
	Pack column with: co-encap. gas generator (1.0 g) and sand (100 g)	
	Without encapsulated foamer	With encapsulated foamer (2.0 g)
1	0.2	0.4
1.5	11.5	11.4
2	23.7	23.5
3	33.1	45.6
4	38.7	54.3
5	39.8	59.5
6	40.4	62.1
8	40.3	65.2
10	40.3	66.8
20	40.2	67.4

[040] Results in Table 4 below demonstrate that the co-encapsulated gas generator gives higher percent fluid recovery than the separate gas generator. Note, based on comparison of the acid active weights, the separate generators can produce at least six times more gas than the co-encapsulated gas generator if completely reacted.

EXAMPLE 3

[041] The advantage of using a co-encapsulated acid (citric acid) and base (sodium bicarbonate) system compared to encapsulating them separately is shown in the Table 4 below.

TABLE 4

ADVANTAGE OF CO-ENCAPSULATION OF ACID AND BASE IN THE SAME ENCAPSULATION VS SEPARATE ENCAPSULATED ACID AND BASE

Time (min)	Percent fluid recovery (%)	
	Pack column with: encap. gas generator, encap. foamer (2.0 g) and sand (100 g)	
	Co-encapsulated acid and base[a]	Separately encap. acid and encap. base[b]
2	2.8	9.3
4	6.9	16.8
10	25.7	29.6
15	64.1	39.5
20	82.5	50.2
25	85.5	55.0
30	88.0	65.4
40	88.8	69.7
50	88.8	71.6
60	88.7	72.8

[a] Co-encapsulated acid and base: 2.0 g (58 wt% of base and 12 wt% of acid)
[b] Encapsulated acid (50% active): 3.2 g; encapsulated base (70% active): 2.8 g

[042] Since there is less total active material in the co-encapsulated acid and base, it does not provide as much recovery initially but does at longer times (more than 15 minutes).

EXAMPLE 4

ABSORPTION ON POROUS MEDIA

[043] Porous ceramic proppants with about 20% porosity made by Carbo Ceramics, Inc absorbed 18% by weight foamer at atmospheric pressure (no pressure or vacuum applied). The foamers are Specialty Intermediates OFI-4880 foamer concentrate and Harcros Foamer 846-64. A second batch was made with less loading of foamer since the final material appeared wet. 10% (wt) of heated OFI-4880 was added to the room temperature porous ceramic proppant and after 15 minutes of mixing, the foamer was absorbed into the ceramic proppant. The foamers were placed in an oven to make them less viscous and more pourable. The final product was relatively free flowing thus concluding that the foamer absorbed completely. Another sample using the same method as above was made except replacing OFI-4880 with Harcros Foamer 846-64. Again the sample was free flowing.

[044] In addition, porous ceramic proppants (20/40) were mixed with CESI CapFoam SI in ratios of 9, 10 and 15%. After initial mixing, the 9 and 10% mixtures flowed freely.

EXAMPLE 5

ADSORPTION ONTO SUBSTRATE

[045] For the encapsulated foamers, we determine that the maximum amount of Foamer LLF (a viscous liquid) that can be adsorbed onto diatomaceous earth (DE) and still give free-flowing particles was about 50%.

[046] It is clear that the present invention is well adapted to carry out its objectives and attain the ends and advantages mentioned above as well as those inherent therein. For the purposes of this disclosure and the appended claims, the term "well treatment operation" shall refer both to deliquification and stimulation operations. The phrases "loading the substrate" and "substrate has been loaded" shall refer to the process and results of: (i) of adsorbing or absorbing a selected formulation onto the substrate; or (ii) packing a solid formulation into a porous substrate. While presently preferred embodiments of the invention have been described in varying detail for purposes of disclosure, it will be understood that numerous changes may be made which will readily suggest themselves to those skilled in the art and which are encompassed within the spirit of the invention disclosed and claimed herein.

It is claimed:

1. A foam generating system for use in well treatment operations, the foam generating system comprising:

a first plurality of substrates, wherein each of the first plurality of substrates has been loaded with a foam generating chemical and wherein the each of the first plurality of substrates is encapsulated with an exterior coating;

a first plurality of gas generating capsules, wherein each of the first plurality of gas generating capsules includes an acidic component encapsulated within an exterior coating; and

a second plurality of gas generating capsules, wherein each of the second plurality of gas generating capsules includes a carbonate or bicarbonate component encapsulated within an exterior coating.

2. The foam generating system of claim 1, wherein the acidic component and the carbonate or bicarbonate component are encapsulated together within one coating.

3. The foam generating system of claim 1, wherein the acidic component is an organic acid selected from the group consisting of lactic acid, acetic acid, formic acid, citric acid, oxalic acid and uric acid.

4. The foam generating system of claim 1, wherein the carbonate or bicarbonate component is selected from the group consisting of alkali metal, alkaline earth metal, and ammonium carbonates and bicarbonates.

5. The foam generating system of claim 1, further comprising a second plurality of substrates, wherein each of the second plurality of substrates has been loaded with a foam enhancing chemical.

6. The foam generating system of claim 5, wherein each of the first and second pluralities of substrates comprise a porous media.

7. The foam generating system of claim 5, wherein each of the first and second pluralities of substrates are selected from the group consisting of finely divided minerals, fibers, ground almond shells, ground walnut shells, ground coconut shells, water-insoluble adsorbents including activated carbon and/or coals, silica particulates, precipitated silicas, silica (quartz sand), alumina, silica-alumina such as silica gel, mica, silicate, orthosilicates or metasilicates, calcium silicate, sand, bauxite, kaolin, talc, zirconia, boron and glass, glass microspheres or beads, fly ash, zeolites, diatomaceous earth, fuller's earth and organic synthetic high molecular weight water-insoluble adsorbents.

8. The foam generating system of claim 5 comprising:

between about 0 and 99 % by weight of gas generating capsules;

between about 0 and 99 % by weight of foam generating substrates; and

between about 0 and 99 % by weight of foam enhancing substrates.

9. The foam generating system of claim 8 comprising:

between about 10 and 90 % by weight of gas generating capsules;

between about 10 and 80% by weight of foam generating substrates; and

between about 10 and 80 % by weight of foam enhancing substrates.

10. The foam generating system of claim 9 comprising:

between about 15 and 80 % by weight of gas generating capsules;

between about 20 and 80% by weight of foam generating substrates; and

between about 20 and 80 % by weight of foam enhancing substrates.

11. The foam generating system of claim 5, wherein each of the second plurality of substrates is not encapsulated with an exterior coating.

12. The foam generating system of claim 5, wherein each of the second plurality of substrates is encapsulated with an exterior coating.

13. The foam generating system of claim 12, wherein the exterior coatings of the first and second pluralities of substrates are lipid or other coatings, such as waxes and polymers.

14. The foam generating system of claim 12, wherein the exterior coatings of the first and second pluralities of substrates are partially hydrogenated vegetable oil.

15. The foam generating system of claim 12, wherein the exterior coatings on the first plurality of substrates is configured to release not later than the time the exterior coatings of the first and second pluralities of gas generating capsules release.

16. The foam generating system of claim 12, wherein the exterior coatings on the first plurality of substrates is made from multiple layers of the same or different materials with the same or different thicknesses to release before or at the same time as the exterior coatings of the first and second pluralities of gas generating capsules .

17. The foam generating system of claim 12, wherein the exterior coatings of the first plurality of substrates have a different thickness than the exterior coatings of the second plurality of substrates.

18. The foam generating system of claim 1, wherein the foam generating chemical is selected from the group consisting of nonionic, anionic, cationic, amphoteric/zwitterionic foaming surfactants, and polymers, and mixtures thereof.

19. The foam generating system of claim 1, wherein the foam generating chemical is an anionic surfactant selected from the group consisting of alkyl sulfate,

alkyl ether sulfate, alkyl sulfonate, alkyl benzene sulfonate, alkyl ether sulfonate, and mixtures thereof.

20. The foam generating system of claim 1, further comprising a solid form foam enhancing chemical.

21. The foam generating system of claim 20, wherein the solid form foam enhancing chemical is encapsulated with an exterior coating.

22. The foam generating system of claim 21, wherein the foam enhancing chemical is selected from a group consisting of amphoteric/zwitterionic surfactants, anionic surfactants, nonionic surfactants, cationic surfactants, polymers, and solvents, such as mutual solvents, and mixtures thereof.

23. A method for treating a well, the method comprising the steps of:

providing a first plurality of substrates, wherein each of the first plurality of substrates has been treated with a foam generating chemical and wherein the absorbed or adsorbed substrate of each of the first plurality of substrates is encapsulated with an exterior coating;

providing a second plurality of substrates, wherein each of the second plurality of substrates has been treated with a foam enhancing chemical;

providing a first plurality of gas generating capsules, wherein each of the first plurality of gas generating capsules includes an acidic component encapsulated within an exterior coating;

providing a second plurality of gas generating capsules, wherein each of the second plurality of gas generating capsules includes a carbonate or bicarbonate encapsulated within an exterior coating;

mixing the first plurality of substrates, the second plurality of substrates, the first plurality of gas generating capsules and the second plurality of gas generating capsules into a carrier fluid to form a gas generation system; and

pumping the gas generating system into the well.

24. A foam generating system for use in a well treatment operation, the foam generating system comprising:

a foam generating component;

a foam enhancing component;

a first plurality of gas generating capsules, wherein each of the first plurality of gas generating capsules includes an acidic component encapsulated within an exterior coating; and

a second plurality of gas generating capsules, wherein each of the second plurality of gas generating capsules includes a carbonate or bicarbonate encapsulated within an exterior coating.

25. The foam generating system of claim 24, wherein the foam enhancing component comprises a solid form foam enhancing chemical.

26. The foam generating system of claim 25, wherein the solid form foam enhancing component is encapsulated with an exterior coating.

27. The foam generating system of claim 26, wherein the foam generating component comprises a first plurality of substrates, wherein each of the first plurality of substrates has been treated with a foam generating chemical.

28. The foam generating system of claim 27, wherein each of the first plurality of substrates is encapsulated with an exterior coating.

29. The foam generating system of claim 24, wherein the foam generating component comprises a solid form foam generating components.

30. The foam generating system of claim 29, wherein the solid form foam generating chemical is encapsulated within an exterior coating.

31. The foam generating system of claim 30, wherein the foam enhancing component comprises a second plurality of substrates, wherein each of the second plurality of substrates has been treated with a foam enhancing chemical.

32. The foam generating system of claim 31, wherein each of the second plurality of substrates is encapsulated with an exterior coating.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 11/45969

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - E21B 21/14 (2011.01)
USPC - 166/353; 166/354; 175/7
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 (8) - E21B 21/14 (2011.01)
USPC - 166/353; 166/354; 175/7

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)
PubWEST (PGPB,USPT,USOC,EPAB,JPAB) Terms - downhole wellbore foam acid base encapsulated time release coating capsule surfactant substrate zeolite shells silica ash carrier particles proppant carbonate bicarbonate anionic cationic
Google - (downhole OR wellbore) foam surfactant-(substrate OR zeolite OR shells OR silica OR ash)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 6,992,048 B2 (REDDY, ET AL.) 31 January 2006 (31.01.2006), col 1, ln 39-44; col 4, ln 8-12; col 4, ln 42-53; col 5, ln 60 to col 6, ln 21 X 24-26 Y 1-23, 27-32	24-26 --- 1-23, 27-32
Y	US 6,554,071 B1 (REDDY, ET AL.) 29 April 2003 (29.04.2003), col 6, ln 61 to col 7, ln 9 Y 1-23, 27-32	1-23, 27-32
A	US 2011/0155372 A1 (PANGA, ET AL.) 30 June 2011 (30.06.2011), entire document	1-32
A	US 2008/0217017 A1 (BROWN, ET AL.) 11 September 2008 (11.09.2008), entire document	1-32
A	US 2009/0301731 A1 (MCDANIEL, ET AL.) 10 December 2009 (10.12.2009), entire document	1-32
A	US 2006/0157248 A1 (HOEFER, ET AL.) 20 July 2006 (20.07.2006), entire document	1-32

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

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
07 December 2011 (07.12.2011)	16 DEC 2011
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

Form PCT/ISA/210 (second sheet) (July 2009)

PATENT COOPERATION TREATY

From the
INTERNATIONAL SEARCHING AUTHORITY

To: STEVEN C. BRUESS
MERCHANT & GOULD P.C.
P.O. BOX 2903
MINNEAPOLIS, MN 55402-0903

PCT

WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY

(PCT Rule 43*bis*.1)

Date of mailing *(day/month/year)*	07 DEC 2015
Applicant's or agent's file reference 4697.2WOU1	**FOR FURTHER ACTION** See paragraph 2 below

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US2015/048634	04 September 2015	04 September 2014

International Patent Classification (IPC) or both national classification and IPC
IPC(8) - C09K 8/68 (2015.01)
CPC - C09K 8/68 (2015.10)

Applicant FLEX-CHEM HOLDING COMPANY, LLC

1. This opinion contains indications relating to the following items:

- ☒ Box No. I Basis of the opinion
- ☐ Box No. II Priority
- ☐ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- ☐ Box No. IV Lack of unity of invention
- ☒ Box No. V Reasoned statement under Rule 43*bis*.1(a)(i) with regard to novelty, inventive step and industrial applicability; citations and explanations supporting such statement
- ☐ Box No. VI Certain documents cited
- ☐ Box No. VII Certain defects in the international application
- ☐ Box No. VIII Certain observations on the international application

2. **FURTHER ACTION**

If a demand for international preliminary examination is made, this opinion will be considered to be a written opinion of the International Preliminary Examining Authority ("IPEA") except that this does not apply where the applicant chooses an Authority other than this one to be the IPEA and the chosen IPEA has notified the International Bureau under Rule 66.1*bis*(b) that written opinions of this International Searching Authority will not be so considered.

If this opinion is, as provided above, considered to be a written opinion of the IPEA, the applicant is invited to submit to the IPEA a written reply together, where appropriate, with amendments, before the expiration of 3 months from the date of mailing of Form PCT/ISA/220 or before the expiration of 22 months from the priority date, whichever expires later.

For further options, see Form PCT/ISA/220.

Name and mailing address of the ISA/	Date of completion of this opinion	Authorized officer
Mail Stop PCT, Attn: ISA/US Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	16 October 2015	Blaine Copenheaver PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

Form PCT/ISA/237 (cover sheet) (January 2015)

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US2015/048634

Box No. I Basis of this opinion

1. With regard to the **language**, this opinion has been established on the basis of:

   ☒ the international application in the language in which it was filed.

   ☐ a translation of the international application into _____ which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1(b)).

2. ☐ This opinion has been established taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 43*bis*.1(a)).

3. ☐ With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, this opinion has been established on the basis of a sequence listing:

   a. ☐ forming part of the international application as filed:

      ☐ in the form of an Annex C/ST.25 text file.

      ☐ on paper or in the form of an image file.

   b. ☐ furnished together with the international application under PCT Rule 13*ter*.1(a) for the purposes of international search only in the form of an Annex C/ST.25 text file.

   c. ☐ furnished subsequent to the international filing date for the purposes of international search only:

      ☐ in the form of an Annex C/ST.25 text file (Rule 13*ter*.1(a)).

      ☐ on paper or in the form of an image file (Rule 13*ter*.1(b) and Administrative Instructions, Section 713).

4. ☐ In addition, in the case that more than one version or copy of a sequence listing has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that forming part of the application as filed or does not go beyond the application as filed, as appropriate, were furnished.

5. Additional comments:

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US2015/048634

Box No. V **Reasoned statement under Rule 43*bis*.1(a)(i) with regard to novelty, inventive step and industrial applicability; citations and explanations supporting such statement**

1. Statement

Novelty (N)	Claims	1-20	YES
	Claims	None	NO
Inventive step (IS)	Claims	None	YES
	Claims	1-20	NO
Industrial applicability (IA)	Claims	1-20	YES
	Claims	None	NO

2. Citations and explanations:

Claims 1-3 and 7-15 lack an inventive step under PCT Article 33(3) as being obvious over Dawson et al. (hereafter Dawson) in view of Robb et al. (hereafter Robb).

Regarding claim 1, Dawson discloses a fracturing fluid (Abstract) comprising: a time-released form of a metal complexing agent (Para. [0017]; Para. [0031]), but fails to explicitly disclose wherein the fracturing fluid is a slick-water fracturing fluid comprising a friction reducer. However, Robb is in the field of treatment fluids for subterranean formations (Robb Abstract) and teaches a slick-water fracturing fluid comprising a friction reducer (Robb Para. [0004]; Para. [0005]; Para. [0013]). It would have been obvious to one of ordinary skill in the art at the time of the invention to modify the fracturing fluid of Dawson to be a slick-water fracturing fluid comprising a friction reducer as taught by Robb. The motivation would have been that slick-water fracturing fluids comprising friction reducers are commonly used in hydraulic fracturing and require complexing agents to improve the performance of said friction reducers (Robb Para. [0004]; Para. [0005]; Para. [0013]); therefore, a time-released form of complexing agents would sustain the performance of the friction reducers in the slick-water fracturing fluids over a period of time.

Regarding claim 2, Dawson in view of Robb discloses the slick-water fracturing fluid of claim 1, but Dawson fails to explicitly disclose wherein the metal complexing agent is citric acid. However, Robb teaches citric acid as a metal complexing agent (Robb Para. [0028], ...citric acid...). It would have been obvious to one of ordinary skill in the art at the time of the invention to modify the fracturing fluid of Dawson to include citric acid as a metal complexing agent as taught by Robb. The motivation would have been that citric acid can be used to improve the performance of friction reducing polymers used in slick-water fracturing fluids (Robb Para. [0028]; Para. [0004]).

Regarding claim 3, Dawson in view of Robb discloses the slick-water fracturing fluid of claim 2. Dawson further discloses wherein the metal complexing agent is encapsulated (Para. [0017]; Para. [0031]).

Regarding claim 7, Dawson in view of Robb discloses the slick-water fracturing fluid of claim 1. Dawson further discloses wherein the metal complexing agent is present in the fracturing fluid in an amount of about 0.1 pound per thousand gallons to about 50 pounds per thousand gallons (Para. [0040]; Para. [0044]).

Regarding claim 8, Dawson in view of Robb discloses the slick-water fracturing fluid of claim 7. Dawson further discloses wherein the metal complexing agent is present in the fracturing fluid in an amount of about 0.5 pound per thousand gallons to about 25 pounds per thousand gallons (Para. [0040]; Para. [0044]).

Regarding claim 9, Dawson in view of Robb discloses the slick-water fracturing fluid of claim 7. Dawson further discloses wherein the metal complexing agent is present in the fracturing fluid in an amount of about 2 pounds per thousand gallons to about 5 pounds per thousand gallons (Para. [0040]; Para. [0044]).

Regarding claim 10, Dawson discloses a method for fracturing (Abstract), comprising: adding a time-released form of a metal-complexing agent to a fracturing fluid (Para. [0017]; Para. [0031]), wherein the time-release form of the metal-complexing agent is added in an amount of about 0.1 pound per thousand gallons to about 50 pounds per thousand gallons (Para. [0040]; Para. [0044]); and introducing the combined fracturing fluid and time-released form of a metal complexing agent into a subterranean zone (Para. [0017]), but fails to explicitly disclose wherein the fracturing is slick-water fracturing, and wherein the fracturing fluid is a slick-water fracturing fluid. However, Robb is in the field of treatment fluids for subterranean formations (Robb Abstract) and teaches slick-water fracturing using a slick-water fracturing fluid (Robb Para. [0004]; Para. [0005]; Para. [0013]). It would have been obvious to one of ordinary skill in the art at the time of the invention to modify the fracturing using a fracturing fluid in the method of Dawson to be a slick-water fracturing using a slick-water fracturing fluid as taught by Robb. The motivation would have been that slick-water fracturing fluids comprising friction reducers are commonly used in hydraulic fracturing and require complexing agents to improve the performance of said friction reducers (Robb Para. [0004]; Para. [0005]; Para. [0013]); therefore, a time-released form of complexing agents would sustain the performance of the friction reducers in the slick-water fracturing fluids over a period of time.

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US2015/048634

Supplemental Box

In case the space in any of the preceding boxes is not sufficient.
Continuation of:

Regarding claim 11, Dawson in view of Robb discloses the method for slick-water fracturing of claim 10. Dawson further discloses the metal-complexing agent (Para. [0017]; Para. [0031]), but fails to explicitly disclose wherein the metal-complexing agent is a biodegradable chelating agent. However, Robb teaches a biodegradable chelating agent (Robb Para. [0028], ...citric acid...; citric acid is inherently biodegradable). It would have been obvious to one of ordinary skill in the art at the time of the invention to modify the metal-complexing agent in the method of Dawson to be a biodegradable chelating agent as taught by Robb. The motivation would have been to select a complexing agent that does not adversely affect the environment and upon introduction into a fracture.

Regarding claim 12, Dawson in view of Robb discloses the method for slick-water fracturing of claim 11. Dawson further discloses the metal-complexing agent (Para. [0017]; Para. [0031]), but fails to explicitly disclose wherein the metal-complexing agent is citric acid. However, Robb teaches citric acid (Robb Para. [0028]). It would have been obvious to one of ordinary skill in the art at the time of the invention to modify the metal-complexing agent in the method of Dawson to be citric acid as taught by Robb. The motivation would have been that citric acid can be used to improve the performance of friction reducing polymers used in slick-water fracturing fluids (Robb Para. [0028]; Para. [0004]).

Regarding claim 13, Dawson in view of Robb discloses the method for slick-water fracturing of claim 12. Dawson further discloses wherein the time-released form of the metal-complexing agent is added in an amount of about 0.5 pound per thousand gallons to about 25 pounds per thousand gallons (Para. [0040]; Para. [0044]).

Regarding claim 14, Dawson in view of Robb discloses the method for slick-water fracturing of claim 13. Dawson further discloses the time-release form of the metal-complexing agent is added in an amount of about 2 pounds per thousand gallons to about 5 pounds per thousand gallons (Para. [0040]; Para. [0044]).

Regarding claim 15, Dawson discloses a fracturing fluid (Abstract) comprising: a time-released form of a metal complexing agent (Para. [0017]; Para. [0031]), wherein the time released form of the metal complexing agent is present in the fracturing fluid at about 0.1 pound per thousand gallons to about 50 pounds per thousand gallons (Para. [0040]; Para. [0044]), but fails to explicitly disclose wherein the fracturing fluid is a slick-water fracturing fluid comprising a friction reducing polymer. However, Robb is in the field of treatment fluids for subterranean formations (Robb Abstract) and teaches a slick-water fracturing fluid comprising a friction reducing polymer (Robb Para. [0004]; Para. [0005]; Para. [0013]). It would have been obvious to one of ordinary skill in the art at the time of the invention to modify the fracturing fluid of Dawson to be a slick-water fracturing fluid comprising a friction reducing polymer as taught by Robb. The motivation would have been that slick-water fracturing fluids comprising friction reducing polymers are commonly used in hydraulic fracturing and require complexing agents to improve the performance of said friction reducers (Robb Para. [0004]; Para. [0005]; Para. [0013]); therefore, a time-released form of complexing agents would sustain the performance of the friction reducers in the slick-water fracturing fluids over a period of time.

Claims 4 and 5 lack an inventive step under PCT Article 33(3) as being obvious over Dawson in view of Robb and Cesi Chemical, Inc. (hereafter Cesi).

Regarding claim 4, Dawson in view of Robb discloses the slick-water fracturing fluid of claim 3. Dawson further discloses wherein the metal complexing agent is encapsulated by a first coating (Para. [0017]; Para. [0031]), but fails to explicitly disclose wherein the first coating is a paraffin coating. However, Cesi is in the field of fracturing (Cesi Abstract; Para. [001]) and teaches a paraffin coating (Cesi, Paras. [027] and [028]). It would have been obvious to one of ordinary skill in the art at the time of the invention to modify the first coating in the fracturing fluid of Dawson to be a paraffin coating as taught by Cesi. The motivation would have been to provide a coating that can prevent the premature release of a compound (Cesi Paras. [027] and [028]).

Regarding claim 5, Dawson in view of Robb discloses the slick-water fracturing fluid of claim 3. Dawson further discloses wherein the metal complexing agent is encapsulated by a first coating (Para. [0017]; Para. [0031]), but fails to explicitly disclose wherein the first coating is a cottonseed oil coating. However, Cesi teaches a cottonseed oil coating (Cesi Para. [027]). It would have been obvious to one of ordinary skill in the art at the time of the invention to modify the first coating in the fracturing fluid of Dawson to be a cottonseed oil coating as taught by Cesi. The motivation would have been to provide a coating that can prevent the premature release of a compound (Cesi Para. [027]).

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US2015/048634

Supplemental Box

In case the space in any of the preceding boxes is not sufficient.
Continuation of:

Claim 6 lacks an inventive step under PCT Article 33(3) as being obvious over Dawson in view of Robb, Cesi and Reddy et al. (hereafter Reddy).

Regarding claim 6, Dawson in view of Robb and Cesi discloses the slick-water fracturing fluid of claim 4. Dawson further discloses wherein the metal complexing agent is encapsulated by a first coating (Para. [0017]; Para. [0031]), but fails to explicitly disclose wherein the metal complexing agent is encapsulated by a second coating, the second coating being a porous cross-linked hydrophilic polymer. However, Reddy is in the field of encapsulated chemicals for use in controlled time release applications (Reddy Abstract) and teaches a second coating, the second coating being a porous cross-linked hydrophilic polymer (Reddy Col. 3 Lns. 8-27). It would have been obvious to one of ordinary skill in the art at the time of the invention to modify the metal complexing agent encapsulated by a first coating in the fracturing fluid of Dawson by encapsulating the metal complexing agent by a second coating, the second coating being a porous cross-linked hydrophilic polymer as taught by Reddy. The motivation would have been to provide a coating that will prevent the substantial dissolution of an encapsulated chemical for a selected time period (Reddy Col. 3 Lns. 8-27).

Claims 16-20 lack an inventive step under PCT Article 33(3) as being obvious over Dawson in view of Robb and Reddy.

Regarding claim 16, Dawson in view of Robb discloses the slick-water fracturing fluid of claim 15. Dawson further discloses wherein the time-released form of the metal complexing agent is encapsulated with a first coating (Para. [0017]; Para. [0031]), but fails to explicitly disclose wherein the metal complexing agent is encapsulated within a second coating. However, Reddy is in the field of encapsulated chemicals for use in controlled time release applications (Reddy Abstract) and teaches a chemical encapsulated by a second coating (Reddy Col. 3 Lns. 8-27). It would have been obvious to one of ordinary skill in the art at the time of the invention to modify the time-released form of the metal complexing agent encapsulated with a first coating in the fracturing fluid of Dawson by encapsulating the metal complexing agent within a second coating as taught by Reddy. The motivation would have been that the second coating can be used to prevent the substantial dissolution of an encapsulated chemical for a selected time period (Reddy Col. 3 Lns. 8-27).

Regarding claim 17, Dawson in view of Robb and Reddy discloses the slick-water fracturing fluid of claim 16. Dawson further discloses the time-released metal complexing agent (Para. [0017]; Para. [0031]), wherein the time-released metal complexing agent is solid (Para. [0038]), but fails to explicitly disclose wherein the time-released metal complexing agent is citric acid. However, Robb is in the field of treatment fluids for subterranean formations (Robb Abstract) and teaches citric acid as a metal complexing agent (Robb Para. [0028], ...citric acid...). It would have been obvious to one of ordinary skill in the art at the time of the invention to modify the time-released solid metal complexing agent in the fracturing fluid of Dawson to be citric acid as taught by Robb. The motivation would have been that citric acid can be used to improve the performance of friction reducing polymers used in slick-water fracturing fluids (Robb Para. [0028]; Para. [0004]).

Regarding claim 18, Dawson in view of Robb and Reddy discloses the slick-water fracturing fluid of claim 17. Dawson further discloses the first coating (Para. [0017]; Para. [0031]), but fails to explicitly disclose wherein the first coating is a dry hydrophobic film forming material; and a second coating, wherein the second coating is a porous cross-linked hydrophilic polymer. However, Reddy teaches a first coating that is a dry hydrophobic film forming material, and a second coating that is a porous cross-linked hydrophilic polymer (Reddy Col. 3 Lns. 8-27). It would have been obvious to one of ordinary skill in the art at the time of the invention to modify the first coating in the fracturing fluid of Dawson to be a dry hydrophobic film forming material as taught by Reddy; and to modify the fracturing fluid of Dawson to include a porous cross-linked hydrophilic polymer as a second coating as taught by Reddy. The motivation would have been to provide a means for encapsulating water soluble particulate solid chemicals, the hydrophobic film forming material providing a dry shield on the encapsulated chemical and the hydrophilic coating prevent substantial dissolution of the encapsulated chemical for a selected time period (Reddy Col. 3 Lns. 8-27).

Regarding claim 19, Dawson in view of Robb and Reddy discloses the slick-water fracturing fluid of claim 17. Dawson further discloses wherein the time released form of the metal complexing agent is present in the fracturing fluid at about 0.5 pounds per thousand gallons to about 25 pounds per thousand gallons (Para. [0040]; Para. [0044]).

Regarding claim 20, Dawson in view of Robb and Reddy discloses the slick-water fracturing fluid of claim 18. Dawson further discloses wherein the time released form of the metal complexing agent is present in the fracturing fluid at about 2 pounds per thousand gallons to about 5 pounds per thousand gallons (Para. [0040]; Para. [0044]).

Claims 1-20 meet the criteria set out in PCT Article 33(4), and thus have industrial applicability because the subject matter claimed can be made or used in industry.

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference 4697.2WOU1	FOR FURTHER ACTION	see Form PCT/ISA/220 as well as, where applicable, item 5 below.
International application No. PCT/US2015/048634	International filing date *(day/month/year)* 04 September 2015	(Earliest) Priority Date *(day/month/year)* 04 September 2014
Applicant FLEX-CHEM HOLDING COMPANY, LLC		

This international search report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This international search report consists of a total of 9 sheets.

☐ It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**

a. With regard to the **language**, the international search was carried out on the basis of:

☒ the international application in the language in which it was filed.

☐ a translation of the international application into _____ which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1(b)).

b. ☐ This international search report has been established taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 43.6*bis*(a)).

c. ☐ With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, see Box No. I.

2. ☐ **Certain claims were found unsearchable** (see Box No. II).

3. ☐ **Unity of invention is lacking** (see Box No. III).

4. With regard to the **title**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2, by this Authority as it appears in Box No. IV. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. With regard to the **drawings**,

a. the figure of the **drawings** to be published with the abstract is Figure No. _____

☐ as suggested by the applicant.

☐ as selected by this Authority, because the applicant failed to suggest a figure.

☐ as selected by this Authority, because this figure better characterizes the invention.

b. ☐ none of the figures is to be published with the abstract.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2015/048634

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - C09K 8/68 (2015.01)
CPC - C09K 8/68 (2015.10)
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(8) - C09K 8/00, 8/60, 8/62, 8/66, 8/68 (2015.01)
CPC - C09K 8/00, 8/60, 8/62, 8/66, 8/68, 2208/28 (2015.10)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC - 166/308.2; 507/200, 203; IPC(8) - C09K 8/00, 8/60, 8/62, 8/66, 8/68; CPC - C09K 8/00, 8/60, 8/62, 8/66, 8/68, 2208/28 (keyword delimited)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Orbit, Google Patents, Google.
Search terms used: fracturing fluid time released complexing agent citric acid friction reducer delayed sustained controlled coating chelating paraffin cottonseed oil hydrophilic porous cross-linked polymer

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2002/0160920 A1 (DAWSON et al) 31 October 2002 (31.10.2002) entire document	1-20
Y	US 2009/0298721 A1 (ROBB et al) 03 December 2009 (03.12.2009) entire document	1-20
Y	WO 2013/019188 A1 (CESI CHEMICAL INC) 07 February 2013 (07.02.2013) entire document	4-6
Y	US 6,527,051 B1 (REDDY et al) 04 March 2003 (04.03.2003) entire document	6, 16-20

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
16 October 2015	07 DEC 2015
Name and mailing address of the ISA/ Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer Blaine Copenheaver PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

Form PCT/ISA/210 (second sheet) (January 2015)

Electronic Patent Application Fee Transmittal

Application Number:	14686237
Filing Date:	14-Apr-2015
Title of Invention:	STIMULATION OF WELLS IN NANO-DARCY SHALE FORMATIONS
First Named Inventor/Applicant Name:	Andrew Bryce Conway
Filer:	Brian Peter McCall/Amy Miller
Attorney Docket Number:	04697.0001USU1

Filed as Small Entity

Filing Fees for Utility under 35 USC 111(a)

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				
Extension-of-Time:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Miscellaneous:				
SUBMISSION- INFORMATION DISCLOSURE STMT	2806	1	90	90
		Total in USD ($)		**90**

Electronic Acknowledgement Receipt

EFS ID:	30746035
Application Number:	14686237
International Application Number:	
Confirmation Number:	2601
Title of Invention:	STIMULATION OF WELLS IN NANO-DARCY SHALE FORMATIONS
First Named Inventor/Applicant Name:	Andrew Bryce Conway
Customer Number:	23552
Filer:	Brian Peter McCall
Filer Authorized By:	
Attorney Docket Number:	04697.0001USU1
Receipt Date:	24-OCT-2017
Filing Date:	14-APR-2015
Time Stamp:	16:23:55
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	CARD
Payment was successfully received in RAM	$90
RAM confirmation Number	102517INTEFSW16243800
Deposit Account	132725
Authorized User	Brian McCall

The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows:

37 CFR 1.16 (National application filing, search, and examination fees)

37 CFR 1.17 (Patent application and reexamination processing fees)

37 CFR 1.19 (Document supply fees)

37 CFR 1.20 (Post Issuance fees)

37 CFR 1.21 (Miscellaneous fees and charges)

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1		2017-10-24--Response-NFOA--04697-0001USU1.PDF	142261 91ea181538316a994e6355ca12ee3205ead14a5d	yes	13

Multipart Description/PDF files in .zip description

Document Description	Start	End
Amendment/Req. Reconsideration-After Non-Final Reject	1	1
Applicant summary of interview with examiner	2	2
Drawings-only black and white line drawings	3	3
Specification	4	4
Claims	5	8
Applicant Arguments/Remarks Made in an Amendment	9	13

Warnings:

Information:

2	Drawings-only black and white line drawings	2017-10-24--Replacement-Figs-1-5--04697-0001USU1.PDF	641747 0f271a6161bb73c5fdef416ea01387c0ec7dfd44	no	5

Warnings:

Information:

3	Information Disclosure Statement (IDS) Form (SB08)	2017-10-24--SIDS-6--04697-0001USU1.PDF	1036351 84784a061e098cf6ecfbb0ac6dc7369e329f211a	no	5

Warnings:

Information:

4	Foreign Reference	EP0326720A1.PDF	515461 ee185345aa5288416325a086893d73a7521a781e	no	9

Warnings:					
Information:					
5	Foreign Reference	EP0505169A1.PDF	533093 d61d8cfa49daf5ebaccd62424fe8aa2e3aad910c	no	11
Warnings:					
Information:					
6	Foreign Reference	WO2009091652A2.PDF	868706 d3f7b4e0338ab71e5e06bfe1c02e42be8b643e15	no	16
Warnings:					
Information:					
7	Foreign Reference	WO2013019188A1-Dismuke.PDF	1033913 3eb35cbd23472246ea33e1b1228c185e39cf97cf	no	33
Warnings:					
Information:					
8	Non Patent Literature	EP-Search-report.PDF	275312 1f8c2631c8872bfb74aeda6ca0dbc110256106ec	no	8
Warnings:					
Information:					
9	Non Patent Literature	2015-12-07-Outgoing-Written-Opinion-of-the-ISA.PDF	318386 f81b537275f04141d23a12d110ed221c7531571f	no	5
Warnings:					
Information:					
10	Non Patent Literature	2015-12-07-Outgoing-ISA-210-International-Search-Report.PDF	97063 285e2865b76869aa94f1ff0c1af3bdae6050ec4c	no	2
Warnings:					
Information:					
11	Non Patent Literature	the-slickwater-story.PDF	185355 5e71927ba7910d34ab5f447bbb52b4a4661b0da5	no	2
Warnings:					
Information:					

12	Non Patent Literature	Huang-Ionically-crosslinked-hydrophilic-polymer-membranes.PDF	1493449 ffdf760e200b72f31c10f4ba856fbf7d000ef835	no	11
Warnings:					
Information:					
13	Non Patent Literature	Ahmed-Hydrogel-2015.PDF	2405440 5a66172f62804a4925bdad4ab1f159b05a3d025e	no	17
Warnings:					
Information:					
14	Non Patent Literature	Akin-Permeability-properties-of-charged-hydrogel-carrying-membranes.PDF	1435227 1d6368be97a6dc5c576167d885139b8e1ad5bec8	no	6
Warnings:					
Information:					
15	Non Patent Literature	MCCURDY-ProceedingsoftheTechnicalWorkshops.PDF	2842895 c1ee1b2773d8fbac8df7438bf9503942a96241a3	no	122
Warnings:					
Information:					
16	Fee Worksheet (SB06)	fee-info.pdf	30481 4ad95fcfadfe03051f0af6db23cccf14702737e6	no	2
Warnings:					
Information:					
			Total Files Size (in bytes):	13855140	

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

PTO/SB/06 (09-11)
Approved for use through 1/31/2014. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

PATENT APPLICATION FEE DETERMINATION RECORD Substitute for Form PTO-875	Application or Docket Number 14/686,237	Filing Date 04/14/2015	☐ To be Mailed

ENTITY: ☐ LARGE ☒ SMALL ☐ MICRO

APPLICATION AS FILED – PART I

FOR	(Column 1) NUMBER FILED	(Column 2) NUMBER EXTRA	RATE ($)	FEE ($)
☐ BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A	N/A	
☐ SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A	N/A	
☐ EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A	N/A	
TOTAL CLAIMS (37 CFR 1.16(i))	minus 20 =	*	X $ =	
INDEPENDENT CLAIMS (37 CFR 1.16(h))	minus 3 =	*	X $ =	
☐ APPLICATION SIZE FEE (37 CFR 1.16(s))	If the specification and drawings exceed 100 sheets of paper, the application size fee due is $310 ($155 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).			
☐ MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))				
* If the difference in column 1 is less than zero, enter "0" in column 2.			TOTAL	

APPLICATION AS AMENDED – PART II

AMENDMENT	10/24/2017	(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	RATE ($)	ADDITIONAL FEE ($)
	Total (37 CFR 1.16(i))	* 17	Minus	** 20	= 0	X $40 =	0
	Independent (37 CFR 1.16(h))	* 2	Minus	***3	= 0	X $210 =	0
	☐ Application Size Fee (37 CFR 1.16(s))						
	☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))						
						TOTAL ADD'L FEE	0

AMENDMENT		(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	RATE ($)	ADDITIONAL FEE ($)
	Total (37 CFR 1.16(i))	*	Minus	**	=	X $ =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=	X $ =	
	☐ Application Size Fee (37 CFR 1.16(s))						
	☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))						
						TOTAL ADD'L FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.
** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".
*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".
The "Highest Number Previously Paid For" (Total or Independent) is the highest number found in the appropriate box in column 1.

SLIE
DESHONNE T. MARTINO

This collection of information is required by 37 CFR 1.16. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**
If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
14/686,237	04/14/2015	Andrew Bryce Conway	04697.0001USU1	2601

23552 7590 10/03/2017

MERCHANT & GOULD P.C.
P.O. BOX 2903
MINNEAPOLIS, MN 55402-0903

EXAMINER	
LOIKITH, CATHERINE A	

ART UNIT	PAPER NUMBER
3674	

NOTIFICATION DATE	DELIVERY MODE
10/03/2017	ELECTRONIC

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Notice of the Office communication was sent electronically on above-indicated "Notification Date" to the following e-mail address(es):

USPTO23552@merchantgould.com

Applicant-Initiated Interview Summary	Application No.	Applicant(s)	
	14/686,237	CONWAY, ANDREW BRYCE	
	Examiner	Art Unit	
	CATHERINE LOIKITH	3674	

All participants (applicant, applicant's representative, PTO personnel):

(1) *CATHERINE LOIKITH*. (3)_____.

(2) *BRIAN McCALL*. (4)_____.

Date of Interview: *26 September 2017*.

Type: ☒ Telephonic ☐ Video Conference
☐ Personal [copy given to: ☐ applicant ☐ applicant's representative]

Exhibit shown or demonstration conducted: ☐ Yes ☒ No.
If Yes, brief description: _____.

Issues Discussed ☐101 ☐112 ☐102 ☒103 ☐Others
(For each of the checked box(es) above, please describe below the issue and detailed description of the discussion)

Claim(s) discussed: *1*.

Identification of prior art discussed: *Horton et al. (US 2011/0053811 A1)*.

Substance of Interview
(For each issue discussed, provide a detailed description and indicate if agreement was reached. Some topics may include: identification or clarification of a reference or a portion thereof, claim interpretation, proposed amendments, arguments of any applied references etc...)

The attorney initiated an interview with the examiner on September 26, 2017 in regards to the Non-final Office action mailed on July 28, 2017. Proposed arguments are attached. Since the font was so small on the request form, an additional document is attached to enlarge the arguments that were presented. The attorney pointed out that in the present invention, it is important for the treatment to penetrate the shale formation to change the characteristics of the formation, whereas Horton teaches an additive that prevents the fluid from entering the formation. The examiner noted that it is important that such a limitation of the fluid leaving the wellbore and entering the formation would only be persuasive if it were recited in the claim language. No amendments are entered at this time, but the attorney will file formal arguments and amendments in the future.

Applicant recordation instructions: The formal written reply to the last Office action must include the substance of the interview. (See MPEP section 713.04). If a reply to the last Office action has already been filed, applicant is given a non-extendable period of the longer of one month or thirty days from this interview date, or the mailing date of this interview summary form, whichever is later, to file a statement of the substance of the interview

Examiner recordation instructions: Examiners must summarize the substance of any interview of record. A complete and proper recordation of the substance of an interview should include the items listed in MPEP 713.04 for complete and proper recordation including the identification of the general thrust of each argument or issue discussed, a general indication of any other pertinent matters discussed regarding patentability and the general results or outcome of the interview, to include an indication as to whether or not agreement was reached on the issues raised.

☒ Attachment

/CATHERINE LOIKITH/ Primary Examiner, Art Unit 3674	

Summary of Record of Interview Requirements

Manual of Patent Examining Procedure (MPEP), Section 713.04, Substance of Interview Must be Made of Record
A complete written statement as to the substance of any face-to-face, video conference, or telephone interview with regard to an application must be made of record in the application whether or not an agreement with the examiner was reached at the interview.

Title 37 Code of Federal Regulations (CFR) § 1.133 Interviews
Paragraph (b)

In every instance where reconsideration is requested in view of an interview with an examiner, a complete written statement of the reasons presented at the interview as warranting favorable action must be filed by the applicant. An interview does not remove the necessity for reply to Office action as specified in §§ 1.111, 1.135. (35 U.S.C. 132)

37 CFR §1.2 Business to be transacted in writing.
All business with the Patent or Trademark Office should be transacted in writing. The personal attendance of applicants or their attorneys or agents at the Patent and Trademark Office is unnecessary. The action of the Patent and Trademark Office will be based exclusively on the written record in the Office. No attention will be paid to any alleged oral promise, stipulation, or understanding in relation to which there is disagreement or doubt.

The action of the Patent and Trademark Office cannot be based exclusively on the written record in the Office if that record is itself incomplete through the failure to record the substance of interviews.

It is the responsibility of the applicant or the attorney or agent to make the substance of an interview of record in the application file, unless the examiner indicates he or she will do so. It is the examiner's responsibility to see that such a record is made and to correct material inaccuracies which bear directly on the question of patentability.

Examiners must complete an Interview Summary Form for each interview held where a matter of substance has been discussed during the interview by checking the appropriate boxes and filling in the blanks. Discussions regarding only procedural matters, directed solely to restriction requirements for which interview recordation is otherwise provided for in Section 812.01 of the Manual of Patent Examining Procedure, or pointing out typographical errors or unreadable script in Office actions or the like, are excluded from the interview recordation procedures below. Where the substance of an interview is completely recorded in an Examiners Amendment, no separate Interview Summary Record is required.

The Interview Summary Form shall be given an appropriate Paper No., placed in the right hand portion of the file, and listed on the "Contents" section of the file wrapper. In a personal interview, a duplicate of the Form is given to the applicant (or attorney or agent) at the conclusion of the interview. In the case of a telephone or video-conference interview, the copy is mailed to the applicant's correspondence address either with or prior to the next official communication. If additional correspondence from the examiner is not likely before an allowance or if other circumstances dictate, the Form should be mailed promptly after the interview rather than with the next official communication.

The Form provides for recordation of the following information:
- Application Number (Series Code and Serial Number)
- Name of applicant
- Name of examiner
- Date of interview
- Type of interview (telephonic, video-conference, or personal)
- Name of participant(s) (applicant, attorney or agent, examiner, other PTO personnel, etc.)
- An indication whether or not an exhibit was shown or a demonstration conducted
- An identification of the specific prior art discussed
- An indication whether an agreement was reached and if so, a description of the general nature of the agreement (may be by attachment of a copy of amendments or claims agreed as being allowable). Note: Agreement as to allowability is tentative and does not restrict further action by the examiner to the contrary.
- The signature of the examiner who conducted the interview (if Form is not an attachment to a signed Office action)

It is desirable that the examiner orally remind the applicant of his or her obligation to record the substance of the interview of each case. It should be noted, however, that the Interview Summary Form will not normally be considered a complete and proper recordation of the interview unless it includes, or is supplemented by the applicant or the examiner to include, all of the applicable items required below concerning the substance of the interview.

A complete and proper recordation of the substance of any interview should include at least the following applicable items:
1) A brief description of the nature of any exhibit shown or any demonstration conducted,
2) an identification of the claims discussed,
3) an identification of the specific prior art discussed,
4) an identification of the principal proposed amendments of a substantive nature discussed, unless these are already described on the Interview Summary Form completed by the Examiner,
5) a brief identification of the general thrust of the principal arguments presented to the examiner,
   (The identification of arguments need not be lengthy or elaborate. A verbatim or highly detailed description of the arguments is not required. The identification of the arguments is sufficient if the general nature or thrust of the principal arguments made to the examiner can be understood in the context of the application file. Of course, the applicant may desire to emphasize and fully describe those arguments which he or she feels were or might be persuasive to the examiner.)
6) a general indication of any other pertinent matters discussed, and
7) if appropriate, the general results or outcome of the interview unless already described in the Interview Summary Form completed by the examiner.

Examiners are expected to carefully review the applicant's record of the substance of an interview. If the record is not complete and accurate, the examiner will give the applicant an extendable one month time period to correct the record.

Examiner to Check for Accuracy

If the claims are allowable for other reasons of record, the examiner should send a letter setting forth the examiner's version of the statement attributed to him or her. If the record is complete and accurate, the examiner should place the indication, "Interview Record OK" on the paper recording the substance of the interview along with the date and the examiner's initials.

Applicant Initiated Interview Request Form

Application No.: 14686237 First Named Applicant: Andrew Bryce Conway
Examiner: Catherine A. Loikith Art Unit: 3674 Status of Application: Pending

Tentative Participants:
(1) Brian McCall (68,734) (2) Examiner Loikith
(3)_____ (4)_____

Proposed Date of Interview: 09/26/2017 **Proposed Time:** 3 (◉AM ◉PM)

Type of Interview Requested:
(1) ☑ Telephonic (2) ☐ Personal (3) ☐ Video Conference

Exhibit To Be Shown or Demonstrated: ☐ YES ☑ NO
If yes, provide brief description:_____

Issues To Be Discussed

Issues (Rej., Obj., etc)	Claims/ Fig. #s	Prior Art	Discussed	Agreed	Not Agreed
(1) 103	1-7, 10-13	Horton	☐	☐	☐
(2)_____	_____	_____	☐	☐	☐
(3)_____	_____	_____	☐	☐	☐
(4)_____	_____	_____	☐	☐	☐

☐ Continuation Sheet Attached ☐ Proposed Amendment or Arguments Attached

Brief Description of Arguments to be Presented: Horton teaches a drilling fluid containing additives that prevent the drilling fluid from leaving the wellbore and entering the formation during the drilling operation while minimizing the effect on the post-drilling characteristics of the formation. This is the opposite of the claimed method, where treatment is injected into a shale formation adjacent to the wellbore to change characteristics of the formati

An interview was conducted on the above-identified application on _____

NOTE: This form should be completed and filed by applicant in advance of the interview (see MPEP § 713.01). If this form is signed by a registered practitioner not of record, the Office will accept this as an indication that he or she is authorized to conduct an interview on behalf of the principal (37 CFR 1.32(a)(3)) pursuant to 37 CFR 1.34. This is not a power of attorney to any above named practitioner. See the Instruction Sheet for this form, which is incorporated by reference. By signing this form, applicant or practitioner is certifying that he or she has read the Instruction Sheet. After the interview is conducted, applicant is advised to file a statement of the substance of this interview (37 CFR 1.133(b)) as soon as possible. This application will not be delayed from issue because of applicant's failure to submit a written record of this interview.

/Brian P. McCall/
Applicant/Applicant's Representative Signature

_____
Examiner/SPE Signature

Brian P. McCall
Typed/Printed Name of Applicant or Representative

608.280.6762
Applicant's/Applicant's Representative's Telephone Number

68734
Registration Number, if applicable

This collection of information is required by 37 CFR 1.133. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 24 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS.

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

Doc Code: M865 or FAI.REQ.INTV

PTOL-413A (08-10)
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Instruction Sheet for:
APPLICANT INITIATED INTERVIEW REQUEST FORM

(Not to be Submitted to the USPTO)

1. If this form is signed by a registered practitioner not of record, the authority to submit the Applicant Initiated Interview Request Form is pursuant to limited authority to act in a representative capacity under 37 CFR 1.34 and further proof of authority to act in a representative capacity may be required. *See* 37 CFR 1.34.

   The Office will accept the signed form as an indication that the registered practitioner not of record is authorized to conduct an interview on behalf of the principal in pursuant to 37 CFR 1.34.

   For more information, see the "Conducting an Interview with a Registered Practitioner Acting in a Representative Capacity" notice which is available on the USPTO Web site at: http://www.uspto.gov/patents/law/notices/2010.jsp.

2. This is not a power of attorney to any named practitioner. Accordingly, any registered practitioner not of record named on the form does not have authority to sign a request to change the correspondence address, a request for express abandonment, a disclaimer, a power of attorney, or other document requiring the signature of the applicant, assignee of the entire interest or an attorney of record. If appropriate, a separate power of attorney to the named practitioner should be executed and filed in the US Patent and Trademark Office.

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2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (*i.e.*, GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspection or an issued patent.
9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

DRAFT

Horton teaches a drilling fluid containing additives that prevent the drilling fluid from leaving the wellbore and entering the formation during the drilling operation while minimizing the effect on the post-drilling characteristics of the formation. This is the opposite of the claimed method, where treatment is injected into a shale formation adjacent to the wellbore to change characteristics of the formation.

PTO/SB/08a (03-15)
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(Not for submission under 37 CFR 1.99)

Application Number	14686237
Filing Date	2015-04-14
First Named Inventor	Andrew Bryce Conway
Art Unit	3676
Examiner Name	Waseem Moorad
Attorney Docket Number	04697.0001USU1

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	First Named Inventor	Andrew Bryce Conway
	Art Unit	3676
	Examiner Name	Waseem Moorad
	Attorney Docket Number	04697.0001USU1

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	1	European Search Report dated August 31, 2017, Application No. EP15780712.4, 7pgs.	

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[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	14686237
Filing Date	2015-04-14
First Named Inventor	Andrew Bryce Conway
Art Unit	3676
Examiner Name	Waseem Moorad
Attorney Docket Number	04697.0001USU1

CERTIFICATION STATEMENT

Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

☒ That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

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See attached certification statement.

The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

A certification statement is not submitted herewith.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/Brian P. McCall/	Date (YYYY-MM-DD)	2017-09-29
Name/Print	Brian P. McCall	Registration Number	68734

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2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.

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6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

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DE ES GB NL

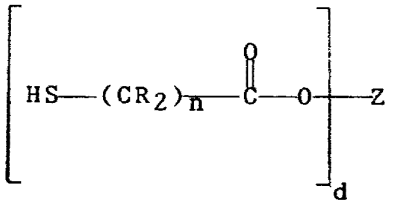
(71) Applicant: **HALLIBURTON COMPANY**
P.O. Drawer 1431
Duncan Oklahoma 73536(US)

(72) Inventor: **Brezinski, Michael**
808 West Beech
Duncan, Oklahoma 73533(US)
Inventor: **Gardner, Tommy R.**
2809 West Beech
Duncan, Oklahoma 73533(US)
Inventor: **Harms, Weldon M.**
Route 2, Box 76
Duncan, Oklahoma 73533(US)
Inventor: **Lane, Jr., James L.**
511 North 11th Street
Duncan, Oklahoma 73533(US)
Inventor: **King, Karen L.**
Route 1, Box 16D
Duncan, Oklahoma 73533(US)

(74) Representative: **Wain, Christopher Paul et al**
A.A. THORNTON & CO.
Northumberland House
303-306 High Holborn
London WC1V 7LE (GB)

(54) Controlling iron in aqueous well fracturing fluids.

(57) Ferric iron contained in a fracturing fluid is prevented from precipitating or otherwise disadvantageously reacting by adding a thioalkyl acid compound to the fracturing fluid. The thioalkyl acid compound reduces ferric ion to ferrous ion which remains in solution at pH levels below about 7.5. The thioalkyl acid compound has the formula:



where n is an integer from 1 to 10; Z is R or M; R is hydrogen, $-(CH_2)_xCH_3$, $-CH_2COOH$ or $-(CH_2)_xC_6H_5$ wherein x is 0 or an integer from 1 to 6; M is sodium, potassium, ammonium, calcium, magnesium or H_3N^+OH; and d is 1 when Z is R, or d is 1 or 2 when Z is M to match the valence of M.

EP 0 599 474 A2

This invention broadly relates to fracturing subterranean well formations to stimulate the production of oil and/or gas therefrom and, more particularly, to controlling iron in aqueous well fracturing fluids to prevent the formation of iron precipitates therein as well as to prevent other undesirable iron reactions.

The stimulation of oil and/or gas production from subterranean formations by fracturing the formations is well known to those skilled in the art. Generally, a fracturing procedure is carried out by pumping a fracturing fluid into the formation at a rate and pressure such that the formation is hydraulically fractured. The fractures are extended in the formation by continued introduction of fracturing fluid therein, and the fractures so formed are often propped open by propping agent, e.g. sand, deposited therein. Also, depending upon the type of rock making up the formation, the fracture faces can be etched with acid to form flow channels therein. Once the fractures have been formed, propping agent has been deposited therein and/or flow channels have been formed in the faces of the fractures, the hydraulic pressure exerted on the formation is released which causes the fracturing fluid to reverse flow out of the formation and the fractures to close leaving permeable passages therein through which oil and/or gas flows from the formation to the wellbore.

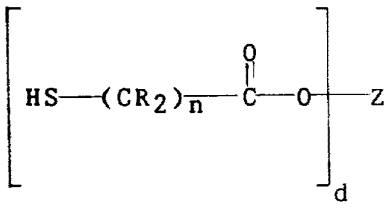
A problem which can be encountered if the fracturing fluid contains dissolved iron is the precipitation of iron compounds such as ferric hydroxide therefrom. Such precipitates can plug or reduce the permeability of the fractured formation whereby the fracturing procedure results in a reduction of oil and/or gas production instead of an increase of such production.

Another problem which can be caused by the presence of dissolved iron in a fracturing fluid comprised of a gelled aqueous polymer solution is the undesirable ferric ion cross-linking of the hydrated polymer whereby the viscosity of the fracturing fluid is undesirably increased and/or inconsistent.

While iron precipitate control additives have been developed and used heretofore, the presence of such additives in viscosified aqueous fracturing fluids can significantly hasten the destruction of the viscosifying hydrated polymer in the fluids and prevent or impede the successful completion of a fracturing procedure.

We have now devised an improved method of controlling iron in an aqueous fracturing fluid whereby ferric ion therein is reduced to ferrous ion which remains in the fracturing fluid without precipitates being produced therefrom.

According to the present invention, there is provided a method of controlling iron in an aqueous fracturing fluid having a pH below 7.5, which method comprises adding a ferric ion reducing agent to said fracturing fluid in an amount sufficient to reduce ferric ion contained therein to ferrous ion, said ferric ion reducing agent being a compound of the general formula:



wherein n is an integer from 1 to 10; Z is R or M; R is hydrogen, $-(CH_2)_xCH_3$, $-CH_2COOH$ or $-(CH_2)_xC_6H_5$ wherein x is 0 or an integer from 1 to 6; M is sodium, potassium, ammonium, calcium, magnesium or H_3N^+OH; and d is 1 when Z is R, or d is 1 or 2 when Z is M to match the valence of M.

By the method of the invention, iron contained in an aqueous fracturing fluid having a pH below about 7.5 is controlled by adding a ferric ion reducing agent to the fracturing fluid in an amount sufficient to prevent the precipitation of ferric compounds or the undesirable cross-linking of polymer in the fracturing fluid. Also, the ferric ion reducing agents of this invention generally do not bring about fracturing fluid viscosity loss to as great a degree as prior art iron control agents used heretofore. The term "controlling" and similar terms when used herein in relation to iron contained in a fracturing fluid mean that ferric iron is reduced to ferrous iron and the pH of the fracturing fluid is maintained below about 7.5 whereby ferrous iron precipitates are not formed.

Ferric iron can find its way into aqueous fracturing fluids in various ways, the most common of which are by way of the water used in forming the fracturing fluid or by the reaction of the formed fracturing fluid with iron containing compounds in the formation being fractured. When ferric iron (+3 oxidation state) exists in the fracturing fluid, it starts to form ferric hydroxide precipitate when the pH of the fluid increases to about 2.5, and it is completely precipitated when the pH reaches about 3.5. Ferrous iron (+2 oxidation state) on the other hand, remains in solution to a pH up to about 7.5.

PHARAOH, EX. 1002
P. 202

The fracturing fluid compositions of this invention are basically comprised of an aqueous solution, e.g. a gelled aqueous polymer solution or a cross-linked gelled aqueous polymer solution, and the ferric ion reducing agent. The compositions may also include one or more buffering agents to help maintain the pH of the fracturing fluid below about 7.5, preferably in the pH range of from about 1 to about 5. In addition, the compositions can include one or more other agents often added to well treatment fluids including additives for removing oxygen therefrom. Also, when the formation being fractured contains reactive sulfides, the fracturing fluid can include one or more agents for preventing the precipitation of ferrous sulfide.

A preferred ferric iron reducing agent is a compound of the above formula wherein n is 1, d is 1 and Z is R. The most preferred ferric iron reducing agent is thioglycolic acid. Other reducing agent which may be used include, for example, α-methylthioglycolic acid, methylthioglycolate. α,α-dimethylthioglycolic acid, α-phenylthioglycolic acid, methyl-α-methylthioglycolate, benzylthioglycolate, α-benzylthioglycolic acid, ammonium thioglycolate, hydroxylammonium thioglycolate, calcium dithioglycolate, β-thiopropionic acid, methyl-β-thiopropionate, sodium-β-thiopropionate and thiomalic acid.

The amount of ferric ion reducing agent effective to reduce substantially all of the ferric ion contained in, or to be contained in, a fracturing fluid composition of this invention depends on the temperature of the reduction reaction environment. A satisfactory rate of reduction is provided by an amount of ferric ion reducing agent which will produce the required reduction in about 1 hour. Generally, the ferric ion reducing agent is combined with a fracturing fluid in a minimum amount of about 0.01% by volume of the fracturing fluid to a maximum amount of about 8% by volume of the fracturing fluid.

A variety of aqueous solutions can be utilized for forming the fracturing fluid compositions of this invention. Generally, the aqueous solution is comprised of water having one or more viscosity increasing hydratable polymers dissolved therein. Examples of commonly utilized such polymers are polysaccarides including galactomannan polymers, glucomannan polymers and their derivatives. Typical of such polymers are guar gum and guar derivatives and modified cellulose such as hydroxyethylcellulose, carboxymethylcellulose, xanthan gum and other cellulose derivatives. Synthetic polymers can also be utilized examples of which include polyacrylamides, poly-2-amino-2-methyl propane sulfonic acid and others. The polymer is generally present in the aqueous solution in an amount in the range of from about 0.1% to about 2% by weight of solution to thereby produce a gelled aqueous polymer fluid having an apparent viscosity in the range of from about 2 cp to about 200 cp as determined using a Fann Model 50 viscometer. The particular concentration of the polymer depends upon the conditions of the well to be fractured and other factors well known to those skilled in the art.

As mentioned above, aqueous polymer solutions can be cross-linked to increase their viscosity by adding a cross-linking compound thereto. Typical such cross-linking compounds are organic chelates of titanium, zirconium, aluminum or other multivalent metals. The selection of an appropriate cross-linking compound depends upon the particular polymer used, and the amount of cross-linking compound depends upon the well conditions and other factors. Generally, a cross-linking compound is added to an aqueous polymer solution in an amount in the range of from about 0.0005% to about 1.2% by weight of the solution to produce a cross-linked gelled aqueous polymer fluid having a viscosity in the range of from about 40 cp to about 6000 cp(.04 to 6 Pa s) as determined using a Fann Model 50 viscometer.

As mentioned above, the gelled aqueous polymer fracturing fluid and/or gelled aqueous cross-linked polymer fracturing fluid must have a pH below about 7.5 to prevent the precipitation of ferrous compounds therefrom. The pH of the fracturing fluid composition can be adjusted if necessary using acids, buffering agents and mixtures of acids and bases. Preferably, the pH of the fracturing fluid is adjusted to a level in the range of from about 1 to about 5 and a buffering agent selected from the group consisting of carbon dioxide, organic acids, e.g., acetic or formic acid, acid salts, e.g., ammonium bisulfite and inorganic acids, e.g., hydrochloric acid or sulfuric acid is added to the fracturing fluid to maintain the pH within that range. The most preferred buffering agent is formic acid.

Other components and additives that can be combined with the compositions of the present invention include acids, sulfide reactants or scavengers such as aldehydes or ketones, surfactants, corrosion inhibitors, fluid loss additives, biocides, non-emulsifying agents and mutual solvents. Such components and additives are well known to those skilled in the art, and their use depends on the conditions of the subterranean formation to be fractured and other factors.

In order to further illustrate the methods and compositions of the present invention, the following examples are given.

PHARAOH, EX. 1002
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Example 1

A quantity of an aqueous treatment fluid recovered from the Antrim Shale formation containing ferric hydroxide precipitate (90 ppm ferric ion) was obtained having a pH of 6.26. The aqueous suspension of ferric hydroxide was divided into samples and various iron control additives including a ferric ion reducing agent of this invention were added to the samples in quantities equivalent to 20 pounds (9.06kg) of additive per 1000 U.S. gallons (3.79m^3) of aqueous suspension. The ferric ion reducing agent of the present invention used was thioglycolic acid and the other additives were prior art iron control additives, namely, citric acid, hydroxylamine and the ferric ion reducing composition described in United States Patent No. 4,683,954 issued on August 4, 1987, i.e., a mixture of hydroxylamine hydrochloride, gluconodeltalactone and a catalytic amount of cuprous ion.

The samples containing the additives were heated from ambient to 125 °F (51 °C) over a time period of about 1 hour. None of the prior art additives reacted with the aqueous ferric hydroxide suspension which retained its original opaque orange color. The sample to which the thioglycolic acid was added reacted whereby the ferric ion in the precipitate was reduced to ferrous ion and dissolved. As the reaction took place, the suspension was converted from opaque orange to a clear colorous solution.

Example 2

An aqueous fracturing fluid containing a guar gum viscosifying polymer in an amount of about 0.36% by weight of the aqueous polymer solution was prepared having a viscosity of 19.5 cp(.0195 Pa s) as determined by a Fann Model 50 viscometer. The polymer solution was divided into two test samples, to one of which was added thioglycolic acid in an amount of 0.05% by weight of the resulting solution. The ferric ion reducing composition described in U.S. Patent No. 4,683,954 issued on August 4, 1987, i.e., a mixture of hydroxylamine hydrochloride, gluconodeltalactone and a catalytic amount of cuprous ion was added to the other polymer solution sample in an amount of about 0.12% by weight of the resulting solution. The viscosities of the test samples containing the additives were continuously monitored over time after the addition of the additives utilizing a Fann Model 50 viscometer at 300 rpm. The results of the tests are set forth and compared in the Table below.

TABLE

Additive Effect on Fracturing Fluid Viscosity

Additive	Additive Quantity, % by wt.	Viscosity, cp (Pa s)							
		Initial	4 min.	5 min.	7 min.	9 min.	15 min.	20 min.	25 min.	30 min.
Additive of this Invention[1]	0.36	19.5 (.0195)	19.5 (.0195)	19.0 (.019)	19.0 (.019)	19.0 (.019)	18.5 (.0185)	18.5 (.0185)	18.0 (.018)	18.0 (.018)
Prior Art Additive[2]	0.36	19.5 (.0195)	19.0 (.019)	18.5 (.0185)	18.0 (.018)	17.5 (.0175)	15.5 (.0155)	14.0 (.014)	12.0 (.012)	11.0 (.011)

[1] Thioglycolic acid

[2] hydroxylamine hydrochloride-gluconodeltalactone-cuprious ion additive of U.S. Patent No. 4,683,954

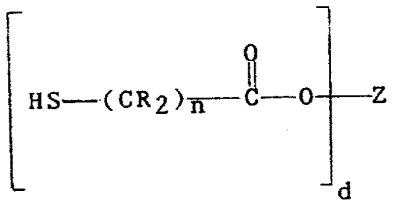
From Table I it can be seen that the ferric ion reducing additive of the present invention causes viscosity reduction to a substantially lesser degree than does the prior art additive tested.

Claims

1. A method of controlling iron in an aqueous fracturing fluid having a pH below 7.5, which method comprises adding a ferric ion reducing agent to said fracturing fluid in an amount sufficient to reduce ferric ion contained therein to ferrous ion, said ferric ion reducing agent being a compound of the

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general formula:



wherein n is an integer from 1 to 10; Z is R or M; R is hydrogen, $-(CH_2)_xCH_3$, $-CH_2COOH$ or $-(CH_2)_xC_6H_5$ wherein x is 0 or an integer from 1 to 6; M is sodium, potassium, ammonium, calcium, magnesium or H_3N^+OH; and d is 1 when Z is R, or d is 1 or 2 when Z is M to match the valence of M.

2. A method according to claim 1, wherein the reducing agent is added to the aqueous fracturing fluid in an amount of from 0.01% to 8% by volume of said fracturing fluid.

3. A method according to claim 1 or 2, wherein n is 1, d is 1 and Z is R.

4. A method according to claim 1,2 or 3, wherein the reducing agent is thioglycolic acid.

5. A method according to claim 1, 2, 3 or 4, wherein the aqueous fracturing fluid is a gelled aqueous polymer solution, a cross-linked gelled aqueous polymer solution, or an emulsion or foam containing a gelled aqueous polymer solution or cross-linked gelled aqueous polymer solution.

6. A method according to claim 5, wherein the fracturing fluid is a gelled aqueous polymer solution containing polymer in an amount of from 0.1% to 2% by weight of said solution.

7. A method according to any of claims 1 to 6, which further comprises adding a buffering agent to the fracturing fluid to maintain the pH of said fracturing fluid in the range from 1 to 5.

8. A method according to claim 7, wherein the buffering agent is carbon dioxide, an organic acid, an acid salt or an inorganic acid.

9. A method according to claim 8, wherein the buffering agent is formic acid.

10. A method of fracturing a subterranean well formation wherein there is used a fracturing fluid made by the method of any of claims 1 to 9.

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(71) Applicant *(for all designated States except US)*: **AKZO NOBEL CHEMICALS INTERNATIONAL B.V.** [NL/NL]; Stationsstraat 77, NL-3811 MH Amersfoort (NL).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **NASR-EL-DIN, Hisham** [CA/US]; 2911 Colton Place, College Station, TX 77845 (US). **DE WOLF, Cornelia, Adriana** [NL/NL]; Kraaiheide 59, NL-6961 PC Eerbeek (NL). **NASR-EL-DIN MAHMOUD, Mohamed, Ahmed** [EG/SA]; KFUPM - Mail Box 1688, Dhahran, 31261 (SA).

(74) Agent: **DE VRIES, Adriaan, Jacobus c.s.**; Akzo Nobel N.V., Legal, IP & Compliance, P.O. Box 9300, NL-6800 SB Arnhem (NL).

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(54) **Title**: TREATMENT OF SHALE FORMATIONS USING A CHELATING AGENT

(57) **Abstract**: The present invention relates to a process fortreatinga shaleformation comprising introducing a fluid containing glutamic acid N,N-diacetic acid or a salt thereof (GLDA), methylglycine N,N-diacetic acid or a salt thereof (MGDA),and/or N- hydroxyethyl ethylenediamine N,N',N'-triacetic acid or a salt thereof (HEDTA) into the formationwhich process may optionally contain an additional fracturing step.

Treatment of shale formations using a chelating agent

The present invention relates to a process for treating shale formations with a fluid that contains glutamic acid N,N-diacetic acid or a salt thereof (GLDA), methylglycine N,N-diacetic acid or a salt thereof (MGDA), and/or N-hydroxyethyl ethylenediamine N,N',N'-triacetic acid or a salt thereof (HEDTA).

Subterranean formations from which oil and/or gas can be recovered can contain several solid materials contained in porous or fractured rock formations. The naturally occurring hydrocarbons, such as oil and/or gas, are trapped by the overlying rock formations with lower permeability. The reservoirs are found using hydrocarbon exploration methods and often one of the purposes of withdrawing the oil and/or gas therefrom is to improve the permeability of the formations. The rock formations can be distinguished by their major components and one category is formed by the so-called shale formations, which contain very fine particles of many different clays covered with organic materials to which gas and/or oil are adsorbed. Shale amongst others contains many clay minerals like kaolinite, illite, chlorite, smectite, and montmorillonite and as well, quartz, feldspars, carbonates, pyrite, organic matter, and cherts.

One process to make a formation more permeable is a matrix acidizing process, wherein an acidic fluid is introduced into the formations trapping the oil and/or gas, the acidic fluid dissolving the carbonate and creating high permeability streaks, which enhances well performance.

In the oil industry, there are two generally recognized ways to improve the flow of oil or gas from shale, matrix acidizing and hydraulic fracturing. In the first process acids are applied to partly dissolve the shale rock, thus creating flow channels and increasing the permeability of the formation. In the second treatment pressure is

applied to open the shale formation by creating fractures. The common way to explore oil and/or gas from shale formations by hydraulic fracturing is treatment with water at neutral pH. Reactive fluids are better as they etch the surface of the fractures, creating flow channels which enhance the conductivity of the fracture and rock permeability around the fracture. The choice between acidizing or hydraulic fracturing is often determined by the natural permeability of the shale formation. Hydraulic fracturing is more often preferred in a lower permeability shale.

SPE 106815, Surface Reactive Fluid's Effect on Shale, from Bill Grieser et al., presented at the 2007 SPE Production and Operations Symposium held in Oklahoma City Oklahoma USA, March 31-April 3, 2007, discloses that though shale only exhibits an insignificant bulk solubility in acids, reactive fluids seem to be capable of enhancing gas diffusion into and through narrow-aperture induced fractures and increasing surface area for flow of gas from the shale matrix. The reactive fluid tested in this document is a fluid containing 3 wt% HCl or a fluid containing 5 wt% acetic acid. The reactive fluid is said to cause the shale to become acid-etched and gas to flow.

US 3,700,280 discloses the production of oil from a shale formation using a chelating agent such as EDTA. In this document it is indicated that for removing the oil from the shale a first step involves treating the shale with a high temperature fluid or steam and then subsequently recovering the decomposed dawsonite in the shale with a chelating agent solution. US 3,700,028 does not disclose the use of GLDA, MGDA, and/or HEDTA, nor does it acknowledge the exploration of oil and/or gas by an acidificaton or acid etching step.

GB 2420577 discloses an aqueous fluid containing a choline salt to reduce shale swelling. It is said that scale control additives may be added which can be a chelating agent like for example a salt of EDTA or NTA.

US 2006/0073984 discloses a fracturing fluid containing a chelating agent chosen from a group of alternatives, such as for example HEDTA, that serves as a shale hydration inhibition agent, an agent that prevents a fractured shale formation to swell. Nowhere in this document it is disclosed or suggested that the fluid described therein that may contain HEDTA serves to treat the fractured shale formation as defined herein i.e. to increase permeability by partly dissolving the formation, remove small particles and/or inorganic scale. In addition this document does not contain any hint to choose HEDTA from the list of alternatives disclosed.

WO 2009/086954 discloses the good solubility of GLDA in acidic solutions. Because of this good solubility, the document discloses the use of GLDA as a chemical in the oil field for example in a fracturing process. However, this document does not explicitly disclose a process to treat a subterranean shale formation comprising a fluid containing GLDA to achieve a treatment of the formation i.e. to increase permeability by at least partly dissolving the formation, remove small particles and/or inorganic scale. Also in this document no suggestion is made that a fluid containing GLDA would be capable of achieving a beneficial effect in a shale formation.

US 2008/200354 discloses a method to clean a wellbore that contains a filter cake with a fluid containing an iminodiacetic acid. The iminodiacetic acid may be selected from a group of compounds, also listing GLDA. The document specifies that filter cakes can give superior stability in shale formations, and as such that the breaker fluid can be used in several well types, but the breaker fluid is only disclosed to break down the filter cake and no disclosure of it having any effect on the formation itself is made.

Shale formations contain various types of clay minerals and a high concentration of very fine particles. As a result, the use of acids like HCl, phosphoric acid or acetic acid will give an insufficient acid etching effect. In addition, contacting shale with these acids was found to give poor results in some cases, for example acetic acid leads to undesired swelling effects in the formation, hydrogen chloride to undesired corrosivity side effects, and phosphoric acid is highly undesired in the environment. The capability of the conventional acids to desorb oil and/or gas from the shale formation was also found to be subject to improvement.

An effective reactive fluid should be compatible with the asphaltene in the kerogen, prevent iron precipitation, be compatible with the clays, give no environmental issue with flow back, give better flowback, have low viscosity so it can penetrate into the small fractures and micro channels, dissolve carbonates and other inorganic components, and help to release the adsorbed oil/gas from the organic layer.

The present invention aims to provide a process in which many of the above attendant disadvantages of treating shale with an acid like HCl are avoided and which leads to the benefits as indicated above.

It has been found that when using a fluid for the formation treatment in which GLDA, MGDA, and/or HEDTA are used, the above disadvantages are avoided to a great extent and further improvements in exploring oil and/or gas from the shale were found.

Accordingly, the present invention provides a process for treating a shale formation comprising introducing a fluid containing L-glutamic acid N,N-diacetic acid or a salt thereof (GLDA), methylglycine N,N-diacetic acid or a salt thereof (MGDA), and/or

N-hydroxyethyl ethylenediamine N,N',N'-triacetic acid or a salt thereof (HEDTA) into the formation.

The term treating in this application is intended to cover any treatment of the formation with the fluid. It specifically covers treating the shale formation with the fluid to achieve at least one of (i) an increased permeability by at least partial dissolution of the formation, (ii) the removal of small particles, and (iii) the removal of inorganic scale, and so enhance the well performance and enable an increased production of oil and/or gas from the formation. At the same time it may cover cleaning of the wellbore and descaling of the oil/gas production well and production equipment.

When the treatment as indicated above, resulting in increased permeability by at least partial dissolution of the formation, is done with an acidic fluid at a pressure below the fracture pressure of the formation, the treatment is normally understood to be an acidizing treatment. When done above fracture pressure, the same treatment is considered an acidic fracturing treatment. Both acidizing treatment processes and acidic fracturing treatment processes are covered by the present invention.

Surprisingly, it was found that GLDA, MGDA, and HEDTA do not degrade the shale in the formation to give many small particles, as is the case with acidic treatment fluids based on other acids like HCl. GLDA, MGDA, and/or HEDTA act much more selectively on the carbonate in the formation and dissolve this carbonate material, leaving the other constituents in the shale quite unaffected. Therefore, when using the process of the invention, the disadvantages caused by many fines, which are primarily to do with fines migration causing particles suspended in the produced fluid to bridge the pore throats near the wellbore, and so reducing well productivity, can be largely avoided. Damage created by fines

usually is located within a radius of 3 to 5 ft [1 to 2 m] of the wellbore, but can also occur in gravel-pack completions. In addition, the process of the invention provides an improved permeability of the formation.

In addition, it was found that GLDA, MGDA and HEDTA are fully compatible with the clays present in the shale and do not induce clay swelling, in contrast to HCl. Clay swelling, the process in which a liquid is absorbed between the layers of the clay, results in an increase in the volume of the clay particles and can thus result in the blockage of the narrow pores, reducing the permeability of the formation and thus ultimately leading to a reduced flow of oil and/ or gas towards the wellbore.

In a preferred embodiment the process of the invention involves an additional fracturing step (when the fluid of the invention is acidic to give an acidic fracturing process). Accordingly, the invention also relates to a process for treating a shale formation comprising a step of fracturing the shale formation and a step of introducing a fluid containing glutamic acid N,N-diacetic acid or a salt thereof (GLDA), methylglycine N,N-diacetic acid or a salt thereof (MGDA), and/or N-hydroxyethyl ethylenediamine N,N',N'-triacetic acid or a salt thereof (HEDTA) into the formation, wherein the fracturing step can take place before introducing the fluid into the formation, while introducing the fluid into the formation or subsequent to introducing the fluid into the formation.

If fracturing takes place while introducing the fluid into the formation, the fluid containing GLDA, MGDA, and/or HEDTA can function as both the treatment and the fracturing fluid and will be introduced into the formation under a pressure above the fracture pressure of the treated formation. In this way, the process has a real economic benefit as instead of two fluids only one fluid needs to be used.

It was found that a fracturing step gives the fluid a better flow through the formation, and makes it possible for a higher area of the formation to be treated

with the fluid containing GLDA, MGDA, and/or HEDTA, thus enabling a higher oil and/or gas production from the shale.

In addition, the fluid containing GLDA, MGDA, and/or HEDTA was found to be very suitable for recycling fracturing fluid and transporting particles, fines, deposits created by fracturing the shale formation. For example, the fluid containing GLDA, MGDA, and/or HEDTA was found to be useful in keeping the fractures formed by the fracturing step open and in addition capable of transporting any particles, fines, deposits outside the formation, while at the same time it was found to be capable of creating further channels into the formation as well as etched surfaces thereon by dissolving certain acid-soluble constituents, like carbonates, in the shale.

In addition, it was found that the fluid containing GLDA, MGDA and/or HEDTA does not weaken the shale, increasing the longevity of the formed fractures as they are less prone to closure due to the formation pressure.

In addition it was established that in the processes of the present invention the fluid used does not only increase the permeability but also plays a role in limiting swelling of the shale which swelling would negatively affect the created permeability improvement.

Moreover, it was found that the fluids of the invention are very suitable for desorbing the kerogen, gas and/or oil from the shale formation and are additionally compatible to a high extent with the kerogen, crude oil and/or gas. Contrary to what is suggested in prior art documents when treating shale with chelating agents, when using the fluids of the present invention less heating is needed as the fluids of the present invention have a much more favourable pH profile and are so compatible with the oil, gas, and organics to which they are adsorbed that they

need not be liquefied to the same extent by heat but give a good desorption and flow at a much lower temperature already.

In addition, the fluids of the present invention require much lower amounts of -and sometimes even can do without - certain additives, like especially antisludge additves, corrosion inhibitors, and corrosion inhibitor intensifiers. Especially when the fluids of the present invention have a low pH, they need significantly lower amounts of these additives while having the same effectiveness.

The GLDA, MGDA, and/or HEDTA are preferably used in an amount of between 1 and 30 wt%, more preferably between 3 and 30 wt%, even more preferably between 5 and 20 wt%, on the basis of the total weight of the fluid.

Salts of GLDA, MGDA, and/or HEDTA that can be used are their alkali metal, alkaline earth metal, or ammonium full and partial salts. Also mixed salts containing different cations can be used. Preferably, the sodium, potassium, and ammonium full or partial salts of GLDA, MGDA, and/or HEDTA are used.

In a preferred embodiment GLDA is used, as this material gives clearly the best results. This is amongst others because it was found that HEDTA leaches iron from the chlorite clay minerals more than it leaches calcium from calcite. Leaching more iron from chlorite may cause some fines migration. If the shale formation contains high percentage of chlorite, it is not advised to use HEDTA. In addition, MGDA also does not give as good results as GLDA because it is not as selective on calcite as GLDA. Another advantage of both GLDA and HEDTA is that these compounds are better for use in higher concentrations, in the case of GLDA in even more concentrated form than any of the other chelating agents over a broad pH range.

The fluids of the invention are preferably aqueous fluids, i.e. they preferably contain water as a solvent for the other ingredients, though other solvents may be added as well, as further explained below.

The pH of the fluids of the invention can range from 1.7 to 14. Preferably, however, it is between 3 and 13, as in the very acidic ranges of 1.7 to 3 and the very alkaline range of 13 to 14 some undesired side effects may be caused by the fluids in the formation, such as too fast dissolution of carbonate giving excessive CO_2 formation or an increased risk of reprecipitation. For a better carbonate dissolving capacity the pH is preferably acidic. On the other hand, it must be realized that highly acidic solutions are more expensive to well tubulars. Consequently, the solution even more preferably has a pH of 3 to 6.

The shale formation contains preferably at least a portion of a calcareous shale type.

The fluid may contain other additives that improve the functionality of the stimulation action and minimize the risk of damage as a consequence of the said treatment, as is known to anyone skilled in the art.

The fluid of the invention may in addition contain one or more of the group of anti-sludge agents, (water-wetting or emulsifying) surfactants, corrosion inhibitors, mutual solvents, corrosion inhibitor intensifiers, foaming agents, viscosifiers, wetting agents, diverting agents, oxygen scavengers, carrier fluids, fluid loss additives, friction reducers, stabilizers, rheology modifiers, gelling agents, scale inhibitors, breakers, salts, brines, pH control additives such as further acids and/or bases, bactericides/biocides, particulates, crosslinkers, salt substitutes (such as tetramethyl ammonium chloride), relative permeability modifiers, sulfide

scavengers, fibres, nanoparticles, consolidating agents (such as resins and/or tackifiers), combinations thereof, or the like.

The mutual solvent is a chemical liquid additive that is soluble in oil, water, acids (often HCl based), and other well treatment fluids, (see also http://www.glossary.oilfield.slb.com). In many cases the mutal solvent makes that the oil and water based liquids which are ordinarily immiscible liquids combine with each other, and in preferred embodiments form a clear solution. Mutual solvents are routinely used in a range of applications, controlling the wettability of contact surfaces before, during and/or after a treatment, and preventing or breaking emulsions. Mutual solvents are used, as insoluble formation fines pick up organic film from crude oil. These particles are partially oil-wet and partially water-wet. This causes them to collect materials at any oil-water interface, which can stabilize various oil-water emulsions. Mutual solvents remove organic films leaving them water-wet, thus emulsions and particle plugging are eliminated. If a mutual solvent is employed, it is preferably selected from the group which includes, but is not limited to, lower alcohols such as methanol, ethanol, 1-propanol, 2-propanol, and the like, glycols such as ethylene glycol, propylene glycol, diethylene glycol, dipropylene glycol, polyethylene glycol, polypropylene glycol, polyethylene glycol-polyethylene glycol block copolymers, and the like, and glycol ethers such as 2-methoxyethanol, diethylene glycol monomethyl ether, and the like, substantially water/oil-soluble esters, such as one or more C2-esters through C10-esters, and substantially water/oil-soluble ketones, such as one or more C2-C10 ketones. The mutual solvent is preferably present in an amount of 1 to 50 wt% on total fluid.

A preferred water/oil-soluble ketone is methyl ethyl ketone.
A preferred substantially water/oil-soluble alcohol is methanol.
A preferred substantially water/oil-soluble ester is methyl acetate.

A more preferred mutual solvent is ethylene glycol monobutyl ether, generally known as EGMBE

The amount of glycol solvent in the solution is preferably about 1 wt% to about 10 wt%, more preferably between 3 and 5 wt%. More preferably, the ketone solvent may be present in an amount from 40 wt% to about 50 wt%; the substantially water-soluble alcohol may be present in an amount within the range of about 20 wt% to about 30 wt%; and the substantially water/oil-soluble ester may be present in an amount within the range of about 20 wt% to about 30 wt%, each amount being based upon the total weight of the solvent in the fluid.

In one embodiment the mutual solvent can be used as a preflush or postflush material, i.e. in such embodiment will be introduced into the formation before or after the treatment with the treatment fluid.

The surfactant can be any surfactant known in the art and can be nonionic, cationic, anionic, and zwitterionic. Preferably, the surfactant is nonionic or anionic. Even more preferably, the surfactant is anionic.

The nonionic surfactant of the present composition is preferably selected from the group consisting of alkanolamides, alkoxylated alcohols, alkoxylated amines, amine oxides, alkoxylated amides, alkoxylated fatty acids, alkoxylated fatty amines, alkoxylated alkyl amines (e.g., cocoalkyl amine ethoxylate), alkyl phenyl polyethoxylates, lecithin, hydroxylated lecithin, fatty acid esters, glycerol esters and their ethoxylates, glycol esters and their ethoxylates, esters of propylene glycol, sorbitan, ethoxylated sorbitan, polyglycosides and the like, and mixtures thereof. Alkoxylated alcohols, preferably ethoxylated alcohols, optionally in combination with (alkyl) polyglycosides, are the most preferred nonionic surfactants.

The anionic (sometimes zwitterionic, as two charges are combined into one compound) surfactants may comprise any number of different compounds, including sulfonates, hydrolyzed keratin, sulfosuccinates, taurates, betaines, modified betaines, alkylamidobetaines (e.g., cocoamidopropyl betaine).

Examples of surfactants that are also foaming agents that may be utilized to foam and stabilize the treatment fluids of this invention include, but are not limited to, betaines, amine oxides, methyl ester sulfonates, alkylamidobetaines such as cocoamidopropyl betaine, alpha-olefin sulfonate, trimethyl tallow ammonium chloride, C8 to C22 alkyl ethoxylate sulfate, and trimethyl coco ammonium chloride.

Suitable surfactants may be used in a liquid or powder form.

Where used, the surfactants may be present in the fluid in an amount sufficient to prevent incompatibility with formation fluids, other treatment fluids, or wellbore fluids at reservoir temperature.

In an embodiment where liquid surfactants are used, the surfactants are generally present in an amount in the range of from about 0.01% to about 5.0% by volume of the fluid.

In one embodiment, the liquid surfactants are present in an amount in the range of from about 0.1% to about 2.0% by volume of the fluid, more preferably between 0.1 and 1 volume %.

In embodiments where powdered surfactants are used, the surfactants may be present in an amount in the range of from about 0.001% to about 0.5% by weight of the fluid.

The antisludge agent can be chosen from the group of mineral and/or organic acids as also used to stimulate hydrocarbon bearing formations. The function of the acid is to dissolve acid-soluble materials so as to clean or enlarge the flow

channels of the formation leading to the wellbore, allowing more oil and/or gas to flow to the wellbore.

Problems are caused by the interaction of the (usually concentrated, 20-28% HCl) stimulation acid and certain crude oils (e.g. asphaltic oils) in the formation to form sludge. Interaction studies between sludging crude oils and the introduced acid show that permanent rigid solids are formed at the acid-oil interface when the aqueous phase is below a pH of about 4. No films are observed for non-sludging crudes with acid.

These sludges are usually reaction products formed between the acid and the high molecular weight hydrocarbons such as asphaltenes, resins, etc.
Methods for preventing or controlling sludge formation with its attendant flow problems during the acidization of crude-containing formations include adding "anti-sludge" agents to prevent or reduce the rate of formation of crude oil sludge, which anti-sludge agents stabilize the acid-oil emulsion and include alkyl phenols, fatty acids, and anionic surfactants. Frequently used as the surfactant is a blend of a sulfonic acid derivative and a dispersing surfactant in a solvent. Such a blend generally has dodecyl benzene sulfonic acid (DDBSA) or a salt thereof as the major dispersant, i.e. anti-sludge, component.

The carrier fluids are aqueous solutions which in certain embodiments contain a Bronsted acid to keep the pH in the desired range and/or contain an inorganic salt, preferably NaCl or KCl.

Corrosion inhibitors may be selected from the group of amine and quaternary ammonium compounds and sulfur compounds. Examples are diethyl thiourea (DETU), which is suitable up to 185°F (about 85°C), alkyl pyridinium or quinolinium salt, such as dodecyl pyridinium bromide (DDPB), and sulfur compounds, such as

thiourea or ammonium thiocyanate, which are suitable for the range 203-302°F (about 95-150°C), benzotriazole (BZT), benzimidazole (BZI), dibutyl thiourea, a proprietary inhibitor called TIA, and alkyl pyridines.

In general, the most successful inhibitor formulations for organic acids and chelating agents contain amines, reduced sulfur compounds or combinations of a nitrogen compound (amines, quats or polyfunctional compounds), and a sulfur compound. The amount of corrosion inhibitor is preferably less than 2 volume %, more preferably between 0.01 and 1 volume %, even more preferably between 0.1 and 1 volume% on total fluid.

One or more corrosion inhibitor intensifiers may be added, such as for example formic acid, potassium iodide, antimony chloride, or copper iodide.

One or more salts may be used as rheology modifiers to modify the rheological properties (e.g., viscosity and elastic properties) of the treatment fluids. These salts may be organic or inorganic.

Examples of suitable organic salts include, but are not limited to, aromatic sulfonates and carboxylates (such as p-toluene sulfonate and naphthalene sulfonate), hydroxynaphthalene carboxylates, salicylate, phthalate, chlorobenzoic acid, phthalic acid, 5-hydroxy-1-naphthoic acid, 6-hydroxy-1-naphthoic acid, 7-hydroxy-1-naphthoic acid, 1-hydroxy-2-naphthoic acid, 3-hydroxy-2-naphthoic acid, 5-hydroxy-2-naphthoic acid, 7-hydroxy-2-naphthoic acid, 1,3-dihydroxy-2-naphthoic acid, 3,4-dichlorobenzoate, trimethyl ammonium hydrochloride and tetramethyl ammonium chloride.

Examples of suitable inorganic salts include water-soluble potassium, sodium, and ammonium halide salts (such as potassium chloride and ammonium chloride), calcium chloride, calcium bromide, magnesium chloride, sodium formate, potassium formate, cesium formate, and zinc halide salts. A mixture of salts may also be used, but it should be noted that preferably chloride salts are mixed with

chloride salts, bromide salts with bromide salts, and formate salts with formate salts.

Wetting agents that may be suitable for use in this invention include crude tall oil, oxidized crude tall oil, surfactants, organic phosphate esters, modified imidazolines and amidoamines, alkyl aromatic sulfates and sulfonates, and the like, and combinations or derivatives of these and similar such compounds that should be well known to one of skill in the art.

The foaming gas may be air, nitrogen or carbon dioxide. Nitrogen is preferred.

Gelling agents in a preferred embodiment are polymeric gelling agents.
Examples of commonly used polymeric gelling agents include, but are not limited to, biopolymers, polysaccharides such as guar gums and derivatives thereof, cellulose derivatives, synthetic polymers like polyacrylamides and viscoelastic surfactants, and the like. These gelling agents, when hydrated and at a sufficient concentration, are capable of forming a viscous solution.
When used to make an aqueous-based treatment fluid, a gelling agent is combined with an aqueous fluid and the soluble portions of the gelling agent are dissolved in the aqueous fluid, thereby increasing the viscosity of the fluid.

Viscosifiers may include natural polymers and derivatives such as xantham gum and hydroxyethyl cellulose (HEC) or synthetic polymers and oligomers such as poly(ethylene glycol) [PEG], poly(diallyl amine), poly(acrylamide), poly(amino-methyl propyl sulfonate) [AMPS polymer], poly(acrylonitrile), poly(vinyl acetate), poly(vinyl alcohol), poly(vinyl amine), poly(vinyl sulfonate), poly(styryl sulfonate), poly(acrylate), poly(methyl acrylate), poly(methacrylate), poly(methyl methacrylate), poly(vinyl pyrrolidone), poly(vinyl lactam) and co-, ter-, and quarter-polymers of the following (co-)monomers: ethylene, butadiene, isoprene, styrene,

divinyl benzene, divinyl amine, 1,4-pentadiene-3-one (divinyl ketone), 1,6-heptadiene-4-one (diallyl ketone), diallyl amine, ethylene glycol, acrylamide, AMPS, acrylonitrile, vinyl acetate, vinyl alcohol, vinyl amine, vinyl sulfonate, styryl sulfonate, acrylate, methyl acrylate, methacrylate, methyl methacrylate, vinyl pyrrolidone, and vinyl lactam. Yet other viscosifiers include clay-based viscosifiers, especially laponite and other small fibrous clays such as the polygorskites (attapulgite and sepiolite). When using polymer-containing viscosifiers, the viscosifiers may be used in an amount of up to 5% by weight of the fluid.

Examples of suitable brines include calcium bromide brines, zinc bromide brines, calcium chloride brines, sodium chloride brines, sodium bromide brines, potassium bromide brines, potassium chloride brines, sodium nitrate brines, sodium formate brines, potassium formate brines, cesium formate brines, magnesium chloride brines, sodium sulfate, potassium nitrate, and the like. A mixture of salts may also be used in the brines, but it should be noted that preferably chloride salts are mixed with chloride salts, bromide salts with bromide salts, and formate salts with formate salts.

The brine chosen should be compatible with the formation and should have a sufficient density to provide the appropriate degree of well control.
Additional salts may be added to a water source, e.g., to provide a brine, and a resulting treatment fluid, in order to have a desired density.
The amount of salt to be added should be the amount necessary for formation compatibility, such as the amount necessary for the stability of clay minerals, taking into consideration the crystallization temperature of the brine, e.g., the temperature at which the salt precipitates from the brine as the temperature drops.
Preferred suitable brines may include seawater and/or formation brines.

Salts may optionally be included in the fluids of the present invention for many purposes, including for reasons related to compatibility of the fluid with the formation and the formation fluids.

To determine whether a salt may be beneficially used for compatibility purposes, a compatibility test may be performed to identify potential compatibility problems.

From such tests, one of ordinary skill in the art will, with the benefit of this disclosure, be able to determine whether a salt should be included in a treatment fluid of the present invention.

Suitable salts include, but are not limited to, calcium chloride, sodium chloride, magnesium chloride, potassium chloride, sodium bromide, potassium bromide, ammonium chloride, sodium formate, potassium formate, cesium formate, and the like. A mixture of salts may also be used, but it should be noted that preferably chloride salts are mixed with chloride salts, bromide salts with bromide salts, and formate salts with formate salts.

The amount of salt to be added should be the amount necessary for the required density for formation compatibility, such as the amount necessary for the stability of clay minerals, taking into consideration the crystallization temperature of the brine, e.g., the temperature at which the salt precipitates from the brine as the temperature drops.

Salt may also be included to increase the viscosity of the fluid and stabilize it, particularly at temperatures above 180°F (about 82°C).

Examples of suitable pH control additives which may optionally be included in the treatment fluids of the present invention are acid compositions and/or bases.

A pH control additive may be necessary to maintain the pH of the treatment fluid at a desired level, e.g., to improve the effectiveness of certain breakers and to reduce corrosion on any metal present in the wellbore or formation, etc.

One of ordinary skill in the art will, with the benefit of this disclosure, be able to recognize a suitable pH for a particular application.

In one embodiment, the pH control additive may be an acid composition.

Examples of suitable acid compositions may comprise an acid, an acid-generating compound, and combinations thereof.

Any known acid may be suitable for use with the treatment fluids of the present invention.

Examples of acids that may be suitable for use in the present invention include, but are not limited to, organic acids (e.g., formic acids, acetic acids, carbonic acids, citric acids, glycolic acids, lactic acids, ethylene diamine tetraacetic acid (EDTA), and the like), inorganic acids (e.g., hydrochloric acid, hydrofluoric acid, phosphonic acid, p-toluene sulfonic acid, and the like), and combinations thereof. Preferred acids are HCl (to an amount compatible with the illite content) and organic acids.

Examples of acid-generating compounds that may be suitable for use in the present invention include, but are not limited to, esters, aliphatic polyesters, ortho esters, which may also be known as ortho ethers, poly(ortho esters), which may also be known as poly(ortho ethers), poly(lactides), poly(glycolides), poly(epsilon-caprolactones), poly(hydroxybutyrates), poly(anhydrides), or copolymers thereof. Derivatives and combinations also may be suitable.

The term "copolymer" as used herein is not limited to the combination of two polymers, but includes any combination of polymers, e.g., terpolymers and the like.

Other suitable acid-generating compounds include: esters including, but not limited to, ethylene glycol monoformate, ethylene glycol diformate, diethylene glycol diformate, glyceryl monoformate, glyceryl diformate, glyceryl triformate, methylene glycol diformate, and formate esters of pentaerythritol.

The pH control additive also may comprise a base to elevate the pH of the fluid.

Generally, a base may be used to elevate the pH of the mixture to greater than or equal to about 7.

Having the pH level at or above 7 may have a positive effect on a chosen breaker

being used and may also inhibit the corrosion of any metals present in the wellbore or formation, such as tubing, screens, etc.

In addition, having a pH greater than 7 may also impart greater stability to the viscosity of the treatment fluid, thereby enhancing the length of time that viscosity can be maintained.

This could be beneficial in certain uses, such as in longer-term well control and in diverting.

Any known base that is compatible with the gelling agents of the present invention can be used in the fluids of the present invention.

Examples of suitable bases include, but are not limited to, sodium hydroxide, potassium carbonate, potassium hydroxide, sodium carbonate, and sodium bicarbonate.

One of ordinary skill in the art will, with the benefit of this disclosure, recognize the suitable bases that may be used to achieve a desired pH elevation.

In some embodiments, the treatment fluid may optionally comprise a further chelating agent.

When added to the treatment fluids of the present invention, the chelating agent may chelate any dissolved iron (or other divalent or trivalent cation) that may be present in the aqueous fluid and prevent any undesired reactions being caused.

Such chelating agent may e.g. prevent such ions from crosslinking the gelling agent molecules.

Such crosslinking may be problematic because, *inter alia*, it may cause filtration problems, injection problems, and/or cause permeability problems once more.

Any suitable chelating agent may be used with the present invention.

Examples of suitable chelating agents include, but are not limited to, citric acid, nitrilotriacetic acid (NTA), any form of ethylene diamine tetraacetic acid (EDTA), diethylene triamine pentaacetic acid (DTPA), propylene diamine tetraacetic acid (PDTA), ethylene diamine-N,N"-di(hydroxyphenylacetic) acid (EDDHA), ethylene

diamine-N,N"-di-(hydroxy-methylphenyl acetic acid (EDDHMA), ethanol diglycine (EDG), trans-1,2-cyclohexylene dinitrilotetraacetic acid (CDTA), glucoheptonic acid, gluconic acid, sodium citrate, phosphonic acid, salts thereof, and the like.

In some embodiments, the chelating agent may be a sodium, potassium or ammonium salt.

Generally, the chelating agent may be present in an amount sufficient to prevent undesired side effects of divalent or trivalent cations that may be present, and thus also functions as a scale inhibitor.

One of ordinary skill in the art will, with the benefit of this disclosure, be able to determine the proper concentration of a chelating agent for a particular application.

In some embodiments, the fluids of the present invention may contain bactericides or biocides, *inter alia*, to protect the subterranean formation as well as the fluid from attack by bacteria. Such attacks can be problematic because they may lower the viscosity of the fluid, resulting in poorer performance, such as poorer sand suspension properties, for example.

Any bactericides known in the art are suitable. Biocides and bactericides that protect against bacteria that may attack GLDA, MGDA, HEDTA, or sulfates are preferred

An artisan of ordinary skill will, with the benefit of this disclosure, be able to identify a suitable bactericide and the proper concentration of such bactericide for a given application.

Examples of suitable bactericides and/or biocides include, but are not limited to, phenoxyethanol, ethylhexyl glycerine, benzyl alcohol, methyl chloroisothiazolinone, methyl isothiazolinone, methyl paraben, ethyl paraben, propylene glycol, bronopol, benzoic acid, imidazolinidyl urea, a 2,2-dibromo-3-nitrilopropionamide, and a 2-bromo-2-nitro-1,3–propane diol. In one embodiment, the bactericides are present in the fluid in an amount in the range of from about 0.001% to about 1.0% by weight of the fluid.

Fluids of the present invention also may comprise breakers capable of reducing the viscosity of the fluid at a desired time.

Examples of such suitable breakers for fluids of the present invention include, but are not limited to, oxidizing agents such as sodium chlorites, sodium bromate, hypochlorites, perborate, persulfates, and peroxides, including organic peroxides. Other suitable breakers include, but are not limited to, suitable acids and peroxide breakers, triethanol amine, as well as enzymes that may be effective in breaking. The breakers can be used as is or encapsulated.

Examples of suitable acids may include, but are not limited to, hydrochloric acid, hydrofluoric acid, formic acid, acetic acid, citric acid, lactic acid, glycolic acid, etc, and combinations of these acids.

A breaker may be included in a treatment fluid of the present invention in an amount and form sufficient to achieve the desired viscosity reduction at a desired time.

The breaker may be formulated to provide a delayed break, if desired.

The fluids of the present invention also may comprise suitable fluid loss additives. Such fluid loss additives may be particularly useful when a fluid of the present invention is used in a fracturing application or in a fluid used to seal a formation against invasion of fluid from the wellbore.

Any fluid loss agent that is compatible with the fluids of the present invention is suitable for use in the present invention.

Examples include, but are not limited to, starches, silica flour, gas bubbles (energized fluid or foam), benzoic acid, soaps, resin particulates, relative permeability modifiers, degradable gel particulates, diesel or other hydrocarbons dispersed in fluid, and other immiscible fluids.

Another example of a suitable fluid loss additive is one that comprises a degradable material.

Suitable examples of degradable materials include polysaccharides such as

dextran or cellulose; chitins; chitosans; proteins; aliphatic polyesters; poly(lactides); poly(glycolides); poly(glycolide-co-lactides); poly(epsilon-caprolactones); poly(3-hydroxybutyrates); poly(3-hydroxybutyrate-co-hydroxyvalerates); poly(anhydrides); aliphatic poly(carbonates); poly(ortho esters); poly(amino acids); poly(ethylene oxides); poly(phosphazenes); derivatives thereof; or combinations thereof.

In some embodiments, a fluid loss additive may be included in an amount of about 5 to about 2,000 lbs/Mgal (about 600 to about 240,000 g/Mliter) of the fluid.

In some embodiments, the fluid loss additive may be included in an amount from about 10 to about 50 lbs/Mgal (about 1,200 to about 6,000 g/Mliter) of the fluid.

In certain embodiments, a stabilizer may optionally be included in the fluids of the present invention.

It may be particularly advantageous to include a stabilizer if a chosen fluid is experiencing viscosity degradation.

One example of a situation where a stabilizer might be beneficial is where the BHT (bottom hole temperature) of the wellbore is sufficient to break the fluid by itself without the use of a breaker.

Suitable stabilizers include, but are not limited to, sodium thiosulfate, methanol, and salts such as formate salts and potassium or sodium chloride.

Such stabilizers may be useful when the fluids of the present invention are utilized in a subterranean formation having a temperature above about 200°F (about 93°C). If included, a stabilizer may be added in an amount of from about 1 to about 50 lbs/Mgal (about 120 to about 6,000 g/Mliter) of fluid.

Scale inhibitors may be added to the fluids of the present invention, for example, when such fluids are not particularly compatible with the formation waters in the formation in which they are used.

These scale inhibitors may include water-soluble organic molecules with carboxylic acid, aspartic acid, maleic acids, sulfonic acids, phosphonic acid, and phosphate

ester groups including copolymers, ter-polymers, grafted copolymers, and derivatives thereof.

Examples of such compounds include aliphatic phosphonic acids such as diethylene triamine penta (methylene phosphonate) and polymeric species such as polyvinyl sulfonate.

The scale inhibitor may be in the form of the free acid but is preferably in the form of mono- and polyvalent cation salts such as Na, K, Al, Fe, Ca, Mg, NH_4. Any scale inhibitor that is compatible with the fluid in which it will be used is suitable for use in the present invention.

Suitable amounts of scale inhibitors that may be included in the fluids of the present invention may range from about 0.05 to 100 gallons per about 1,000 gallons (i.e. 0.05 to 100 liters per 1,000 liters) of the fluid.

Any particulates such as proppant, gravel that are commonly used in subterranean operations in formations may be used in the present invention (e.g., sand, gravel, bauxite, ceramic materials, glass materials, wood, plant and vegetable matter, nut hulls, walnut hulls, cotton seed hulls, cement, fly ash, fibrous materials, composite particulates, hollow spheres and/or porous proppant).

It should be understood that the term "particulate" as used in this disclosure includes all known shapes of materials including substantially spherical materials, oblong, fibre-like, ellipsoid, rod-like, polygonal materials (such as cubic materials), mixtures thereof, derivatives thereof, and the like.

In some embodiments, coated particulates may be suitable for use in the treatment fluids of the present invention. It should be noted that many particulates also act as diverting agents. Further diverting agents are viscoelastic surfactants and in-situ gelled fluids.

Oxygen scavengers may be needed to enhance the thermal stability of the GLDA, MGDA, HEDTA or NTA. Examples thereof are sulfites and ethorbates.

Friction reducers can be added in an amount of up to 0.2 vol%. Suitable examples are viscoelastic surfactants and enlarged molecular weight polymers.

Crosslinkers can be chosen from the group of multivalent cations that can crosslink polymers such as Al, Fe, B, Ti, Cr, and Zr, or organic crosslinkers such as polyethylene amides, formaldehyde.

Sulfide scavengers can suitably be an aldehyde or ketone.

Viscoelastic surfactants can be chosen from the group of amine oxides or carboxyl betaine based surfactants.

The fluids can be used at basically any temperature encountered when treating a subterranean formation. Though subterranean formations normally have a temperature higher than room temperature, due to the fact that they sometimes are accessed through deep sea water, this means in practice a temperature of between 35 and 400°F (about 2 and 204°C). Preferably, the fluids are used at a temperature where they best achieve the desired effects, which means a temperature of between 77 and 300°F (about 25 and 149°C).

High temperature applications may benefit from the presence of an oxygen scavenger in an amount of less than about 2 volume percent of the solution.

At the same time the fluids can be used at an increased pressure. Often fluids are pumped into the formation under pressure. Preferably, the pressure used is below fracture pressure, i.e. the pressure at which a specific formation is susceptible to

fracture. Fracture pressure can vary a lot depending on the formation treated, but is well known by the person skilled in the art.

In the process of the invention the fluid can be flooded back from the formation. Even more preferably, (part of) the solution is recycled.

It must be realized, however, that GLDA, and MGDA, being biodegradable chelating agents, will not flow back completely and therefore are not recyclable to the full extent.

Claims:

1. A process for treating a shale formation comprising introducing a fluid containing glutamic acid N,N-diacetic acid or a salt thereof (GLDA), methylglycine N,N-diacetic acid or a salt thereof (MGDA), and/or N-hydroxyethyl ethylenediamine N,N',N'-triacetic acid or a salt thereof (HEDTA) into the formation.

2. The process for treating a shale formation of claim 1 comprising an additional step of fracturing the shale formation wherein the fracturing step can take place before introducing the fluid into the formation, while introducing the fluid into the formation or subsequent to introducing the fluid into the formation

3. The process of claim 2, wherein the fluid containing glutamic acid N,N-diacetic acid or a salt thereof (GLDA), methylglycine N,N-diacetic acid or a salt thereof (MGDA), and/or N-hydroxyethyl ethylenediamine N,N',N'-triacetic acid or a salt thereof (HEDTA) is also the fracturing fluid in the fracturing step.

4. The process of any one of claims 1 to 3, wherein the fluid contains between 3 and 30 wt% of GLDA, MGDA, and/or HEDTA based on the total weight of the fluid.

5. The process of any one of claims 1 to 4, wherein the fluid contains GLDA.

6. The process of any one of claims 1 to 5, wherein the fluid has a pH of between 3 and 13.

7. The process of claim 6, wherein the pH is between 3 and 6.

8. The process of any one of claims 1 to 7, wherein the process is done at a temperature of between 77 and 300°F (about 25 and 149°C).

9. The process of any one of claims 1 to 8, wherein the fluid contains water as a solvent.

10. The process of any one of claims 1 to 9, wherein the fluid in addition contains a further additive from the group of other solvents like alcohols, glycols, and further organic solvents, mutual solvents, anti-sludge agents, surfactants, corrosion inhibitors, corrosion inhibitor intensifiers, foaming agents, viscosifiers, wetting agents, diverting agents, oxygen scavengers, carrier fluids, fluid loss additives, friction reducers, stabilizers, rheology modifiers, gelling agents, scale inhibitors, breakers, salts, brines, pH control additives, bactericides/biocides, particulates, crosslinkers, salt substitutes, relative permeability modifiers, sulfide scavengers, fibres, nanoparticles, and consolidating agents.

11. The process of claim 10, wherein the surfactant is a nonionic or anionic surfactant.

12. The process of claim 10 or 11, wherein the surfactant is present in an amount of 0.1 to 2 volume % on total fluid volume.

13. The process of any one of claims 10 to 12, wherein the corrosion inhibitor is present in an amount of 0.01 to 2 volume % on total fluid volume.

14. The process of any one of claims 10 to 13, wherein the mutual solvent is present in an amount of 1 to 50 wt% on total fluid weight.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/060950

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K8/68 C09K8/60 C09K8/74
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

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, 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 2006/041822 A2 (MI LLC [US]) 20 April 2006 (2006-04-20)	1-14
Y	page 4, lines 4-13,29-37 page 8, lines 15-20; example 3 the whole document	1-14

X	US 2006/073984 A1 (PATEL ARVIND D [US] ET AL) 6 April 2006 (2006-04-06) cited in the application	1-14
Y	the whole document	1-14

X	US 2008/200354 A1 (JONES ANDREW G K [ZA] ET AL) 21 August 2008 (2008-08-21) cited in the application	1-10
Y	paragraphs [0007], [0029], [0032], [0036], [0048] the whole document	1-14

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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 :

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

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" 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 September 2012	20/09/2012

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

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

PHARAOH, EX. 1002
P. 234

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/060950

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	GB 2 420 577 A (CLEARWATER INT LLC [US]) 31 May 2006 (2006-05-31) cited in the application page 13, line 13 page 25, lines 14-19 page 35, lines 6-14 claims 1,5,6 the whole document -----	1-14

1

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

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2012/060950

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2006041822 A2	20-04-2006	AR 054693 A1	11-07-2007
		CA 2581891 A1	20-04-2006
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		US 2006116296 A1	01-06-2006
		US 2008039345 A1	14-02-2008

Electronic Acknowledgement Receipt

EFS ID:	30521269
Application Number:	14686237
International Application Number:	
Confirmation Number:	2601
Title of Invention:	STIMULATION OF WELLS IN NANO-DARCY SHALE FORMATIONS
First Named Inventor/Applicant Name:	Andrew Bryce Conway
Customer Number:	23552
Filer:	Brian Peter McCall/Amy Miller
Filer Authorized By:	Brian Peter McCall
Attorney Docket Number:	04697.0001USU1
Receipt Date:	29-SEP-2017
Filing Date:	14-APR-2015
Time Stamp:	14:28:30
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Information Disclosure Statement (IDS) Form (SB08)	2017-09-29--SIDS-5--04697-0001USU1.PDF	1035085 40749bd8cb6547ed1cb996206b78daa00832bbed	no	4

Warnings:

Information:					
2	Foreign Reference	D1-EP0599474A2.PDF	362223 38ce702d2e69d3a3a9e815042d46809bcae09e91	no	5
Warnings:					
Information:					
3	Foreign Reference	D3-WO2012171857A1.PDF	1211703 66856dba29993121a6c02ad3e38009cb9acb5c08	no	31
Warnings:					
Information:					
4	Non Patent Literature	EP-search-report-and-written-opinion-dated-8-31-17.PDF	182402 10da00b03c7cdd4642e87fe202fcabb4e6bf4d0d	no	7
Warnings:					
Information:					
			Total Files Size (in bytes):	2791413	

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<u>New Applications Under 35 U.S.C. 111</u>
If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.
<u>National Stage of an International Application under 35 U.S.C. 371</u>
If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.
<u>New International Application Filed with the USPTO as a Receiving Office</u>
If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

UNITED STATES PATENT AND TRADEMARK OFFICE

USPTO Automated Interview Request (AIR)

Sep 18 2017

This paper requesting to schedule and/or conduct an interview is appropriate because:

This submission is requested to be accepted as an authorization for this interview to communicate via the internet. Recognizing that Internet communications are not secure, I hereby authorize the USPTO to communicate with the undersigned concerning scheduling of the interview via video conference, instant messaging, or electronic mail, and to conduct the interview in accordance with office practice including video conferencing.

Name(s):
Brian McCall

S-signature:
/Brian McCall/

Registration Number:
68734

U.S. Application Number:
14686237

Confirmation Number:
2601

E-mail Address:
bmccall@merchantgould.com

Phone Number:
6082806762

Proposed Time of Interview:
9-26-2017 3:00 PM ET

Prefered Interview Type:
Telephonic

I am the applicant or applicant's representative for this application.

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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
14/686,237	04/14/2015	Andrew Bryce Conway	04697.0001USU1	2601

23552 7590 07/28/2017

MERCHANT & GOULD P.C.
P.O. BOX 2903
MINNEAPOLIS, MN 55402-0903

EXAMINER
LOIKITH, CATHERINE A

ART UNIT	PAPER NUMBER
3674	

NOTIFICATION DATE	DELIVERY MODE
07/28/2017	ELECTRONIC

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Notice of the Office communication was sent electronically on above-indicated "Notification Date" to the following e-mail address(es):

USPTO23552@merchantgould.com

Office Action Summary	Application No. 14/686,237	Applicant(s) CONWAY, ANDREW BRYCE	
	Examiner CATHERINE LOIKITH	Art Unit 3674	AIA (First Inventor to File) Status Yes

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTHS FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

1)☒ Responsive to communication(s) filed on *06 July 2017*.

☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on _____.

2a)☐ This action is **FINAL**. 2b)☒ This action is non-final.

3)☐ An election was made by the applicant in response to a restriction requirement set forth during the interview on _____; the restriction requirement and election have been incorporated into this action.

4)☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims*

5)☒ Claim(s) *1-17* is/are pending in the application.

5a) Of the above claim(s) *14-17* is/are withdrawn from consideration.

6)☐ Claim(s) _____ is/are allowed.

7)☒ Claim(s) *1-13* is/are rejected.

8)☐ Claim(s) _____ is/are objected to.

9)☐ Claim(s) _____ are subject to restriction and/or election requirement.

* If any claims have been determined allowable, you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information, please see http://www.uspto.gov/patents/init_events/pph/index.jsp or send an inquiry to PPHfeedback@uspto.gov.

Application Papers

10)☒ The specification is objected to by the Examiner.

11)☒ The drawing(s) filed on *4/14/15* is/are: a)☐ accepted or b)☒ objected to by the Examiner.

Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).

Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).

Priority under 35 U.S.C. § 119

12)☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

Certified copies:

a)☐ All b)☐ Some** c)☐ None of the:

1.☐ Certified copies of the priority documents have been received.

2.☐ Certified copies of the priority documents have been received in Application No. _____.

3.☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

** See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

1) ☒ Notice of References Cited (PTO-892)

2) ☒ Information Disclosure Statement(s) (PTO/SB/08a and/or PTO/SB/08b) Paper No(s)/Mail Date _____.

3) ☐ Interview Summary (PTO-413) Paper No(s)/Mail Date. _____ .

4) ☐ Other: _____.

PHARAOH, EX. 1002
P. 241

DETAILED ACTION

Notice of Pre-AIA or AIA Status

The present application, filed on or after March 16, 2013, is being examined under the first inventor to file provisions of the AIA.

Election/Restrictions

Applicant's election without traverse of Species I in the reply filed on July 6, 2017 is acknowledged.

Drawings

The drawings are objected to because Figures 2-4 are very grainy and unclear. New figures are requested. Corrected drawing sheets in compliance with 37 CFR 1.121(d) are required in reply to the Office action to avoid abandonment of the application. Any amended replacement drawing sheet should include all of the figures appearing on the immediate prior version of the sheet, even if only one figure is being amended. The figure or figure number of an amended drawing should not be labeled as "amended." If a drawing figure is to be canceled, the appropriate figure must be removed from the replacement sheet, and where necessary, the remaining figures must be renumbered and appropriate changes made to the brief description of the several views of the drawings for consistency. Additional replacement sheets may be necessary to show the renumbering of the remaining figures. Each drawing sheet submitted after the filing date of an application must be labeled in the top margin as either "Replacement Sheet" or "New Sheet" pursuant to 37 CFR 1.121(d). If the changes are not accepted by the examiner, the applicant will be notified and informed of any required

corrective action in the next Office action. The objection to the drawings will not be held in abeyance.

Specification

Applicant is reminded of the proper language and format for an abstract of the disclosure.

The abstract should be in narrative form and generally limited to a single paragraph on a separate sheet within the range of 50 to 150 words in length. The abstract should describe the disclosure sufficiently to assist readers in deciding whether there is a need for consulting the full patent text for details.

The language should be clear and concise and should not repeat information given in the title. **It should avoid using phrases which can be implied**, such as, "The disclosure concerns," "The disclosure defined by this invention," "The disclosure describes," etc. In addition, the form and legal phraseology often used in patent claims, such as "means" and "said," should be avoided.

The abstract of the disclosure is objected to because it contains the implied phrase "This disclosure describes". Correction is required. See MPEP § 608.01(b).

Claim Rejections - 35 USC § 112

> The following is a quotation of 35 USC 112(b):
> (b) CONCLUSION.—The specification shall conclude with one or more claims particularly pointing out and distinctly claiming the subject matter which the inventor or a joint inventor regards as the invention.
>
> The following is a quotation of 35 USC 112 (pre-AIA), second paragraph:
> The specification shall conclude with one or more claims particularly pointing out and distinctly claiming the subject matter which the applicant regards as his invention.

Claim 10 is rejected under 35 USC 112(b) or 35 USC 112 (pre-AIA), second paragraph, as being indefinite for failing to particularly point out and distinctly claim the

subject matter which the inventor or a joint inventor, or for pre-AIA the applicant regards as the invention.

Regarding claim 10, the phrase "such as" renders the claim indefinite because it is unclear whether the limitations following the phrase are part of the claimed invention. See MPEP § 2173.05(d).

Claim 10 recites the limitation "the induced fractures" in the last line. There is insufficient antecedent basis for this limitation in the claim.

Claim 10 is also rejected as being indefinite since it requires "hydraulic fracturing" and "propagation of the induced fractures." It is unclear how this is possible as the pressure range in claim 1 (as elected in the response filed July 6, 2017) is less than the fracture pressure. Therefore, claim 10 is not within the pressure range defined in claim 1 and is indefinite.

Claim Rejections - 35 USC § 103

In the event the determination of the status of the application as subject to AIA 35 USC 102 and 103 (or as subject to pre-AIA 35 USC 102 and 103) is incorrect, any correction of the statutory basis for the rejection will not be considered a new ground of rejection if the prior art relied upon, and the rationale supporting the rejection, would be the same under either status.

The following is a quotation of 35 USC 103 which forms the basis for all obviousness rejections set forth in this Office action:

> A patent for a claimed invention may not be obtained, notwithstanding that the claimed invention is not identically disclosed as set forth in section 102, if the differences between the claimed invention and the prior art are such that the claimed invention as a whole would have been obvious before the effective filing date of the claimed invention to a person having

ordinary skill in the art to which the claimed invention pertains. Patentability shall not be negated by the manner in which the invention was made.

Claims 1-7 and 10-13 are rejected under 35 USC 103 as being unpatentable over Horton et al. (US 2011/0053811 A1) ("Horton").

Referring to claim 1: Horton teaches a method for stimulating a well in formation comprising:

providing a treatment mixture containing a metal complexing agent (paragraph [0037]) at a pH;

injecting the treatment mixture into the well at a pressure less than a fracture pressure of the formation (since Horton does not explicitly teach injecting at a pressure above a fracture pressure, and since Horton teaches using the method in applications other than fracturing [0022]) until at least some of the treatment mixture contacts the formation;

maintaining the treatment mixture in contact with the formation for a contact time, thereby allowing the metal complexing agent to bind with at least some naturally-occurring metals contained within the formation (Abstract and paragraph [0037]); and

removing the treatment mixture from the well after the contact time, thereby removing the bound naturally-occurring metals from the formation (paragraph [0016]) and thereby improving the hydrocarbon production of the well relative to the hydrocarbon production immediately prior to performance of the method.

While Horton teaches removing fluids that damage the permeability of the wellbore (paragraph [0026]), which would be beneficial in a low permeability nano-dacry shale formation, Horton does not specifically teach stimulating a well in a nano-darcy

shale formation. It would have been obvious to one of ordinary skill in the art before the effective filing date of the claimed invention to have modified the method taught by Horton to be used in a well in a nano-darcy shale formation in order to improve permeability and enhance production.

Horton does not specifically teach the weight percent of the metal complexing agent. It would have been obvious to one of ordinary skill in the art before the effective filing date of the claimed invention to have modified the weight percent of the metal complexing agent to be between about 0.1% and 95% since it has been held that where the general conditions of a claim are disclosed in the prior art, discovering the optimum or workable ranges involves only routine skill in the art. *In re Aller*, 105 USPQ 233.

While Horton teaches modifying the pH of the mixture (paragraph [0024]), Horton does not specifically teach a pH of between about 0 and 10. It would have been obvious to one of ordinary skill in the art before the effective filing date of the claimed invention to have modified the pH to be between about 0 and 10 since it has been held that where the general conditions of a claim are disclosed in the prior art, discovering the optimum or workable ranges involves only routine skill in the art. *In re Aller*, 105 USPQ 233.

While Horton inherently teaches a contact time between the treatment mixture and the formation, Horton does not specifically teach a contact time of between about 1 minute and 100 days. It would have been obvious to one of ordinary skill in the art before the effective filing date of the claimed invention to have modified the contact time to be between about 1 minute and 100 days since it has been held that where the

general conditions of a claim are disclosed in the prior art, discovering the optimum or workable ranges involves only routine skill in the art. *In re Aller*, 105 USPQ 233.

Referring to claim 2: Horton does not specifically teach the metal complexing agent is citric acid. It would have been obvious to one of ordinary skill in the art before the effective filing date of the claimed invention to have modified the metal complexing agent taught by Horton to be citric acid since it has been held to be within the general skill of a worker in the art to select a known material on the basis of its suitability for the intended use as a matter of obvious design choice. *In re Leshin*, 125 USPQ 416.

Referring to claims 3-5, 12 and 13: Horton teaches the metal complexing agent may be ethylenediaminetetraacetic acid (EDTA) (paragraph [0037]), acetic acid (paragraph [0037]), at least one of ethylenediaminetetraacetic acid (EDTA) (paragraph [0037]), propylenediaminetetraacetic acid (PDTA), nitrilotriacetic acid (NTA), N-(2-hydroxyethyl)ethylenediaminetriacetic acid (HEDTA), diethylenetriaminepentaacetic acid (DTPA), hydroxyethyliminodiacetic acid (HEIDA), cyclohexylenediaminetetraacetic acid (CDTA), diphenylaminesulfonic acid (DPAS), ethylenediaminedi(o-hydroxyphenylacetic) acid (EDDHA), glucoheptonic acid, gluconic acid, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, phthalic acid, terephthalic acid, aconitic acid, carballylic acid, trimesic acid, isocitric acid, citric acid, or any salt or derivative of any of the previously listed compounds, glutamic acid diacetic acid (GLDA) (paragraph [0037]), methylglycine diacetic acid (MGDA), (3-alanine diacetic acid (p-ADA), ethylenediaminedi succinic acid, S,S- ethylenediaminedi succinic acid (EDDS),

iminodisuccinic acid (IDS), hydroxyiminodisuccinic acid (HIDS), polyamino disuccinic acids, N-bis[2-(1,2- dicarboxyethoxy)ethyl]glycine (BCA6), N-bis[2-(1,2-dicarboxyethoxy)ethyl]aspartic acid (BCA5), N-bis[2-(1,2-dicarboxyethoxy)ethyl]methylglycine (MCBA5), N-tris[(1,2- dicarboxyethoxy)ethyl]amine (TCA6), N-methyliminodiacetic acid (MIDA), iminodiacetic acid (IDA), N-(2-acetamido)iminodiacetic acid (ADA), hydroxymethyl- iminodiacetic acid, 2-(2-carboxyethylamino) succinic acid (CEAA), 2-(2-carboxymethylamino) succinic acid (CMAA), diethylenetriamine- N,N"-disuccinic acid, triethylenetetramine-N,N"'- disuccinic acid, 1,6- hexamethylenediamine-N,N'-disuccinic acid, tetraethylenepentamine- N,N""-disuccinic acid, 2-hydroxypropylene-1,3-diamine-N,N'-disuccinic acid, 1,2-propylenediamine-N,N'-disuccinic acid, 1,3-propylenediamine-N,N'-disuccinic acid, cis-cyclohexanediamine-N,N'-disuccinic acid, trans-cyclohexanediamine- N,N'-disuccinic acid, ethylenebi s(oxyethylenenitrilo)-N,N'-di succinic acid, glucoheptanoic acid, cysteic acid-N,N- diacetic acid, cysteic acid-N-monoacetic acid, alanine-N-monoacetic acid, N-(3- hydroxysuccinyl) aspartic acid, N-[2-(3- hydroxysuccinyl)]-L-serine, aspartic acid-N,N-diacetic acid, aspartic acid-N- monoacetic acid, any salt thereof, any derivative thereof, or any combination thereof, or acetic acid, acrylates, dihydroxymaleic acid, salts of dihydroxymaleic acid, EDTA (ethylenediamine tetraacetic acid) (paragraph [0037]), salts of EDTA, erythorbic acid, erythroboric acid, formic acid, gluconodeltalactone, GLDA (glutamic acid N,N-diacetic acid), salts of GLDA, HEDTA (hydroxyethylenediamine triacetic acid), salts of HEDTA, HEIDA (disodium ethanoldiglycine), salts of HEIDA, MGDA (methylglycine N,N-diacetic acid), salts of

MGDA, NTA (nitriolotriacetic acid), organic metal complexers, ligands, porphyrins, pigments, peptides, saccharides, nucleic acids, phosphonic acid, polyacrylic acid and citric acid in an amount sufficient to sequester at least a portion of a metal compound.

Referring to claim 6: Horton teaches the treatment mixture comprises metal complexing agent; a corrosion inhibitor; a biocide; a mutual solvent; and a surfactant (paragraph [0024]). Horton does not teach specific percentages or ranges of these additives. It would have been obvious to one of ordinary skill in the art before the effective filing date of the claimed invention to have modified the amounts of the metal complexing agent; the corrosion inhibitor; the biocide; the mutual solvent; and the surfactant to be within the ranges claimed since it has been held that where the general conditions of a claim are disclosed in the prior art, discovering the optimum or workable ranges involves only routine skill in the art. *In re Aller*, 105 USPQ 233. Although Horton teaches inhibiting polymer deposition (abstract), Horton does not specifically teach between 1 and 10,000 ppm of a colloidal silica deposition inhibitor. It would have been obvious to one of ordinary skill in the art before the effective filing date of the claimed invention to have modified the mixture to include between 1 and 10,000 ppm of a colloidal silica deposition inhibitor since it has been held that where the general conditions of a claim are disclosed in the prior art, discovering the optimum or workable ranges involves only routine skill in the art. *In re Aller*, 105 USPQ 233, and since it has been held to be within the general skill of a worker in the art to select a known material on the basis of its suitability for the intended use as a matter of obvious design choice. *In re Leshin*, 125 USPQ 416.

Referring to claim 7: While Horton teaches pH control additives and pH buffers are known in the art, Horton does not specifically teach between 0.1 and 95% of acid(s) as pH modifier. It would have been obvious to one of ordinary skill in the art before the effective filing date of the claimed invention to have modified the mixture taught by Horton to include between 0.1 and 95% of acid(s) as pH modifier since it has been held that where the general conditions of a claim are disclosed in the prior art, discovering the optimum or workable ranges involves only routine skill in the art. *In re Aller*, 105 USPQ 233, and since it has been held to be within the general skill of a worker in the art to select a known material on the basis of its suitability for the intended use as a matter of obvious design choice. *In re Leshin*, 125 USPQ 416.

Referring to claim 10: Horton teaches injecting the treatment mixture containing a metal complexing agent such as citric acid or EDTA in combination with hydraulic fracturing and injecting into the formation in conjunction with propagation of the induced fractures (paragraph [0022]).

Referring to claim 11: Horton teaches monitoring at least one of pH and well pressure during the maintaining operation; and initiating the removing operation based on results of the monitoring operation (paragraph [0031]).

Claims 8 and 9 are rejected under 35 USC 103 as being unpatentable over Horton and in view of Conway et al. (US 2015/0114653 A1) ("Conway").

Referring to claim 8: Horton does not specifically teach alternately injecting a first amount of treatment mixture and a second amount of a diverting mixture into the well. Conway teaches a method of stimulating a well in a nano-darcy shale formation

(paragraph [0008]) comprising providing a treatment mixture containing a metal complexing agent (paragraph [0008]) and alternately injecting a first amount of treatment mixture and a second amount of a diverting mixture into the well (paragraph [0047]). It would have been obvious to one of ordinary skill in the art before the effective filing date of the claimed invention to have modified the method taught by Horton to include alternately injecting a first amount of treatment mixture and a second amount of a diverting mixture into the well as taught by Conway in order to avoid "fluid thief zones" (Conway - paragraph [0045]).

Referring to claim 9: While Horton teaches injecting the treatment mixture until the pressure within the well reaches a predetermined target pressure and that it is known to abandon the well (paragraph [0004]), Horton does not specifically teach injecting the treatment mixture until the pressure within the well reaches a predetermined target pressure calculated based on the fracture pressure of the nano-darcy shale formation; and upon reaching the target pressure, shutting in the well. Conway teaches injecting the treatment mixture until the pressure within the well reaches a predetermined target pressure calculated based on the fracture pressure of the nano-darcy shale formation (paragraph [0051]); and upon reaching the target pressure, shutting in the well (paragraph [0052]). It would have been obvious to one of ordinary skill in the art before the effective filing date of the claimed invention to have modified the method taught by Horton to include injecting the treatment mixture until the pressure within the well reaches the target pressure calculated based on the fracture

pressure of the formation and shutting in the well as taught by Conway in order to have more control over the contact time between the mixture and the well.

Conclusion

Any inquiry concerning this communication or earlier communications from the examiner should be directed to CATHERINE LOIKITH whose telephone number is (571)270-7822. The examiner can normally be reached on Monday-Friday, 9:00am-5:30pm.

Examiner interviews are available via telephone, in-person, and video conferencing using a USPTO supplied web-based collaboration tool. To schedule an interview, applicant is encouraged to use the USPTO Automated Interview Request (AIR) at http://www.uspto.gov/interviewpractice.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Doug Hutton can be reached on 571-272-4137. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see http://pair-direct.uspto.gov. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a USPTO Customer Service Representative or access to the automated information system, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.

/CATHERINE LOIKITH/
Primary Examiner, Art Unit 3674

7/23/17

Notice of References Cited	Application/Control No. 14/686,237	Applicant(s)/Patent Under Reexamination CONWAY, ANDREW BRYCE	
	Examiner CATHERINE LOIKITH	Art Unit 3674	Page 1 of 1

U.S. PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Name	CPC Classification	US Classification
*	A	US-2015/0114653 A1	04-2015	Conway; Andrew Bryce	C09K8/52	166/308.2
	B	US-				
	C	US-				
	D	US-				
	E	US-				
	F	US-				
	G	US-				
	H	US-				
	I	US-				
	J	US-				
	K	US-				
	L	US-				
	M	US-				

FOREIGN PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Country	Name	CPC Classification
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	P					
	Q					
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NON-PATENT DOCUMENTS

*		Include as applicable: Author, Title Date, Publisher, Edition or Volume, Pertinent Pages)
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	X	

*A copy of this reference is not being furnished with this Office action. (See MPEP § 707.05(a).)
Dates in MM-YYYY format are publication dates. Classifications may be US or foreign.

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BIB DATA SHEET

CONFIRMATION NO. 2601

SERIAL NUMBER	FILING or 371(c) DATE RULE	CLASS	GROUP ART UNIT	ATTORNEY DOCKET NO.
14/686,237	04/14/2015	166	3674	04697.0001USU1

APPLICANTS
Flex-Chem Holding Company, LLC, Weatherford, OK;

INVENTORS
Andrew Bryce Conway, Weatherford, OK;

**** CONTINUING DATA **************************
This appln claims benefit of 61/979,210 04/14/2014
and claims benefit of 62/087,899 12/05/2014

**** FOREIGN APPLICATIONS **************************

**** IF REQUIRED, FOREIGN FILING LICENSE GRANTED **** ** SMALL ENTITY **
04/24/2015

Foreign Priority claimed ☐ Yes ☑ No 35 USC 119(a-d) conditions met ☐ Yes ☐ No Verified and Acknowledged /CATHERINE A LOIKITH/ Examiner's Signature	☐ Met after Allowance Initials	STATE OR COUNTRY	SHEETS DRAWINGS	TOTAL CLAIMS	INDEPENDENT CLAIMS
		OK	5	17	2

ADDRESS

MERCHANT & GOULD P.C.
P.O. BOX 2903
MINNEAPOLIS, MN 55402-0903
UNITED STATES

TITLE

STIMULATION OF WELLS IN NANO-DARCY SHALE FORMATIONS

FILING FEE RECEIVED		
800	FEES: Authority has been given in Paper No._____ to charge/credit DEPOSIT ACCOUNT No._____ for following:	☐ All Fees ☐ 1.16 Fees (Filing) ☐ 1.17 Fees (Processing Ext. of time) ☐ 1.18 Fees (Issue) ☐ Other _____ ☐ Credit

Doc code: IDS
Doc description: Information Disclosure Statement (IDS) Filed

PTO/SB/08a (03-15)
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INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	14686237
Filing Date	2015-04-14
First Named Inventor	Andrew Bryce Conway
Art Unit	3676
Examiner Name	
Attorney Docket Number	04697.0001USU1

U.S.PATENTS Remove

Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
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Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	20130210684	A1	2013-08-15	Ballard	
	2	20150005204	A1	2015-01-01	Alwattari et al.	
	3	20080110621	A1	2008-05-15	Montgomery et al.	
	4	20110053811	A1	2011-03-03	Horton et al.	
	5	20130157905	A1	2013-06-20	Saini et al.	

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT

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Examiner Name	
Attorney Docket Number	04697.0001USU1

Examiner Initial*	Cite No	Foreign Document Number[3]	Country Code[2] i	Kind Code[4]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear	T[5]
	1							

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NON-PATENT LITERATURE DOCUMENTS Remove

Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]
	1		

If you wish to add additional non-patent literature document citation information please click the Add button Add

EXAMINER SIGNATURE

Examiner Signature	/Catherine Loikith/	Date Considered	07/21/2017

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /CAL/

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	14686237
Filing Date	2015-04-14
First Named Inventor	Andrew Bryce Conway
Art Unit	3676
Examiner Name	
Attorney Docket Number	04697.0001USU1

CERTIFICATION STATEMENT

Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

See attached certification statement.

The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

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Signature	/Brian P. McCall/	Date (YYYY-MM-DD)	2016-09-06
Name/Print	Brian P. McCall	Registration Number	68734

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Doc code: IDS
Doc description: Information Disclosure Statement (IDS) Filed

PTO/SB/08a (03-15)
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(Not for submission under 37 CFR 1.99)

Application Number	14686237
Filing Date	2015-04-14
First Named Inventor	Andrew Bryce Conway
Art Unit	3676
Examiner Name	Waseem Moorad
Attorney Docket Number	04697.0001USU1

U.S.PATENTS Remove

Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	4815537	A	1989-03-28	Jones	
	2	6110875	A	2000-08-29	Tjon-Joe-Pin	

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Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
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Examiner Initial*	Cite No	Foreign Document Number[3]	Country Code[2] i	Kind Code[4]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear	T[5]
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Attorney Docket Number	04697.0001USU1

Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]
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Examiner Signature	/Catherine Loikith/	Date Considered	07/21/2017

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[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

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OR

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Index of Claims	Application/Control No.	Applicant(s)/Patent Under Reexamination
	14686237	CONWAY, ANDREW BRYCE
	Examiner	**Art Unit**
	CATHERINE LOIKITH	3674

✓	Rejected	-	Cancelled	N	Non-Elected	A	Appeal
=	Allowed	÷	Restricted	I	Interference	O	Objected

☐ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

CLAIM		DATE								
Final	Original	05/01/2017	07/23/2017							
	1	÷	✓							
	2	÷	✓							
	3	÷	✓							
	4	÷	✓							
	5	÷	✓							
	6	÷	✓							
	7	÷	✓							
	8	÷	✓							
	9	÷	✓							
	10	÷	✓							
	11	÷	✓							
	12	÷	✓							
	13	÷	✓							
	14	÷	N							
	15	÷	N							
	16	÷	N							
	17	÷	N							

Doc code: IDS
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Filing Date	2015-04-14
First Named Inventor	Andrew Bryce Conway
Art Unit	3676
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Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	4089787		1978-05-16	Lybarger et al.	
	2	5944446		1999-08-31	Hocking	
	3	7906463		2011-03-15	Starkey, II et al.	

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	1	20050150520	A1	2015-07-14	Gill et al.	
	2	20060124302	A1	2006-06-15	Gupta et al.	
	3	20120125626	A1	2012-05-24	Constantine	

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	4	20130269936		2013-10-17	Reyes et al.	

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	1	2013081609	WO	A1	2013-06-06	Ayers et al.		☐
	2	2013173634	WO	A1	2013-11-21	Yean et al.		☐
	3	2009086954	WO	A1	2009-07-16	De Wolf et al.		☐

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	1	International Search Report for Application No. PCT/US2015/25399 mailed July 8, 2015, 2pgs.	☐
	2	Written Opinion of the International Searching Authority for Application No. PCT/US2015/25399 mailed July 8, 2015, 5pgs.	☐
	3	Notification of Transmittal of the International Search Report and the Written Opinion of the International Searching Authority, or the Declaration for Application No. PCT/US2015/25399 mailed July 8, 2015, 1pg.	☐

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	4	FRENIER, et al., Use of Highly Acid-Soluble Chelating Agents in Well Stimulation Services, SPE Annual Technical Conference and Exhibition, October 1-4, 2000, Dallas, Texas, https://www.onepetro.org/conference-paper/SPE-63242-MS.	☐

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	1	4986356		1991-01-22	Lockhardt et al.	
	2	5223159		1993-06-29	Smith et al.	
	3	5224546		1993-07-06	Smith et al.	
	4	5346010		1994-09-13	Adams et al.	
	5	6265355		2001-07-24	Lai et al.	
	6	6331513		2001-12-18	Zaid et al.	
	7	6435277		2002-08-20	Qu et al.	
	8	6436880		2002-08-20	Frenier	

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	9	6569814		2003-05-27	Brady et al.	
	10	6638896		2003-10-28	Tibbles et al.	
	11	7013974		2006-03-21	Hanes, Jr.	
	12	7159658		2007-01-09	Frost et al.	
	13	7192908		2007-03-20	Frenier et al.	
	14	7208529		2007-04-24	Crews	
	15	7306041		2007-12-11	Milne et al.	
	16	7527103		2009-05-05	Huang et al.	
	17	7928040		2011-04-19	Sanders et al.	
	18	8071511		2011-12-06	Welton et al.	
	19	8312929		2012-11-20	Frenier et al.	

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	Art Unit	3676
	Examiner Name	
	Attorney Docket Number	04697.0001USU1

	20	8567503		2013-10-29	Welton et al.	
	21	8567504		2013-10-29	Welton et al.	
	22	8584757		2013-11-19	Reyes	

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U.S.PATENT APPLICATION PUBLICATIONS Remove

Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	20060142166	A1	2006-06-29	Thomas	
	2	20100294498	A1	2010-11-25	Svoboda et al.	
	3	20110053811	A1	2011-03-03	Horton et al.	
	4	20110237470	A1	2011-09-29	Li et al.	
	5	20110263466	A1	2011-10-27	Rose	
	6	20130213657	A1	2013-08-22	Dobson, Jr. et al.	

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(**Not for submission under 37 CFR 1.99)**

Application Number	14686237
Filing Date	2015-04-14
First Named Inventor	Andrew Bryce Conway
Art Unit	3676
Examiner Name	
Attorney Docket Number	04697.0001USU1

	7	20130261032	A1	2013-10-03	Ladva et al.	
	8	20130274154	A1	2013-10-17	Nasr-El-Din et al.	
	9	20130274155	A1	2013-10-17	Nasr-El-Din et al.	
	10	20130303412	A1	2013-11-14	Luyster et al.	
	11	20140116696	A1	2014-05-01	Reyes	
	12	20140124205	A1	2014-05-08	Nasr-El-Din et al.	
	13	20140151042	A1	2014-06-05	Faugerstrom et al.	
	14	20130269944	A1	2013-10-17	Reyes et al.	
	15	20130269941	A1	2013-10-17	Reyes et al.	

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Examiner Initial*	Cite No	Foreign Document Number[3]	Country Code[2] i	Kind Code[4]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear	T[5]

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	14686237
Filing Date	2015-04-14
First Named Inventor	Andrew Bryce Conway
Art Unit	3676
Examiner Name	
Attorney Docket Number	04697.0001USU1

	1	2012116032	WO	A1	2012-08-30	Faugerstrom et al.		☐
	2	20100276152		A1	2010-11-04	De Wolf et al.		☐

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NON-PATENT LITERATURE DOCUMENTS Remove

Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]
	1	EPA, Proceedings of the Technical Workshops for the Hydraulic Fracturing Study: Chemical & Analytical Methods, EPA 600/R-11/066, May 2011, 122pgs.	☐
	2	AL-HARTHY, et al., Options for High-Temperature Well Stimulation, Oilfield Review, Winter 2008/2009: 20, No. 4., 11pgs.	☐
	3	XU, et al., On Modeling of Chemical Stimulation of an Enhanced Geothermal System using a High pH Solution with Chelating Agent, August 2009,30pgs.	☐
	4	PORTIER, et al., CREGE, Review on chemical stimulation techniques in oil industry and applications to geothermal systems, May 2007, 34pgs.	☐
	5	NASIR, Effects of Acid Additives on Spent Acid Flowback Through Carbonate Cores, May 2012, 125pgs.	☐
	6	WEIDNER, Chemical Additive Selection in Matrix Acidizing, May 2011, 95pgs.	☐
	7	CIVAN, et al., Rigorous Modeling of Gas Transport in Nano-darcy Shale Porous Media under Extreme Pore Proximity and Elevated Pressure Conditions, Proceedings of the International Conference on Heat Transfer and Fluid Flow, Paper No. 208, August 2014, 2pgs.	☐

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	14686237
	Filing Date	2015-04-14
	First Named Inventor	Andrew Bryce Conway
	Art Unit	3676
	Examiner Name	
	Attorney Docket Number	04697.0001USU1

	8	BWA, Geogard(R) SX - Amorphous Silica Control, Product Information, 2013, 2pgs.	☐
	9	NGUYEN, Well Design Spring 2013 Power Point, 44pgs.	☐
	10	CAPUTO, Shale Plays: Basic Geologic and Engineering Concepts, AAPL's 57th Annual Meeting, Boston June 2011, 71pgs.	☐
	11	Notification of Transmittal of The International Search Report and The Written Opinion of the International Searching Authority, or the Declaration, PCT/US2014/062440, February 13, 2015, 1 pg.	☐
	12	International Search Report, PCT/US2014/062440, February 13, 2015, 2pgs.	☐
	13	Written Opinion of the International Searching Authority, PCT/US2014/062440, February 13, 2015, 6pgs.	☐

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EXAMINER SIGNATURE

Examiner Signature	/Catherine Loikith/	Date Considered	07/21/2017

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	14686237
Filing Date	2015-04-14
First Named Inventor	Andrew Bryce Conway
Art Unit	3676
Examiner Name	
Attorney Docket Number	04697.0001USU1

CERTIFICATION STATEMENT

Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

☐ That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

☐ See attached certification statement.

☐ The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

☒ A certification statement is not submitted herewith.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/Brian P. McCall/	Date (YYYY-MM-DD)	2015-07-13
Name/Print	Brian P. McCall	Registration Number	68734

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1 hour to complete, including gathering, preparing and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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The information provided by you in this form will be subject to the following routine uses:

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EAST Search History

EAST Search History (Prior Art)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
S1	1	(14/686237).APP.	US-PGPUB	OR	OFF	2017/05/01 10:56
S2	50	("4815537" | "6110875" | "20130210684" | "20150005204" | "20080110621" | "20110053811" | "20130157905" | "4089787" | "5944446" | "7906463" | "20050150520" | "20060124302" | "20120125626" | "20130269936" | "4986356" | "5223159" | "5224546" | "5346010" | "6265355" | "6331513" | "6435277" | "6436880" | "6569814" | "6638896" | "7013974" | "7159658" | "7192908" | "7208529" | "7306041" | "7527103" | "7928040" | "8071511" | "8312929" | "8567503" | "8567504" | "8584757" | "20060142166" | "20100294498" | "20110237470" | "20110263466" | "20130213657" | "20130261032" | "20130274154" | "20130274155" | "20130303412" | "20140116696" | "20140124205" | "20140151042" | "20130269944" | "20130269941").PN.	US-PGPUB; USPAT	OR	ON	2017/05/01 10:58
S3	91	(nanodarcy nano$1darcy nano ADJ darcy) WITH shale	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/05/01 11:12
S4	6441	(E21B43/16).CPC.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/05/01 11:13
S5	8	S3 AND S4	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/05/01 11:13
S6	13	S3 AND (shale formation) WITH metal	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/05/01 11:14

S7	7	S3 AND (shale formation) WITH metal WITH natural$2	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/05/01 11:15
S8	123	(nanodarcy nano$1darcy nano ADJ darcy) WITH (formation shale)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/05/01 11:17
S9	14	S8 AND (shale formation) WITH metal	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/05/01 11:17
S10	29	S8 AND (metal WITH complex$4 citric WITH acid edta ethylenediaminetetraacetic acetic WITH acid)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/05/01 11:19
S15	71336	ethylenediaminetetraacetic ADJ acid	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/07/21 11:24
S16	26539	ethylenediamine ADJ tetraacetic ADJ acid	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/07/21 11:25
S22	50	("4815537" | "6110875" | "20130210684" | "20150005204" | "20080110621" | "20110053811" | "20130157905" | "4089787" | "5944446" | "7906463" | "20050150520" | "20060124302" | "20120125626" | "20130269936" | "4986356" | "5223159" | "5224546" | "5346010" | "6265355" | "6331513" | "6435277" | "6436880" | "6569814" | "6638896" | "7013974" | "7159658" | "7192908" | "7208529" | "7306041" | "7527103" | "7928040" | "8071511" | "8312929" | "8567503" | "8567504" | "8584757" | "20060142166" | "20100294498" | "20110237470" | "20110263466" | "20130213657" | "20130261032" | "20130274154" | "20130274155" | "20130303412" | "20140116696" | "20140124205" | "20140151042" | "20130269944" |	US-PGPUB; USPAT	OR	ON	2017/07/21 11:31

		"20130269941").PN.				
S23	9	(("2012116032") or ("20100276152")).PN.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2017/07/21 11:33
S24	2	(("20140151042") or ("20100276152")).PN.	US-PGPUB; USPAT	OR	OFF	2017/07/21 11:34
S40	77	shale WITH formation AND (below less lower) WITH fractur$3 WITH pressure AND complex$3 WITH metal	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/07/21 11:59
S41	9632	(E21B43/16 OR E21B43/25).CPC.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/07/21 11:59
S42	11	S40 AND (nanodarcy nano ADJ darcy)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/07/21 12:00
S43	10	S40 AND (shale formation) WITH (nanodarcy nano ADJ darcy)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/07/21 12:01
S44	1	("6265355").PN.	USPAT	OR	OFF	2017/07/21 12:06
S45	2	"14252038"	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/07/21 12:10
S46	1	"14525038"	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/07/21 12:10
S47	15	(("2013081609") or ("2013173634") or ("2009086954")).PN.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT;	OR	OFF	2017/07/21 12:28

			IBM_TDB			
S48	13	metal WITH complex$3 AND (shale formation) WITH (nanodarcy nano ADJ darcy)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/07/21 14:55
S49	12	S48 AND shale	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/07/21 14:55
S50	129	permeability AND (shale formation) WITH (nanodarcy nano ADJ darcy)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/07/21 14:58
S51	126	permeability SAME (shale formation) WITH (nanodarcy nano ADJ darcy)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/07/21 14:58
S52	3	(US-20150114653-$ or US-20110053811-$).did. or (US-6265355-$).did.	US-PGPUB; USPAT	OR	ON	2017/07/21 15:21
S53	3	S52 AND (citric edta acetic)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/07/21 15:21
S54	3	(US-20150114653-$ or US-20110053811-$).did. or (US-6265355-$).did.	US-PGPUB; USPAT	OR	ON	2017/07/23 13:52
S55	4356	metal WITH complex$3 AND diver$4 WITH (fluid mixture material)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/07/23 14:05
S56	287	S55 AND shale	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/07/23 14:10
S57	71	metal WITH complex$3 AND diver$4 WITH (fluid mixture material) WITH alternat$4	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT;	OR	ON	2017/07/23 14:10

			IBM_TDB			
S58	11	metal WITH complex$3 AND diver$4 WITH (fluid mixture material) WITH alternat$4 AND shale	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/07/23 14:10

EAST Search History (Interference)

<This search history is empty>

7/23/2017 2:28:24 PM
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Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	14686237	CONWAY, ANDREW BRYCE
	Examiner	Art Unit
	CATHERINE LOIKITH	3674

CPC- SEARCHED		
Symbol	Date	Examiner
E21B 43/16, 43/25	7/21/2017	CAL

CPC COMBINATION SETS - SEARCHED		
Symbol	Date	Examiner

US CLASSIFICATION SEARCHED			
Class	Subclass	Date	Examiner

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SEARCH NOTES		
Search Notes	Date	Examiner
text searches in EAST	7/21/2017	CAL

INTERFERENCE SEARCH			
US Class/ CPC Symbol	US Subclass / CPC Group	Date	Examiner

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant:	Andrew Bryce Conway	Examiner:	Catherine A Loikith
Serial No.:	14/686,237	Group Art Unit:	3674
Filed:	April 14, 2015	Docket No.:	04697.0001USU1
Customer No.:	23552	Confirmation No.:	2601
Title:	Stimulation of Wells in Nano-Darcy Shale Formations		

RESPONSE TO RESTRICTION REQUIREMENT

Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

Attention Commissioner:

This is in response to the Restriction Requirement mailed May 8, 2017. Applicant submits the following Remarks.

A listing of claims are included with this paper.

Remarks are included with this paper.

Listing of Claims:

This listing of claims will replace all prior versions and listings of claims in the application.

1. (Original) A method for stimulating a well in a nano-darcy shale formation comprising:

providing a treatment mixture containing between about 0.1% and 95% by weight metal complexing agent at a pH of between about 0 and 10;

injecting the treatment mixture into the well at a pressure less than a fracture pressure of the nano-darcy shale formation until at least some of the treatment mixture contacts the nano-darcy shale formation;

maintaining the treatment mixture in contact with the nano-darcy shale formation for a contact time of between about 1 minute to 100 days, thereby allowing the metal complexing agent to bind with at least some naturally-occurring metals contained within the nano-darcy shale formation; and

removing the treatment mixture from the well after the contact time, thereby removing the bound naturally-occurring metals from the non-darcy shale formation and thereby improving the hydrocarbon production of the well relative to the hydrocarbon production immediately prior to performance of the method.

2. (Original) The method of claim 1 wherein the metal complexing agent is citric acid.

3. (Original) The method of claim 1 wherein the metal complexing agent is ethylenediaminetetraacetic acid (EDTA).

4. (Original) The method of claim 1 wherein the metal complexing agent is acetic acid.

5. (Original) The method of claim 1 wherein the metal complexing agent includes at least one of ethylenediaminetetraacetic acid (EDTA), propylenediaminetetraacetic acid (PDTA), nitrilotriacetic acid (NTA), N-(2- hydroxyethyl)ethylenediaminetriacetic acid (HEDTA), diethylenetriaminepentaacetic acid (DTPA), hydroxyethyliminodiacetic acid (HEIDA),

cyclohexylenediaminetetraacetic acid (CDTA), diphenylaminesulfonic acid (DPAS), ethylenediaminedi(o-hydroxyphenylacetic) acid (EDDHA), glucoheptonic acid, gluconic acid, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, phthalic acid, terephthalic acid, aconitic acid, carballylic acid, trimesic acid, isocitric acid, citric acid, or any salt or derivative of any of the previously listed compounds.

6. (Original) The method of claim 1 wherein the treatment mixture comprises:
between about 0.1% and 95% by weight metal complexing agent;
between 1 and 10,000 parts per million (ppm) of a corrosion inhibitor;
between 1 and 10,000 ppm of a biocide;
between 1 and 10,000 ppm of a colloidal silica deposition inhibitor;
between 1 and 500 gallons per thousand gallons (gpt) of a mutual solvent; and
between 1 and 2000 parts per million of a surfactant.

7. (Original) The method of claim 1 wherein the treatment mixture further comprises between 0.1 and 95% of acid(s) as pH modifier.

8. (Original) The method of claim 1 wherein the injecting operation further comprises:
alternately injecting a first amount of treatment mixture and a second amount of a diverting mixture into the well.

9. (Original) The method of claim 1 wherein the injecting operation further comprises:
injecting the treatment mixture until the pressure within the well reaches a predetermined target pressure calculated based on the fracture pressure of the nano-darcy shale formation; and
upon reaching the target pressure, shutting in the well.

10. (Original) The method of claim 1 wherein the injecting operation further comprises:
injecting the treatment mixture containing a metal complexing agent such as citric acid or EDTA in combination with hydraulic fracturing and injecting into the formation in conjunction with propagation of the induced fractures.

11. (Original) The method of claim 1 further comprising:
monitoring at least one of pH and well pressure during the maintaining operation; and
initiating the removing operation based on results of the monitoring operation.

12. (Original) The method of claim 1 further wherein the metal complexing agent is selected from glutamic acid diacetic acid (GLDA), methylglycine diacetic acid (MGDA), β-alanine diacetic acid (β-ADA), ethylenediaminedisuccinic acid, S,S- ethylenediaminedisuccinic acid (EDDS), iminodisuccinic acid (IDS), hydroxyiminodisuccinic acid (HIDS), polyamino disuccinic acids, N-bis[2-(l,2- dicarboxyethoxy)ethyl]glycine (BCA6), N-bis[2-(l,2-dicarboxyethoxy)ethyl]aspartic acid (BCA5), N-bis[2-(l,2- dicarboxyethoxy)ethyl]methylglycine (MCBA5), N-tris[(l,2- dicarboxyethoxy)ethyl]amine (TCA6), N-methyliminodiacetic acid (MIDA), iminodiacetic acid (IDA), N-(2-acetamido)iminodiacetic acid (ADA), hydroxymethyl-iminodiacetic acid, 2-(2-carboxyethylamino) succinic acid (CEAA), 2-(2-carboxymethylamino) succinic acid (CMAA), diethylenetriamine- N,N"-disuccinic acid, triethylenetetramine-N,N"'-disuccinic acid, 1,6- hexamethylenediamine-N,N'-disuccinic acid, tetraethylenepentamine-N,N""- disuccinic acid, 2-hydroxypropylene-l,3-diamine-N,N'-disuccinic acid, 1,2-propylenediamine-N,N'-disuccinic acid, l,3-propylenediamine-N,N'-disuccinic acid, cis-cyclohexanediamine-N,N'-disuccinic acid, trans-cyclohexanediamine- N,N'-disuccinic acid, ethylenebis(oxyethylenenitrilo)-N,N'-disuccinic acid, glucoheptanoic acid, cysteic acid-N,N-diacetic acid, cysteic acid-N-monoacetic acid, alanine-N-monoacetic acid, N-(3-hydroxysuccinyl) aspartic acid, N-[2-(3- hydroxysuccinyl)]-L-serine, aspartic acid-N,N-diacetic acid, aspartic acid-N- monoacetic acid, any salt thereof, any derivative thereof, or any combination thereof.

13. (Original) The method of claim 1 further wherein the metal complexing agent is selected from acetic acid, acrylates, dihydroxymaleic acid, salts of dihydroxymaleic acid, EDTA (ethylenediamine tetraacetic acid), salts of EDTA, erythorbic acid, erythroboric acid, formic acid, gluconodeltalactone, GLDA (glutamic acid N,N-diacetic acid), salts of GLDA, HEDTA (hydroxyethylenediamine triacetic acid), salts of HEDTA, HEIDA (disodium ethanoldiglycine), salts of HEIDA, MGDA (methylglycine N,N-diacetic acid), salts of MGDA, NTA

(nitriolotriacetic acid), organic metal complexers, ligands, porphyrins, pigments, peptides, saccharides, nucleic acids, phosphonic acid, polyacrylic acid and citric acid in an amount sufficient to sequester at least a portion of a metal compound.

14. (Withdrawn) A method for fracturing and stimulating a well in a nano-darcy shale formation comprising:

providing a treatment mixture containing between about 0.1% and 95% by weight metal complexing agent at a pH of between about 0 and 10;

injecting the treatment mixture into the well at a pressure greater than a fracture pressure of the nano-darcy shale formation until at least some of the treatment mixture enters fractures in the nano-darcy shale formation, thereby allowing the metal complexing agent to bind with at least some naturally-occurring metals contained within the nano-darcy shale formation; and

removing spent treatment mixture and fracturing fluids from the well after the fractures are created, thereby removing the bound naturally-occurring metals from the non-darcy shale formation.

15. (Withdrawn) The method of claim 14 wherein the injecting operation is part of a fracturing operation that causes the fractures to occur in the nano-darcy shale formation.

16. (Withdrawn) The method of claim 14 further comprising:

fracturing the nano-darcy shale formation; and

wherein the injecting operation occurs after the fracturing operation causes the fractures to occur in the nano-darcy shale formation.

17. (Withdrawn) The method of claim 16 wherein the injecting operation includes injecting proppant into the fractures to occur in the nano-darcy shale formation.

REMARKS

This is in response to the Office Action issued May 8, 2017. The Office Action states that claims 1-17 are subject to restriction and species election requirements. Claims 14-17 are hereby withdrawn. Claims 1-17 are currently pending.

I. Restriction Requirement

The Office Action categorized the claims into the following species:

- Species I – directed to "a method of stimulating a nano-darcy shale formation comprising treatment at a pressure less than a fracture pressure"; and
- Species II – directed to "a method of stimulating a nano-darcy shale formation comprising treatment at a pressure greater than a fracture pressure."

In response to the restriction requirement, Applicants hereby elect Species I, without traverse, for examination in this application. Elected claims 1-13 read on the elected species. Thus, claims 1-13 remain pending and claims 14-17 are withdrawn. Applicants expressly reserve the right to pursue unelected and/or cancelled subject matter without prejudice in one or more continuation and/or divisional applications.

II. Conclusion

Applicants believe that the pending claims are in condition for allowance. If it would be helpful to obtain favorable consideration of this case, the Examiner is encouraged to call and discuss this case with the undersigned.

This paper constitutes a request for any needed extension of time and an authorization to charge all fees therefore to deposit account No. 13-2725, if not otherwise specifically requested. The undersigned hereby authorizes the charge of any fees created by the filing of this document or any deficiency of fees submitted herewith to be charged to deposit account No. 13-2725.

Respectfully submitted,
MERCHANT & GOULD P.C.
P.O. Box 2903
Minneapolis, Minnesota 55402-0903
(608) 280-6762

Date: July 6, 2017

/Brian P. McCall/
Name: Brian P. McCall
Reg. No.: 68,734

Electronic Acknowledgement Receipt

EFS ID:	29698077
Application Number:	14686237
International Application Number:	
Confirmation Number:	2601
Title of Invention:	STIMULATION OF WELLS IN NANO-DARCY SHALE FORMATIONS
First Named Inventor/Applicant Name:	Andrew Bryce Conway
Customer Number:	23552
Filer:	Brian Peter McCall
Filer Authorized By:	
Attorney Docket Number:	04697.0001USU1
Receipt Date:	06-JUL-2017
Filing Date:	14-APR-2015
Time Stamp:	11:53:26
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1		2017-07-06--Response-to-Restriction-Req--04697-0001USU1.PDF	111783 96a3ab3254e477c0ba94e613fe0bd49ad559513d	yes	8

	Multipart Description/PDF files in .zip description		
	Document Description	**Start**	**End**
	Response to Election / Restriction Filed	1	1
	Claims	2	6
	Applicant Arguments/Remarks Made in an Amendment	7	8
Warnings:			
Information:			
	Total Files Size (in bytes):	111783	

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

PTO/SB/06 (09-11)
Approved for use through 1/31/2014. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

PATENT APPLICATION FEE DETERMINATION RECORD Substitute for Form PTO-875	Application or Docket Number 14/686,237	Filing Date 04/14/2015	☐ To be Mailed

ENTITY: ☐ LARGE ☒ SMALL ☐ MICRO

APPLICATION AS FILED – PART I

FOR	(Column 1) NUMBER FILED	(Column 2) NUMBER EXTRA	RATE ($)	FEE ($)
☐ BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A	N/A	
☐ SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A	N/A	
☐ EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A	N/A	
TOTAL CLAIMS (37 CFR 1.16(i))	minus 20 =	*	X $ =	
INDEPENDENT CLAIMS (37 CFR 1.16(h))	minus 3 =	*	X $ =	
☐ APPLICATION SIZE FEE (37 CFR 1.16(s))	If the specification and drawings exceed 100 sheets of paper, the application size fee due is $310 ($155 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).			
☐ MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))				
* If the difference in column 1 is less than zero, enter "0" in column 2.			TOTAL	

APPLICATION AS AMENDED – PART II

AMENDMENT	07/06/2017	(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	RATE ($)	ADDITIONAL FEE ($)
	Total (37 CFR 1.16(i))	* 17	Minus	** 20	= 0	X $40 =	0
	Independent (37 CFR 1.16(h))	* 2	Minus	***3	= 0	X $210 =	0
	☐ Application Size Fee (37 CFR 1.16(s))						
	☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))						
						TOTAL ADD'L FEE	0

AMENDMENT		(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	RATE ($)	ADDITIONAL FEE ($)
	Total (37 CFR 1.16(i))	*	Minus	**	=	X $ =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=	X $ =	
	☐ Application Size Fee (37 CFR 1.16(s))						
	☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))						
						TOTAL ADD'L FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.
** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".
*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".
The "Highest Number Previously Paid For" (Total or Independent) is the highest number found in the appropriate box in column 1.

SLIE
VONDA GALE

This collection of information is required by 37 CFR 1.16. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

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www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
14/686,237	04/14/2015	Andrew Bryce Conway	04697.0001USU1	2601

23552 7590 05/08/2017

MERCHANT & GOULD P.C.
P.O. BOX 2903
MINNEAPOLIS, MN 55402-0903

EXAMINER
LOIKITH, CATHERINE A

ART UNIT	PAPER NUMBER
3674	

NOTIFICATION DATE	DELIVERY MODE
05/08/2017	ELECTRONIC

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Notice of the Office communication was sent electronically on above-indicated "Notification Date" to the following e-mail address(es):

USPTO23552@merchantgould.com

Office Action Summary	Application No. 14/686,237	Applicant(s) CONWAY, ANDREW BRYCE	
	Examiner CATHERINE LOIKITH	Art Unit 3674	AIA (First Inventor to File) Status Yes

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 2 MONTHS FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

1)☒ Responsive to communication(s) filed on *14 April 2015*.

☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on _____.

2a)☐ This action is **FINAL**. 2b)☐ This action is non-final.

3)☐ An election was made by the applicant in response to a restriction requirement set forth during the interview on _____; the restriction requirement and election have been incorporated into this action.

4)☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims*

5)☒ Claim(s) *1-17* is/are pending in the application.

5a) Of the above claim(s) _____ is/are withdrawn from consideration.

6)☐ Claim(s) _____ is/are allowed.

7)☐ Claim(s) _____ is/are rejected.

8)☐ Claim(s) _____ is/are objected to.

9)☒ Claim(s) *1-17* are subject to restriction and/or election requirement.

* If any claims have been determined allowable, you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information, please see http://www.uspto.gov/patents/init_events/pph/index.jsp or send an inquiry to PPHfeedback@uspto.gov.

Application Papers

10)☐ The specification is objected to by the Examiner.

11)☐ The drawing(s) filed on _____ is/are: a)☐ accepted or b)☐ objected to by the Examiner.

Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).

Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).

Priority under 35 U.S.C. § 119

12)☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

Certified copies:

a)☐ All b)☐ Some** c)☐ None of the:

1.☐ Certified copies of the priority documents have been received.

2.☐ Certified copies of the priority documents have been received in Application No. _____.

3.☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

** See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

1) ☐ Notice of References Cited (PTO-892)

2) ☐ Information Disclosure Statement(s) (PTO/SB/08a and/or PTO/SB/08b) Paper No(s)/Mail Date _____.

3) ☐ Interview Summary (PTO-413) Paper No(s)/Mail Date. _____ .

4) ☐ Other: _____.

PHARAOH, EX. 1002
P. 295

DETAILED ACTION

The present application, filed on or after March 16, 2013, is being examined under the first inventor to file provisions of the AIA.

Election/Restrictions

No claims are generic to the following disclosed patentably distinct species:

Species I directed towards a method of stimulating a nano-darcy shale formation comprising treatment at a pressure less than a fracture pressure; and

Species II directed towards a method of stimulating a nano-darcy shale formation comprising treatment at a pressure greater than a fracture pressure.

The species are independent or distinct because as disclosed the different species have mutually exclusive characteristics for each identified species. In addition, these species are not obvious variants of each other based on the current record.

Applicant is required under 35 U.S.C. 121 to elect a single disclosed species, or a single grouping of patentably indistinct species, for prosecution on the merits to which the claims shall be restricted if no generic claim is finally held to be allowable.

There is a search and/or examination burden for the patentably distinct species as set forth above because at least the following reason(s) apply:

The Species are not obvious variants of one another.

Applicant is advised that the reply to this requirement to be complete must include (i) an election of a species or a grouping of patentably indistinct species to be examined even though the requirement may be traversed (37 CFR 1.143) **and (ii) identification of the claims encompassing the elected species** or grouping of

patentably indistinct species, including any claims subsequently added. An argument that a claim is allowable or that all claims are generic is considered nonresponsive unless accompanied by an election.

The election may be made with or without traverse. To preserve a right to petition, the election must be made with traverse. If the reply does not distinctly and specifically point out supposed errors in the election of species requirement, the election shall be treated as an election without traverse. Traversal must be presented at the time of election in order to be considered timely. Failure to timely traverse the requirement will result in the loss of right to petition under 37 CFR 1.144. If claims are added after the election, applicant must indicate which of these claims are readable on the elected species or grouping of patentably indistinct species.

Should applicant traverse on the ground that the species, or groupings of patentably indistinct species from which election is required, are not patentably distinct, applicant should submit evidence or identify such evidence now of record showing the species to be obvious variants or clearly admit on the record that this is the case. In either instance, if the examiner finds one of the species unpatentable over the prior art, the evidence or admission may be used in a rejection under 35 U.S.C. 103 or pre-AIA 35 U.S.C. 103(a) of the other species.

Upon the allowance of a generic claim, applicant will be entitled to consideration of claims to additional species which depend from or otherwise require all the limitations of an allowable generic claim as provided by 37 CFR 1.141.

Any inquiry concerning this communication or earlier communications from the examiner should be directed to CATHERINE LOIKITH whose telephone number is (571)270-7822. The examiner can normally be reached on Monday-Friday, 9:00am-5:30pm.

Examiner interviews are available via telephone, in-person, and video conferencing using a USPTO supplied web-based collaboration tool. To schedule an interview, applicant is encouraged to use the USPTO Automated Interview Request (AIR) at http://www.uspto.gov/interviewpractice.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Doug Hutton can be reached on 571-272-4137. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see http://pair-direct.uspto.gov. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a USPTO Customer Service Representative or access to the automated information system, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.

/CATHERINE LOIKITH/
Primary Examiner, Art Unit 3674
5/1/17

Index of Claims	Application/Control No.	Applicant(s)/Patent Under Reexamination
	14686237	CONWAY, ANDREW BRYCE
	Examiner	**Art Unit**
	CATHERINE LOIKITH	3674

✓	Rejected	-	Cancelled	N	Non-Elected	A	Appeal
=	Allowed	÷	Restricted	I	Interference	O	Objected

☐ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

CLAIM		DATE								
Final	Original	05/01/2017								
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PTO/SB/08a (03-15)
Approved for use through 07/31/2016. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	14686237
Filing Date	2015-04-14
First Named Inventor	Andrew Bryce Conway
Art Unit	3676
Examiner Name	Waseem Moorad
Attorney Docket Number	04697.0001USU1

U.S.PATENTS Remove

Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	4815537	A	1989-03-28	Jones	
	2	6110875	A	2000-08-29	Tjon-Joe-Pin	

If you wish to add additional U.S. Patent citation information please click the Add button. Add

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Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
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INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	14686237
	Filing Date	2015-04-14
	First Named Inventor	Andrew Bryce Conway
	Art Unit	3676
	Examiner Name	Waseem Moorad
	Attorney Docket Number	04697.0001USU1

Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]
	1		

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EXAMINER SIGNATURE

Examiner Signature		Date Considered	

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	14686237
Filing Date	2015-04-14
First Named Inventor	Andrew Bryce Conway
Art Unit	3676
Examiner Name	Waseem Moorad
Attorney Docket Number	04697.0001USU1

CERTIFICATION STATEMENT

Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

See attached certification statement.

The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

☒ A certification statement is not submitted herewith.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/Brian P. McCall/	Date (YYYY-MM-DD)	2017-01-31
Name/Print	Brian P. McCall	Registration Number	68734

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1 hour to complete, including gathering, preparing and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C. 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether the Freedom of Information Act requires disclosure of these record s.

2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.

3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.

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5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.

6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.

9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

Electronic Acknowledgement Receipt

EFS ID:	28222617
Application Number:	14686237
International Application Number:	
Confirmation Number:	2601
Title of Invention:	STIMULATION OF WELLS IN NANO-DARCY SHALE FORMATIONS
First Named Inventor/Applicant Name:	Andrew Bryce Conway
Customer Number:	23552
Filer:	Brian Peter McCall/Amy Miller
Filer Authorized By:	Brian Peter McCall
Attorney Docket Number:	04697.0001USU1
Receipt Date:	31-JAN-2017
Filing Date:	14-APR-2015
Time Stamp:	16:51:53
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Information Disclosure Statement (IDS) Form (SB08)	2017-01-31--SIDS-4--04697-0001USU1.PDF	1034891 2dca674b31987a733f56d522e59913f19f2e5c68	no	4

Warnings:

Information:	
Total Files Size (in bytes):	1034891

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New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

PTO/SB/08a (03-15)
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INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	14686237
Filing Date	2015-04-14
First Named Inventor	Andrew Bryce Conway
Art Unit	3676
Examiner Name	
Attorney Docket Number	04697.0001USU1

U.S.PATENTS Remove

Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
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Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	20130210684	A1	2013-08-15	Ballard	
	2	20150005204	A1	2015-01-01	Alwattari et al.	
	3	20080110621	A1	2008-05-15	Montgomery et al.	
	4	20110053811	A1	2011-03-03	Horton et al.	
	5	20130157905	A1	2013-06-20	Saini et al.	

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	14686237
Filing Date	2015-04-14
First Named Inventor	Andrew Bryce Conway
Art Unit	3676
Examiner Name	
Attorney Docket Number	04697.0001USU1

Examiner Initial*	Cite No	Foreign Document Number[3]	Country Code[2] i	Kind Code[4]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear	T[5]
	1							

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NON-PATENT LITERATURE DOCUMENTS Remove

Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]
	1		

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Examiner Signature		Date Considered	

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[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	14686237
	Filing Date	2015-04-14
	First Named Inventor	Andrew Bryce Conway
	Art Unit	3676
	Examiner Name	
	Attorney Docket Number	04697.0001USU1

CERTIFICATION STATEMENT

Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

See attached certification statement.

The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

☒ A certification statement is not submitted herewith.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/Brian P. McCall/	Date (YYYY-MM-DD)	2016-09-06
Name/Print	Brian P. McCall	Registration Number	68734

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1 hour to complete, including gathering, preparing and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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Electronic Acknowledgement Receipt

EFS ID:	26835243
Application Number:	14686237
International Application Number:	
Confirmation Number:	2601
Title of Invention:	STIMULATION OF WELLS IN NANO-DARCY SHALE FORMATIONS
First Named Inventor/Applicant Name:	Andrew Bryce Conway
Customer Number:	23552
Filer:	Brian Peter McCall
Filer Authorized By:	
Attorney Docket Number:	04697.0001USU1
Receipt Date:	06-SEP-2016
Filing Date:	14-APR-2015
Time Stamp:	11:19:06
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Information Disclosure Statement (IDS) Form (SB08)	2016-09-06--SIDS-3--04697-0001USU1.PDF	1035034 de7cf688b0bea9da1ef8901f9ad4ee71143eee0f	no	4

Warnings:

Information:	
Total Files Size (in bytes):	1035034

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New Applications Under 35 U.S.C. 111

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National Stage of an International Application under 35 U.S.C. 371

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New International Application Filed with the USPTO as a Receiving Office

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APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
14/686,237	04/14/2015	Andrew Bryce Conway	04697.0001USU1

CONFIRMATION NO. 2601

23552
MERCHANT & GOULD P.C.
P.O. BOX 2903
MINNEAPOLIS, MN 55402-0903

PUBLICATION NOTICE



Title:STIMULATION OF WELLS IN NANO-DARCY SHALE FORMATIONS

Publication No.US-2015-0292308-A1
Publication Date:10/15/2015

NOTICE OF PUBLICATION OF APPLICATION

The above-identified application will be electronically published as a patent application publication pursuant to 37 CFR 1.211, et seq. The patent application publication number and publication date are set forth above.

The publication may be accessed through the USPTO's publically available Searchable Databases via the Internet at www.uspto.gov. The direct link to access the publication is currently http://www.uspto.gov/patft/.

The publication process established by the Office does not provide for mailing a copy of the publication to applicant. A copy of the publication may be obtained from the Office upon payment of the appropriate fee set forth in 37 CFR 1.19(a)(1). Orders for copies of patent application publications are handled by the USPTO's Office of Public Records. The Office of Public Records can be reached by telephone at (703) 308-9726 or (800) 972-6382, by facsimile at (703) 305-8759, by mail addressed to the United States Patent and Trademark Office, Office of Public Records, Alexandria, VA 22313-1450 or via the Internet.

In addition, information on the status of the application, including the mailing date of Office actions and the dates of receipt of correspondence filed in the Office, may also be accessed via the Internet through the Patent Electronic Business Center at www.uspto.gov using the public side of the Patent Application Information and Retrieval (PAIR) system. The direct link to access this status information is currently http://pair.uspto.gov/. Prior to publication, such status information is confidential and may only be obtained by applicant using the private side of PAIR.

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Office of Data Managment, Application Assistance Unit (571) 272-4000, or (571) 272-4200, or 1-888-786-0101

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U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	14686237
Filing Date	2015-04-14
First Named Inventor	Andrew Bryce Conway
Art Unit	3676
Examiner Name	
Attorney Docket Number	04697.0001USU1

U.S.PATENTS Remove

Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	4089787		1978-05-16	Lybarger et al.	
	2	5944446		1999-08-31	Hocking	
	3	7906463		2011-03-15	Starkey, II et al.	

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U.S.PATENT APPLICATION PUBLICATIONS Remove

Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	20050150520	A1	2015-07-14	Gill et al.	
	2	20060124302	A1	2006-06-15	Gupta et al.	
	3	20120125626	A1	2012-05-24	Constantine	

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	14686237
	Filing Date	2015-04-14
	First Named Inventor	Andrew Bryce Conway
	Art Unit	3676
	Examiner Name	
	Attorney Docket Number	04697.0001USU1

	4	20130269936		2013-10-17	Reyes et al.	

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Examiner Initial*	Cite No	Foreign Document Number[3]	Country Code[2] ¡	Kind Code[4]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear	T[5]
	1	2013081609	WO	A1	2013-06-06	Ayers et al.		☐
	2	2013173634	WO	A1	2013-11-21	Yean et al.		☐
	3	2009086954	WO	A1	2009-07-16	De Wolf et al.		☐

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Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]
	1	International Search Report for Application No. PCT/US2015/25399 mailed July 8, 2015, 2pgs.	☐
	2	Written Opinion of the International Searching Authority for Application No. PCT/US2015/25399 mailed July 8, 2015, 5pgs.	☐
	3	Notification of Transmittal of the International Search Report and the Written Opinion of the International Searching Authority, or the Declaration for Application No. PCT/US2015/25399 mailed July 8, 2015, 1pg.	☐

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	14686237
	Filing Date	2015-04-14
	First Named Inventor	Andrew Bryce Conway
	Art Unit	3676
	Examiner Name	
	Attorney Docket Number	04697.0001USU1

	4	FRENIER, et al., Use of Highly Acid-Soluble Chelating Agents in Well Stimulation Services, SPE Annual Technical Conference and Exhibition, October 1-4, 2000, Dallas, Texas, https://www.onepetro.org/conference-paper/SPE-63242-MS.	☐

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EXAMINER SIGNATURE

Examiner Signature		Date Considered	

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

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CERTIFICATION STATEMENT

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☐ See attached certification statement.

☐ The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

☒ A certification statement is not submitted herewith.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/Brian P. McCall/	Date (YYYY-MM-DD)	2015-08-06
Name/Print	Brian P. McCall	Registration Number	68734

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9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

PATENT COOPERATION TREATY

From the INTERNATIONAL SEARCHING AUTHORITY

To: STEVEN C. BRUESS
MERCHANT & GOULD P.C.
P.O. BOX 2903
MINNEAPOLIS, MN 55402-0903

PCT

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL SEARCH REPORT AND THE WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY, OR THE DECLARATION

(PCT Rule 44.1)

Applicant's or agent's file reference 4697.1WOU1	Date of mailing *(day/month/year)* 08 JUL 2015 **FOR FURTHER ACTION** See paragraphs 1 and 4 below
International application No. PCT/US 15/25399	International filing date *(day/month/year)* 10 April 2015 (10.04.2015)
Applicant FLEX-CHEM HOLDING COMPANY, LLC	

1. ☒ The applicant is hereby notified that the international search report and the written opinion of the International Searching Authority have been established and are transmitted herewith.

   Filing of amendments and statement under Article 19:
   The applicant is entitled, if he so wishes, to amend the claims of the international application (see Rule 46):

   When? The time limit for filing such amendments is normally two months from the date of transmittal of the international search report.

   How? Directly to the International Bureau of WIPO preferably through ePCT or on paper to, 34 chemin des Colombettes 1211 Geneva 20, Switzerland, Facsimile No.: +41 22 338 82 70

   For more detailed instructions, see *PCT Applicant's Guide*, International Phase, paragraphs 9.004 – 9.011.

2. ☐ The applicant is hereby notified that no international search report will be established and that the declaration under Article 17(2)(a) to that effect and the written opinion of the International Searching Authority are transmitted herewith.

3. ☐ **With regard to any protest** against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that:
   - ☐ the protest together with the decision thereon has been transmitted to the International Bureau together with any request to forward the texts of both the protest and the decision thereon to the designated Offices.
   - ☐ no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.

4. **Reminders**

   The applicant may **submit comments on an informal basis on the written opinion of the International Searching Authority** to the International Bureau. These comments will be made available to the public after international publication. The International Bureau will send a copy of such comments to all designated Offices unless an international preliminary examination report has been or is to be established.

   Shortly after the expiration of **18 months from the priority date, the international application will be published** by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the international application, or of the priority claim, must reach the International Bureau before the completion of the technical preparations for international publication (Rules 90*bis*.1 and 90*bis*.3).

   Within **19 months** from the priority date, but only in respect of some designated Offices, a demand for international preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase **until 30 months** from the priority date (in some Offices even later); otherwise, the applicant must, **within 20 months** from the priority date, perform the prescribed acts for **entry into the national phase** before those designated Offices. In respect of other designated Offices, the time limit of **30 months** (or later) will apply even if no demand is filed within 19 months. For details about the applicable time limits, Office by Office, see www.wipo.int/pct/en/texts/time_limits.html and the *PCT Applicant's Guide*, National Chapters.

   Within **19 months from the priority date, the applicant may request that a supplementary international search be carried out** by a different International Searching Authority that offers this service (Rule 45*bis*.1). The procedure for requesting supplementary international search is described in the *PCT Applicant's Guide*, International Phase, paragraphs 8.006-8.032.

Name and mailing address of the ISA/ Mail Stop PCT, Attn: ISA/US Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer Lee W. Young PCT Helpdesk: 571-272-4300 Telephone No. PCT OSP: 571-272-7774

Form PCT/ISA/220 (July 2014)

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference 4697.1WOU1	FOR FURTHER ACTION	see Form PCT/ISA/220 as well as, where applicable, item 5 below.
International application No. PCT/US 15/25399	International filing date *(day/month/year)* 10 April 2015 (10.04.2015)	(Earliest) Priority Date *(day/month/year)* 14 April 2014 (14.04.2014)
Applicant FLEX-CHEM HOLDING COMPANY, LLC		

This international search report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This international search report consists of a total of 2 sheets.

☐ It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**

a. With regard to the **language**, the international search was carried out on the basis of:

☒ the international application in the language in which it was filed.

☐ a translation of the international application into _____ which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1(b)).

b. ☐ This international search report has been established taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 43.6*bis*(a)).

c. ☐ With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, see Box No. I.

2. ☐ **Certain claims were found unsearchable** (see Box No. II).

3. ☐ **Unity of invention is lacking** (see Box No. III).

4. With regard to the **title**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2, by this Authority as it appears in Box No. IV. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. With regard to the **drawings**,

a. the figure of the drawings to be published with the abstract is Figure No. 1

☒ as suggested by the applicant.

☐ as selected by this Authority, because the applicant failed to suggest a figure.

☐ as selected by this Authority, because this figure better characterizes the invention.

b. ☐ none of the figures is to be published with the abstract.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 15/25399

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - E21B 43/22, 43/28, 43/28; C09K 8/60 (2015.01)
CPC - C09K 8/607; E21B 43/25
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(8) - E21B 43/22, 43/28, 43/28; C09K 8/60 (2015.01)
CPC - C09K 8/607; E21B 43/25

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
CPC - E21B 43/16, 43/28, 43/283; C09K 8/58, 8/60, 8/608, 8/62, 8/72

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Patbase; Google Patents; Google Scholar; Google Web; Espacenet; Search Terms: acetic*, acid*, biocid*, bind*, borehole*, bound*, chel*, citric, clay*, complex*, concentration*, corro*, downhole*, EDTA, ethylenediaminetetraacetic, fluid*, formation*, frac*, inhibit*, inject*, introduc*, liquid*, measur*, metal*, mix*, monitor*, nanodarcy*, pH, ppm*,

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	WO 2013/081609 A1 (Ayers et al.) 06 June 2013 (06.06.2013), para [002], [0042], [00156], [00178]	1-5, 7-10 and 12-17 --- 6 and 11
Y	US 2005/0150520 A1 (Gill et al.) 14 July 2005 (14.07.2005), para [0039], [0042]	6
Y	US 2006/0124302 A1 (Gupta et al.) 15 June 2006 (15.06.2006), para [0022], [0035]	6
Y	US 2012/0125626 A1 (Constantine) 24 May 2012 (24.05.2012), para [0018]	11
A	WO 2013/173634 A1 (Yean et al.) 21 November 2013 (21.11.2013), para [0035]-[0036]	1-17
A	US 2013/0269944 A1 (Reyes et al.) 17 October 2013 (17.10.2013), para [0020], [0037]-[0038]	1-17

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

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
04 June 2015 (04.06.2015)	08 JUL 2015
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

Form PCT/ISA/210 (second sheet) (January 2015)

PATENT COOPERATION TREATY

From the
INTERNATIONAL SEARCHING AUTHORITY

To: STEVEN C. BRUESS
MERCHANT & GOULD P.C.
P.O. BOX 2903
MINNEAPOLIS, MN 55402-0903

PCT

WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY

(PCT Rule 43*bis*.1)

Date of mailing *(day/month/year)*	08 JUL 2015
Applicant's or agent's file reference 4697.1WOU1	FOR FURTHER ACTION See paragraph 2 below

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US 15/25399	10 April 2015 (10.04.2015)	14 April 2014 (14.04.2014)

International Patent Classification (IPC) or both national classification and IPC
IPC(8) - E21B 43/22, 43/28, 43/28; C09K 8/60 (2015.01)
CPC - C09K 8/607; E21B 43/25

Applicant FLEX-CHEM HOLDING COMPANY, LLC

1. This opinion contains indications relating to the following items:

- ☒ Box No. I Basis of the opinion
- ☐ Box No. II Priority
- ☐ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- ☐ Box No. IV Lack of unity of invention
- ☒ Box No. V Reasoned statement under Rule 43*bis*.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- ☐ Box No. VI Certain documents cited
- ☐ Box No. VII Certain defects in the international application
- ☐ Box No. VIII Certain observations on the international application

2. **FURTHER ACTION**

If a demand for international preliminary examination is made, this opinion will be considered to be a written opinion of the International Preliminary Examining Authority ("IPEA") except that this does not apply where the applicant chooses an Authority other than this one to be the IPEA and the chosen IPEA has notified the International Bureau under Rule 66.1 *bis*(b) that written opinions of this International Searching Authority will not be so considered.

If this opinion is, as provided above, considered to be a written opinion of the IPEA, the applicant is invited to submit to th IPEA a written reply together, where appropriate, with amendments, before the expiration of 3 months from the date of mailing of Fom PCT/ISA/220 or before the expiration of 22 months from the priority date, whichever expires later.

For further options, see Form PCT/ISA/220.

Name and mailing address of the ISA/US	Date of completion of this opinion	Authorized officer:
Mail Stop PCT, Attn: ISA/US Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	04 June 2015 (04.06.2015)	Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

Form PCT/ISA/237 (cover sheet) (January 2015)

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US 15/25399

Box No. I Basis of this opinion

1. With regard to the **language**, this opinion has been established on the basis of:
   - [x] the international application in the language in which it was filed.
   - [ ] a translation of the international application into _____ which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1(b)).

2. [ ] This opinion has been established taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 43*bis*.1(a)).

3. [ ] With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, this opinion has been established on the basis of a sequence listing:
   - a. [ ] forming part of the international application as filed:
     - [ ] in the form of an Annex C/ST.25 text file.
     - [ ] on paper or in the form of an image file.
   - b. [ ] furnished together with the international application under PCT Rule 13*ter*.1(a) for the purposes of international search only in the form of an Annex C/ST.25 text file.
   - c. [ ] furnished subsequent to the international filing date for the purposes of international search only:
     - [ ] in the form of an Annex C/ST.25 text file (Rule 13*ter*.1(a)).
     - [ ] on paper or in the form of an image file (Rule 13*ter*.1(b) and Administrative Instructions, Section 713).

4. [ ] In addition, in the case that more than one version or copy of a sequence listing has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that forming part of the application as filed or does not go beyond the application as filed, as appropriate, were furnished.

5. Additional comments:

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US 15/25399

Box No. V **Reasoned statement under Rule 43*bis*.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

1. Statement

Novelty (N)	Claims	2, 4, 6-8, 11 and 16-17	YES
	Claims	1, 3, 5, 9-10 and 12-15	NO
Inventive step (IS)	Claims	None	YES
	Claims	1-17	NO
Industrial applicability (IA)	Claims	1-17	YES
	Claims	None	NO

2. Citations and explanations:

Claims 1, 3, 5, 9-10 and 12-15 lack novelty under PCT Article 33(2) as being anticipated by WO 2013/081609 A1 to Ayers et al. (hereinafter 'Ayers').

Regarding claim 1, Ayers discloses a method for stimulating a well (para [002]) in a nano-darcy shale formation (intended use) comprising:
providing a treatment mixture containing between about 0.1 % and 95% by weight metal complexing agent (para [00156], 'the alkali metal chelate concentration is greater than about 0.2%') at a pH of between about 0 and 10 (para [00156], 'the composition pH is less than about 10');
injecting the treatment mixture into the well at a pressure less than a fracture pressure of the nano-darcy shale formation until at least some of the treatment mixture contacts the nano-darcy shale formation (para [0042], 'procedure is applied or performed at pressures below the formation fracturing pressure');
maintaining the treatment mixture in contact with the nano-darcy shale formation for a contact time of between about 1 minute to 100 days (para [00178]), thereby allowing the metal complexing agent to bind with at least some naturally-occurring metals contained within the nano-darcy shale formation (para [002], 'alkali metal chelate can serve the purpose of scavenging ionic or bound phases of metals in a formation'); and
removing the treatment mixture from the well after the contact time, thereby removing the bound naturally-occurring metals from the non-darcy shale formation and thereby improving the hydrocarbon production of the well relative to the hydrocarbon production immediately prior to performance of the method (para [00170], 'removed from the wellbore after introduction').

Regarding claim 3, Ayers discloses the method of claim 1 and further wherein the metal complexing agent is ethylenediaminetetraacetic acid (EDTA) (para [00151], 'EDTA').

Regarding claim 5, Ayers discloses the method of claim 1 and further wherein the metal complexing agent includes at least one of ethylenediaminetetraacetic acid (EDTA), propylenediaminetetraacetic acid (PDTA), nitrilotriacetic acid (NTA), N-(2-29 hydroxyethyl)ethylenediaminetriacetic acid (HEDTA), diethylenetriaminepentaacetic acid (DTPA), hydroxyethyliminodiacetic acid (HEIDA), cyclohexylenediaminetetraacetic acid (CDT A), diphenylaminesulfonic acid (DPAS), ethylenediaminedi(o-hydroxyphenylacetic) acid (EDD HA), glucoheptonic acid, gluconic acid, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, phthalic acid, terephthalic acid, aconitic acid, carballylic acid, trimesic acid, isocitric acid, citric acid, or any salt or derivative of any of the previously listed compounds (para [00151], 'EDTA').

Regarding claim 9, Ayers discloses the method of claim 1 and further wherein the injecting operation further comprises:
injecting the treatment mixture until the pressure within the well reaches a predetermined target pressure calculated based on the fracture pressure of the nanodarcy shale formation (para [0042]); and
upon reaching the target pressure, shutting in the well (para [00170], 'wellbore may be sealed after introducing the composition').

Regarding claim 10, Ayers discloses the method of claim 1 and further wherein the injecting operation further comprises:
injecting the treatment mixture containing a metal complexing agent such as citric acid or EDTA (para [00151], 'EDTA') in combination with hydraulic fracturing and injecting into the formation in conjunction with propagation of the induced fractures (para [0098], 'The composition can be applied with sufficient time allowed for the composition to generate 02 or C02 gas and gas pressure with sufficient mechanical energy and/or action to physically alter, fragment, rubblize, fracture, crack, pit, and/or create fluid preferential pathways within a portion of the treated subterranean formation').

— See supplemental box —

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US 15/25399

Supplemental Box

In case the space in any of the preceding boxes is not sufficient.
Continuation of:
Box V.2 - Citations and explanations

Regarding claim 12, Ayers discloses the method of claim 1 and further wherein the metal complexing agent is selected from glutamic acid diacetic acid (GLDA), methylglycine diacetic acid (MGDA), ()-alanine diacetic acid ((3-ADA), ethylenediaminedisuccinic acid, S,Sethylenediaminedisuccinic acid (EDDS), iminodisuccinic acid (IDS), hydroxyiminodisuccinic acid (HIDS), polyamino disuccinic acids, N-bis[2-(l,2-dicarboxyethoxy)ethyl]glycine (BCA6), N-bis[2-(l,2- dicarboxyethoxy)ethyl]aspartic acid (BCA5), N-bis[2-(l,2-dicarboxyethoxy)ethyl]methylglycine (MCBA5), Ntris[(l,2- dicarboxyethoxy)ethyl]amine (TCA6), N-methyliminodiacetic acid (MIDA), iminodiacetie acid (IDA), N-(2-acetamido)iminodiacetic acid (ADA), hydroxymethyl-iminodiacetic acid, 2-(2-carboxyethylamino) succinic acid (CEAA), 2-(2-carboxymethylamino) succinic acid (CMAA), diethylenetriamine- N,N"-disuccinic acid, triethylenetetramine-N,N'"-disuccinic acid, 1,6-hexamethylenediamine-N,N'-disuccinic acid, tetraethylenepentamine-N,N""disuccinic acid, 2-hydroxypropylene-1,3-diamine-N,N'-disuccinic acid, 1,2-propylenediamine-N,N'-disuccinic acid, 1,3-propylenediamine-N,N'-disuccinic acid, cis-cyclohexanediamine-N,N'-disuccinic acid, trans-cyclohexanediamine- N,N'-disuccinic acid, ethylenebis(oxyethylenenitrilo)-N,N'-disuccinic acid, glucoheptanoic acid, cysteic acid-N,N-diacetic acid, cysteic acid-N-monoacetic acid, alanine-Nmonoacetic acid, N-(3-hydroxysuccinyl) aspartic acid, N-[2-(3- hydroxysuccinyl)]-Lserine, aspartic acid-N,N-diacetic acid, aspartic acid-N- monoacetic acid, any salt thereof, any derivative thereof, or any combination thereof (para [00151], 'EDDS').

Regarding claim 13, Ayers discloses the method of claim 1 and further wherein the metal complexing agent is selected from acetic acid, acrylates, dihydroxymaleic acid, salts of dihydroxymaleic acid, EDTA (ethylenediamine tetraacetic acid), salts of EDTA, erythorbic acid, erythroboric acid, formic acid, gluconodeltalactone, GLDA (glutamic acid N,N-diacetic acid), salts of GLDA, HEDT A (hydroxyethylenediamine triacetic acid), salts of HEDTA, HEIDA (disodium ethanoldiglycine), salts of HEIDA, MGDA (methylglycine N,N-diacetic acid), salts of MGDA, NTA (nitriolotriacetic acid), organic metal complexers, ligands, porphyrins, pigments, peptides, saccharides, nucleic acids, phosphonic acid, polyacrylic acid and citric acid in an amount sufficient to sequester at least a portion of a metal compound (para [00151], 'EDTA').

Regarding claim 14, Ayers discloses a method for fracturing and stimulating a well (para [0002]) in a nano-darcy shale formation (intended use) comprising:
providing a treatment mixture containing between about 0.1 % and 95% by weight metal complexing agent (para [00156], 'the alkali metal chelate concentration is greater than about 0.2%') at a pH of between about 0 and 10 (para [00156], 'the composition pH is less than about 10');
injecting the treatment mixture into the well at a pressure greater than a fracture pressure of the nano-darcy shale formation until at least some of the treatment mixture enters fractures in the nano-darcy shale formation (para [0098], 'The composition can be applied with sufficient time allowed for the composition to generate 02 or C02 gas and gas pressure with sufficient mechanical energy and/or action to physically alter, fragment, rubblize, fracture, crack, pit, and/or create fluid preferential pathways within a portion of the treated subterranean formation'), thereby allowing the metal complexing agent to bind with at least some naturally-occurring metals contained within the nano-darcy shale formation (para [002], 'alkali metal chelate can serve the purpose of scavenging ionic or bound phases of metals in a formation'); and
removing spent treatment mixture and fracturing fluids from the well after the fractures are created, thereby removing the bound naturally-occurring metals from the non-darcy shale formation (para [00170], 'removed from the wellbore after introduction').

Regarding claim 15, Ayers discloses the method of claim 14 and further wherein the injecting operation is part of a fracturing operation that causes the fractures to occur in the nano-darcy shale formation (para [0098], 'The composition can be applied with sufficient time allowed for the composition to generate 02 or C02 gas and gas pressure with sufficient mechanical energy and/or action to physically alter, fragment, rubblize, fracture, crack, pit, and/or create fluid preferential pathways within a portion of the treated subterranean formation').

Claims 2, 4, 7-8 and 16-17 lack an inventive step under PCT Article 33(3) as being obvious over Ayers.

Regarding claim 2, Ayers discloses the method of claim 1. While Ayers does not specifically disclose wherein the metal complexing agent is citric acid, Ayers does include the addition of citric acid (para [00160]). It would have been obvious to a person of ordinary skill in the art that the citric acid would also function as a complexing agent.

Regarding claim 4, Ayers discloses the method of claim 1. While Ayers does not specifically disclose wherein the metal complexing agent is acetic acid, Ayers does disclose the addition of acetic acid (para [00160]). It would have been obvious to a person of ordinary skill in the art that the citric acid would also function as a complexing agent.

Regarding claim 7, Ayers discloses the method of claim 1 and further wherein the treatment mixture further comprises acid(s) as a pH modifier (para [00160]) but does not specifically disclose between 0.1 and 95% of acid(s) as pH modifier. However, it would be mere routine experimentation to add more or less acid depending upon the amount of pH modification required for a particular application.

Regarding claim 8, Ayers discloses the method of claim 1 and in a specific embodiment, further wherein the injecting operation further comprises:
alternately injecting a first amount of treatment mixture and a second amount of a diverting mixture into the well (para [00223], 'The entire volume of treatment solution was allowed to gravity flow into the test wellbore. Following, a 100 gal water chase was slowly pumped (8 gpm) behind the treatment solution to displace the treatment solution from the wellbore and into the targeted subterranean formation'). It would have been obvious to a person of ordinary skill in the art to use a diverting mixture as disclosed in a specific embodiment of Ayers for the general method in order to ensure the composition fully enters the formation and does not remain in the wellbore.

--- See supplemental box ---

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US 15/25399

Supplemental Box

In case the space in any of the preceding boxes is not sufficient.
Continuation of:
Box V.2 - Citations and explanations

Regarding claim 16, Ayers discloses the method of claim 14 and further comprising:
fracturing the nano-darcy shale formation (para [0098]) and in a further embodiment wherein the injecting operation occurs after the fracturing operation causes the fractures to occur in the nano-darcy shale formation (para [00103], 'The a composition can be applied to a portion of the wellbore or a portion of a subterranean formation before, during, and/or after the application, igniting, shooting, firing, setting off, or detonating of explosive materials, propellants, or seismic instruments that cause sufficient pressure, gas wave, or shock wave to fracture, shatter, rubblize, and/or propagate treatment into a portion of a subterranean formation'). It would have been obvious to a person of ordinary skill in the art that the general method of Ayers could be applied to a formation that was previously fractured as disclosed in one of the optional embodiments of Ayers.

Regarding claim 17, Ayers discloses the method of claim 16 and further wherein the injecting operation includes injecting proppant into the fractures to occur in the nano-darcy shale formation (para [00103], 'The composition can be added to an existing treatment composition including explosive fluids or gels, peroxygens, acids, polymers, proppants').

Claim 11 lacks an inventive step under PCT Article 33(3) as being obvious over Ayers in view of US 2012/0125626 A1 (Constantine).

Regarding claim 11, Ayers discloses the method of claim I but does not specifically disclose further comprising: monitoring at least one of pH and well pressure during the maintaining operation; and initiating the removing operation based on results of the monitoring operation. However, Constantine dsicloses monitoring at least one of pH and well pressure during the maintaining operation (para [0018]); and initiating the removing operation based on results of the monitoring operation (para [0018]). It would have been obvious to a person of ordinary skill in the art to use pH measurement as disclosed in Constantine a means of measuring the reaction progress of Ayers in order to know when to move to the next steps of the method.

Claim 6 lacks an inventive step under PCT Article 33(3) as being obvious over Ayers in view of US 2005/0150520 A1 to Gill et al. (hereinafter 'Gill') in view of US 2006/0124302 A1 to Gupta et al. (hereinafter 'Gupta').

Regarding claim 6, Ayers discloses the method of claim 1 and further wherein the treatment mixture comprises:
between about 0.1 % and 95% by weight metal complexing agent (para [00156], 'the alkali metal chelate concentration is greater than about 0.2%');
a biocide (para [00102]);
between 1 and 500 gallons per thousand gallons (gpt) of a mutual solvent (para [00158], 'composition has a concentration in water of 0.01% to 99.9%'); and
between 1 and 2000 parts per million of a surfactant (para [00161]) but Ayers does not specifically disclose between 1 and 10,000 parts per million (ppm) of a corrosion inhibitor; between 1 and 10,000 ppm of a biocide; and between 1 and 10,000 ppm of a colloidal silica deposition inhibitor.
Gill discloses disclose between 1 and 10,000 parts per million (ppm) of a corrosion inhibitor (para [0039], 'corrosion inhibitor is added to reach a concentration of from about 50 ppm to about 500 ppm'); and
between 1 and 10,000 ppm of a biocide (para [0042], 'the amount of biocide added is that amount sufficient to have a concentration of from about 1 ppm to about 500 ppm').
Gupta discloses between 1 and 10,000 ppm of a colloidal silica deposition inhibitor (para [0022], 'Suitable scale inhibitors include strong acidic materials such as a phosphonic acid, a phosphoric acid or a phosphorous acid, phosphate esters'; para [0035], 'the amount of scale inhibitor in the well treating composite may be as low as 1 ppm').
It would have been obvious to a person of ordinary skill in the art to incorporate additional additives as disclosed in Gill and Gupta to the composition disclosed in Ayers depending upon the characteristics of the particular formation being treated.

Claims 1-17 have industrial applicability as defined by PCT Article 33(4) because the subject matter can be made or used in industry.

Electronic Acknowledgement Receipt

EFS ID:	23130434
Application Number:	14686237
International Application Number:	
Confirmation Number:	2601
Title of Invention:	STIMULATION OF WELLS IN NANO-DARCY SHALE FORMATIONS
First Named Inventor/Applicant Name:	Andrew Bryce Conway
Customer Number:	23552
Filer:	Brian Peter McCall
Filer Authorized By:	
Attorney Docket Number:	04697.0001USU1
Receipt Date:	06-AUG-2015
Filing Date:	14-APR-2015
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Application Type:	Utility under 35 USC 111(a)

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Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Information Disclosure Statement (IDS) Form (SB08)	2015-08-06-IDS-2-04697-0001USU1.PDF	1035767 4d7aa234ce4a628ab04bbfdca6a04efaa0184c06	no	5

Warnings:	
Information:	

2	Non Patent Literature	FRENIER-SPE-63242-MS.PDF	305490 c453e022e4b46965b5d55c05f7b8b53de4cc1103	no	12
Warnings:					
Information:					
3	Non Patent Literature	ISA-220-7-8-15--Notification-of-Transmittal-of-ISR-and-Written-Opinion.PDF	70281 6f6a9102458810ac25f7cf4763d6db0977086de2	no	1
Warnings:					
Information:					
4	Non Patent Literature	ISA-210-International-Search-Report--7-8-15.PDF	98600 a52cc856eafb49e787512eb4533a66c09e100c9c	no	2
Warnings:					
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5	Non Patent Literature	Written-Opinion-of-the-ISA--7-8-15.PDF	313368 6038513b2742492f9ce843aecdaa7509b47094f2	no	5
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		Total Files Size (in bytes):	1823506		

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<u>New Applications Under 35 U.S.C. 111</u>
If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

<u>National Stage of an International Application under 35 U.S.C. 371</u>
If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

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If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	14686237
Filing Date	2015-04-14
First Named Inventor	Andrew Bryce Conway
Art Unit	3676
Examiner Name	
Attorney Docket Number	04697.0001USU1

U.S.PATENTS						Remove
Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	4986356		1991-01-22	Lockhardt et al.	
	2	5223159		1993-06-29	Smith et al.	
	3	5224546		1993-07-06	Smith et al.	
	4	5346010		1994-09-13	Adams et al.	
	5	6265355		2001-07-24	Lai et al.	
	6	6331513		2001-12-18	Zaid et al.	
	7	6435277		2002-08-20	Qu et al.	
	8	6436880		2002-08-20	Frenier	

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	9	6569814		2003-05-27	Brady et al.	
	10	6638896		2003-10-28	Tibbles et al.	
	11	7013974		2006-03-21	Hanes, Jr.	
	12	7159658		2007-01-09	Frost et al.	
	13	7192908		2007-03-20	Frenier et al.	
	14	7208529		2007-04-24	Crews	
	15	7306041		2007-12-11	Milne et al.	
	16	7527103		2009-05-05	Huang et al.	
	17	7928040		2011-04-19	Sanders et al.	
	18	8071511		2011-12-06	Welton et al.	
	19	8312929		2012-11-20	Frenier et al.	

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	Attorney Docket Number	04697.0001USU1

	20	8567503		2013-10-29	Welton et al.	
	21	8567504		2013-10-29	Welton et al.	
	22	8584757		2013-11-19	Reyes	

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Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	20060142166	A1	2006-06-29	Thomas	
	2	20100294498	A1	2010-11-25	Svoboda et al.	
	3	20110053811	A1	2011-03-03	Horton et al.	
	4	20110237470	A1	2011-09-29	Li et al.	
	5	20110263466	A1	2011-10-27	Rose	
	6	20130213657	A1	2013-08-22	Dobson, Jr. et al.	

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	7	20130261032	A1	2013-10-03	Ladva et al.	
	8	20130274154	A1	2013-10-17	Nasr-El-Din et al.	
	9	20130274155	A1	2013-10-17	Nasr-El-Din et al.	
	10	20130303412	A1	2013-11-14	Luyster et al.	
	11	20140116696	A1	2014-05-01	Reyes	
	12	20140124205	A1	2014-05-08	Nasr-El-Din et al.	
	13	20140151042	A1	2014-06-05	Faugerstrom et al.	
	14	20130269944	A1	2013-10-17	Reyes et al.	
	15	20130269941	A1	2013-10-17	Reyes et al.	

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
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	Filing Date	2015-04-14
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	Art Unit	3676
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	Attorney Docket Number	04697.0001USU1

	1	2012116032	WO	A1	2012-08-30	Faugerstrom et al.		☐
	2	20100276152		A1	2010-11-04	De Wolf et al.		☐

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Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]
	1	EPA, Proceedings of the Technical Workshops for the Hydraulic Fracturing Study: Chemical & Analytical Methods, EPA 600/R-11/066, May 2011, 122pgs.	☐
	2	AL-HARTHY, et al., Options for High-Temperature Well Stimulation, Oilfield Review, Winter 2008/2009: 20, No. 4., 11pgs.	☐
	3	XU, et al., On Modeling of Chemical Stimulation of an Enhanced Geothermal System using a High pH Solution with Chelating Agent, August 2009,30pgs.	☐
	4	PORTIER, et al., CREGE, Review on chemical stimulation techniques in oil industry and applications to geothermal systems, May 2007, 34pgs.	☐
	5	NASIR, Effects of Acid Additives on Spent Acid Flowback Through Carbonate Cores, May 2012, 125pgs.	☐
	6	WEIDNER, Chemical Additive Selection in Matrix Acidizing, May 2011, 95pgs.	☐
	7	CIVAN, et al., Rigorous Modeling of Gas Transport in Nano-darcy Shale Porous Media under Extreme Pore Proximity and Elevated Pressure Conditions, Proceedings of the International Conference on Heat Transfer and Fluid Flow, Paper No. 208, August 2014, 2pgs.	☐

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	Filing Date	2015-04-14
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	Art Unit	3676
	Examiner Name	
	Attorney Docket Number	04697.0001USU1

	8	BWA, Geogard(R) SX - Amorphous Silica Control, Product Information, 2013, 2pgs.	☐
	9	NGUYEN, Well Design Spring 2013 Power Point, 44pgs.	☐
	10	CAPUTO, Shale Plays: Basic Geologic and Engineering Concepts, AAPL's 57th Annual Meeting, Boston June 2011, 71pgs.	☐
	11	Notification of Transmittal of The International Search Report and The Written Opinion of the International Searching Authority, or the Declaration, PCT/US2014/062440, February 13, 2015, 1 pg.	☐
	12	International Search Report, PCT/US2014/062440, February 13, 2015, 2pgs.	☐
	13	Written Opinion of the International Searching Authority, PCT/US2014/062440, February 13, 2015, 6pgs.	☐

If you wish to add additional non-patent literature document citation information please click the Add button Add

EXAMINER SIGNATURE

Examiner Signature		Date Considered	

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

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	First Named Inventor	Andrew Bryce Conway
	Art Unit	3676
	Examiner Name	
	Attorney Docket Number	04697.0001USU1

CERTIFICATION STATEMENT

Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

☐ That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

☐ See attached certification statement.

☐ The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

☒ A certification statement is not submitted herewith.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/Brian P. McCall/	Date (YYYY-MM-DD)	2015-07-13
Name/Print	Brian P. McCall	Registration Number	68734

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1 hour to complete, including gathering, preparing and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C. 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether the Freedom of Information Act requires disclosure of these record s.

2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.

3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.

4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).

5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.

6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.

9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

PATENT COOPERATION TREATY

From the
INTERNATIONAL SEARCHING AUTHORITY

To: STEVEN C. BRUESS
MERCHANT & GOULD P.C.
P.O. BOX 2903
MINNEAPOLIS, MN 55402-0903

PCT

WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY

(PCT Rule 43*bis*.1)

Date of mailing *(day/month/year)*	13 FEB 2015
Applicant's or agent's file reference 4697.3WOU1	**FOR FURTHER ACTION** See paragraph 2 below

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US2014/062440	27 October 2014	25 October 2013

International Patent Classification (IPC) or both national classification and IPC
IPC(8) - E21B 43/22 (2014.01)
CPC - E21B 43/25 (2014.11)

Applicant CONWAY, ANDREW BRYCE

1. This opinion contains indications relating to the following items:

- ☒ Box No. I Basis of the opinion
- ☐ Box No. II Priority
- ☐ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- ☐ Box No. IV Lack of unity of invention
- ☒ Box No. V Reasoned statement under Rule 43*bis*.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- ☐ Box No. VI Certain documents cited
- ☐ Box No. VII Certain defects in the international application
- ☐ Box No. VIII Certain observations on the international application

2. **FURTHER ACTION**

If a demand for international preliminary examination is made, this opinion will be considered to be a written opinion of the International Preliminary Examining Authority ("IPEA") except that this does not apply where the applicant chooses an Authority other than this one to be the IPEA and the chosen IPEA has notified the International Bureau under Rule 66.1 *bis*(b) that written opinions of this International Searching Authority will not be so considered.

If this opinion is, as provided above, considered to be a written opinion of the IPEA, the applicant is invited to submit to th IPEA a written reply together, where appropriate, with amendments, before the expiration of 3 months from the date of mailing of Fom PCT/ISA/220 or before the expiration of 22 months from the priority date, whichever expires later.

For further options, see Form PCT/ISA/220.

Name and mailing address of the ISA/US	Date of completion of this opinion	Authorized officer:
Mail Stop PCT, Attn: ISA/US Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	31 December 2014	Blaine R. Copenheaver PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

Form PCT/ISA/237 (cover sheet) (July 2011)

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US2014/062440

Box No. I Basis of this opinion

1. With regard to the **language**, this opinion has been established on the basis of:

   ☒ the international application in the language in which it was filed.

   ☐ a translation of the international application into _____ which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1(b)).

2. ☐ This opinion has been established taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 43*bis*.1(a))

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, this opinion has been established on the basis of a sequence listing filed or furnished:

   a. (means)

      ☐ on paper

      ☐ in electronic form

   b. (time)

      ☐ in the international application as filed

      ☐ together with the international application in electronic form

      ☐ subsequently to this Authority for the purposes of search

4. ☐ In addition, in the case that more than one version or copy of a sequence listing has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that in the application as filed or does not go beyond the application as filed, as appropriate, were furnished.

5. Additional comments:

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US2014/062440

Box No. V **Reasoned statement under Rule 43*bis*.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

1. Statement

Novelty (N)	Claims	1-20	YES
	Claims	None	NO
Inventive step (IS)	Claims	None	YES
	Claims	1-20	NO
Industrial applicability (IA)	Claims	1-20	YES
	Claims	None	NO

2. Citations and explanations:

Claims 1-5, 7, 8 and 12-17 lack an inventive step under PCT Article 33(3) as being obvious over Reyes et al. (hereafter Reyes) in view of Lybarger et al. (hereafter Lybarger).

Regarding claim 1, Reyes discloses a method for remediating a subterranean-formed metal-polymer complex in a well in a subterranean formation (Para. [0071] used in remediation operations within a subterranean formation) comprising: providing a metal-polymer complex remediation mixture containing between about 0.1% and 95% by weight metal complexing agent (Para. [0013] alkali metal complexing agent comprising cyclic polyether; Para. [0037]); injecting the metal-polymer complex remediation mixture into the well at a pressure less than a fracture pressure of the subterranean formation until at least some of the metal-polymer complex remediation mixture contacts the subterranean formed metal-polymer complex (Para. [0014] introducing the treatment fluid into subterranean formation); thereby allowing the metal complexing agent to cause the subterranean-formed metal-polymer complex to dissociate and dissolve, thereby creating a low viscosity flow back fluid comprising the spent metal-polymer complex remediation mixture and the metal-polymer complex components (Para. [0003] an acid to dissolve at least a portion of the material); and removing the low viscosity flow back fluid from the well after the contact time (Paras. [0071];[0002];[0003]), thereby improving the hydrocarbon production of the well relative to the hydrocarbon production immediately prior to performance of the method (Para. [0003] improve the formations rate of hydrocarbon production). Reyes fails to explicitly disclose maintaining the metal-polymer complex remediation mixture in contact with the subterranean-formed metal-polymer complex for a contact time of between about 1 minute and about 100 days. Lybarger is in the field of well-treating process for dissolving a siliceous material within a well borehole (Lybarger, Col. 1, Lines 7-9). Lybarger teaches maintaining the remediation mixture in contact with the subterranean-formed metal-polymer complex for a contact time of between about 1 minute and about 100 days (Lybarger, Fig. 1. dissolved solids over time). It would have been obvious to one of ordinary skill in the art at the time of the invention that the remediation mixture of Reyes to be used over an extended period of time as taught by Lybarger. The motivation for doing so would be to increase net dissolved solids (Lybarger, Fig. 1. Net dissolved solids increase over time).

Regarding claim 2, Reyes in view of Lybarger discloses the method of claim 1. Reyes further discloses wherein the metal complexing agent is citric acid (Para. [0049] citric acid).

Regarding claim 3, Reyes in view of Lybarger discloses the method of claim 1. Reyes further discloses wherein the metal complexing agent is acetic acid (Para. [0046] acetic acid).

Regarding claim 4, Reyes in view of Lybarger discloses the method of claim 1. Reyes further discloses wherein the metal complexing agent is ethylenediaminetetraacetic acid (EDTA) (Para. [0049] EDTA).

Regarding claim 5, Reyes in view of Lybarger discloses the method of claim 1. Reyes further discloses wherein the metal complexing agent includes at least one of ethylenediaminetetraacetic acid (EDT A), propylenediaminetetraacetic acid (PDTA), nitrilotriacetic acid (NT A), N-(2- hydroxyethyl)ethylenediaminetriacetic acid (HEDTA), diethylenetriaminepentaacetic 5 acid (DTPA), hydroxyethyliminodiacetic acid (HEIDA), cyclohexylenediaminetetraacetic acid (CDTA), diphenylaminesulfonic acid (DPAS), ethylenediaminedi (o-hydroxyphenylacetic) acid (EDDHA), glucoheptonic acid, gluconic acid, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, phthalic acid, terephthalic acid, aconitic acid, carballylic acid, trimesic acid, isocitric acid, citric acid, or any salt or derivative of any of the previously listed compounds (Para. [0049] EDTA).

Regarding claim 7, Reyes in view of Lybarger discloses the method of claim 1. Reyes further discloses wherein the metal-polymer complex remediation mixture further comprises acid(s) as pH modifier (Para. [0057] pH control agents; Para. [0015], treatment fluid having a pH ranging between 0 and about 8). Reyes fails to explicitly disclose wherein the metal-polymer complex remediation mixture further comprises between 0.1 and 95% of acid(s) as pH modifier. It would have been obvious to one of ordinary skill in the art at the time the invention was made to modify the treatment fluid of Reyes to include between 0.1 and 95% of acid(s) as pH modifier, since where the general conditions of the claim are disclosed in the prior art, discovering the optimum or workable ranges involves only routine skill in the art. The motivation for doing so would be promote initial silicon dissolution and aid in maintaining the silicon in a dissolved (Reyes, Para. [0006]).

Regarding claim 8, Reyes in view of Lybarger discloses the method of claim 1. Reyes further disclsoes wherein the injecting operation further comprises: alternately injecting a first amount of metal-polymer complex remediation mixture and a second amount of a diverting mixture into the well (Para. [0057] optionally further comprise ...particulate diverters; Para. [0014]).

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US2014/062440

Supplemental Box

In case **the space in any of the preceding boxes is not sufficient.**
Continuation of:

Regarding claim 12, Reyes in view of Lybarger discloses the method of claim 1. Reyes further disclsoes further wherein the metal complexing agent is selected from glutamic acid diacetic acid (GLDA), methylglycine diacetic acid 20 (MGDA), ()-alanine diacetic acid (()-ADA), ethylenediaminedisuccinic acid, S,Sethylenediaminedisuccinic acid (EDDS), iminodisuccinic acid (IDS), hydroxyiminodisuccinic acid (HIDS), polyamino disuccinic acids, N-bis[2-(l,2- dicarboxyethoxy)ethyl]glycine (BCA6), N-bis[2-(l,2- dicarboxyethoxy)ethyl]aspartic acid (BCA5), N-bis[2-(1,2- dicarboxyethoxy)ethyl]methylglycine (MCBA5), N- 25 tris[(l,2- dicarboxyethoxy)ethyl]amine (TCA6), N-methyliminodiacetic acid (MIDA), iminodiacetic acid (IDA), N-(2-acetamido)iminodiacetic acid (ADA), hydroxymethyl-iminodiacetic acid, 2-(2-carboxyethylamino) succinic acid (CEAA), 2-(2-carboxymethylamino) succinic acid (CMAA), diethylenetriamine- N,N"disuccinic acid, triethylenetetramine-N,N"'-disuccinic acid, 1,6- 30 hexamethylenediamine-N,N'-disuccinic acid, tetraethylenepentamine-N,N""- -26-disuccinic acid, 2-hydroxypropylene-1,3-diamine-N,N' -disuccinic acid, l ,2- propylenediamine-N,N'-disuccinic acid, 1,3-propylenediamine-N,N'-disuccinic acid, cis-cyclohexanediamine-N,N'-disuccinic acid, trans-cyclohexanediamine- N,N'disuccinic acid, ethylenebis(oxyethylenenitrilo)-N,N'-disuccinic acid, glucoheptanoic 5 acid, cysteic acid-N,N-diacetic acid, cysteic acid-N-monoacetic acid, alanine-Nmonoacetic acid, N-(3-hydroxysuccinyl) aspartic acid, N-[2-(3- hydroxysuccinyi)]-Lserine, aspartic acid-N,N-diacetic acid, aspartic acid-N- monoacetic acid, any salt thereof, any derivative thereof, or any combination thereof (Para. [0050]).

Regarding claim 13, Reyes in view of Lybarger discloses the method of claim 1. Reyes further disclsoes further wherein the metal complexing agent is selected from acetic acid, acrylates, dihydroxymaleic acid, salts of dihydroxymaleic acid, EDT A (ethylenediamine tetraacetic acid), salts of EDT A, erythorbic acid, erythroboric acid, formic acid, gluconodeltalactone, GLDA (glutamic acid N,Ndiacetic acid), salts of GLDA, HEDT A (hydroxyethylenediamine triacetic acid), salts 15 of HEDT A, HE IDA (disodium ethanoldiglycine), salts of HE IDA, MGDA 20 (methylglycine N,N-diacetic acid), salts of MGDA, NTA (nitriolotriacetic acid), organic metal complexers, ligands, porphyrins, pigments, peptides, saccharides, nucleic acids, phosphonic acid, polyacrylic acid and citric acid in an amount sufficient to sequester at least a portion of a metal compound (Para. [0049]).

Regarding claim 14, Reyes in view of Lybarger discloses the method of claim 1. Reyes further disclsoes wherein the metal-polymer complex remediation mixture comprises between about 0.1% and about 60% by weight metal complexing agent (Para. [0037]).

Regarding claim 15, Reyes in view of Lybarger discloses the method of claim 1. Reyes fails to explicitly disclose wherein the contact time is between about 4 hours and about 4 days. Lybarger teaches wherein the contact time is between about 4 hours and about 4 days (Lybarger, Fig. 1 Time 0-29 hours). It would have been obvious to one of ordinary skill in the art at the time of the invention that the remediation mixture of Reyes to be used over an extended period of time as taught by Lybarger. The motivation for doing so would be to increase net dissolved solids (Lybarger, Fig. 1. Net dissolved solids increase over time).

Regarding claim 16, Reyes discloses a method for remediating a low-producing well in a hydrocarbon bearing subterranean formation, comprising: fracturing the hydrocarbon-bearing subterranean formation (Para. [0025] alkali metal complexing agent may be used in conjunction with a stimulation operation (e.g., a fracturing operation)); monitoring the production of the well; and after observing a well production decrease, determining that a subterranean formed metal-polymer complex has formed in the well (Para. [0007] precipitation of insoluble fluorosilicates and aluminosilicate can block pore throats and undo desirable permeability increase initially achieved by the acidizing operation; Para. [0022]); providing a metal-polymer complex remediation mixture containing between about 0.1% and 95% by weight metal complexing agent (Para. [0013] alkali metal complexing agent comprising cyclic polyether; Para. 0037]); injecting the metal-polymer complex remediation mixture into the well at a pressure less than a fracture pressure of the subterranean formation until at least some of the metal-polymer complex remediation mixture contacts the subterranean formed metal-polymer complex (Para. [0014] introducing the treatment fluid into subterranean formation); allowing the metal complexing agent to cause the subterranean-formed metal-polymer complex to dissociate and dissolve, thereby creating a low viscosity flow back fluid comprising the spent metal-polymer complex remediation mixture and the metal-polymer complex components (Para. [0003] an acid to dissolve at least a portion of the material); and removing the low viscosity flow back fluid from the well after the contact time (Paras. [0071];[0002];[0003]), thereby improving the hydrocarbon production of the well relative to the hydrocarbon production immediately prior to performance of the method (Para. [0003] improve the formations rate of hydrocarbon production). Reyes fails to explicitly disclose maintaining the metal-polymer complex remediation mixture in contact with the subterranean-formed metal-polymer complex for a contact time of between about 1 minute and about 100 days. Lybarger teaches maintaining the remediation mixture in contact with the subterranean-formed metal-polymer complex for a contact time of between about 1 minute and about 100 days (Lybarger, Fig. 1. dissolved solids over time). It would have been obvious to one of ordinary skill in the art at the time of the invention that the remediation mixture of Reyes to be used over an extended period of time as taught by Lybarger. The motivation for doing so would be to increase net dissolved solids (Lybarger, Fig. 1. Net dissolved solids increase over time).

Regarding claim 17, Reyes in view of Lybarger discloses the method of claim 16, wherein the metal complexing agent includes at least one of ethylenediaminetetraacetic acid (EDTA) , propylenediaminetetraacetic acid (PDTA), nitrilotriacetic acid (NT A), N-(2- hydroxyethyl) ethylenediaminetriacetic acid (HEDTA), diethylenetriaminepentaacetic acid (DTPA), hydroxyethyliminodiacetic acid (HEIDA), cyclohexylenediaminetetraacetic acid (CDTA), diphenylaminesulfonic acid (DPAS), ethylenediaminedi(o-hydroxyphenylacetic) acid (EDDHA), glucoheptonic acid, gluconic acid, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, phthalic acid, terephthalic acid, aconitic acid, carballylic acid, trimesic acid, isocitric acid, citric acid, or any salt or derivative of any of the previously listed compounds (Para. [0049]).

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No. PCT/US2014/062440

Supplemental Box

In case **the space in any of the preceding boxes is not sufficient.**
Continuation of:

Claims 6 and 18 lack an inventive step under PCT Article 33(3) as being obvious over Reyes in view of Lybarger, and Starkey, II et al., (hereafter Starkey).

Regarding claim 6, Reyes in view of Lybarger discloses the method of claim 1. Reyes further discloses wherein the metal-polymer complex remediation mixture comprises: between about 1% and 95% by weight metal complexing agent (Para. [0013] alkali metal complexing agent; agent; Para. [0037]); a corrosion inhibitor (Para. [0057] corrosion inhibitors); a colloidal silica deposition inhibitor (Para. [0057] scale inhibitors); and a mutual solvent (Para. [0035] may comprise an organic solvent). Reyes fails to explicitly disclose between 1 and 10,000 ppm of a biocide. Starkey is in the field of biocides for well stimulation and treatment fluids (Starkey, Col. 2, Lines 38-53). Starkey discloses biocides used in well treatment fluids (Col. 1, Ln. 55, biocides and oxygen scavengers are frequently added to the well treatment fluid; Col. 2, Line 66-Col. 3, Line 15). It would have been obvious to one of ordinary skill in the art to modify the remediation mixture of Reyes to add biocide as taught by Starkey. The motivation for doing so would be to control bacterial growth in the well (Starkey, Col. 1, Ln. 57, to control bacterial growth). Reyes fails to explicitly disclose between 1 and 10,000 parts per million (ppm) of a corrosion inhibitor; between 1 and 10,000 ppm of a colloidal silica deposition inhibitor; and between 1 and 500 gallons per thousand gallons (gpt) of a mutual solvent. It would have been obvious to one of ordinary skill in the art at the time the invention was made to modify the treatment fluid of Reyes to include between 1 and 10,000 parts per million (ppm) of a corrosion inhibitor; between 1 and 10,000 ppm of a colloidal silica deposition inhibitor; and between 1 and 500 gallons per thousand gallons (gpt) of a mutual solvent, since where the general conditions of the claim are disclosed in the prior art, discovering the optimum or workable ranges involves only routine skill in the art. The motivation for doing so would be promote initial silicon dissolution and aid in maintaining the silicon in a dissolved (Reyes, Para. [0006]).

Regarding claim 18, Reyes in view of Lybarger discloses the method of claim 17. Reyes further discloses wherein remediation mixture comprises: between about 0.1% and 60% by weight metal complexing agent (Para. [0013] alkali metal complexing agent; agent; Para. [0037]); between about 1% and 95% by weight metal complexing agent (Para. [0013] alkali metal complexing agent; agent; Para. [0037]); a corrosion inhibitor (Para. [0057] corrosion inhibitors); a colloidal silica deposition inhibitor (Para. [0057] scale inhibitors); and a mutual solvent (Para. [0035] may comprise an organic solvent). Reyes fails to explicitly disclose wherein the contact time is between about 1 minute and about 100 days. Lybarger teaches maintaining the remediation mixture in contact with the subterranean-formed metal-polymer complex for a contact time of between about 1 minute and about 100 days (Lybarger, Fig. 1. dissolved solids over time). It would have been obvious to one of ordinary skill in the art at the time of the invention that the remediation mixture of Reyes to be used over an extended period of time as taught by Lybarger. The motivation for doing so would be to increase net dissolved solids (Lybarger, Fig. 1. Net dissolved solids increase over time). Reyes fails to explicitly disclose between 1 and 10,000 ppm of a biocide. Starkey is in the field of biocides for well stimulation and treatment fluids (Starkey, Col. 2, Lines 38-53). Starkey discloses biocides used in well treatment fluids (Col. 1, Ln. 55, biocides and oxygen scavengers are frequently added to the well treatment fluid; Col. 2, Line 66-Col. 3, Line 15). It would have been obvious to one of ordinary skill in the art to modify the remediation mixture of Reyes to add biocide as taught by Starkey. The motivation for doing so would be to control bacterial growth in the well (Starkey, Col. 1, Ln. 57, to control bacterial growth). Reyes fails to explicitly disclose between 1 and 10,000 parts per million (ppm) of a corrosion inhibitor; between 1 and 10,000 ppm of a colloidal silica deposition inhibitor; and between 1 and 500 gallons per thousand gallons (gpt) of a mutual solvent. It would have been obvious to one of ordinary skill in the art at the time the invention was made to modify the treatment fluid of Reyes to include between 1 and 10,000 parts per million (ppm) of a corrosion inhibitor; between 1 and 10,000 ppm of a colloidal silica deposition inhibitor; and between 1 and 500 gallons per thousand gallons (gpt) of a mutual solvent, since where the general conditions of the claim are disclosed in the prior art, discovering the optimum or workable ranges involves only routine skill in the art. The motivation for doing so would be promote initial silicon dissolution and aid in maintaining the silicon in a dissolved (Reyes, Para. [0006]).

Claims 9-11, 19 and 20 lacks an inventive step under PCT Article 33(3) as being obvious over Reyes in view of Lybarger and Hocking.

Regarding claim 9, Reyes in view of Lybarger discloses the method of claim 1. Reyes fails to explicitly disclose wherein the injecting operation further comprises: injecting the metal-polymer complex remediation mixture to completion or until pressure within the well reaches a predetermined target that does not cause substantial fracturing of the formation. Hocking teaches monitoring subterranean formations for targeted actions (Hocking, Col. 2, Ln. 55-58, in a computer generated feedback signal to modify the injection pressures and flow rates, and thus develop an injected geometry optimum for the containment or remediation application). It would have been obvious to one of skill in the art at the time of the invention to modify the method of Reyes to include the optimum control as taught by Hocking. The motivation for doing so would be to control the pressure of the well, and therefore the size of the fracture, whether it is to make larger, or keep the same (Hocking, Col. 1, Lns. 26-28, improved process to control the orientation, shape, size and aperture of induced fractures in the ground).

Regarding claim 10, Reyes in view of Lybarger discloses the method of claim 1. Reyes fails to explicitly disclose wherein the injecting operation further comprises: injecting the metal-polymer complex remediation mixture until the pressure within the well reaches a predetermined target pressure calculated based on the fracture pressure of the subterranean formation; and upon reaching the target pressure, shutting in the well. Hocking teaches monitoring subterranean formations for targeted actions (Hocking, Col. 2, Lns. 55-58, in a computer generated feedback signal to modify the injection pressures and flow rates, and thus develop an injected geometry optimum for the containment or remediation application). It would have been obvious to one of skill in the art at the time of the invention to modify the method of Reyes to include the optimum control as taught by Hocking. The motivation for doing so would be to control the pressure of the well, and therefore the size of the fracture, whether it is to make larger, or keep the same (Hocking, Col. 1, Lns. 26-28, improved process to control the orientation, shape, size and aperture of induced fractures in the ground).

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US2014/062440

Supplemental Box

In case **the space in any of the preceding boxes is not sufficient.**
Continuation of:

Regarding claim 11, Reyes in view of Lybarger discloses the method of claim 1. Reyes fails to explicitly disclose the method further comprising: monitoring at least one of pH and well pressure during the maintaining operation; and initiating the removing operation based on results of the monitoring operation. Hocking teaches monitoring subterranean formations for targeted actions (Hocking, Col. 2, Lns. 55-58, in a computer generated feedback signal to modify the injection pressures and flow rates, and thus develop an injected geometry optimum for the containment or remediation application). It would have been obvious to one of skill in the art at the time of the invention to modify the method of Reyes to include the optimum control as taught by Hocking. The motivation for doing so would be to control the pressure of the well, and therefore the size of the fracture, whether it is to make larger, or keep the same (Hocking, Col. 1, Lns. 26-28, improved process to control the orientation, shape, size and aperture of induced fractures in the ground).

Regarding claim 19, Reyes in view of Lybarger discloses the method of claim 16. Reyes fails to explicitly disclose wherein the injecting operation further comprises: injecting the remediation mixture until the pressure within the well reaches a predetermined target pressure calculated based on the fracture pressure of the hydrocarbon-bearing subterranean formation; and upon reaching the target pressure, shutting in the well. Hocking teaches monitoring subterranean formations for targeted actions (Hocking, Col. 2, Lns. 55-58, in a computer generated feedback signal to modify the injection pressures and flow rates, and thus develop an injected geometry optimum for the containment or remediation application). It would have been obvious to one of skill in the art at the time of the invention to modify the method of Reyes to include the optimum control as taught by Hocking. The motivation for doing so would be to control the pressure of the well, and therefore the size of the fracture, whether it is to make larger, or keep the same (Hocking, Col. 1, Lns. 26-28, improved process to control the orientation, shape, size and aperture of induced fractures in the ground).

Regarding claim 20, Reyes in view of Lybarger discloses the method of claim 19. Reyes fails to explicitly disclose the method further comprising: monitoring at least one of pH and well pressure during the maintaining operation; and initiating the removing operation based on results of the monitoring operation. Hocking teaches monitoring subterranean formations for targeted actions (Hocking, Col. 2, Lns. 55-58, in a computer generated feedback signal to modify the injection pressures and flow rates, and thus develop an injected geometry optimum for the containment or remediation application). It would have been obvious to one of skill in the art at the time of the invention to modify the method of Reyes to include the optimum control as taught by Hocking. The motivation for doing so would be to control the pressure of the well, and therefore the size of the fracture, whether it is to make larger, or keep the same (Hocking, Col. 1, Lns. 26-28, improved process to control the orientation, shape, size and aperture of induced fractures in the ground).

Claims 1-20 meet the criteria set out in PCT Article 33(4), and thus have industrial applicability because the subject matter claimed can be made or used in industry.

PATENT COOPERATION TREATY

From the INTERNATIONAL SEARCHING AUTHORITY

To: STEVEN C. BRUESS
MERCHANT & GOULD P.C.
P.O. BOX 2903
MINNEAPOLIS, MN 55402-0903

PCT

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL SEARCH REPORT AND THE WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY, OR THE DECLARATION

(PCT Rule 44.1)

Applicant's or agent's file reference 4697.3WOU1	Date of mailing *(day/month/year)* 13 FEB 2015 **FOR FURTHER ACTION** See paragraphs 1 and 4 below
International application No. PCT/US2014/062440	International filing date *(day/month/year)* 27 October 2014
Applicant CONWAY, ANDREW BRYCE	

1. ☒ The applicant is hereby notified that the international search report and the written opinion of the International Searching Authority have been established and are transmitted herewith.

   Filing of amendments and statement under Article 19:
   The applicant is entitled, if he so wishes, to amend the claims of the international application (see Rule 46):

   When? The time limit for filing such amendments is normally two months from the date of transmittal of the international search report.

   How? Directly to the International Bureau of WIPO preferably through ePCT or on paper to, 34 chemin des Colombettes 1211 Geneva 20, Switzerland, Facsimile No.: +41 22 338 82 70

   For more detailed instructions, see *PCT Applicant's Guide,* International Phase, paragraphs 9.004 – 9.011.

2. ☐ The applicant is hereby notified that no international search report will be established and that the declaration under Article 17(2)(a) to that effect and the written opinion of the International Searching Authority are transmitted herewith.

3. ☐ **With regard to any protest** against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that:
   ☐ the protest together with the decision thereon has been transmitted to the International Bureau together with any request to forward the texts of both the protest and the decision thereon to the designated Offices.
   ☐ no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.

4. **Reminders**

   The applicant may **submit comments on an informal basis on the written opinion of the International Searching Authority** to the International Bureau. These comments will be made available to the public after international publication. The International Bureau will send a copy of such comments to all designated Offices unless an international preliminary examination report has been or is to be established.

   Shortly after the expiration of **18 months from the priority date, the international application will be published** by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the international application, or of the priority claim, must reach the International Bureau before the completion of the technical preparations for international publication (Rules 90*bis*.1 and 90*bis*.3).

   Within **19 months** from the priority date, but only in respect of some designated Offices, a demand for international preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase **until 30 months** from the priority date (in some Offices even later); otherwise, the applicant must, **within 20 months** from the priority date, perform the prescribed acts for **entry into the national phase** before those designated Offices. In respect of other designated Offices, the time limit of **30 months** (or later) will apply even if no demand is filed within 19 months. For details about the applicable time limits, Office by Office, see www.wipo.int/pct/en/texts/time_limits.html and the *PCT Applicant's Guide,* National Chapters.

   Within **19 months from the priority date, the applicant may request that a supplementary international search be carried out** by a different International Searching Authority that offers this service (Rule 45*bis*.1). The procedure for requesting supplementary international search is described in the *PCT Applicant's Guide,* International Phase, paragraphs 8.006-8.032.

Name and mailing address of the ISA/ Mail Stop PCT, Attn: ISA/US Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer Blaine R. Copenheaver PCT Helpdesk: 571-272-4300 Telephone No. PCT OSP: 571-272-7774

Form PCT/ISA/220 (July 2014)

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference 4697.3WOU1	**FOR FURTHER ACTION**	see Form PCT/ISA/220 as well as, where applicable, item 5 below.
International application No. PCT/US2014/062440	International filing date *(day/month/year)* 27 October 2014	(Earliest) Priority Date *(day/month/year)* 25 October 2013
Applicant CONWAY, ANDREW BRYCE		

This international search report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This international search report consists of a total of 2 sheets.

☐ It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**

   a. With regard to the **language**, the international search was carried out on the basis of:

   ☒ the international application in the language in which it was filed.

   ☐ a translation of the international application into _____ which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1(b)).

   b. ☐ This international search report has been established taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 43.6*bis*(a)).

   c. ☐ With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, see Box No. I.

2. ☐ **Certain claims were found unsearchable** (see Box No. II).

3. ☐ **Unity of invention is lacking** (see Box No. III).

4. With regard to the **title**,

   ☒ the text is approved as submitted by the applicant.

   ☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

   ☒ the text is approved as submitted by the applicant.

   ☐ the text has been established, according to Rule 38.2, by this Authority as it appears in Box No. IV. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. With regard to the **drawings**,

   a. the figure of the **drawings** to be published with the abstract is Figure No. 8

   ☒ as suggested by the applicant.

   ☐ as selected by this Authority, because the applicant failed to suggest a figure.

   ☐ as selected by this Authority, because this figure better characterizes the invention.

   b. ☐ none of the figures is to be published with the abstract.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2014/062440

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - E21B 43/22 (2014.01)
CPC - E21B 43/25 (2014.11)
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(8) - C09K 8/03, 8/32; E21B 43/22, 43/25 (2014.01)
CPC - C09K 8/588; E21B 43/25 (2014.11) (keyword delimited)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC - 166/53, 300; 507/215, 224, 225, 228 (keyword delimited)

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

Orbit, Google Patents, Google Scholar
Search terms used: EDTA, well remediation, control, pressure

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2013/0269944 A1 (REYES et al) 17 October 2013 (17.10.2013) entire document	1-20
Y	US 4,089,787 A (LYBARGER et al) 16 May 1978 (16.05.1978) entire document	1-20
Y	US 7,906,463 B2 (STARKEY II et al) 15 March 2011 (15.03.2011) entire document	6, 18
Y	US 5,944,446 A (HOCKING) 31 August 1999 (31.08.1999) entire document	9-11, 19, 20

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

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
31 December 2014	13 FEB 2015
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Blaine R. Copenheaver PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

Form PCT/ISA/210 (second sheet) (July 2009)

Electronic Acknowledgement Receipt

EFS ID:	22898698
Application Number:	14686237
International Application Number:	
Confirmation Number:	2601
Title of Invention:	STIMULATION OF WELLS IN NANO-DARCY SHALE FORMATIONS
First Named Inventor/Applicant Name:	Andrew Bryce Conway
Customer Number:	23552
Filer:	Brian Peter McCall
Filer Authorized By:	
Attorney Docket Number:	04697.0001USU1
Receipt Date:	13-JUL-2015
Filing Date:	14-APR-2015
Time Stamp:	16:28:03
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Information Disclosure Statement (IDS) Form (SB08)	2015-07-13-IDS--04697-0001USU1.PDF	614205 9e318243c3c8c6e4fbf463a4fbe933f74ea8c68f	no	8

Warnings:	
Information:	

2	Non Patent Literature	Intl-Written-Opinion-02-13-2015.PDF	437769 bee7058ae8eb5373fae11dd18ebca031555bac61	no	6
Warnings:					
Information:					
3	Non Patent Literature	Notification-of-Transmittal-ISR-WO-02-13-15.PDF	76916 0b148b5b9ed6fb4806c7dfd2925c0802a6992e05	no	1
Warnings:					
Information:					
4	Non Patent Literature	Intl-Search-Report-02-13-15.PDF	98258 1171997475 24f2e83dd0a649ef6dae1acfbcd161	no	2
Warnings:					
Information:					
5	Non Patent Literature	Nguyen-Well-Design-PPT-2013.PDF	1040260 e61c76efde2abc655e38c6ac544e7ce72f2e7a8c	no	44
Warnings:					
Information:					
6	Non Patent Literature	PORTIER-review-on-chemical-stimulation.PDF	1511544 a064c19fe52e6e8bd5dceaf758596d57b2147b2b	no	34
Warnings:					
Information:					
7	Non Patent Literature	AL-Harthy-options-for-high-temperature-well-stimulation2.pdf	7928721 423918df32e1c9ee53d5652b85f936c3df33643e	no	11
Warnings:					
Information:					
8	Non Patent Literature	CAPUTO-03-caputo-aapl-shale-play-seminar-part1-final2.pdf	17908012 67b48c39d32aa84cb45da34b35ba402766f28c3d	no	71
Warnings:					
Information:					
9	Non Patent Literature	CIVAN-Rigorous-Modeling-in-Nano-darcy-shale-article2.pdf	141608 f240b2a030c6250c7dde54c131f0a9315a8b5878	no	2
Warnings:					
Information:					
10	Non Patent Literature	Geogard-SX-GP-WF2.pdf	383583 423b9d25fc4c7a027ad21f20e41d8ce35f4fecfd	no	2
Warnings:					
Information:					

11	Non Patent Literature	NASIR-EFFECTS-OF-ACID-ADDITIVES-ON-SPENT-ACID-FLOWBACK-THROUGH-CARBONATE-CORES2.pdf	5624659 4d5e452f5e3d990371d070347dcd5107f17e586f	no	125
Warnings:					
Information:					
12	Non Patent Literature	EPA-Proceedings-of-the-Technical-Workshops-for-the-Hydraulic-Fracturing-Study2.pdf	2842880 333037d7e3c71aba5d1b779564a7ed1d8780fc69	no	122
Warnings:					
Information:					
13	Non Patent Literature	WEIDNER-CHEMICAL-ADDITIVE-SELECTION-IN-MATRIX-ACIDIZING2.pdf	4016451 f2b241e1b8a8013db3c2ec02f5acc823bfa5c8ba	no	95
Warnings:					
Information:					
14	Non Patent Literature	XU-Modeling-of-chemical-stimulation2.pdf	340224 631e2acd24167d5b89ad4ee87bd7934f85f2fe22	no	30
Warnings:					
Information:					
		Total Files Size (in bytes):	42965090		

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
14/686,237	04/14/2015	Andrew Bryce Conway	04697.0001USU1

CONFIRMATION NO. 2601

23552
MERCHANT & GOULD P.C.
P.O. BOX 2903
MINNEAPOLIS, MN 55402-0903

POA ACCEPTANCE LETTER

OC000000075213296

Date Mailed: 05/18/2015

NOTICE OF ACCEPTANCE OF POWER OF ATTORNEY

This is in response to the Power of Attorney filed 05/13/2015.

The Power of Attorney in this application is accepted. Correspondence in this application will be mailed to the above address as provided by 37 CFR 1.33.

Questions about the contents of this notice and the requirements it sets forth should be directed to the Office of Data Management, Application Assistance Unit, at **(571) 272-4000** or **(571) 272-4200** or **1-888-786-0101**.

/sibrahim/

PTO/AIA/80 (07-12)
Approved for use through 11/30/2014. OMB 0651-0035
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
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POWER OF ATTORNEY TO PROSECUTE APPLICATIONS BEFORE THE USPTO

I hereby revoke all previous powers of attorney given in the application identified in the attached statement under 37 CFR 3.73(c).

I hereby appoint:

☒ Practitioners associated with Customer Number: 23552

OR

☐ Practitioner(s) named below (if more than ten patent practitioners are to be named, then a customer number must be used):

Name	Registration Number	Name	Registration Number

An attorney(s) or agent(s) to represent the undersigned before the United States Patent and Trademark Office (USPTO) in connection with any and all patent applications assigned only to the undersigned according to the USPTO assignment records or assignments documents attached to this form in accordance with 37 CFR 3.73(c).

Please change the correspondence address for the application identified in the attached statement under 37 CFR 3.73(c) to:

☒ The address associated with Customer Number: 23552

OR

☐

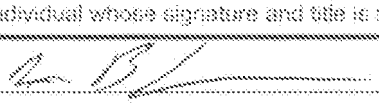
Firm or Individual Name			
Address			
City		State	Zip
Country			
Telephone		Email	

Assignee Name and Address: Flex-Chem Holding Company, LLC
700 N. Wilson Rd.
Weatherford, OK 73096

A copy of this form, together with a statement under 37 CFR 3.73(c) (Form PTO/AIA/96 or equivalent) is required to be Filed in each application in which this form is used. The statement under 37 CFR 3.73(c) may be completed by one of The practitioners appointed in this form, and must identify the application in which this Power of Attorney is to be filed.

SIGNATURE of Assignee of Record

The individual whose signature and title is supplied below is authorized to act on behalf of the assignee

Signature		Date	May 11, 2015
Name	Andrew Bryce Conway	Telephone	580-772-2386
Title	Technical Director		

This collection of information is required by 37 CFR 1.31, 1.32 and 1.33. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 3 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

PTO/AIA/96 (08-12)
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U.S. Patent and Trademark Office;U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of1995, no persons arerequired to respond to a collection of information unless it displays a valid OMB control number.

STATEMENT UNDER 37 CFR 3.73(c)

Applicant/Patent Owner: Flex-Chem Holding Company, LLC

Application No./Patent No.: 14/686,237 Filed/Issue Date: 04/14/15

Titled: Stimulation of Wells in Nano-Darcy Shale Formations

Flex-Chem Holding Company, LLC, a corporation

(Name of Assignee) (Type of Assignee, e.g., corporation, partnership, university, government agency, etc.)

states that, for the patent application/patent identified above, it is (choose **one** of options 1, 2, 3 or 4 below):

1. ☑ The assignee of the entire right, title, and interest.

2. ☐ An assignee of less than the entire right, title, and interest (check applicable box):

   ☐ The extent (by percentage) of its ownership interest is _____%. Additional Statement(s) by the owners holding the balance of the interest must be submitted to account for 100% of the ownership interest.

   ☐ There are unspecified percentages of ownership. The other parties, including inventors, who together own the entire right, title and interest are:

   Additional Statement(s) by the owner(s) holding the balance of the interest must be submitted to account for the entire right, title, and interest.

3. ☐ The assignee of an undivided interest in the entirety (a complete assignment from one of the joint inventors was made). The other parties, including inventors, who together own the entire right, title, and interest are:

   Additional Statement(s) by the owner(s) holding the balance of the interest must be submitted to account for the entire right, title, and interest.

4. ☐ The recipient, via a court proceeding or the like (*e.g.*, bankruptcy, probate), of an undivided interest in the entirety (a complete transfer of ownership interest was made). The certified document(s) showing the transfer is attached.

The interest identified in option 1, 2 or 3 above (not option 4) is evidenced by either (choose **one** of options A or B below):

A. ☑ An assignment from the inventor(s) of the patent application/patent identified above. The assignment was recorded in the United States Patent and Trademark Office at Reel 035616, Frame 0069, or for which a copy thereof is attached.

B. ☐ A chain of title from the inventor(s), of the patent application/patent identified above, to the current assignee as follows:

1. From: _____ To: _____

   The document was recorded in the United States Patent and Trademark Office at

   Reel _____, Frame _____, or for which a copy thereof is attached.

2. From: _____ To: _____

   The document was recorded in the United States Patent and Trademark Office at

   Reel _____, Frame _____, or for which a copy thereof is attached.

This collection of information is required by37 CFR3.73(b). The information is required toobtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentialityis governed by35 U.S.C. 122and 37 CFR1.11 and1.14. Thiscollection is estimated to take 12 minutes to complete, including gathering, preparing, and submittingthe completed application form to the USPTO.Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent tothe Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS.**SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450**

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

PTO/AIA/96 (08-12)
Approved for use through 01/31/2013. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

STATEMENT UNDER 37 CFR 3.73(c)

3. From: _____ To: _____

The document was recorded in the United States Patent and Trademark Office at

Reel _____, Frame _____, or for which a copy thereof is attached.

4. From: _____ To: _____

The document was recorded in the United States Patent and Trademark Office at

Reel _____, Frame _____, or for which a copy thereof is attached.

5. From: _____ To: _____

The document was recorded in the United States Patent and Trademark Office at

Reel _____, Frame _____, or for which a copy thereof is attached.

6. From: _____ To: _____

The document was recorded in the United States Patent and Trademark Office at

Reel _____, Frame _____, or for which a copy thereof is attached.

☐ Additional documents in the chain of title are listed on a supplemental sheet(s).

☑ As required by 37 CFR 3.73(c)(1)(i), the documentary evidence of the chain of title from the original owner to the assignee was, or concurrently is being, submitted for recordation pursuant to 37 CFR 3.11.

[NOTE: A separate copy (i.e., a true copy of the original assignment document(s)) must be submitted to Assignment Division in accordance with 37 CFR Part 3, to record the assignment in the records of the USPTO. See MPEP 302.08]

The undersigned (whose title is supplied below) is authorized to act on behalf of the assignee.

/Brian P. McCall/	2015-05-13
Signature	Date
Brian P. McCall	68,734
Printed or Typed Name	Title or Registration Number

Privacy Act Statement

The **Privacy Act of 1974 (P.L. 93-579)** requires that yoube given certain informationin connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, pleasebe advised that: (1) the general authority forthe collection of thisinformation is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and(3) the principal purpose forwhich the information isused by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent applicationor patent. If you do not furnish the requested information,the U.S. Patent and Trademark Office may not be able to process and/or examineyour submission,which may result in termination of proceedings or abandonment of the applicationor expiration of the patent.

The informationprovided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether disclosure of these records is required by the Freedom of Information Act.
2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the informationin order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an InternationalApplication filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (*i.e.*, GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, arecord may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspection or an issued patent.
9. A record from thissystem of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

Electronic Acknowledgement Receipt

EFS ID:	22333092
Application Number:	14686237
International Application Number:	
Confirmation Number:	2601
Title of Invention:	STIMULATION OF WELLS IN NANO-DARCY SHALE FORMATIONS
First Named Inventor/Applicant Name:	Andrew Bryce Conway
Customer Number:	23552
Filer:	Brian Peter McCall/Amy Miller
Filer Authorized By:	Brian Peter McCall
Attorney Docket Number:	04697.0001USU1
Receipt Date:	13-MAY-2015
Filing Date:	14-APR-2015
Time Stamp:	12:39:05
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Power of Attorney	2015-05-13-POA--04697-0001USU1.PDF	353215 bb746ccbfd38f2098a613e034c51e3dfd226c1a9	no	1

Warnings:	
Information:	

2	Assignee showing of ownership per 37 CFR 3.73	2015-05-13-373Stmt--04697-0001USU1.PDF	119211 9bc363ccb5360fc933fbdb9a38178b8f03027592	no	3

Warnings:	
Information:	
Total Files Size (in bytes):	472426

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New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

PATENT APPLICATION FEE DETERMINATION RECORD Substitute for Form PTO-875	Application or Docket Number 14/686,237

APPLICATION AS FILED - PART I

	(Column 1)	(Column 2)	SMALL ENTITY		OR	OTHER THAN SMALL ENTITY	
FOR	NUMBER FILED	NUMBER EXTRA	RATE($)	FEE($)		RATE($)	FEE($)
BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A	N/A	70		N/A	
SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A	N/A	300		N/A	
EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A	N/A	360		N/A	
TOTAL CLAIMS (37 CFR 1.16(i))	17 minus 20 =	*	x 40 =	0.00	OR		
INDEPENDENT CLAIMS (37 CFR 1.16(h))	2 minus 3 =	*	x 210 =	0.00			
APPLICATION SIZE FEE (37 CFR 1.16(s))	If the specification and drawings exceed 100 sheets of paper, the application size fee due is $310 ($155 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).			0.00			
MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))				0.00			
* If the difference in column 1 is less than zero, enter "0" in column 2.			TOTAL	730		TOTAL	

APPLICATION AS AMENDED - PART II

		(Column 1)		(Column 2)	(Column 3)	SMALL ENTITY		OR	OTHER THAN SMALL ENTITY	
		CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA	RATE($)	ADDITIONAL FEE($)		RATE($)	ADDITIONAL FEE($)
AMENDMENT A	Total (37 CFR 1.16(i))	*	Minus	**	=	x =		OR	x =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=	x =		OR	x =	
	Application Size Fee (37 CFR 1.16(s))									
	FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							OR		
						TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

		(Column 1)		(Column 2)	(Column 3)					
		CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA	RATE($)	ADDITIONAL FEE($)		RATE($)	ADDITIONAL FEE($)
AMENDMENT B	Total (37 CFR 1.16(i))	*	Minus	**	=	x =		OR	x =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=	x =		OR	x =	
	Application Size Fee (37 CFR 1.16(s))									
	FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							OR		
						TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.
** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".
*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".
The "Highest Number Previously Paid For" (Total or Independent) is the highest found in the appropriate box in column 1.

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UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NUMBER	FILING or 371(c) DATE	GRP ART UNIT	FIL FEE REC'D	ATTY.DOCKET.NO	TOT CLAIMS	IND CLAIMS
14/686,237	04/14/2015	3674	800	04697.0001USU1	17	2

CONFIRMATION NO. 2601

23552
MERCHANT & GOULD P.C.
P.O. BOX 2903
MINNEAPOLIS, MN 55402-0903

FILING RECEIPT

OC000000074814540

Date Mailed: 04/28/2015

Receipt is acknowledged of this non-provisional patent application. The application will be taken up for examination in due course. Applicant will be notified as to the results of the examination. Any correspondence concerning the application must include the following identification information: the U.S. APPLICATION NUMBER, FILING DATE, NAME OF APPLICANT, and TITLE OF INVENTION. Fees transmitted by check or draft are subject to collection. Please verify the accuracy of the data presented on this receipt. **If an error is noted on this Filing Receipt, please submit a written request for a Filing Receipt Correction. Please provide a copy of this Filing Receipt with the changes noted thereon. If you received a "Notice to File Missing Parts" for this application, please submit any corrections to this Filing Receipt with your reply to the Notice. When the USPTO processes the reply to the Notice, the USPTO will generate another Filing Receipt incorporating the requested corrections**

Inventor(s)

Andrew Bryce Conway, Weatherford, OK;

Applicant(s)

Flex-Chem Holding Company, LLC, Weatherford, OK

Assignment For Published Patent Application

Flex-Chem Holding Company, LLC, Weatherford, OK

Power of Attorney: None

Domestic Priority data as claimed by applicant

This appln claims benefit of 61/979,210 04/14/2014
and claims benefit of 62/087,899 12/05/2014

Foreign Applications for which priority is claimed (You may be eligible to benefit from the **Patent Prosecution Highway** program at the USPTO. Please see http://www.uspto.gov for more information.) - None.
Foreign application information must be provided in an Application Data Sheet in order to constitute a claim to foreign priority. See 37 CFR 1.55 and 1.76.

Permission to Access - A proper **Authorization to Permit Access to Application by Participating Offices** (PTO/SB/39 or its equivalent) has been received by the USPTO.

If Required, Foreign Filing License Granted: 04/24/2015
The country code and number of your priority application, to be used for filing abroad under the Paris Convention, is **US 14/686,237**
Projected Publication Date: 10/15/2015
Non-Publication Request: No

Early Publication Request: No
**** SMALL ENTITY ****
Title

STIMULATION OF WELLS IN NANO-DARCY SHALE FORMATIONS

Preliminary Class

166

Statement under 37 CFR 1.55 or 1.78 for AIA (First Inventor to File) Transition Applications: No

PROTECTING YOUR INVENTION OUTSIDE THE UNITED STATES

Since the rights granted by a U.S. patent extend only throughout the territory of the United States and have no effect in a foreign country, an inventor who wishes patent protection in another country must apply for a patent in a specific country or in regional patent offices. Applicants may wish to consider the filing of an international application under the Patent Cooperation Treaty (PCT). An international (PCT) application generally has the same effect as a regular national patent application in each PCT-member country. The PCT process **simplifies** the filing of patent applications on the same invention in member countries, but **does not result** in a grant of "an international patent" and does not eliminate the need of applicants to file additional documents and fees in countries where patent protection is desired.

Almost every country has its own patent law, and a person desiring a patent in a particular country must make an application for patent in that country in accordance with its particular laws. Since the laws of many countries differ in various respects from the patent law of the United States, applicants are advised to seek guidance from specific foreign countries to ensure that patent rights are not lost prematurely.

Applicants also are advised that in the case of inventions made in the United States, the Director of the USPTO must issue a license before applicants can apply for a patent in a foreign country. The filing of a U.S. patent application serves as a request for a foreign filing license. The application's filing receipt contains further information and guidance as to the status of applicant's license for foreign filing.

Applicants may wish to consult the USPTO booklet, "General Information Concerning Patents" (specifically, the section entitled "Treaties and Foreign Patents") for more information on timeframes and deadlines for filing foreign patent applications. The guide is available either by contacting the USPTO Contact Center at 800-786-9199, or it can be viewed on the USPTO website at http://www.uspto.gov/web/offices/pac/doc/general/index.html.

For information on preventing theft of your intellectual property (patents, trademarks and copyrights), you may wish to consult the U.S. Government website, http://www.stopfakes.gov. Part of a Department of Commerce initiative, this website includes self-help "toolkits" giving innovators guidance on how to protect intellectual property in specific countries such as China, Korea and Mexico. For questions regarding patent enforcement issues, applicants may call the U.S. Government hotline at 1-866-999-HALT (1-866-999-4258).

LICENSE FOR FOREIGN FILING UNDER

Title 35, United States Code, Section 184

Title 37, Code of Federal Regulations, 5.11 & 5.15

GRANTED

The applicant has been granted a license under 35 U.S.C. 184, if the phrase "IF REQUIRED, FOREIGN FILING LICENSE GRANTED" followed by a date appears on this form. Such licenses are issued in all applications where the conditions for issuance of a license have been met, regardless of whether or not a license may be required as set forth in 37 CFR 5.15. The scope and limitations of this license are set forth in 37 CFR 5.15(a) unless an earlier license has been issued under 37 CFR 5.15(b). The license is subject to revocation upon written notification. The date indicated is the effective date of the license, unless an earlier license of similar scope has been granted under 37 CFR 5.13 or 5.14.

This license is to be retained by the licensee and may be used at any time on or after the effective date thereof unless it is revoked. This license is automatically transferred to any related applications(s) filed under 37 CFR 1.53(d). This license is not retroactive.

The grant of a license does not in any way lessen the responsibility of a licensee for the security of the subject matter as imposed by any Government contract or the provisions of existing laws relating to espionage and the national security or the export of technical data. Licensees should apprise themselves of current regulations especially with respect to certain countries, of other agencies, particularly the Office of Defense Trade Controls, Department of State (with respect to Arms, Munitions and Implements of War (22 CFR 121-128)); the Bureau of Industry and Security, Department of Commerce (15 CFR parts 730-774); the Office of Foreign AssetsControl, Department of Treasury (31 CFR Parts 500+) and the Department of Energy.

NOT GRANTED

No license under 35 U.S.C. 184 has been granted at this time, if the phrase "IF REQUIRED, FOREIGN FILING LICENSE GRANTED" DOES NOT appear on this form. Applicant may still petition for a license under 37 CFR 5.12, if a license is desired before the expiration of 6 months from the filing date of the application. If 6 months has lapsed from the filing date of this application and the licensee has not received any indication of a secrecy order under 35 U.S.C. 181, the licensee may foreign file the application pursuant to 37 CFR 5.15(b).

SelectUSA

The United States represents the largest, most dynamic marketplace in the world and is an unparalleled location for business investment, innovation, and commercialization of new technologies. The U.S. offers tremendous resources and advantages for those who invest and manufacture goods here. Through SelectUSA, our nation works to promote and facilitate business investment. SelectUSA provides information assistance to the international investor community; serves as an ombudsman for existing and potential investors; advocates on behalf of U.S. cities, states, and regions competing for global investment; and counsels U.S. economic development organizations on investment attraction best practices. To learn more about why the United States is the best country in the world to develop technology, manufacture products, deliver services, and grow your business, visit http://www.SelectUSA.gov or call +1-202-482-6800.

PTO/AIA/01 (06-12)
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DECLARATION (37 CFR 1.63) FOR UTILITY OR DESIGN APPLICATION USING AN APPLICATION DATA SHEET (37 CFR 1.76)

Title of Invention	STIMULATION OF WELLS IN NANO-DARCY SHALE FORMATIONS

As the below named inventor, I hereby declare that:

This declaration is directed to:

☐ The attached application, or

☒ United States application or PCT international application number 14/686,237

filed on April 14, 2015

The above-identified application was made or authorized to be made by me.

I believe that I am the original inventor or an original joint inventor of a claimed invention in the application.

I hereby acknowledge that any willful false statement made in this declaration is punishable under 18 U.S.C. 1001 by fine or imprisonment of not more than five (5) years, or both.

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LEGAL NAME OF INVENTOR

Inventor: Andrew Bryce Conway Date (Optional): 4-16-15

Signature: BC

Note: An application data sheet (PTO/SB/14 or equivalent), including naming the entire inventive entity, must accompany this form or must have been previously filed. Use an additional PTO/AIA/01 form for each additional inventor.

This collection of information is required by 35 U.S.C. 115 and 37 CFR 1.63. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 1 minute to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

STIMULATION OF WELLS IN NANO-DARCY SHALE FORMATIONS

RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application No. 62/087,899, filed December 5, 2014, and U.S. Provisional Application No. 61/979,210, filed April 14, 2014, which applications are hereby incorporated by reference.

INTRODUCTION

[0002] The darcy is a unit of permeability for fluids in a porous material. Nano-darcy shale formations refer to those shale formations having an average permeability in at least one direction of less than 1 micro-darcy or less than $1x10^{-6}$ darcy. In nano-darcy shale formations, the range of average pore sizes within the shale spans the size of the hydrocarbons trapped in the shale, e.g., the natural gas molecules and the molecules of the various crude oil constituents. That is, the average pore size within the shale may be smaller, approximately the same size or larger than the size of the hydrocarbons. This differs from higher permeability shale formations in which the average pores sizes are substantially larger than the various hydrocarbon molecule sizes.

[0003] While permeability is a useful measurement, the determination of average pore size from a permeability measurement relies on assumptions about the shapes of the grains or pores in the subsurface. Shale formations are a mixture of clay minerals and larger particles. Clay minerals are not normally spherically shaped and also exhibit electro-static properties not found in non-clay materials. Thus, as nano-darcy shale formations are typically very high in clay content, they do not exhibit the same behaviors as more permeable formations, even more permeable shale formations.

[0004] Well stimulation refers to the treatment of an existing well to increase its recovery of hydrocarbons or other substances from the subsurface. Because of the different nature of nano-darcy shale formations, typical well stimulation techniques have been found to be ineffective or much less effective than in higher permeability formations.

[0005] An extreme form of well stimulation is referred to as hydraulic fracturing. Hydraulic fracturing of oil and gas wells is conducted by pumping fluids at high pressures and high velocities through a vertical and, usually, a horizontal section of a well. The well contains a well casing and, in some wells, tubing inside the casing. Perforations or ports in the casing are adjacent to targeted intervals of subterranean formations containing a hydrocarbon or target

product. In hydraulic fracturing, the pressure exerted on the formation is greater than the pressure required to substantially fracture the formation, a pressure referred to as the fracture pressure of the formation which is a function of the formation' properties and the depth where the fractures are desired. One test for determining the fracture pressure is the Leak-off test. Applying a pressure equal to or greater than the fracture pressure causes the formation to fracture, creating an extensive fracture network.

[0006] After the fractures or cracks are initiated, pumping is continued, allowing the fractures to propagate. Once the fracture has gained sufficient fracture width, a proppant such as sand is added to the fluid and is transported into the fracture system, partially filling the fracture network. After the desired amount of proppant is placed in the fractures, additional water-based fluid is pumped to flush the casing of any proppant that may have settled in the casing. On completion of the fracturing process, the well is opened, allowing a portion of the fracturing fluids to be recovered. As the pressure is relieved, the fracture closes onto the proppant, creating a conductive pathway needed to accelerate oil and gas recovery from the formation. Hydraulic fracturing is expensive because of the large amounts of fluids and high pressures involved.

STIMULATION OF WELLS IN NANO-DARCY SHALE FORMATIONS

[0007] This disclosure describes formulations and methods for stimulating the production from wells in nano-darcy shale formations. In one embodiment, the method includes injecting a treatment mixture containing a metal complexing agent such as citric acid or EDTA into a shale formation adjacent to a well at a pressure below the fracture pressure of the formation. A sufficient contact time is allowed and then the treatment mixture is pumped from the subsurface. This has been shown to stimulate well production in nano-darcy shale formations. In another embodiment, the method includes staging the treatment mixture containing a metal complexing agent such as citric acid or EDTA in combination with hydraulic fracturing and injecting into the formation in conjunction with propagation of the induced fractures. Without being held to a particular theory, based on an analysis of the extracted spent treatment fluid it appears that the metal complexing agent binds with naturally occurring metals in the formation, and particularly divalent and/or trivalent metal ions, which are then extracted with the spent treatment mixture. This removal of naturally occurring metals may be increasing the permeability of the formation in the contact region adjacent to the well, thereby causing the increased production.

[0008] In one aspect, this disclosure describes a method for stimulating a well in a nano-darcy shale formation. The method includes providing a treatment mixture containing between about 0.1% and 95% by weight metal complexing agent at a pH of between about 0 and 10; injecting the treatment mixture into the well at a pressure less than a fracture pressure of the nano-darcy shale formation until at least some of the treatment mixture contacts the nano-darcy shale formation; maintaining the treatment mixture in contact with the nano-darcy shale formation for a contact time of between about 1 minute to 100 days, thereby allowing the metal complexing agent to bind with at least some naturally-occurring metals contained within the nano-darcy shale formation; and removing the treatment mixture from the well after the contact time, thereby removing the bound naturally-occurring metals from the non-darcy shale formation and thereby improving the hydrocarbon production of the well relative to the hydrocarbon production immediately prior to performance of the method. In the method, the metal complexing agent may be one or more of citric acid, ethylene diaminet etra acetic acid (EDTA), acetic acid, or any of a number of compounds described below.

[0009] Another aspect of this disclosure is method for fracturing and stimulating a well in a nano-darcy shale formation. The method includes providing a treatment mixture containing between about 0.1% and 95% by weight metal complexing agent at a pH of between about 0 and 10; injecting the treatment mixture into the well at a pressure greater than a fracture pressure of the nano-darcy shale formation until at least some of the treatment mixture enters fractures in the nano-darcy shale formation, thereby allowing the metal complexing agent to bind with at least some naturally-occurring metals contained within the nano-darcy shale formation; and removing spent treatment mixture and fracturing fluids from the well after the fractures are created, thereby removing the bound naturally-occurring metals from the non-darcy shale formation. The injecting operation may be part of a fracturing operation that causes the fractures to occur in the nano-darcy shale formation. The method may further include fracturing the nano-darcy shale formation; and wherein the injecting operation occurs after the fracturing operation causes the fractures to occur in the nano-darcy shale formation.

[0010] These and various other features as well as advantages which characterize the systems and methods described herein will be apparent from a reading of the following detailed description and a review of the associated drawings. Additional features are set forth in the description which follows, and in part will be apparent from the description, or may be learned by practice of the technology. The benefits and features of the technology will be realized and

attained by the structure particularly pointed out in the written description and claims hereof as well as the appended drawings.

[0011] It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory and are intended to provide further explanation of the invention as claimed.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] The following drawing figures, which form a part of this application, are illustrative of described technology and are not meant to limit the scope of the invention as claimed in any manner, which scope shall be based on the claims appended hereto.

[0013] FIG. 1 is an embodiment of a method of well stimulation.

[0014] FIG. 2 illustrates a plot of aluminum, barium, manganese, strontium, sulfate; and pH vs. time in samples taken from a horizontal well completed in the Woodford Shale formation and stimulated using the technique of FIG. 1 on day 0.

[0015] FIG. 3 illustrates a plot of calcium, magnesium and pH vs. time in samples taken from a horizontal well completed in the Woodford Shale formation from the same experiment as FIG. 2.

[0016] FIG. 4 illustrates a plot of iron and pH vs. time in samples taken from a horizontal well completed in the Woodford Shale formation from the same experiment as FIG. 2.

[0017] FIG. 5 illustrates performing the stimulation treatment as part of a fracturing operation.

DETAILED DESCRIPTION

[0018] Although the techniques introduced above and discussed in detail below may be implemented for stimulating any subsurface extractions from nano-darcy formations, the present disclosure will discuss the implementation of these techniques in an oil and gas well for the purpose of extracting hydrocarbons. The reader will understand that the technology described in the context of an oil and gas well could be adapted for use with other systems such as water well and solution mining wells or any other situation in which the permeability of the subsurface needs to be reduced.

[0019] This disclosure describes formulations and methods for stimulating the production from wells in nano-darcy shale formations. In one embodiment, the method includes injecting a treatment mixture containing a metal complexing agent such as citric acid or EDTA into a nano-darcy shale formation adjacent to a well at a pressure below the fracture pressure of the formation. A sufficient contact time is allowed and then the treatment mixture is pumped from

the subsurface. This has been shown to stimulate well production in nano-darcy shale formations. Without being held to a particular theory, based on an analysis of the extracted spent treatment fluid it appears that the metal complexing agent binds with naturally occurring metals in the formation (possibly by forming a complex with the metals and removing them from the shale), and particularly divalent metal ions, which are then extracted with the spent fluid. This removal of naturally occurring metals may be increasing the permeability of the formation in the contact region adjacent to the well, thereby causing the increased production.

[0020] In an alternative embodiment, the well stimulation treatment is applied as part of the fracturing process. It is anticipated that proper integration of the well stimulation treatment with the fracturing process will achieve a better production result than fracturing without stimulation. Both embodiments, the fracturing embodiment and the stimulation embodiment done below the fracture pressure of the formation, are described in greater detail below.

[0021] The present disclosure relates to a process to sequester and remove metal cations from partially soluble silicon-bearing clay minerals naturally present in a subterranean formation. Whether the metallic ions are present from natural sources in the reservoir rock prior to drilling into the formation or formed through interactions with drilling, completion, or reservoir stimulation (hydraulic fracturing or acid stimulation) fluids, the use of metal chelating substances to dissolve or disperse materials that are, or can, restrict flow into the well bore is presented as a commercial method to restore or enhance the productivity of well bores that are restricted with such materials. For example, the introduction of hydraulic fracturing fluids and/or acid treatments that release metal ions through their interaction with the formation materials, such as aluminum, barium, calcium, magnesium, manganese, iron, strontium, boron and other metals or metalloids. Such metallic or metalloid ions may form ion complexes with sulfur bearing ions such as sulfide and sulfate, hydroxide ions, and silicon bearing ions such as silicates; for example calcium magnesium silicate, that may precipitate or otherwise form flow restrictions in the porous space of the reservoir rock in the well bore. Specifically, metallic ion complexes such as aluminum hydroxide, aluminum silicate, calcium hydroxide, calcium magnesium silicate, iron hydroxide, iron silicate, magnesium hydroxide, magnesium silicate, or other metal hydroxide, and/or silicon complexes, or metal sulfide or metal sulfate scales; that through formation of solid or colloidal substances may form restrictions that limit the permeability of reservoir rock to producing hydrocarbons.

[0022] Introduction and maintenance of a metal-complexing agent into the formation allows for the metals to be bound and subsequently removed. For the purposes of this disclosure, a metal-complexing agent may be any chemical that can bind with a metal regardless of the binding mechanism and includes sequestration agents, reducing agents, chelating agents, ligands porphyrins, pigments, peptides, saccharides and/or nucleic acids. In some embodiments, the metal-complexing agent is a chelating agent, an alkali metal salt thereof, a non-alkali metal salt thereof, or any combination thereof may be included in the treatment fluids described herein. In some embodiments, the chelating agent may be biodegradable. Although use of a biodegradable chelating agent may be particularly advantageous in some embodiments of the present disclosure, there is no requirement to do so, and, in general, any suitable chelating agent may be used. As used herein, the term "biodegradable" refers to a substance that can be broken down by exposure to environmental conditions including native or non-native microbes, sunlight, air, heat, and the like. Use of the term "biodegradable" does not imply a particular degree of biodegradability, mechanism of biodegradability, or a specified biodegradation half-life.

[0023] In some embodiments, A partially soluble or colloidal metal ion complex, such as, for example, calcium magnesium silicate, is solubilized using, for example, one or a combination of the following chelation chemicals (chelating agent): Acetic Acid, Acrylates, Dihydroxymaleic Acid, Salts of Dihydroxymaleic Acid, EDTA (ethylenediamine tetraacetic acid), Salts of EDTA, erythorbic acid, erythroboric acid, Formic Acid, Gluconodeltalactone, GLDA (glutamic acid N,N-diacetic acid), Salts of GLDA, HEDTA (hydroxyethylenediamine triacetic acid), Salts of HEDTA, HEIDA (disodium ethanoldiglycine), Salts of HEIDA, MGDA (methylglycine N,N-diacetic acid), Salts of MGDA, NTA (nitriolotriacetic acid), Organic Metal Complexers, Phosphonic Acid, Polyacrylic Acid and notably Citric Acid in an amount sufficient to sequester at least a portion of any metal compounds and there by dissolve or disperse materials that can restrict the flow path to the well bore and the overall permeability of the well bore and reservoir rock system. It should be understood that although chelation chemical(s) (chelating agent(s), chelator(s)) have been provided herein by way of example, any chelation chemical may be utilized in accordance with the present process, so long as the chelation chemical functions in accordance with the present disclosure as described herein.

[0024] In some embodiments, suitable chelating agents may include common chelating agent compounds such as, for example, ethylenediaminetetraacetic acid (EDTA), propylenediaminetetraacetic acid (PDTA), nitrilotriacetic acid (NTA), N-(2-

hydroxyethyl)ethylenediaminetriacetic acid (HEDTA), diethylenetriaminepentaacetic acid (DTPA), hydroxyethyliminodiacetic acid (HEIDA), cyclohexylenediaminetetraacetic acid (CDTA), diphenylaminesulfonic acid (DPAS), ethylenediaminedi(o-hydroxyphenylacetic) acid (EDDHA), glucoheptonic acid, gluconic acid, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, phthalic acid, terephthalic acid, aconitic acid, carballylic acid, trimesic acid, isocitric acid, citric acid, any salt thereof, any derivative thereof, and the like. It is to be noted that NTA may be considered to be a biodegradable compound, but it may have undesirable toxicity issues.

[0025] In some embodiments, suitable chelating agents may include biodegradable chelating agents such as, for example, glutamic acid diacetic acid (GLDA), methylglycine diacetic acid (MGDA), β-alanine diacetic acid (β-ADA), ethylenediaminedisuccinic acid, S,S-ethylenediaminedisuccinic acid (EDDS), iminodisuccinic acid (IDS), hydroxyiminodisuccinic acid (HIDS), polyamino disuccinic acids, N-bis[2-(l,2- dicarboxyethoxy)ethyl]glycine (BCA6), N-bis[2-(l,2- dicarboxyethoxy)ethyl]aspartic acid (BCA5), N-bis[2-(l,2-dicarboxyethoxy)ethyl]methylglycine (MCBA5), N-tris[(l,2- dicarboxyethoxy)ethyl]amine (TCA6), N-methyliminodiacetic acid (MIDA), iminodiacetic acid (IDA), N-(2-acetamido)iminodiacetic acid (ADA), hydroxymethyl-iminodiacetic acid, 2-(2-carboxyethylamino) succinic acid (CEAA), 2-(2-carboxymethylamino) succinic acid (CMAA), diethylenetriamine- N,N"-disuccinic acid, triethylenetetramine-N,N"'-disuccinic acid, 1,6-hexamethylenediamine-N,N'-disuccinic acid, tetraethylenepentamine-N,N""- disuccinic acid, 2-hydroxypropylene-l,3-diamine-N,N'-disuccinic acid, 1,2- propylenediamine-N,N'-disuccinic acid, l,3-propylenediamine-N,N'-disuccinic acid, cis-cyclohexanediamine-N,N'-disuccinic acid, trans-cyclohexanediamine- N,N'-disuccinic acid, ethylenebis(oxyethylenenitrilo)-N,N'-disuccinic acid, glucoheptanoic acid, cysteic acid-N,N-diacetic acid, cysteic acid-N-monoacetic acid, alanine-N-monoacetic acid, N-(3-hydroxysuccinyl) aspartic acid, N-[2-(3- hydroxysuccinyl)]-L-serine, aspartic acid-N,N-diacetic acid, aspartic acid-N- monoacetic acid, any salt thereof, any derivative thereof, or any combination thereof.

[0026] In an alternative embodiment, the metal-complexing agent may be a suitable sequestering agent such as polysuccinimide, polyaspartic acid, and polymers, oligomers, chains or block-copolymers of the twenty two essential amino acids containing metal complexing groups such as carboxylic acids, phosphonic acids, sulfonic acids and boronic acids.

[0027] In one embodiment, the chelating agent is provided between about 0.05% weight volume to about 60% weight volume. However, any suitable range may be used including from 1% to 40%, and between 2% and 20%. In some embodiments, the amount of chelating agent may be even higher as some chelating agents may be provided with additives as described in greater detail below.

[0028] The well stimulation mixture can contain the metal complexing agent as well as multiple chemical additives as desired. The additives may include biocide, scale inhibitor, clay control additive, oxygen scavenger and surfactant that assist fluid recovery. To keep the fracturing treatments affordable, only minimal amounts of these additives are used. Each additive is normally liquid-based and is metered separately into the treatment fluid and mixed with water and other additives in the blender. The blender includes a 5- to 15-barrel tub with agitation devices. The additive concentrations are commonly expressed in parts per million (ppm) or as gallons of additive per 1000 gallons of water (abbreviated as gallons per thousand or gpt). The additives typically are composed of a chemical that provides the desired function such as scale inhibition and a solvent, commonly water, alcohol or oil.

[0029] Another additive that may be used is a corrosion inhibitor. Corrosion inhibitors reduce corrosion of the well components. In an embodiment, quaternary ammonium compounds typically referred to as quaternary amines are used as a corrosion inhibitor in trace amounts to 2,000 ppm. However, any suitable corrosion inhibitor may be used in any amount as desired. Other examples of possible corrosion inhibitors include quaternary amine compounds commonly used for protection of metal in the presence of high or low pH and/or dissolved oxygen bearing fluids, such as Flex Chem FC-181 and many other similar formulations used in well maintenance activities. Quaternary ammonium compounds, acetylenic alcohols, amide and oxylalkylated alcohols, quinoline quaternary ammonium alkyl amine salts and surfactants, nonyl phenol surfactants, alkyl thioamides, oxyalkylated phenols, alkyl pyridine benzyl quaternary ammonium chloride, benzyl quaternary ammonium chloride, aliphatic amines, cocoamine diquaternary ammonium chloride, imadazoline, polyamide, modified amido polyamine, alkylamidomine, amido imadazoline, alkyl phosphate ester, potassium salt of a glycol phosphate ester, amine salt of poly-phosphate ester, tallow diamine ethoxylate, polyacid, amine salt of polyphosphonic acid, organic acid-amine salt, crude dimerized fatty acids or tall oil dimer-trimer acids.

[0030] Surfactants such as sodium lauryl sulfate and many other surfactant materials that could be selected based on their compatibility with the other materials in the chelating solution and pH of the final solution.

[0031] Another additive that may be used is a biocide. For example, in an embodiment trace amounts to 5,000 ppm tributyl tetradecyl phosphonium chloride (TTPC) may be used as a biocide. Any suitable biocide may be used in any amount as desired. Biocidal agents could include glutaraldehyde, quaternary amine compounds such as alkyl dimethyl benzyl ammonium chloride (ADBAC), sodium chlorite (which would generate chlorine dioxide in-situ), TTPC, isothiazolin compounds, thione based compounds, and many other agents approved for use in the well maintenance activities. Other examples of possible biocides include chlorine dioxide, didecyldimethyl ammonium chloride (DDAC) and brominated propionamide.

[0032] Dispersing agents such as Dow Acumer 5000 or Versaflex Si to enhance the removal of colloidal silicon bearing materials and many other dispersing agents that could assist with recovering colloidal material residue from the well bore.

[0033] Another additive that may be used is a colloidal silica deposition inhibitor. The use of a colloidal silica deposition inhibitor, sometimes also referred to as amorphous silica control compound, prevents silica scale precipitation within the wells during the treatment process. One example of a colloidal silica deposition inhibitor is an aqueous solution of organic additive based on phosphino carboxylic acid copolymer, a commercial version of which is sold under the trademark GEOGARD SX. Any suitable colloidal silica deposition inhibitor may be used. Other examples of possible colloidal silica deposition inhibitors include such materials as phosphate, phosphate ester, or phosphonate compounds; polymaleic, or acrylate compounds such as polyacrylic acid scale inhibitors commonly used for such applications in well maintenance activities.

[0034] Another additive that may be used is a mutual solvent. Mutual solvents are soluble in oil, water and acid-based mixtures and may be used in a range of applications, such as removing heavy hydrocarbon deposits, controlling the wettability of contact surfaces before, during or after a stimulation treatment, and preventing or breaking emulsions. A commonly used mutual solvent is ethylene glycol monobutyl ether, generally known as EGMBE or 2-butoxy ethanol. Any suitable mutual solvent may be used. Other examples of possible mutual solvents include compounds such as ethylene glycol monobutyl ether or FCS-280 or other compounds commonly used for such applications in well maintenance activities.

[0035] Acid may also be used as an additive in order to control the pH of the treatment mixture. In an embodiment hydrochloric acid may be used from trace amounts to about 30% by weight. Any suitable acid may be used as needed. Other examples of possible acids include aqua regia, arsenic acid, boric acid, carbonic acid, chloric acid, chromic acid, fluoroantimonic acid, fluoroboric acid, fluorosulfuric acid, fulminic acid, hexafluorophosphoric acid, hexafluorosilicic acid, hydrobromic acid, hydrofluoric acid, hydrogen iodide, hypochlorous acid, hypofluorous acid, hypophosphoric acid, iodic acid, nitric acid, nitrosyl-O-hydroxide, nitrous acid, orthocarbonic acid, perchloric acid, permanganic acid, perrhenic acid, pertechnetic acid, phosphoric acid, silicic acid, sulfuric acid, thiocyanic acid, titanic acid, tungstic acid or xenic acid.

[0036] In some wells, well stimulation using the novel treatment mixtures designed herein may be made more cost efficient by alternating the injection of the treatment mixture with the injection of a diverting material. Many wells have high volume sections within the well flow paths that are referred to as fluid thief zones in that they represent a volume that must be filed during the treatment process but the fluid in that zone is ineffective at its task (in this case complexing with metal cations in the nano-darcy formation). To address this, a diverting material such as particles of polylactic acid in a brine mixture may be used. Diverting materials are designed to take up larger volumes without interfering with the delivery of treatment chemicals to the target zones. Diverting materials are relatively inert with respect to the treatment chemicals and are also designed to allow easy passage of the treatment chemicals around volumes that they occupy. In addition, many diverting materials are designed to breakdown and be easily recoverable after some period of time such as days or weeks.

[0037] Diverting materials and mixtures other than particles of polylactic acid in a brine mixture may also be used. Diverting agents such as benzoic acid flakes, polylactic acid, solid or water soluble ball sealers, rock salt, encapsulated solid chelators, etc., other diverting agents. For example, mixtures using products consisting of various polymers blended with waxes and other solid hydrocarbons polymers blended with waxes and other solid hydrocarbons have been used as diverting material. Diverting materials are designed to be relatively inert with respect to the treatment chemicals and are also designed to allow easy passage of the treatment chemicals.

[0038] In an embodiment, a stimulation program may include alternating between injecting an amount of treatment mixture, followed by injecting an amount of a diverting mixture until such time as the well pressure achieves a target pressure, such as a pre-determined target pressure, the

fracture pressure for the formation or a threshold amount above or below the pre-determined fracture pressure from the formation calculated based on the fracture pressure.

[0039] FIG. 1 illustrates one such stimulation program, in this case done below the fracture pressure of the formation. In the program 100, the treatment mixture is obtained in a provide treatment mixture operation 102. The treatment mixture may be made or completed on site in a batch process or an amount of treatment mixture may be brought to the site prior to the stimulation of the well. Any of the embodiments of the treatment mixture described above may be used.

[0040] A provide diverting mixture operation 104 is also performed in which a diverting mixture is either generated at the site prior to use or a mixture is brought to the site pre-made. Any diverting mixture as described above may be used. This operation 104, is also optional and may not be needed if it is determined that there will be relatively little lose to thief zones of the treatment mixture during the treatment process.

[0041] Next, the treatment mixture and the diverting mixture (if any) are injected in an injection operation 106. In an embodiment, the two mixtures are alternately injected in alternating injection operation 106. As described above, predetermined amounts of the mixtures may be alternately injected or the injection amounts may be varied. In an embodiment, for example, the injection operation alternately injects 150 barrels of treatment mixture and 150 barrels of diverting mixture.

[0042] In one embodiment, injection continues until such time as the well pressure achieves a target pressure. The target pressure may be a pre-determined target pressure based on knowledge of the operator. Alternatively, the target pressure may be the fracture pressure for the formation or a threshold amount above or below the fracture pressure from the formation. Any suitable technique such as the Leak-off test may be used to determine fracture pressure.

[0043] Upon reaching the target pressure, a well shut in operation 108 is performed. In the shut in operation 108, the well is closed and the treatment mixture is trapped in the well.

[0044] The well is then maintained in the shut in state in a maintain shut in operation 110. This provides contact time for the treatment mixture allowing the treatment chemicals to react with the shale formation and bind some of the natural metals to the treatment mixture. During this period, the pressure may slowly decrease and the pH may change due to reactions occurring in the subsurface. The contact time provided may be any amount from 1 minute to 100 days. However, it appears that 1 to 3 days may be preferable. Other examples of acceptable ranges of

contact times include: from 3 hours to 7 days; from 6 hours to 5 days; from 12 hours to 45 days; from 18 hours to 3 days and from 1 to 2 days. Too long or too short a contact time may result in lowered performance. Too short a time may not allow sufficient time for the treatment mixture to complex with the naturally occurring metals in the formation. Too long a contact time may result in bound metals precipitating within the well or formation before they can be removed with the spent treatment mixture. It is anticipated that the optimum time may need to be determined empirically for each formation or even each depth or region of a formation. In this case, determining the contact time may be considered an additional step in the stimulation process. This step may include testing multiple wells at different contact times, using a downhole monitoring device or other mechanism to determine when sufficient solubilizing of the formation metals has been achieved or by some ex-situ method such as by calculation or lab testing of formation materials.

[0045] The method ends with the extraction of the treatment mixture in a mixture removal operation 112. In the removal operation 112, the well opened and the mixtures are pumped out of the well. The mixtures will include bound metals from the subsurface. Again, without being held to a particular theory, based on an analysis of the extracted treatment mixtures and laboratory testing it appears that the metal complexing agent is forming metal complexes and/or binding with naturally occurring metals in the formation, and particularly divalent metal ions, which are then extracted with the spent treatment mixture. This removal of naturally occurring metals may be increasing the permeability of the formation in the contact region adjacent to the well, thereby causing the increased production of the well after the stimulation using the techniques described above.

[0046] FIG. 5 illustrates performing the stimulation treatment as part of a fracturing operation. In the process of hydraulic fracturing, fluid is injected into the well at a pressure that induces fractures in the reservoir rock. Pumping is continued after the fractures are initiated, which causes the fractures to propagate and widen sufficiently to allow a proppant material to enter the fractures. Stages of fluids of different composition are injected sequentially to induce, propagate and prop the fractures. One example of an injection sequence is:

1. An initial acid (sometimes referred to as the “pre-pad stage”), typically containing hydrochloric acid, to clear the wellbore and perforations.
2. A conditioning (or “pad stage”) to open the fractures, and containing chemicals to condition fluid pathways.

3. A proppant stage which carries the proppant material into the opened fractures, and normally containing a polymer to increase the proppant carrying capacity.
4. A flushing stage to clean excess chemicals and proppant from the wellbore.

The above sequence and/or individual steps, or stages as they are sometimes called below, may be repeated as needed or desired.

[0047] In the fracturing process embodiment of the well stimulation treatment, a stimulation treatment mixture containing a metal complexing agent such as citric acid or EDTA could be placed in any of the stages, or as an additional stage anywhere in a fracturing injection sequence, such as the one described above. The placement within the injection sequence of the treatment mixture injection would affect where the treatment goes within the formation and, therefore, control the resulting effects on the formation.

[0048] In the fracturing process embodiment of the well stimulation treatment, a stimulation treatment mixture containing a metal complexing agent such as citric acid or EDTA could be placed in any of the stages, or as an additional stage anywhere in a fracturing injection sequence, such as the one described above. The placement within the injection sequence of the treatment mixture injection would affect where the treatment goes within the formation and, therefore, control the resulting effects on the formation.

[0049] For example, injecting the stimulation treatment mixture before the pad stage would make the stimulation treatment mixture contact the formation during the stage that opens the fracture and, thus, make it the first fluid to contact the surface of the newly-induced fractures. Assuming fluids, including the treatment mixture, from the early stages leaks off into the formation, placing the stimulation treatment mixture before the pad stage would allow the treatment mixture to leak off into the formation matrix before other chemicals in the pad stage affect the fracture face.

[0050] As another example, placing the stimulation treating mixture in the proppant stage would allow the chemicals in the pad stage to affect the contact of the fracture face before the treatment mixture contacts the fracture face. If the chemicals in the pad stage alters the rock along the fracture face it could potentially affect the penetration of the treatment mixture. In the extreme case, if chemicals in the pad stage prevent fluid leakoff it could potentially prevent the stimulation treatment mixtures from penetrating into the formation matrix.

[0051] If a goal is to sequester ions from reservoir rock matrix (e.g., to increase the permeability of the rock near the fracture), it may be desirable to inject the treatment mixture early in the sequence to get maximum penetration. On the other hand, if the goal is to sequester ions from other sources, such as displaced or introduced ions, it may be desirable to place the treatment later in the sequence. Thus, the injection sequence can be tailored to specific goals depending on the conditions at the wellhead and in the formation. In an embodiment, determination of the optimum stage for including injection At this time an optimum treatment mixture placement in combination with hydraulic fracturing has not been experimentally determined and we would like to secure as much treatment design flexibility as possible.

[0052] Fluids used in all stages of well fracturing contain chemical additives that may include acids, hydrocarbons, gums, polymers, solids, surfactants, scale inhibitors, disinfectants, etc. In the current state-of-the-art the formulations and placements are designed to facilitate and optimize the hydraulic pumping without the design or aim of treating the hydrocarbon-bearing formations with metal complexing agents.

[0053] Acids, commonly hydrochloric, citric, etc., may be added in initial stages to clean wellbore debris such as cement from fluid paths and control iron released from the steel well components by the harsh chemicals, and the formulations and volumes are designed to be mostly spent within the wellbore with preferably no entry into the fracture, as that would be wasted and, therefore, cost inefficient. Additional chemistries are formulated to further facilitate the hydraulic pumping by facilitating flow and proppant placement with minimal chemical effect on the formation past the fracture face.

[0054] Loss of fluid into the formation during hydraulic fracturing decreases hydraulic efficiency. In applications where fluid loss may affect hydraulics of the fracturing operation additives such as diverting materials, polymers, particulates, fine sand, hydrocarbons, etc., are commonly added to fracturing fluids to minimize leakoff of fracturing fluids into the formation and improve fluid hydraulic efficiency. In more permeable formations some initial fluid may spurt into the formation matrix before a barrier, or wall cake, is formed by the fluid additives, which slows or prevents further leakoff. In less permeable formations the fluid additives may prevent significant spurt from occurring.

[0055] Chemical interactions of fluid formulations during fracturing may be affected by placement and staging of specific formulations, other chemistries and sequential placement of the other chemistries. Chemical formulations in early fluid stages that may spurt into the formation

potentially have more access to the formation matrix than later stages that enter the fracture after a wall cake is formed, and if such chemical formulations were applied in a fluid stage that did not contain additional additives the chemical interaction of the chemical formulations with the formation matrix could potentially be affected less by the subsequent additives.

[0056] The stimulation treatment can be adapted to treat hydrocarbon-bearing formations with metal complexing agents. The chemical formulations are as described earlier during fracturing. The fracturing embodiments may include sequencing the well stimulation mixture in combination with hydraulic fracturing in ways to treat the formation differently.

[0057] In one embodiment, the well stimulation mixture could be formulated and injected in an initial stage that opens the fracture and contacts the formation before additional chemical additives. There are a number of ways this could be achieved. For example, a well stimulation mixture of sufficient volume to propagate through the induced fracture and contact the formation before a potential barrier or wall cake is formed could be injected between the pre-pad and pad stages or the pre-pad and/or pad stage could be modified with chemical amendments and/or design to achieve formation treatment.

[0058] In another embodiment, the well stimulation mixture could be formulated and injected in a stage containing a diverting or leakoff-minimizing material. Initially a limited amount of treatment mixture might contact the formation as wall cake is formed and treatment mixture has initial access to diverting material and wall cake inner face, outer face and wall cake matrix. In such a case the treatment of the formation might be influenced by other chemistries in the inclusive and/or prior stage(s). This method of treatment could be applied by injecting a new stage or modifying a stage containing other materials and formulations.

[0059] In another embodiment, the well stimulation mixture could be formulated and injected in post-diversion/wall cake stage such as a proppant stage. In this case immediate access of the stimulation treatment mixture is primarily limited to outer face of wall cake and other stage materials/chemicals. Treatment of the formation might be influenced by other chemistries of prior stages and might be delayed by some amount of time for the stimulation treatment mixture to penetrate the diverting material/wall cake. This method of treatment could be applied by injecting a new stage or modifying a stage containing other materials and formulations.

[0060] In another embodiment, the well stimulation mixture could be formulated and injected in a trailing or flushing stage at a pressure below the fracture pressure as described with reference to FIG. 1. Treatment of the formation might be influenced by other chemistries of prior stages

and might be delayed by some amount of time for the treatment mixture to penetrate the diverting material/wall cake. This method of treatment could be applied by injecting a new stage or modifying a stage containing other materials and formulations.

[0061] Turning now to the embodiment of FIG. 5, a well stimulation treatment program as part of a fracturing process is described in greater detail. In the program 500, the treatment mixture is obtained in a provide treatment mixture operation 502. The treatment mixture may be made or completed on site in a batch process or an amount of treatment mixture may be brought to the site prior to the stimulation of the well. Any of the embodiments of the treatment mixture described above may be used.

[0062] A provide fracturing fluids operation 504 is also performed in which the various fracturing fluids necessary for the fracturing operation are either generated at the site prior to use or brought to the site pre-made. Fracturing operations and the various fracturing fluids for each stage of the fracturing operation are known in the art.

[0063] Next, a combined fracturing/stimulation operation 506 is performed. As described above, different embodiments are possible depending upon when during the fracturing process the well stimulation mixture is incorporated.

[0064] FIG. 5 specifically illustrates the embodiment in which the well stimulation mixture is injected in the initial stage of the fracturing operation. In the embodiment illustrated, a pre-pad stage 508 is performed, as described above, to clear the wellbore and perforations. This may include injecting an acid or other pre-pad formulation.

[0065] The pre-pad stage 508 is then followed by a stimulation injection operation 510. In this operation 510, the stimulation treatment mixture is injected at a pressure above the fracturing pressure of the formation in order to create the initial fractures.

[0066] A proppant stage 512 is then performed in which proppant material is injected and forced into the opened fractures. In an embodiment, the injected proppant mixture may include polymers and other chemicals to increase the proppant carrying capacity and reduce the pressure needed to inject the proppant.

[0067] Next, a flushing stage 514 is performed in which excess chemicals and proppant from the wellbore. In this embodiment, spent well stimulation treatment mixture, bound with metals from the subsurface formation, will also be recovered. It is believed, based on the laboratory results and the results observed from stimulation below the fracturing pressure, that the combined fracturing/stimulation embodiments described above will result in a higher production rate for

the well that would be achieved without the use of the stimulation treatment mixture. Again, without being held to a particular theory, this is presumably because of the affect the stimulation treatment mixture has on the formation. By binding with naturally occurring metals in the formation, and particularly divalent metal ions, it is believed that the permeability of the formation near the fractures is increased, thereby causing the increased production of the well that would otherwise be observed.

[0068] As discussed above, the entire process may be repeated until sufficient fracturing has been achieved. Other embodiments of the method 500 are possible. In addition to changing any of the specific components of the mixtures as described above, changes to when and how the mixtures are produced and injected may be made without departing from the teaching of this disclosure.

EXAMPLES

Example 1

[0069] A laboratory analysis was performed in which an embodiment of the treatment mixture was mixed with a sample of nano-darcy shale material obtained from well cuttings of a well drilled into the Barnett Shale Formation, a nano-darcy shale formation. The embodiment of the treatment mixture was as follows: 10% by weight citric acid; 2000 ppm of quaternary amine; 5000 ppm of TTPC; 10000 ppm of GEOGARD SX colloidal silica deposition inhibitor; 20 gpt of 2-butoxy ethanol; and 10% by weight hydrochloric acid in an aqueous mixture.

[0070] The Barnett Shale material was mixed with the embodiment described above and allowed to soak for 96 hours at 179 degrees F. An analysis of various metals was performed by Inductively Coupled Plasma (ICP) on treatment mixture removed from the shale material after the end of the 96 hours. The results, provided below, show that the treatment mixture is effective at binding with metals naturally occurring in the nano-darcy shale formation.

	Aluminum	**Arsenic**	**Barium**	**Boron**	**Calcium**	**Iron**	**Potassium**
mg/L	710.8	1.9	2.0	37.3	21.7	2,808	192.6
mg/Kg	31,796.0	85.0	89.5	1,668.53	970.7	125,609	8615.5

	Magnesium	Manganese	Sodium	Silicon	Strontium
mg/L	68.2	53.1	30.8	8.9	0.8
mg/Kg	3,050.8	2,375.3	1,377.8	398.1	35.8

	Molybdenum	Antimony
mg/L	<0.3	10.8
mg/Kg	<13.4	483.1

Example 2

[0071] A laboratory analysis was performed in which an embodiment of the treatment mixture was mixed with a sample of nano-darcy shale material obtained from well cuttings of a well drilled into the Cana Woodford Shale Formation, a nano-darcy shale formation. The embodiment of the treatment mixture was as follows: 10% by weight citric acid; 2000 ppm of quaternary amine; 5000 ppm of TTPC; 10000 ppm of GEOGARD SX colloidal silica deposition inhibitor (aqueous solution of organic additive based on phosphino carboxylic acid copolymer); 20 gpt of 2-butoxy ethanol; and 10% by weight hydrochloric acid in an aqueous mixture.

[0072] A 4.471g sample of the Cana Woodford Shale material was mixed with 200 ml of the embodiment described above and allowed to soak for 96 hours at 179 degrees F. An ICP analysis of various metals was performed on treatment mixture removed from the shale material after 1 hour and another at the end of the 96 hours. The results, provided below, show that the treatment mixture is effective at binding with metals naturally occurring in the nano-darcy shale formation.

Time Removed	Aluminum	Antimony	Arsenic	Barium	Boron	Calcium	IronTot
hours	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
1	102	0.210	0.190	2.70	6.87	344	150
96	2,994	6.165	5.578	79.26	201.67	10,098	4,403

Time Removed	Potassium	Magnesium	Manganese	Molybdenum	Silicon
hours	mg/L	mg/L	mg/L	mg/L	mg/L
1	49.8	233	4.35	0.450	211
96	1,461.9	6,840	127.70	13.210	6,194

Time Removed	Sodium	Strontium
hours	mg/L	mg/L
1	20.9	3.77
96	613.5	110.67

Example 3

[0073] An experiment was performed in a well located in the nano-darcy Woodford shale formation in Canadian County, Oklahoma. In this experiment the following 1200 barrel treatment mixture was used: 10% by weight citric acid; 2000 ppm of quaternary amine; 5000 ppm of TTPC; 10000 ppm of GEOGARD SX colloidal silica deposition inhibitor (aqueous solution of organic additive based on phosphino carboxylic acid copolymer); and 20 gpt of 2-butoxy ethanol. A diverting material was also used comprising different sizes of poly lactic acid particles in a 10.2 pound/gallon brine mixture to create a diverting mixture. The treatment and diverting mixtures were alternately injected into the well in amounts of 150 barrels each until completion. After completion the well was shut in and the treatment mixture maintained in the well for 4 days.

[0074] The treatment mixture was then extracted and analyzed for metal content including aluminum, iron, magnesium and silicon. The following table is a list of results of the analysis.

					Rw.	Al	Fe	Mg	Si
Sample #:	Day:	Time:	pH:	Sp. Gr.	Ohm-M	mg/L	mg/L	mg/L	mg/L
Pre-Job		9:00	7.07	1.0049	0.650	0.18	<0.18	5.28	41.4
1	1	12:00	7.38	1.0050	0.800	118	1,399	586	26
2	2	14:00	6.19	1.0250	0.340	300	2,304	1,270	104
3	2	15:00	6.28	1.0262	0.340	303	2,156	1,294	116

					Rw.	Al	Fe	Mg	Si
Sample #:	Day:	Time:	pH:	Sp. Gr.	Ohm-M	mg/L	mg/L	mg/L	mg/L
4	2	16:00	6.24	1.0247	0.340	295	1,926	1,271	110
5	2	18:00	6.25	1.0250	0.320	333	2,017	1,457	98
6	2	19:00	6.17	1.0258	0.320	333	1,846	1,389	107
7	2	20:00	6.26	1.0251	0.315	319	1,746	1,366	87
8	2	22:00	6.23	1.0263	0.330	321	1,730	1,361	91
9	3	0:00	6.30	1.0250	0.320	330	1,593	1,416	92
10	3	2:00	6.33	1.0247	0.340	331	1,468	1,396	91
11	3	4:00	6.25	1.0249	0.300	372	1,725	1,601	110
12	3	6:00	6.25	1.0271	0.310	347	1,567	1,496	82
13	3	8:00	6.34	1.0277	0.320	376	1,673	1,593	69
14	3	10:00	6.24	1.0279	0.320	379	1,668	1,621	72
15	3	12:00	6.20	1.0280	0.310	391	1,703	1,714	81
16	3	14:00	6.19	1.0301	0.295	403	1,726	1,744	72
17	3	16:00	6.20	1.0307	0.300	418	1,772	1,805	85
18	3	18:00	6.18	1.0310	0.280	440	1,816	1,849	89
19	3	20:00	6.16	1.0317	0.295	434	1,750	1,872	114
20	3	22:00	6.22	1.0320	0.295	438	1,765	1,886	74
21	4	0:00	6.16	1.0320	0.290	434	1,754	1,857	104
22	4	2:00	6.20	1.0314	0.300	481	1,828	1,975	89
23	4	4:00	6.23	1.0312	0.280	463	1,766	1,918	106
24	4	6:00	6.16	1.0315	0.280	448	1,675	1,873	111
25	4	8:00	6.37	1.0310	0.280	464	1,714	1,887	58
26	4	10:00	6.32	1.0306	0.270	498	1,782	1,933	67
27	4	12:00	6.34	1.0303	0.275	478	1,734	1,886	72
28	4	14:00	6.33	1.0300	0.280	508	1,785	1,951	106
29	4	16:00	6.31	1.0304	0.290	490	1,657	1,844	82
30	4	18:00	6.35	1.0300	0.295	492	1,686	1,867	61
31	5	12:00	6.35	1.0299	0.300	529	1,705	1,895	66
32	6	12:00	6.35	1.0300	0.300	421	1,256	1,486	47
33	7	12:00	6.36	1.0300	0.300	436	1,276	1,489	72
34	8	12:00	6.38	1.0294	0.300	464	1,636	1,794	70
35	9	11:00	6.40	1.0295	0.300	414	1,206	1,440	81

					Rw.	Al	Fe	Mg	Si
Sample #:	Day:	Time:	pH:	Sp. Gr.	Ohm-M	mg/L	mg/L	mg/L	mg/L
36	10	10:30	6.39	1.0300	0.300	470	1,716	1,863	71
37	11	10:00	6.54	1.0240	0.290	414	1,226	1,402	68
38	12	9:00	6.59	1.0230	0.285	364	1,090	1,239	56
39	13	10:00	6.51	1.0195	0.305	241	803	888	95
40	14	17:30	6.50	1.0215	0.300	400	1,194	1,401	80
41	15	13:30	6.54	1.0219	0.299	314	951	1,110	89
42	16	12:00	6.52	1.0200	0.300	252	810	942	98
43	17	15:30	6.52	1.0205	0.300	334	1,016	1,212	113
44	18	10:30	6.53	1.0195	0.300	252	807	964	101
45	19	10:00	6.53	1.0200	0.305	233	749	872	92
46	20	12:00	6.44	1.0183	0.305	167	625	670	86
47	21	11:00	6.50	1.0158	0.305	242	793	916	100
48	22	13:30	6.45	1.0175	0.310	225	760	861	94
49	23	12:30	6.38	1.0171	0.310	232	784	917	105
50	24	12:30	6.60	1.0164	0.310	189	669	769	93

[0075] In the experiment, after the shut in period, the well was pumped and samples of extracted flowback liquids were obtained and analyzed for various constituents over a 24 day period. The data shows a trend similar to the laboratory analyses of a high initial recovery of metals that trails off significantly over the first 3-7 days.

[0076] In addition, the subsequent well production rates were determined and compared to the production rate of the well prior to stimulation. The comparison showed that the gas production showed an 11 to 1 improvement in product rates. The liquid hydrocarbon production showed a 5 to 1 improvement after stimulation.

Example 4

[0077] FIGS. 2 through 4 illustrate some results obtained from the use of embodiments of the stimulation treatment mixtures described above.

[0078] FIG. 2 illustrates a plot of aluminum, barium, manganese, strontium, sulfate; and pH vs. time in samples taken from flowback out of a horizontal well completed in the Woodford Shale formation.

[0079] FIG. 3 illustrates a plot of calcium, magnesium and pH vs. time in samples taken from a horizontal well completed in the Woodford Shale formation from the same experiment as FIG. 2.

[0080] FIG. 4 illustrates a plot of iron and pH vs. time in samples taken from a horizontal well completed in the Woodford Shale formation.

[0081] Unless otherwise indicated, all numbers expressing quantities of ingredients, properties such as molecular weight, reaction conditions, and so forth used in the specification and claims are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that may vary depending upon the desired properties sought to be obtained.

[0082] As used herein, "about" refers to a degree of deviation based on experimental error typical for the particular property identified. The latitude provided the term "about" will depend on the specific context and particular property and can be readily discerned by those skilled in the art. The term "about" is not intended to either expand or limit the degree of equivalents which may otherwise be afforded a particular value. Further, unless otherwise stated, the term "about" shall expressly include "exactly," consistent with the discussions regarding ranges and numerical data. Concentrations, amounts, and other numerical data may be expressed or presented herein in a range format. It is to be understood that such a range format is used merely for convenience and brevity and thus should be interpreted flexibly to include not only the numerical values explicitly recited as the limits of the range, but also to include all the individual numerical values or sub-ranges encompassed within that range as if each numerical value and sub-range is explicitly recited. As an illustration, a numerical range of "about 4 percent to about 7 percent" should be interpreted to include not only the explicitly recited values of about 4 percent to about 7 percent, but also include individual values and sub-ranges within the indicated range. Thus, included in this numerical range are individual values such as 4.5, 5.25 and 6 and sub-ranges such as from 4-5, from 5-7, and from 5.5-6.5; etc. This same principle applies to ranges reciting only one numerical value. Furthermore, such an interpretation should apply regardless of the breadth of the range or the characteristics being described.

[0083] Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the disclosure are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contain certain

errors necessarily resulting from the standard deviation found in their respective testing measurements.

[0084] It will be clear that the systems and methods described herein are well adapted to attain the ends and advantages mentioned as well as those inherent therein. Those skilled in the art will recognize that the methods and systems within this specification may be implemented in many manners and as such is not to be limited by the foregoing exemplified embodiments and examples. In other words, functional elements being performed by a single or multiple components, in various combinations of hardware and software, and individual functions can be distributed among software applications at either the client or server level. In this regard, any number of the features of the different embodiments described herein may be combined into one single embodiment and alternate embodiments having fewer than or more than all of the features herein described are possible.

[0085] It will be clear that the systems and methods described herein are well adapted to attain the ends and advantages mentioned as well as those inherent therein. Those skilled in the art will recognize that the methods and systems within this specification may be implemented in many manners and as such is not to be limited by the foregoing exemplified embodiments and examples. In this regard, any number of the features of the different embodiments described herein may be combined into one single embodiment and alternate embodiments having fewer than or more than all of the features herein described are possible.

[0086] While various embodiments have been described for purposes of this disclosure, various changes and modifications may be made which are well within the scope of the present disclosure. Numerous other changes may be made which will readily suggest themselves to those skilled in the art and which are encompassed in the spirit of the disclosure.

CLAIMS

What is claimed is:

1. A method for stimulating a well in a nano-darcy shale formation comprising:

providing a treatment mixture containing between about 0.1% and 95% by weight metal complexing agent at a pH of between about 0 and 10;

injecting the treatment mixture into the well at a pressure less than a fracture pressure of the nano-darcy shale formation until at least some of the treatment mixture contacts the nano-darcy shale formation;

maintaining the treatment mixture in contact with the nano-darcy shale formation for a contact time of between about 1 minute to 100 days, thereby allowing the metal complexing agent to bind with at least some naturally-occurring metals contained within the nano-darcy shale formation; and

removing the treatment mixture from the well after the contact time, thereby removing the bound naturally-occurring metals from the non-darcy shale formation and thereby improving the hydrocarbon production of the well relative to the hydrocarbon production immediately prior to performance of the method.

2. The method of claim 1 wherein the metal complexing agent is citric acid.

3. The method of claim 1 wherein the metal complexing agent is ethylenediaminetetraacetic acid (EDTA).

4. The method of claim 1 wherein the metal complexing agent is acetic acid.

5. The method of claim 1 wherein the metal complexing agent includes at least one of ethylenediaminetetraacetic acid (EDTA), propylenediaminetetraacetic acid (PDTA), nitrilotriacetic acid (NTA), N-(2- hydroxyethyl)ethylenediaminetriacetic acid (HEDTA), diethylenetriaminepentaacetic acid (DTPA), hydroxyethyliminodiacetic acid (HEIDA), cyclohexylenediaminetetraacetic acid (CDTA), diphenylaminesulfonic acid (DPAS), ethylenediaminedi(o-hydroxyphenylacetic) acid (EDDHA), glucoheptonic acid, gluconic acid,

oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, phthalic acid, terephthalic acid, aconitic acid, carballylic acid, trimesic acid, isocitric acid, citric acid, or any salt or derivative of any of the previously listed compounds.

6. The method of claim 1 wherein the treatment mixture comprises:

between about 0.1% and 95% by weight metal complexing agent;

between 1 and 10,000 parts per million (ppm) of a corrosion inhibitor;

between 1 and 10,000 ppm of a biocide;

between 1 and 10,000 ppm of a colloidal silica deposition inhibitor;

between 1 and 500 gallons per thousand gallons (gpt) of a mutual solvent; and

between 1 and 2000 parts per million of a surfactant.

7. The method of claim 1 wherein the treatment mixture further comprises between 0.1 and 95% of acid(s) as pH modifier.

8. The method of claim 1 wherein the injecting operation further comprises:

alternately injecting a first amount of treatment mixture and a second amount of a diverting mixture into the well.

9. The method of claim 1 wherein the injecting operation further comprises:

injecting the treatment mixture until the pressure within the well reaches a predetermined target pressure calculated based on the fracture pressure of the nano-darcy shale formation; and

upon reaching the target pressure, shutting in the well.

10. The method of claim 1 wherein the injecting operation further comprises:

injecting the treatment mixture containing a metal complexing agent such as citric acid or EDTA in combination with hydraulic fracturing and injecting into the formation in conjunction with propagation of the induced fractures.

11. The method of claim 1 further comprising:

monitoring at least one of pH and well pressure during the maintaining operation; and

initiating the removing operation based on results of the monitoring operation.

12. The method of claim 1 further wherein the metal complexing agent is selected from glutamic acid diacetic acid (GLDA), methylglycine diacetic acid (MGDA), β-alanine diacetic acid (β-ADA), ethylenediaminedisuccinic acid, S,S- ethylenediaminedisuccinic acid (EDDS), iminodisuccinic acid (IDS), hydroxyiminodisuccinic acid (HIDS), polyamino disuccinic acids, N-bis[2-(l,2- dicarboxyethoxy)ethyl]glycine (BCA6), N-bis[2-(l,2-dicarboxyethoxy)ethyl]aspartic acid (BCA5), N-bis[2-(l,2- dicarboxyethoxy)ethyl]methylglycine (MCBA5), N-tris[(l,2- dicarboxyethoxy)ethyl]amine (TCA6), N-methyliminodiacetic acid (MIDA), iminodiacetic acid (IDA), N-(2-acetamido)iminodiacetic acid (ADA), hydroxymethyl-iminodiacetic acid, 2-(2-carboxyethylamino) succinic acid (CEAA), 2-(2-carboxymethylamino) succinic acid (CMAA), diethylenetriamine- N,N''-disuccinic acid, triethylenetetramine-N,N'''-disuccinic acid, 1,6- hexamethylenediamine-N,N'-disuccinic acid, tetraethylenepentamine-N,N''''- disuccinic acid, 2-hydroxypropylene-l,3-diamine-N,N'-disuccinic acid, 1,2-propylenediamine-N,N'-disuccinic acid, l,3-propylenediamine-N,N'-disuccinic acid, cis-cyclohexanediamine-N,N'-disuccinic acid, trans-cyclohexanediamine- N,N'-disuccinic acid, ethylenebis(oxyethylenenitrilo)-N,N'-disuccinic acid, glucoheptanoic acid, cysteic acid-N,N-diacetic acid, cysteic acid-N-monoacetic acid, alanine-N-monoacetic acid, N-(3-hydroxysuccinyl) aspartic acid, N-[2-(3- hydroxysuccinyl)]-L-serine, aspartic acid-N,N-diacetic acid, aspartic acid-N- monoacetic acid, any salt thereof, any derivative thereof, or any combination thereof.

13. The method of claim 1 further wherein the metal complexing agent is selected from acetic acid, acrylates, dihydroxymaleic acid, salts of dihydroxymaleic acid, EDTA (ethylenediamine tetraacetic acid), salts of EDTA, erythorbic acid, erythroboric acid, formic acid, gluconodeltalactone, GLDA (glutamic acid N,N-diacetic acid), salts of GLDA, HEDTA (hydroxyethylenediamine triacetic acid), salts of HEDTA, HEIDA (disodium ethanoldiglycine), salts of HEIDA, MGDA (methylglycine N,N-diacetic acid), salts of MGDA, NTA (nitriolotriacetic acid), organic metal complexers, ligands, porphyrins, pigments, peptides,

saccharides, nucleic acids, phosphonic acid, polyacrylic acid and citric acid in an amount sufficient to sequester at least a portion of a metal compound.

14. A method for fracturing and stimulating a well in a nano-darcy shale formation comprising:

providing a treatment mixture containing between about 0.1% and 95% by weight metal complexing agent at a pH of between about 0 and 10;

injecting the treatment mixture into the well at a pressure greater than a fracture pressure of the nano-darcy shale formation until at least some of the treatment mixture enters fractures in the nano-darcy shale formation, thereby allowing the metal complexing agent to bind with at least some naturally-occurring metals contained within the nano-darcy shale formation; and

removing spent treatment mixture and fracturing fluids from the well after the fractures are created, thereby removing the bound naturally-occurring metals from the non-darcy shale formation.

15. The method of claim 14 wherein the injecting operation is part of a fracturing operation that causes the fractures to occur in the nano-darcy shale formation.

16. The method of claim 14 further comprising:

fracturing the nano-darcy shale formation; and

wherein the injecting operation occurs after the fracturing operation causes the fractures to occur in the nano-darcy shale formation.

17. The method of claim 16 wherein the injecting operation includes injecting proppant into the fractures to occur in the nano-darcy shale formation.

ABSTRACT OF THE DISCLOSURE

This disclosure describes formulations and methods for stimulating the production from wells in nano-darcy shale formations. In one embodiment, the method includes injecting a treatment mixture containing a metal complexing agent into a nano-darcy shale formation adjacent to a well at a pressure below the fracture pressure of the formation. A sufficient contact time is allowed and then the treatment mixture is pumped from the subsurface. This has been shown to stimulate well production in shale formations. Without being held to a particular theory it appears that the metal complexing agent is binding with naturally occurring metals in the shale formation, and particularly divalent metal ions, which are then extracted with the spent fluid. This removal of naturally occurring metals may be increasing the permeability of the formation in the contact region adjacent to the well, thereby causing the observed increased production.

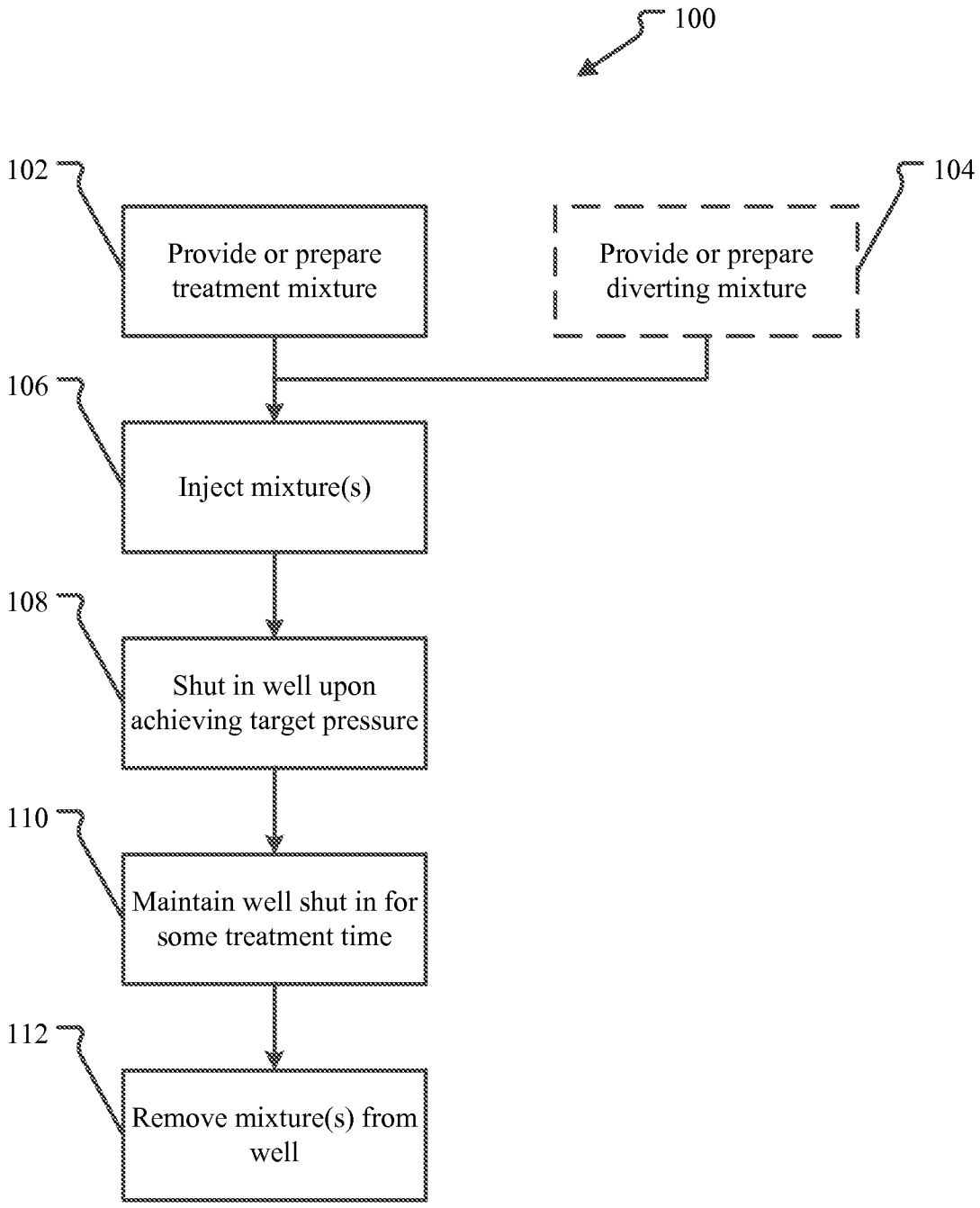

100
102
Provide or prepare treatment mixture
104
Provide or prepare diverting mixture
106
Inject mixture(s)
108
Shut in well upon achieving target pressure
110
Maintain well shut in for some treatment time
112
Remove mixture(s) from well

FIG. 1

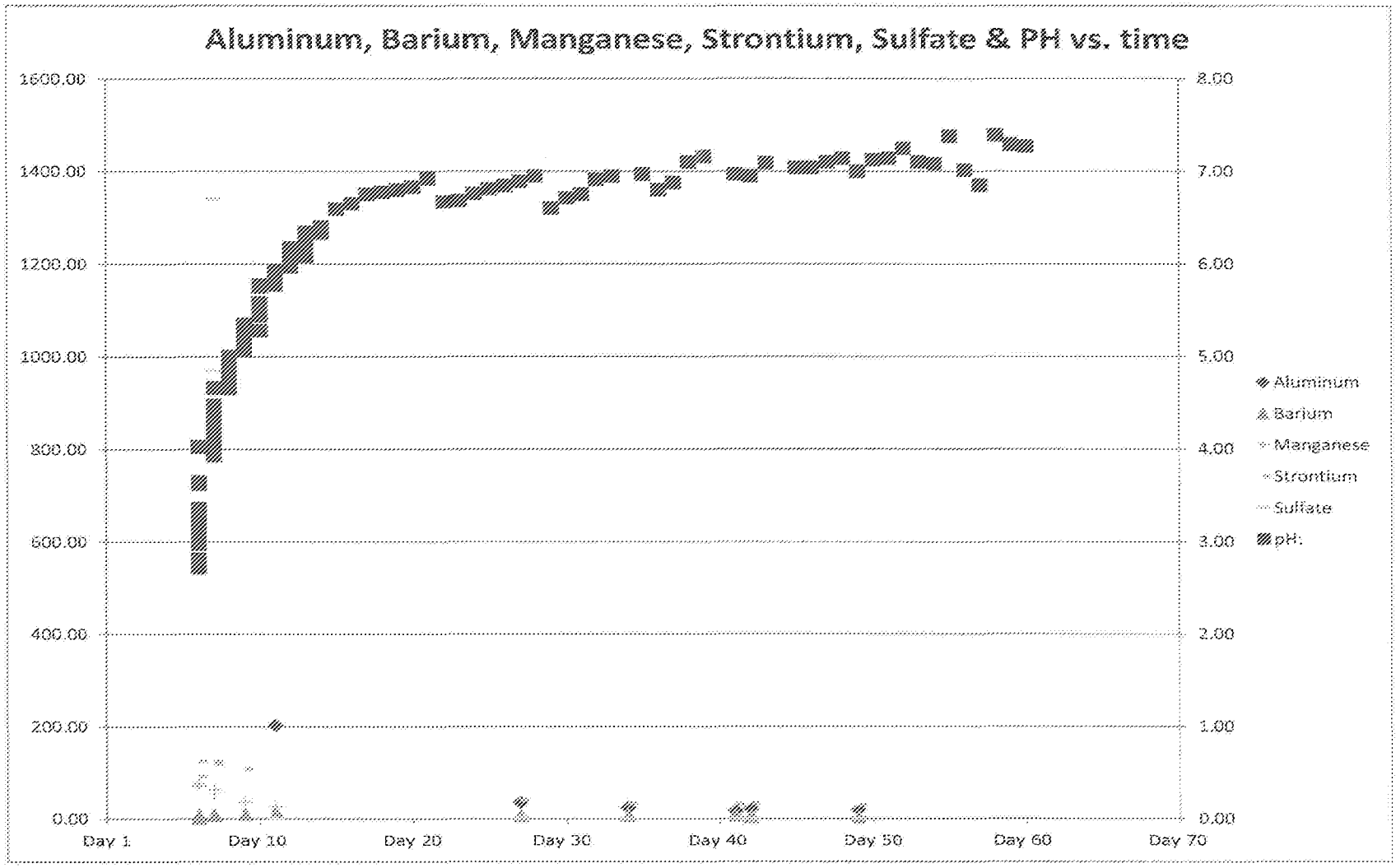

Aluminum, Barium, Manganese, Strontium, Sulfate & PH vs. time
1600.00
1400.00
1200.00
1000.00
800.00
600.00
400.00
200.00
0.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
Day 1
Day 10
Day 20
Day 30
Day 40
Day 50
Day 60
Day 70
Aluminum
Barium
Manganese
Strontium
Sulfate
pH:

FIG. 2

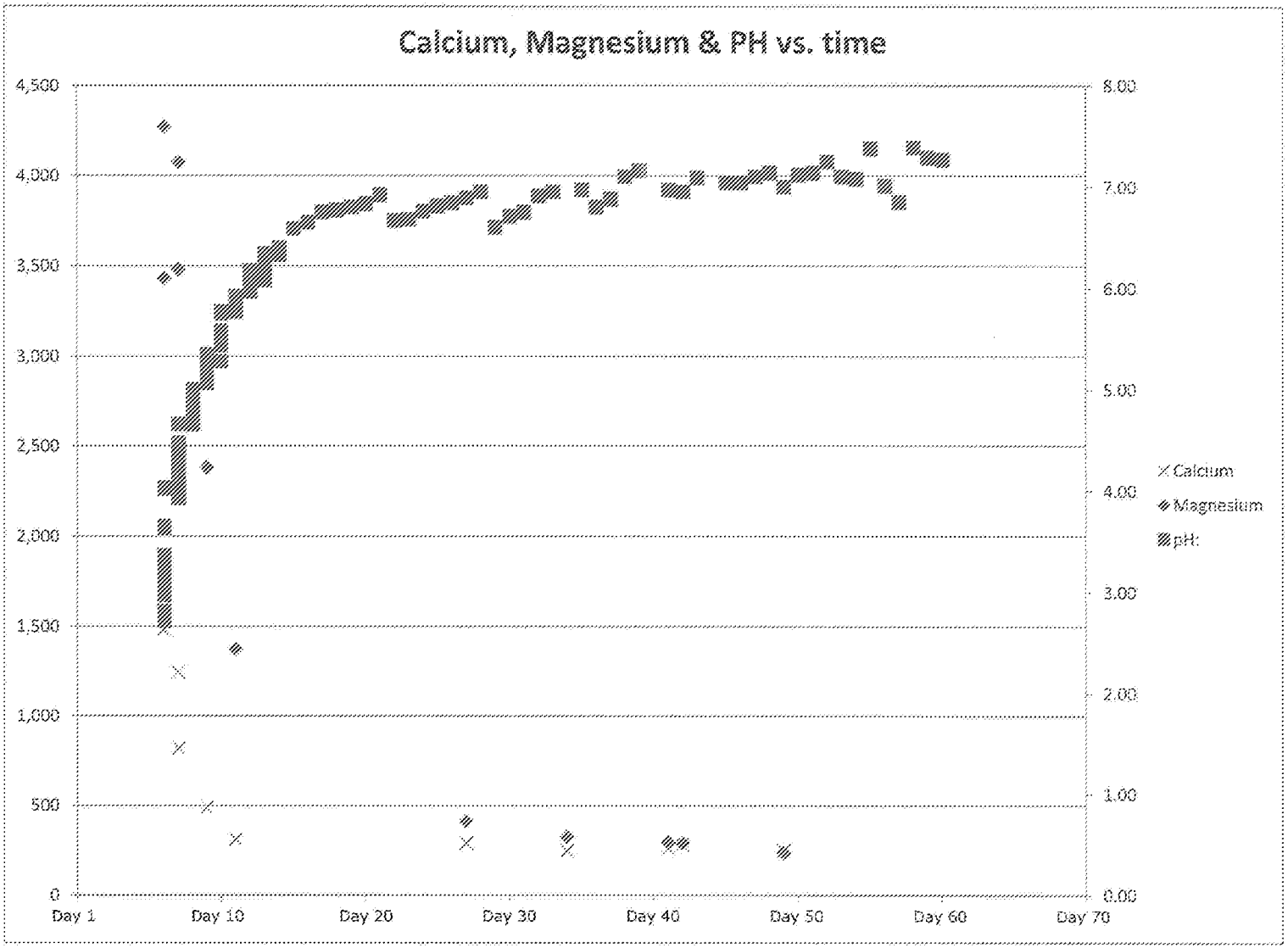


FIG. 3

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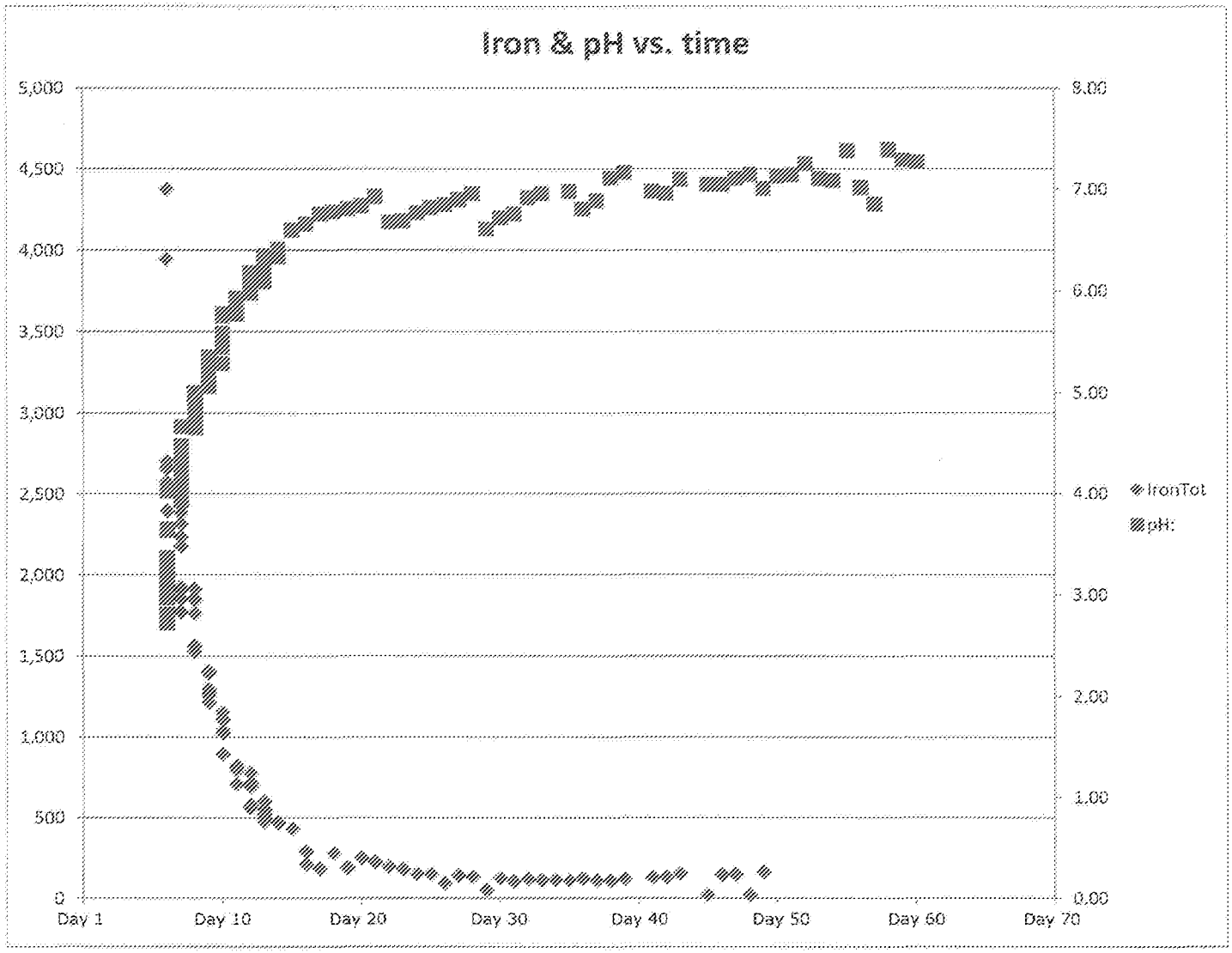


FIG. 4

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P. 393

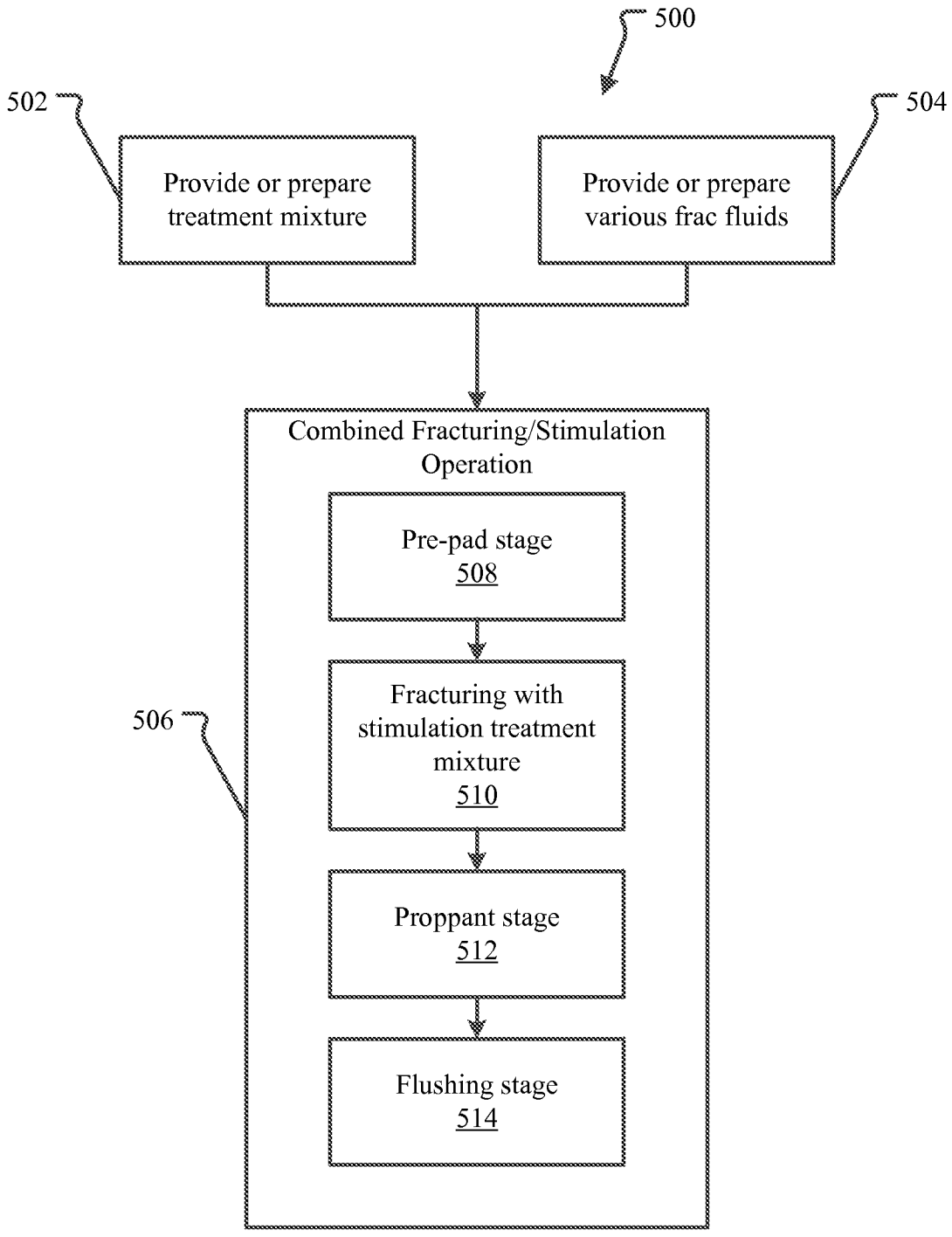

500
502
504
Provide or prepare treatment mixture
Provide or prepare various frac fluids
Combined Fracturing/Stimulation Operation
Pre-pad stage 508
Fracturing with stimulation treatment mixture 510
Proppant stage 512
Flushing stage 514
506

FIG. 5

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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	04697.0001USU1
	Application Number	
Title of Invention	STIMULATION OF WELLS IN NANO-DARCY SHALE FORMATIONS	

The application data sheet is part of the provisional or nonprovisional application for which it is being submitted. The following form contains the bibliographic data arranged in a format specified by the United States Patent and Trademark Office as outlined in 37 CFR 1.76.
This document may be completed electronically and submitted to the Office in electronic format using the Electronic Filing System (EFS) or the document may be printed and included in a paper filed application.

Secrecy Order 37 CFR 5.2

☐ Portions or all of the application associated with this Application Data Sheet may fall under a Secrecy Order pursuant to 37 CFR 5.2 (Paper filers only. Applications that fall under Secrecy Order may not be filed electronically.)

Inventor Information:

Inventor 1 Remove

Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
	Andrew	Bryce	Conway	

Residence Information (Select One) ◉ US Residency ○ Non US Residency ○ Active US Military Service

City	Weatherford	State/Province	OK	Country of Residence i	US

Mailing Address of Inventor:

Address 1	1501 Timbercreek Drive		
Address 2			
City	Weatherford	State/Province	OK
Postal Code	73096	Country i	US

All Inventors Must Be Listed - Additional Inventor Information blocks may be generated within this form by selecting the **Add** button. Add

Correspondence Information:

Enter either Customer Number or complete the Correspondence Information section below.
For further information see 37 CFR 1.33(a).

☐ **An Address is being provided for the correspondence Information of this application.**

Customer Number	23552		
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Application Information:

Title of the Invention	STIMULATION OF WELLS IN NANO-DARCY SHALE FORMATIONS		
Attorney Docket Number	04697.0001USU1	Small Entity Status Claimed	☒
Application Type	Nonprovisional		
Subject Matter	Utility		
Total Number of Drawing Sheets (if any)	5	Suggested Figure for Publication (if any)	

Filing By Reference :

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	Application Number	
Title of Invention	STIMULATION OF WELLS IN NANO-DARCY SHALE FORMATIONS	

Only complete this section when filing an application by reference under 35 U.S.C. 111(c) and 37 CFR 1.57(a). Do not complete this section if application papers including a specification and any drawings are being filed. Any domestic benefit or foreign priority information must be provided in the appropriate section(s) below (i.e., "Domestic Benefit/National Stage Information" and "Foreign Priority Information").

For the purposes of a filing date under 37 CFR 1.53(b), the description and any drawings of the present application are replaced by this reference to the previously filed application, subject to conditions and requirements of 37 CFR 1.57(a).

Application number of the previously filed application	Filing date (YYYY-MM-DD)	Intellectual Property Authority or Country

Publication Information:

☐ Request Early Publication (Fee required at time of Request 37 CFR 1.219)

☐ **Request Not to Publish.** I hereby request that the attached application not be published under 35 U.S.C. 122(b) and certify that the invention disclosed in the attached application **has not and will not** be the subject of an application filed in another country, or under a multilateral international agreement, that requires publication at eighteen months after filing.

Representative Information:

Representative information should be provided for all practitioners having a power of attorney in the application. Providing this information in the Application Data Sheet does not constitute a power of attorney in the application (see 37 CFR 1.32).
Either enter Customer Number or complete the Representative Name section below. If both sections are completed the customer Number will be used for the Representative Information during processing.

Please Select One:	◉ Customer Number	○ US Patent Practitioner	○ Limited Recognition (37 CFR 11.9)
Customer Number	23552		

Domestic Benefit/National Stage Information:

This section allows for the applicant to either claim benefit under 35 U.S.C. 119(e), 120, 121, or 365(c) or indicate National Stage entry from a PCT application. Providing this information in the application data sheet constitutes the specific reference required by 35 U.S.C. 119(e) or 120, and 37 CFR 1.78.
When referring to the current application, please leave the application number blank.

Prior Application Status	Pending		Remove
Application Number	Continuity Type	Prior Application Number	Filing Date (YYYY-MM-DD)
	Claims benefit of provisional	61979210	2014-04-14
Prior Application Status	Pending		Remove
Application Number	Continuity Type	Prior Application Number	Filing Date (YYYY-MM-DD)
	Claims benefit of provisional	62087899	2014-12-05

Additional Domestic Benefit/National Stage Data may be generated within this form by selecting the **Add** button. Add

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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	04697.0001USU1
	Application Number	
Title of Invention	STIMULATION OF WELLS IN NANO-DARCY SHALE FORMATIONS	

Foreign Priority Information:

This section allows for the applicant to claim priority to a foreign application. Providing this information in the application data sheet constitutes the claim for priority as required by 35 U.S.C. 119(b) and 37 CFR 1.55(d). When priority is claimed to a foreign application that is eligible for retrieval under the priority document exchange program (PDX) [i] the information will be used by the Office to automatically attempt retrieval pursuant to 37 CFR 1.55(h)(1) and (2). Under the PDX program, applicant bears the ultimate responsibility for ensuring that a copy of the foreign application is received by the Office from the participating foreign intellectual property office, or a certified copy of the foreign priority application is filed, within the time period specified in 37 CFR 1.55(g)(1).

Remove

Application Number	Country [i]	Filing Date (YYYY-MM-DD)	Access Code [i] (if applicable)

Additional Foreign Priority Data may be generated within this form by selecting the **Add** button. Add

Statement under 37 CFR 1.55 or 1.78 for AIA (First Inventor to File) Transition Applications

☐ This application (1) claims priority to or the benefit of an application filed before March 16, 2013 and (2) also contains, or contained at any time, a claim to a claimed invention that has an effective filing date on or after March 16, 2013.
NOTE: By providing this statement under 37 CFR 1.55 or 1.78, this application, with a filing date on or after March 16, 2013, will be examined under the first inventor to file provisions of the AIA.

Authorization to Permit Access:

☒ Authorization to Permit Access to the Instant Application by the Participating Offices

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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	04697.0001USU1
	Application Number	
Title of Invention	STIMULATION OF WELLS IN NANO-DARCY SHALE FORMATIONS	

If checked, the undersigned hereby grants the USPTO authority to provide the European Patent Office (EPO), the Japan Patent Office (JPO), the Korean Intellectual Property Office (KIPO), the World Intellectual Property Office (WIPO), and any other intellectual property offices in which a foreign application claiming priority to the instant patent application is filed access to the instant patent application. See 37 CFR 1.14(c) and (h). This box should not be checked if the applicant does not wish the EPO, JPO, KIPO, WIPO, or other intellectual property office in which a foreign application claiming priority to the instant patent application is filed to have access to the instant patent application.

In accordance with 37 CFR 1.14(h)(3), access will be provided to a copy of the instant patent application with respect to: 1) the instant patent application-as-filed; 2) any foreign application to which the instant patent application claims priority under 35 U.S.C. 119(a)-(d) if a copy of the foreign application that satisfies the certified copy requirement of 37 CFR 1.55 has been filed in the instant patent application; and 3) any U.S. application-as-filed from which benefit is sought in the instant patent application.

In accordance with 37 CFR 1.14(c), access may be provided to information concerning the date of filing this Authorization.

Applicant Information:

Providing assignment information in this section does not substitute for compliance with any requirement of part 3 of Title 37 of CFR to have an assignment recorded by the Office.

Applicant 1 Remove

If the applicant is the inventor (or the remaining joint inventor or inventors under 37 CFR 1.45), this section should not be completed. The information to be provided in this section is the name and address of the legal representative who is the applicant under 37 CFR 1.43; or the name and address of the assignee, person to whom the inventor is under an obligation to assign the invention, or person who otherwise shows sufficient proprietary interest in the matter who is the applicant under 37 CFR 1.46. If the applicant is an applicant under 37 CFR 1.46 (assignee, person to whom the inventor is obligated to assign, or person who otherwise shows sufficient proprietary interest) together with one or more joint inventors, then the joint inventor or inventors who are also the applicant should be identified in this section.

Clear

(•) Assignee	( ) Legal Representative under 35 U.S.C. 117	( ) Joint Inventor
( ) Person to whom the inventor is obligated to assign.	( ) Person who shows sufficient proprietary interest	

If applicant is the legal representative, indicate the authority to file the patent application, the inventor is:

Name of the Deceased or Legally Incapacitated Inventor :

If the Applicant is an Organization check here. [X]

Organization Name	Flex-Chem Holding Company, LLC

Mailing Address Information:

Address 1	700 N. Wilson Rd.		
Address 2			
City	Weatherford	**State/Province**	OK
Country [i]	US	Postal Code	73096
Phone Number		Fax Number	

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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	04697.0001USU1
	Application Number	
Title of Invention	STIMULATION OF WELLS IN NANO-DARCY SHALE FORMATIONS	

Email Address	

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Assignee Information including Non-Applicant Assignee Information:

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Complete this section if assignee information, including non-applicant assignee information, is desired to be included on the patent application publication . An assignee-applicant identified in the "Applicant Information" section will appear on the patent application publication as an applicant. For an assignee-applicant, complete this section only if identification as an assignee is also desired on the patent application publication.

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If the Assignee or Non-Applicant Assignee is an Organization check here. ☒

Organization Name	Flex-Chem Holding Company, LLC

Mailing Address Information For Assignee including Non-Applicant Assignee:

Address 1	700 N. Wilson Rd.		
Address 2			
City	Weatherford	**State/Province**	OK
Country i	US	Postal Code	73096
Phone Number		Fax Number	
Email Address			

Additional Assignee or Non-Applicant Assignee Data may be generated within this form by selecting the Add button. Add

Signature:

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Signature	/George C. Lewis/			Date (YYYY-MM-DD)	2015-04-14
First Name	George C.	Last Name	Lewis	Registration Number	53214

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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	04697.0001USU1
	Application Number	
Title of Invention	STIMULATION OF WELLS IN NANO-DARCY SHALE FORMATIONS	

This collection of information is required by 37 CFR 1.76. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 23 minutes to complete, including gathering, preparing, and submitting the completed application data sheet form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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Electronic Patent Application Fee Transmittal

Application Number:	
Filing Date:	
Title of Invention:	STIMULATION OF WELLS IN NANO-DARCY SHALE FORMATIONS
First Named Inventor/Applicant Name:	Andrew Bryce Conway
Filer:	George Cone Lewis/Rita Christensen
Attorney Docket Number:	04697.0001USU1

Filed as Small Entity

Filing Fees for Utility under 35 USC 111(a)

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
Utility filing Fee (Electronic filing)	4011	1	70	70
Utility Search Fee	2111	1	300	300
Utility Examination Fee	2311	1	360	360
Pages:				
Claims:				
Miscellaneous-Filing:				
Late Filing Fee for Oath or Declaration	2051	1	70	70
Petition:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				
Extension-of-Time:				
Miscellaneous:				
			Total in USD ($)	800

Electronic Acknowledgement Receipt

EFS ID:	22055025
Application Number:	14686237
International Application Number:	
Confirmation Number:	2601
Title of Invention:	STIMULATION OF WELLS IN NANO-DARCY SHALE FORMATIONS
First Named Inventor/Applicant Name:	Andrew Bryce Conway
Customer Number:	23552
Filer:	George Cone Lewis/Rita Christensen
Filer Authorized By:	George Cone Lewis
Attorney Docket Number:	04697.0001USU1
Receipt Date:	14-APR-2015
Filing Date:	
Time Stamp:	16:09:02
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	Credit Card
Payment was successfully received in RAM	$800
RAM confirmation Number	2739
Deposit Account	132725
Authorized User	LEWIS, GEORGE

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Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1		SPECIFICATION.pdf	210561 b16fd60cc53f26e2c69bbd31a7af4a91d2685dae	yes	28

Multipart Description/PDF files in .zip description		
Document Description	**Start**	**End**
Specification	1	23
Claims	24	27
Abstract	28	28

Warnings:					
Information:					
2	Drawings-only black and white line drawings	FIGURES.pdf	1351396 ff35de3f61c8fd6a3dec5659257c4a5dead1fa78	no	5
Warnings:					
Information:					
3	Application Data Sheet	aia0014.pdf	1561114 5bf85f2104c5fe8d442f3f495928f26f3a1d07c0	no	7
Warnings:					
Information:					
4	Fee Worksheet (SB06)	fee-info.pdf	36930 50273d21af30195990bc4e88eed52a5d6ed470c4	no	2
Warnings:					
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		Total Files Size (in bytes):	3160001		

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If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

SCORE Placeholder Sheet for IFW Content

Application Number: 14686237 Document Date: 04/14/2015

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Form Revision Date: September 30, 2013