From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF THE RECORDING OF A CHANGE

(PCT Rule 92*bis*.1 and Administrative Instructions, Section 422)

To:

CHANDLER, Kimberly
Baker Hughes Incorporated
P.O. Box 4740
Houston, Texas 77210-4740
ÉTATS-UNIS D'AMÉRIQUE

Date of mailing *(day/month/year)*
25 August 2017 (25.08.2017)

Applicant's or agent's file reference
FRC4-58165WO

IMPORTANT NOTIFICATION

International application No.
PCT/US2016/024861

International filing date *(day/month/year)*
30 March 2016 (30.03.2016)

1. The following indications appeared on record concerning:

☒ the applicant ☐ the inventor ☐ the agent ☐ the common representative

Name and Address
BAKER HUGHES INCORPORATED
P.O. Box 4740
Houston, Texas 77210-4740
United States of America

State of Nationality: US
State of Residence: US
Telephone No.: 281-231-3039
Facsimile No.: 281-231-3168
E-mail address:

2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

☐ the person ☒ the name ☒ the address ☐ the nationality ☐ the residence

Name and Address
BAKER HUGHES A GE COMPANY, LLC
17021 Aldine Westfield
Houston, Texas 77073
United States of America

State of Nationality: US
State of Residence: US
Telephone No.: 832-559-4424
Facsimile No.: 281-351-3409
E-mail address: gwengray@bhge.com
☐ Notifications by e-mail authorized

3. Further observations, if necessary:

4. A copy of this notification has been sent to:

☒ the receiving Office
☐ the International Searching Authority
☐ the Authority(ies) specified for supplementary search
☐ the International Preliminary Examining Authority
☒ the designated Offices concerned
☐ the elected Offices concerned
☐ other:

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No. +41 22 338 70 10

Authorized officer
Abbou Farid
e-mail pct.team8@wipo.int
Telephone No. +41 22 338 74 08

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference FRC4-58165WO	**FOR FURTHER ACTION**	see Form PCT/ISA/220 as well as, where applicable, item 5 below.
International application No. **PCT/US2016/024861**	International filing date *(day/month/year)* **30 March 2016 (30.03.2016)**	(Earliest) Priority Date *(day/month/year)* 30 March 2015 (30.03.2015)

Applicant

BAKER HUGHES INCORPORATED

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 **5** 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/US2016/024861

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:
See an extra sheet.

1. ☐ As all required addtional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☒ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of any additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/024861

A. CLASSIFICATION OF SUBJECT MATTER

C09K 8/80(2006.01)i, C09K 8/52(2006.01)i

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 8/80; C08J 11/04; C08J 11/16; E21B 37/00; E21B 21/06; B08B 9/032; B01D 17/02; C09K 8/52

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: superabsorbent polymer, cleanout fluid, casing flush, recycling

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6164380 A (DAVIS, LLOYD KEITH) 26 December 2000 See abstract and claims 1-32.	1-15
A	US 2010-0099781 A1 (TIAN, GONGLU et al.) 22 April 2010 See abstract and claims 1-12.	1-15
A	US 8839859 B2 (IVAN, CATALIN et al.) 23 September 2014 See abstract and claims 1-23.	1-15
A	US 2009-0095324 A1 (CROWTHER, NICHOLAS JOHN et al.) 16 April 2009 See abstract and claims 1-26.	1-15
A	US 6419019 B1 (PALMER, BENTLEY J. et al.) 16 July 2002 See abstract and claims 1-18.	1-15

☐ 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
08 July 2016 (08.07.2016)	**11 July 2016 (11.07.2016)**

Name and mailing address of the ISA/KR
International Application Division
Korean Intellectual Property Office
189 Cheongsa-ro, Seo-gu, Daejeon, 35208, Republic of Korea
Facsimile No. +82-42-481-8578

Authorized officer
KIM, Dong Seok
Telephone No. +82-42-481-5405

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2016/024861

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 6164380 A	26/12/2000	CA 2232092 A1	17/09/1998
		CA 2232092 C	31/12/2002
		EP 0867495 A2	30/09/1998
		EP 0867495 A3	03/02/1999
		EP 0867495 B1	04/06/2003
		US 6016872 A	25/01/2000
US 2010-0099781 A1	22/04/2010	BR PI0920200 A2	15/12/2015
		CN 102197057 A	21/09/2011
		CN 102197057 B	15/04/2015
		EP 2340265 A1	06/07/2011
		EP 2340265 B1	21/01/2015
		JP 2012-506462 A	15/03/2012
		JP 5548210 B2	16/07/2014
		KR 10-2011-0087293 A	02/08/2011
		RU 2011120237 A	27/11/2012
		RU 2518063 C2	10/06/2014
		TW 201022294 A	16/06/2010
		TW I466900 B	01/01/2015
		US 2011-0121231 A1	26/05/2011
		US 2012-292566 A1	22/11/2012
		US 2013-079221 A1	28/03/2013
		US 7910688 B2	22/03/2011
		US 8309682 B2	13/11/2012
		US 8318895 B1	27/11/2012
		US 8487049 B2	16/07/2013
		WO 2010-046267 A1	29/04/2010
US 8839859 B2	23/09/2014	BR PI0706394 A2	22/03/2011
		CA 2600856 A1	19/07/2007
		CA 2600856 C	21/06/2011
		EA 010800 B1	30/12/2008
		EA 200701531 A1	28/02/2008
		EP 1971636 A1	24/09/2008
		EP 1971636 A4	28/01/2009
		MX 2007009884 A	26/09/2007
		NO 20074031 A	14/03/2008
		US 2010-0204066 A1	12/08/2010
		WO 2007-082207 A1	19/07/2007
US 2009-0095324 A1	16/04/2009	EP 2026914 A1	25/02/2009
		GB 0608342 D0	07/06/2006
		GB 0707947 D0	30/05/2007
		GB 2437640 A	31/10/2007
		JP 2009-534187 A	24/09/2009
		WO 2007-125309 A1	08/11/2007
US 6419019 B1	16/07/2002	None	

Invention group I (Claims 1-11) is directed to a method of removing residual proppant in a horizontal or deviated wellbore from a bottom surface of a casing or tubing string after a fracturing operation using a casing flush fluid comprising a superabsorbent polymer (claims 1 and 2), or a method of cleaning out a wellbore using a cleanout fluid comprising a superabsorbent polymer (claims 3-11).

Invention group II (Claims 12-15) is directed to a method of recycling a superabsorbent polymer, the method characterized by: adding water to a fluid containing hydrated particles of the superabsorbent polymer and a plurality of suspended particles that are not the same as the hydrated particles of the superabsorbent polymer; precipitating the suspended particles to form precipitated particles and a slurry comprising hydrated particles of the superabsorbent polymer; removing the precipitated particles; and filtering the slurry through a mesh filter to provide recycled hydrated particles of the superabsorbent polymer; the mesh filter having a mesh size smaller than a predetermined average size of the hydrated particles of the superabsorbent polymer.

PATENT COOPERATION TREATY

From the
INTERNATIONAL SEARCHING AUTHORITY

To:
CHANDLER, Kimberly

BAKER HUGHES INCORPORATED P.O. BOX 4740
HOUSTON, Texas 77210-4740 USA

PCT

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

(PCT Rule 43bis.1)

Date of mailing *(day/month/year)* **11 July 2016 (11.07.2016)**

Applicant's or agent's file reference
FRC4-58165WO

FOR FURTHER ACTION
See paragraph 2 below

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US2016/024861	**30 March 2016 (30.03.2016)**	30 March 2015 (30.03.2015)

International Patent Classification (IPC) or both national classification and IPC
C09K 8/80(2006.01)i, C09K 8/52(2006.01)i

Applicant
BAKER HUGHES INCORPORATED

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 43bis.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 66.1bis(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/KR	Date of completion of this opinion	Authorized officer
International Application Division Korean Intellectual Property Office 189 Cheongsa-ro, Seo-gu, Daejeon, 35208, Republic of Korea Facsimile No. +82-42-481-8578	08 July 2016 (08.07.2016)	KIM, Dong Seok Telephone No. +82-42-481-5405

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US2016/024861

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/US2016/024861

Box No. IV Lack of unity of invention

1. ☐ In response to the invitation (Form PCT/ISA/206) to pay additional fees the applicant has, within the applicable time limit:
   - ☐ paid additional fees
   - ☐ paid additional fees under protest and, where applicable, the protest fee
   - ☐ paid additional fees under protest but the applicable protest fee was not paid
   - ☐ not paid additional fees
2. ☒ This Authority found that the requirement of unity of invention is not complied with and chose not to invite the applicant to pay additional fees.
3. This Authority considers that the requirement of unity of invention in accordance with Rule 13.1, 13.2 and 13.3 is
   - ☐ complied with
   - ☒ not complied with for the following reasons:

Invention group I (Claims 1-11) is directed to a method of removing residual proppant in a horizontal or deviated wellbore from a bottom surface of a casing or tubing string after a fracturing operation using a casing flush fluid comprising a superabsorbent polymer (claims 1 and 2), or a method of cleaning out a wellbore using a cleanout fluid comprising a superabsorbent polymer (claims 3-11).

Invention group II (Claims 12-15) is directed to a method of recycling a superabsorbent polymer, the method characterized by: adding water to a fluid containing hydrated particles of the superabsorbent polymer and a plurality of suspended particles that are not the same as the hydrated particles of the superabsorbent polymer; precipitating the suspended particles to form precipitated particles and a slurry comprising hydrated particles of the superabsorbent polymer; removing the precipitated particles; and filtering the slurry through a mesh filter to provide recycled hydrated particles of the superabsorbent polymer; the mesh filter having a mesh size smaller than a predetermined average size of the hydrated particles of the superabsorbent polymer.

The common technical feature linking invention groups I and II is a fluid comprising a superabsorbent polymer. However, the feature is already disclosed in the prior art document such as US 2014-0024561 A1 (REDDY, B. RAGHAVAM, 23 January 2014, see claim 1). Therefore, the Invention Groups I and II do not relate to a single general inventive concept under PCT Rule 13.1, because they lack the same or corresponding special technical feature contributing over the prior art within the meaning of PCT Rule 13.2.

4. Consequently, this opinion has been established in respect of the following parts of the international application :
   - ☒ all parts.
   - ☐ the parts relating to claims Nos. _____

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US2016/024861

Box No. V Reasoned statement under Rule 43bis.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Claims	1-15	YES
	Claims	NONE	NO
Inventive step (IS)	Claims	1-15	YES
	Claims	NONE	NO
Industrial applicability (IA)	Claims	1-15	YES
	Claims	NONE	NO

2. Citations and explanations :

※ This international search has been carried out on the presumption that claim 6 refers to claim 5 instead of claim 3.

Reference is made to the following documents:

D1: US 6164380 A (DAVIS, LLOYD KEITH) 26 December 2000
D2: US 2010-0099781 A1 (TIAN, GONGLU et al.) 22 April 2010
D3: US 8839859 B2 (IVAN, CATALIN et al.) 23 September 2014
D4: US 2009-0095324 A1 (CROWTHER, NICHOLAS JOHN et al.) 16 April 2009
D5: US 6419019 B1 (PALMER, BENTLEY J. et al.) 16 July 2002

2.1. Novelty and Inventive Step

2.1.1. Claims 1-2

D1, which is considered to be the closest prior art to the subject matter of claim 1, discloses a method of cleaning loose materials from a bore, comprising: injecting under pressure a liquid suspension into a conduit inserted into the bore wherein the conduit and the bore define an annulus therebetween, the bore being oriented in a non-vertical position; and sweeping at least a portion of loose materials from the annulus by directing the liquid suspension through the annulus to the materials, wherein the liquid suspension comprises hydrophilic fibers selected from the group consisting of polyolefin, polyester and nylon, suspended in a liquid (see claim 1 in D1).

Claim 1 differs D1 in that (1) the casing flush fluid comprises a superabsorbent polymer, and (2) the method comprises transporting residual proppant from the bottom surface of the casing or tubing to a fracture. Said features are not disclosed in any of the other available prior art documents D2-D5, nor are they obvious by the documents, taken alone or in combination. Therefore, claim 1 is novel and involves an inventive step under PCT Article 33(2) and 33(3).

Claim 2 is dependent on claim 1. Therefore, claim 2 is novel and involves an inventive step under PCT Article 33(2) and 33(3).

Continued on Supplemental Box

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No.

PCT/US2016/024861

Box No. VII Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

The unit of weights (pound and gallon) mentioned in claims 10-11 is not additionally expressed in terms of the units stipulated by PCT Rule 10.1(a).

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No.

PCT/US2016/024861

Box No. VIII Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

Claim 6, dependent on claim 3, mentions "the recycled hydrated particles". But "recycled hydrated particles" has not been described in claim 3. Thus, claim 6 is not considered to be clearly written as required by PCT Article 6.

Supplemental Box

In case **the space in any of the preceding boxes is not sufficient.**
Continuation of : Box No. V

2.1.2. Claims 3-11

D1, which is considered to be the closest prior art to the subject matter of claim 3, discloses a method of cleaning loose materials from a bore, as described above in point 2.1.1.

Claim 3 differs D1 in that the cleanout fluid comprises a superabsorbent polymer. Said feature is not disclosed in any of the other available prior art documents D2-D5, nor is it obvious by the documents, taken alone or in combination. Therefore, claim 3 is novel and involves an inventive step under PCT Article 33(2) and 33(3).

Claims 4-6 are directly or indirectly dependent on claim 3 and claims 7-11 are directly or indirectly dependent on claim 1 or 3. Therefore, claims 4-11 are novel and involve an inventive step under PCT Article 33(2) and 33(3).

2.1.3. Claims 12-15

D2, which is considered to be the closest prior art to the subject matter of claim 12, discloses a process for the production of a superabsorbent polymer gel with recycled superabsorbent polymer fines comprising the following steps:
(a) treating the superabsorbent polymer fines with a caustic solution containing from about 0.1 to about 12% caustic based on the weight of the superabsorbent polymer fines;
(b) mixing the treated superabsorbent polymer fines obtained in step (a) with a polymerization solution containing at least one cross linking agent and a partially neutralized monomer in which the content of the superabsorbent polymer fines relative to the total amount of the monomer is from about 0.1 to about 30 wt%; and
(c) polymerizing the mixture obtained in step (b) to produce the superabsorbent polymer gel (see claim 1 in D2).

Claim 12 differs from D2 in that the method of recycling a superabsorbent polymer comprises: adding water to a fluid containing hydrated particles of the superabsorbent polymer and a plurality of suspended particles; precipitating the suspended particles to form precipitated particles and a slurry comprising hydrated particles of the superabsorbent polymer; removing the precipitated particles; and filtering the slurry through a mesh filter. Said method is not disclosed in any of the other available prior art documents D1 and D3-D5, nor is it obvious by the documents, taken alone or in combination. Therefore, claim 12 is novel and involves an inventive step under PCT Article 33(2) and 33(3).

Claims 13-15 are directly or indirectly dependent on claim 12. Therefore, claims 13-15 are novel and involve an inventive step under PCT Article 33(2) and 33(3).

Continued on The Next Page

Supplemental Box

In case **the space in any of the preceding boxes is not sufficient.**
Continuation of : Previous Page

2.2. Industrial Applicability

Claims 1-15 are industrially applicable under PCT Article 33(4).

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
6 October 2016 (06.10.2016)

WIPO | PCT

(10) International Publication Number
WO 2016/160899 A1

(51) International Patent Classification:
C09K 8/80 (2006.01) *C09K 8/52* (2006.01)

(21) International Application Number:
PCT/US2016/024861

(22) International Filing Date:
30 March 2016 (30.03.2016)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
62/140,105 30 March 2015 (30.03.2015) US

(71) Applicant: **BAKER HUGHES INCORPORATED** [US/US]; P.O. Box 4740, Houston, Texas 77210-4740 (US).

(72) Inventors: **NELSON, Scott G.**; P.O. Box 4740, Houston, TX 77210-4740 (US). **LI, Leiming**; P.O. Box 4740, Houston, TX 77210-4740 (US). **SUN, Hong**; P.O. Box 4740, Houston, TX 77210-4740 (US). **ZHOU, Jia**; P.O. Box 4740, Houston, TX 77210-4740 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

Published:

— *with international search report (Art. 21(3))*

WO 2016/160899 A1

(54) Title: CASING FLUSH FLUID, RECYCLABLE CLEANOUT FLUIDS, AND APPLICATIONS THEREOF

(57) Abstract: A method of removing residual proppant from a bottom of a casing after a fracturing operation comprises: circulating a casing flush fluid comprising a carrier and a superabsorbent polymer in the casing; and transporting the residual proppant from the bottom of the casing to a fracture created by a hydraulic fracturing operation. A method for cleaning a wellbore comprises: introducing a cleanout fluid through a conduit inserted into the wellbore, the cleanout fluid comprising a carrier fluid and a superabsorbent polymer; and receiving a returning fluid comprising debris at the surface of the wellbore from an annular space between the conduit and a wall of the wellbore.

CASING FLUSH FLUID, RECYCLABLE CLEANOUT FLUIDS, AND APPLICATIONS THEREOF

CROSS REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of United States Patent Application No. 62/140,105, filed March 30, 2015, which is incorporated by reference in its entirety herein.

BACKGROUND

[0002] The disclosure relates to the use of superabsorbent polymers in casing flush fluids and cleanout fluids. The disclosure also relates to methods of recycling superabsorbent polymers from cleanout fluids.

[0003] Nowadays a sizeable percentage of wells are overflushed in order to remove as much proppant from the bottom of the horizontal casing as possible. Proppant such as sand remaining in the bottom of the casing causes issues with the deployment and setting of mechanical tools such as bridge plugs. Leftover proppant can cause a plug to prematurely set in the casing uphole from its intended target depth, or if placed at the proper location can cause the plug to fail to set in order to seal off the already treated portion of the horizontal lateral.

[0004] To combat this many operators have added the pumping of additional fluid that is above that required to flush the casing volume to the perforations. This additional fluid is intended to further flush the casing to remove unwanted proppant, but also carries with it added consequences. The additional fluid adds pumping time to the horsepower used on location, along with additional chemical costs that are associated with the extra treating fluid. It is also known that the overflush of frac stages in horizontal wells contributes to reductions in well productivity. The overflush of the wellbore can also displace proppant further into the fracture, thus harmfully removing proppant from the near wellbore region of the fracture.

[0005] Therefore, there is a need in the art for casing flush fluid having improved efficiencies. There is also a need for well cleanout fluids that are effective to suspend and carry small particles out of the well. It would be a further advantage if the cleanout fluids are recyclable.

BRIEF DESCRIPTION

[0006] A method of removing residual proppant in a horizontal or deviated wellbore from the bottom surface of a casing or tubing string after a fracturing operation comprises: circulating a casing or tubing flush fluid comprising a carrier and a superabsorbent polymer in the wellbore; and transporting the residual proppant from the bottom surface of the casing or tubing to a fracture created by a hydraulic fracturing operation.

[0007] A method of cleaning a wellbore comprises: introducing a cleanout fluid through a conduit inserted into the wellbore, the cleanout fluid comprising a carrier fluid and a superabsorbent polymer present in an amount effective to suspend and carry debris in the wellbore to a surface of the wellbore; and receiving a returning fluid comprising debris at the surface of the wellbore from an annular space between the conduit and a wall of the wellbore.

[0008] A method of recycling a superabsorbent polymer comprises adding water to a fluid containing hydrated particles of the superabsorbent polymer and a plurality of suspended particles that are not the same as the hydrated particles of the superabsorbent polymer; precipitating the suspended particles to form precipitated particles and a slurry comprising hydrated particles of the superabsorbent polymer; removing the precipitated particles; and filtering the slurry through a mesh filter to provide recycled hydrated particles of the superabsorbent polymer; the mesh filter having a mesh size smaller than a predetermined average size of the hydrated particles of the superabsorbent polymer.

DETAILED DESCRIPTION

[0009] It has been found that superabsorbent polymers can be used in casing flush and wellbore cleanout applications. Such applications provide beneficial enhancements to both the ultimate production of a well, and operational improvements to time management efficiency on location. In particular, it has been found that adding superabsorbent polymers to the conventional casing flush fluid greatly improve the ability of the fluid to lift proppant up from the bottom surface of the casing and transport it into the fracture leaving a clean casing string with which to set a bridge plug.

[0010] In an embodiment, a casing flush fluid is provided which comprises a carrier and a superabsorbent polymer present in an amount effective to remove residual proppant from the bottom of the casing. The carrier includes fresh water or brine. The superabsorbent polymer can be used in an amount of about 20 pounds to about 100 pounds or about 30 pounds to about 60 pounds per one thousand gallons of the casing flush fluid.

[0011] Optionally the casing flush fluid is a foam comprising a liquid phase and a gas constituent, wherein the liquid phase comprises a superabsorbent polymer and a carrier such as water or brine and the gas constituent comprises air, nitrogen, carbon dioxide, natural gas and the like, or mixtures thereof or a combination comprising at least one of the foregoing. Nitrogen is specifically mentioned. In an embodiment, the sum of the volumes of the gas constituent and the superabsorbent polymer is greater than about 50%, based on the total volume of the casing flush fluid. As used herein, the volume of the superabsorbent polymer refers to the volume of the superabsorbent polymer in an unhydrated form or in a hydrated form.

[0012] In order to uniformly disperse the gas into the liquid phase of the casing flush fluid, a small amount of a foaming agent can be used to reduce the surface tension and create a "wet" liquid phase. The foaming agent can be mixed into the liquid phase of the casing flush fluid in concentrations ranging from about 0.05 to about 5 volume% or about 0.1 to about 2 volume% based on the total volume of the liquid phase of the casing flush fluid.

[0013] The casing flush fluid can be used to remove residual proppant from the bottom surface of a casing after a fracturing operation. The method comprises circulating a casing flush fluid comprising a carrier and a superabsorbent polymer in the casing; and transporting the residual proppant from the bottom surface of the casing to a fracture created by a hydraulic fracturing operation. In an embodiment, the method further comprises breaking the superabsorbent polymer after the residual proppant is transported from the bottom surface of the casing to the fracture. The broken superabsorbent polymer can then be carried back to the surface of the wellbore through the carrier of the casing flush fluid and by the recovery of the fracturing fluid.

[0014] After the wellbore is flushed with the casing flush fluid, additional operations can be performed. In an embodiment a bridge plug is set after the wellbore is treated with the casing flush fluid. Any bridge plug known in the art can be used.

[0015] Unconventional reservoirs such as shale and tight permeability conventional reservoirs typically require multiple fractures along the horizontal or deviated azimuth wellbore to reach economic production levels and to provide effective drainage. When multiple fractures are required, the casing in a zone of interest, after being perforated and stimulated, must be hydraulically isolated before any new zone of interest can be exploited. Isolation of zones often consists of inserting a mechanical plug, such as a bridge plug, below the zone of interest. The bridge plug hydraulically isolates that portion of the well from a

lower portion (or the rest) of the well. The isolation of the lower zone ensures that high pressure fracturing fluid pumped into the well is directed to the next zone of interest.

[0016] Treating a casing with a casing flush fluid as disclosed herein facilitates the setting of bridge plugs as the flush fluid is effective to remove particulates such as sand from the bottom surface of the casing thus avoiding any undesirable effects that the particulates may have on the proper setting of bridge plugs. The compositions and methods disclosed herein are particularly advantageous for treating horizontal casings where particulates settling out and accumulating can be a concern. Moreover, the improved efficiency allows for the use of less casing flush fluid to provide the desirable cleaning of the casing and avoids the issues associated with overflushing such as reductions in well productivity associated with the over displacement of proppant away from the near wellbore region.

[0017] The superabsorbent polymers can also be used in coiled tubing cleanout fluid due to its capability of suspending and carrying small particles such as proppant and cuttings. A cleanout fluid can comprise a base or carrier fluid and a superabsorbent polymer present in an amount effective to suspend and carry debris in a wellbore to a surface of the wellbore. The carrier can be fresh water or brine. The superabsorbent polymer is used in an amount of about 20 pounds to about 100 pounds or about 30 to about 60 pounds per one thousand gallons of the cleanout fluid.

[0018] Optionally the cleanout fluid comprises various fractions of gas and is selected to compensate for underpressured formations or where liquid cleanout fluid annular velocities are insufficient to lift solids. Such cleanout fluid can be a foam comprising a liquid phase and a gas constituent, wherein the liquid phase comprises a superabsorbent polymer and a carrier. Examples of the gas constituent are air, nitrogen, carbon dioxide, natural gas and the like, or mixtures thereof or a combination comprising at least one of the foregoing. In one embodiment, the gas constituent is nitrogen.

[0019] In order to uniformly disperse the gas into the liquid phase of the cleanout fluid, a small amount of a foaming agent is used to reduce the surface tension and create a "wet" liquid phase. The foaming agent can be mixed into the liquid phase in concentrations ranging from about 0.05 to about 5 volume% or about 0.1 to about 2 volume% based on the total volume of the liquid phase of the cleanout fluid. The "wet" liquid is then pumped down the treatment line and commingled with the gas constituent. The turbulent action created by the gas constituent intermixing with the "wet" liquid provides sufficient dispersion for the formation of a homogeneous, emulsified fluid (foam).

[0020] In an embodiment, the sum of the volumes of the gas constituent and the superabsorbent polymer is greater than about 50%, based on the total volume of the cleanout fluid. As used herein, the volume of the superabsorbent polymer refers to the volume of the superabsorbent polymer in an unhydrated form or in a hydrated form.

[0021] The cleanout fluid can be used to remove debris from a wellbore. A method for cleaning a wellbore comprises: introducing a cleanout fluid through a conduit inserted into the wellbore; and receiving a returning fluid comprising debris at the surface of the wellbore from an annular space between the conduit and a wall of the wellbore.

[0022] The conduit can be a drill string, a casing string, tubing string, coiled tubing or joined tubing. Coiled tubing is preferred. As used herein, coiled tubing refers to a very long metal pipe, which is normally supplied spooled on a large reel. Treatment fluids such as cleanout fluids can be pumped through the coil and pushed into the wellbore rather than relying on gravity. Coiled tubing is not particularly limited and can include any coiled tubing known to a person skilled in the art.

[0023] When the cleanout fluid is circulated back to the ground with the debris from the wellbore, it would be cost efficient to recycle the superabsorbent polymer. A method of recycling a superabsorbent polymer comprises adding water to a fluid containing hydrated particles of the superabsorbent polymer and a plurality of suspended particles that are not the same as the hydrated particles of the superabsorbent polymer; precipitating the suspended particles to form precipitated particles and a slurry comprising hydrated particles of the superabsorbent polymer; removing the precipitated particles; and filtering the slurry through a mesh filter to provide recycled hydrated particles of the superabsorbent polymer; wherein the mesh filter has a mesh size smaller than a predetermined average size of the hydrated particles of the superabsorbent polymer

[0024] The superabsorbent polymer in the fluid circulated back to the ground typically comprises hydrated particles. These hydrated superabsorbent particles can be smaller or lighter or both than the debris carried out of the wellbore. Accordingly after water is added to the returning fluid, the fluid thins out and suspended debris precipitates. Hydrated particles of the superabsorbent polymer, on the other hand, remain dispersed throughout the returning fluid. The precipitated debris can then be removed by decantation or filtration to provide a slurry containing particles of the superabsorbent polymer. The slurry is filtered through a mesh filter having a mesh size smaller than a predetermined average size of the hydrated particles of the superabsorbent polymer. For example, if the hydrated superabsorbent polymer particles have a size around 2 mm, the mesh size used can be 0.5 mm

to 1 mm. The superabsorbent polymer particles on the mesh filter can be rinsed during filtering to further clean the particles. The filtered hydrated superabsorbent polymer particles can be reused alone or together with fresh unhydrated superabsorbent polymers for further operations.

[0025] The components for the casing flush fluid and the cleanout fluid are described in more detail below.

[0026] The carrier for the casing flush fluid and the cleanout fluid can be fresh water or brine. The brine can be, for example, seawater, produced water, completion brine, or a combination comprising at least one of the foregoing. The properties of the brine can depend on the identity and components of the brine. Seawater, for example, can contain numerous constituents including sulfate, bromine, and trace metals, beyond typical halide-containing salts. Produced water can be water extracted from a production reservoir (e.g., hydrocarbon reservoir) or produced from the ground. Produced water can also be referred to as reservoir brine and contain components including barium, strontium, and heavy metals. In addition to naturally occurring brines (e.g., seawater and produced water), completion brine can be synthesized from fresh water by addition of various salts for example, KCl, NaCl, $ZnCl_2$, $MgCl_2$, or $CaCl_2$ to increase the density of the brine, such as about 1 to about 0.6 pounds per gallon of $CaCl_2$ brine. Completion brines typically provide a hydrostatic pressure optimized to counter the reservoir pressures downhole. The above brines can be modified to include one or more additional salts. The additional salts included in the brine can be NaCl, KCl, NaBr, $MgCl_2$, $CaCl_2$, $CaBr_2$, $ZnBr_2$, NH_4Cl, sodium formate, cesium formate, and combinations comprising at least one of the foregoing. The salt can be present in the brine in an amount of about 0.001 to about 50 weight percent (wt.%), specifically about 0.001 to about 40 wt.%, and more specifically about 0.001 to about 25 wt%, based on the weight of the fluid.

[0027] As used herein, a superabsorbent polymer (SAP) is a crosslinked polymer that is capable of absorbing large amounts of aqueous liquids, such as water and brine, with swelling and the formation of a gel or viscous material, and that retains the absorbed fluid under a certain pressure or temperature. The superabsorbent polymer can have internal crosslinks, surface crosslinks, or a combination comprising at least one of the foregoing.

[0028] The SAP comprises a hydrophilic network that retains large amounts of aqueous liquid relative to the weight of the SAP (e.g., in a dry state, the SAP absorbs and retains a weight amount of water equal to or greater than its own weight). The SAPs can be a variety of synthetic organic polymers that react with or absorb water and swell when

contacted with an aqueous fluid. Non-limiting examples of such SAPs are poly(hydroxyC_{1-8} alkyl (meth)acrylate)s such as (2-hydroxyethyl acrylate), poly(meth)acrylamide, poly(vinyl pyrrolidine), poly(vinyl acetate), starch-acrylonitrile grafted copolymer of polyacrylonitrile, carboxymethyl cellulose, crosslinked polyacrylates, sulfonated polystyrene, hydrolyzed polyacrylamide, polyvinyl alcohol, polyethylene oxide, polyvinyl pyrrolidone, polyacrylonitrile, and the like. The foregoing are inclusive of copolymers, for example copolymers of (meth)acrylamide with maleic anhydride, vinyl acetate, ethylene oxide, ethylene glycol, or acrylonitrile, or a combination comprising at least one of the foregoing. A combination of different polymers can be used.

[0029] The SAPs are polymerized from nonionic, anionic, cationic monomers, or a combination comprising at least one of the foregoing. Polymerization can be via free-radical polymerization, solution polymerization, gel polymerization, emulsion polymerization, dispersion polymerization, or suspension polymerization. Moreover, polymerization can be performed in an aqueous phase, in inverse emulsion, or in inverse suspension.

[0030] Examples of nonionic monomers for preparing the preformed synthetic polymers include (meth)acrylamide, alkyl-substituted (meth)acrylamides, aminoalkyl-substituted (meth)acrylamides, alkyliminoalkyl-substituted (meth)acrylamides, vinyl alcohol, vinyl acetate, allyl alcohol, C_{1-8} alkyl (meth)acrylates, hydroxyC_{1-8} alkyl (meth)acrylates such as hydroxyethyl (meth)acrylate, N-vinylformamide, N-vinylacetamide, and (meth)acrylonitrile. As used herein, "poly((meth)acrylamide)s" includes polymer comprising units derived from (meth)acrylamide, alkyl-substituted (meth)acrylamides such as N-C_{1-8} alkyl (meth)acrylamides and N,N-di(C_{1-8} alkyl) (meth)acrylamides, aminoalkyl-substituted (meth)acrylamides such as N,N-di(amino(C_{1-8} alkyl))-substituted (meth)acrylamides, and (N,N-dialkylamino)alkyl-substituted (meth)acrylamides such as (N,N-di(C_{1-8} alkyl)amino)(C_{1-8} alkyl) (meth)acrylamides. Specific examples of the foregoing monomers include methacrylamide, N-methyl acrylamide, N-methyl methacrylamide, N,N-dimethyl acrylamide, N-ethyl acrylamide, N,N-diethyl acrylamide, N-cyclohexyl acrylamide, N-benzyl acrylamide, N,N-dimethylaminopropyl acrylamide, N,N-dimethylaminoethyl acrylamide, N-tert-butyl acrylamide, or a combination comprising at least one of the foregoing. In an embodiment, the poly((meth)acrylamide) is a copolymer of methacrylamide with maleic anhydride, vinyl acetate, ethylene oxide, ethylene glycol, or acrylonitrile, or a combination comprising at least one of the foregoing.

[0031] Examples of anionic monomers include ethylenically unsaturated anionic monomers having acidic groups, for example, a carboxylic group, a sulfonic group, a

phosphonic group, a salt thereof, the corresponding anhydride or acyl halide, or a combination comprising at least one of the foregoing acidic groups. For example, the anionic monomer can be (meth)acrylic acid, ethacrylic acid, maleic acid, maleic anhydride, fumaric acid, itaconic acid, α-chloroacrylic acid, β-cyanoacrylic acid, β -methylacrylic acid, α-phenylacrylic acid, β-acryloyloxypropionic acid, sorbic acid, α-chlorosorbic acid, 2'-methylisocrotonic acid, cinnamic acid, p-chlorocinnamic acid, β-stearyl acid, citraconic acid, mesaconic acid, glutaconic acid, aconitic acid, 2-acrylamido-2-methylpropanesulfonic acid, allyl sulfonic acid, vinyl sulfonic acid, allyl phosphonic acid, vinyl phosphonic acid, a salt thereof, or a combination comprising at least one of the foregoing.

[0032] Examples of cationic monomers include (N,N-di(C_{1-8} alkylamino)(C_{1-8} alkyl) (meth)acrylates (e.g., N,N-dimethylaminoethyl acrylate and N,N-dimethylaminoethyl methacrylate), (wherein the amino group is quaternized to, e.g., a methyl chloride quaternary form), diallyldimethyl ammonium chloride, or any of the foregoing alkyl-substituted (meth)acrylamides and dialkylaminoalkyl-substituted (meth)acrylamides, such as (N,N-di(C_{1-8} alkyl)amino)C_{1-8} alkyl acrylamide, and the quaternary forms thereof such as acrylamidopropyl trimethyl ammonium chloride.

[0033] The superabsorbent polymer can contain both cationic substituents and anionic substituents. The cationic substituents and anionic substituents occur in various stoichiometric proportions, for example, a ratio of about 1:1, or one monomer can be present in a greater stoichiometric amount than the other monomer. Representative amphoteric polymers include terpolymers of nonionic monomers, anionic monomers and cationic monomers.

[0034] In an embodiment, the SAP includes a repeating unit derived from an acrylate, an acrylic acid or a salt thereof, an acrylamide, a vinylpyrrolidone, a vinyl ester (e.g., a vinyl acetate), a vinyl alcohol, a 2-acrylamide-2-methylpropanesulfonic acid, a derivative thereof, or a combination thereof.

[0035] The superabsorbent polymer can include a plurality of crosslinks among the polymer chains of the superabsorbent polymer. The crosslinks can be covalent and result from crosslinking the polymer chains using a crosslinker. The crosslinks are formed before the SAP is combined with the aqueous carrier. The crosslinker can be an ethylenically-unsaturated monomer that contains, for example, two sites of ethylenic unsaturation (i.e., two ethylenically unsaturated double bonds), an ethylenically unsaturated double bond and a functional group that is reactive toward a functional group (e.g., an amide group) of the polymer chains of the superabsorbent polymer, or several functional groups that are reactive

toward functional groups of the polymer chains of the superabsorbent polymer. The degree of crosslinking can be selected so as to control the amount of swelling of the superabsorbent polymer. For example, the degree of crosslinking can be used to control the amount of fluid absorption or the volume expansion of the superabsorbent polymer. Accordingly, when the polymer particles comprise a superabsorbent polymer, the degree of crosslinking can be used to control the amount of fluid absorption or the volume expansion of the polymer particles.

[0036] Exemplary crosslinkers include a di(meth)acrylamide of a diamine such as a diacrylamide of piperazine, a C_{1-8} alkylene bisacrylamide such as methylene bisacrylamide and ethylene bisacrylamide, an N-methylol compounds of an unsaturated amide such as N-methylol methacrylamide or N-methylol acrylamide, a (meth)acrylate esters of a di-, tri-, or tetrahydroxy compound such as ethylene glycol diacrylate, poly(ethyleneglycol) di(meth)acrylate, trimethylopropane tri(meth)acrylate, ethoxylated trimethylol tri(meth)acrylate, glycerol tri(meth)acrylate), ethoxylated glycerol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, ethoxylated pentaerythritol tetra(meth)acrylate, butanediol di(meth)acrylate), a divinyl or diallyl compound such as allyl (meth)acrylate, alkoxylated allyl(meth)acrylate, diallylamide of 2,2'-azobis(isobutyric acid), triallyl cyanurate, triallyl isocyanurate, maleic acid diallyl ester, polyallyl esters, tetraallyloxyethane, triallylamine, and tetraallylethylene diamine, a diols polyol, hydroxyallyl or acrylate compounds, and allyl esters of phosphoric acid or phosphorous acid. Specifically mentioned are water soluble diacrylates such as poly(ethylene glycol) diacrylate (e.g., PEG 200 diacrylate or PEG 400 diacrylate). A combination comprising any of the above-described crosslinkers can also be used. Additional crosslinks are described in US 2014/0332213, US 2014/0332214, and US 2015/0096751.

[0037] When the SAP is in the form of a particle, the particle can includes surface crosslink external to the interior of the particle. The surface crosslinks can result from addition of a surface crosslinker to the superabsorbent polymer particle and subsequent heat treatment. The surface crosslinks can increase the crosslink density of the particle near its surface with respect to the crosslink density of the interior of the particle. Surface crosslinkers can also provide the particle with a chemical property that the superabsorbent polymer did not have before surface crosslinking, and can control the chemical properties of the particle, for example, hydrophobicity, hydrophilicity, and adhesiveness of the superabsorbent polymer to other materials, for example, minerals (e.g., silicates) or other chemicals, for example, petroleum compounds (e.g., hydrocarbons, asphaltene, and the like).

[0038] Surface crosslinkers have at least two functional groups that are reactive with a group of the polymer chains, for example, any of the above crosslinkers, or crosslinkers having reactive functional groups such as an acid (including carboxylic, sulfonic, and phosphoric acids and the corresponding anions), an amide, an alcohol, an amine, or an aldehyde. Exemplary surface crosslinkers include polyols, polyamines, polyaminoalcohols, and alkylene carbonates, such as ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, glycerol, polyglycerol, propylene glycol, diethanolamine, triethanolamine, polypropylene glycol, block copolymers of ethylene oxide and propylene oxide, sorbitan fatty acid esters, ethoxylated sorbitan fatty acid esters, trimethylolpropane, ethoxylated trimethylolpropane, pentaerythritol, ethoxylated pentaerythritol, polyvinyl alcohol, sorbitol, ethylene carbonate, propylene carbonate, and combinations comprising at least one of the foregoing.

[0039] Additional surface crosslinkers include borate, titanate, zirconate, aluminate, chromate, or a combination comprising at least one of the foregoing. Boron crosslinkers include boric acid, sodium tetraborate, encapsulated borates, and the like. Borate crosslinkers can be used with buffers and pH control agents including sodium hydroxide, magnesium oxide, sodium sesquicarbonate, and sodium carbonate, amines (such as hydroxyalkyl amines, anilines, pyridines, pyrimidines, quinolines, pyrrolidines, and carboxylates such as acetates and oxalates), delay agents including sorbitol, aldehydes, sodium gluconate, and the like. Zirconium crosslinkers, e.g., zirconium lactates (e.g., sodium zirconium lactate), triethanolamines, 2,2'-iminodiethanol, or a combination comprising at least one of the foregoing can be used. Titanates crosslinkers can include, for example, lactates, triethanolamines, and the like.

[0040] Preferably the crosslinks are formed before the SAP is combined with the aqueous carrier. Accordingly the casing flush fluid and the cleanout fluid can be free of crosslinking agents. In an embodiment, the superabsorbent polymer does not have any surface crosslinks.

[0041] Non-limiting examples of SAPs include poly 2-hydroxyethyl acrylate, polyalkyl acrylate, polyacrylamide, poly methacrylamide, poly vinylpyrrolidone, poly vinyl acetate, polyacrylic acid, polyacrylic acid salt, or copolymers thereof. As a specific example, the SAP is polyacrylamide having crosslinks that are polyethylene glycol diacrylate. As another specific example, the SAP is a copolymer of acrylamide with, for example, maleic anhydride, vinyl acetate, ethylene oxide, ethylene glycol, acrylonitrile, or a combination thereof. Another specific example of SAP is polyacrylamide having crosslinks that are

polyethylene glycol diacrylate. In some embodiments, the SAP is polyacrylic acid homopolymer or copolymer, wherein the crosslinks are vinyl ester oligomer. In an embodiment, the superabsorbent polymer is a copolymer of acrylic acid and sodium acrylate having crosslinks derived from polyethylene glycol diacrylate.

[0042] The SAP can be in a number of formats, including a particle (e.g., a powder), fiber, strand, braid, and the like, or a combination thereof. The size of the SAP is from 10 μm to 200,000 μm, specifically 50 μm to 10,000 μm, and more specifically 50 μm to 1,000 μm. As used herein, "size" refers to the largest linear dimension, e.g., a diameter in a spherical particle. Particles of the SAP are any shape including spherical, angular, and polyhedral. As used herein, "size" refers to the largest linear dimension, e.g., a diameter in a spherical particle. Particles of the SAP are any shape including spherical, angular, and polyhedral.

[0043] In some embodiments, the casing flush fluid and the cleanout fluid can further comprise a polysaccharide. Exemplary polysaccharides include starch, cellulose, xanthan gum, agar, pectin, alginic acid, tragacanth gum, pluran, gellan gum, tamarind seed gum, cardlan gum, guar gum, arabic, glucomannan, chitin, chitosan, hyaluronic acid, and combinations comprising at least one of the foregoing. The amount of the polysaccharide in the flush fluid or the cleanout fluid is between from about 1 pound of the polysaccharide per thousand gallons of the casing flush or the cleanout fluid (ppt) to about 30 ppt, specifically from about 2 ppt to about 25 ppt or from about 4 ppt to about 20 ppt. In other embodiments, the flush fluid and the cleanout fluid are free of polysaccharides.

[0044] The foaming agent in the cleanout fluid is at least one surfactant. Examples of the foaming agent are non-ionic surfactants, cationic surfactants, anionic surfactants, amphoteric/zwitterionic surfactants, and mixtures thereof. Examples of non-ionic surfactants include, but are not limited to, alkoxylated alcohols or ethers, alkyl ethoxylates, alkylamido ethoxylates, alkylamine ethoxylate, alkyl glucosides, alkoxylated carboxylic acids, sorbitan derivatives where the alkyl chain length varies from 8 to 24, for example, nonylphenol ethoxylate, alkyl ethoxylates, oleyl carboxylic diethylamides, and the like and mixtures thereof. Examples of cationic surfactants include, but are not limited to, monoalkyl quaternary amines such as cocotrimonium chloride, cetyltrimonium chloride, stearyltrimonium chloride, soyatrimonium chloride, and behentrimonium chloride, dialkyl quaternary amines such as dicetyldimethyl ammonium chloride, dicocodimethyl ammonium chloride and distearyldimethyl ammonium chloride, and the like and mixtures thereof. Examples of anionic surfactants include, but are not limited to, fatty carboxylates, alkyl

sarcosinates, alkyl phosphates, alkyl sulfonate, alkyl sulfates and the like and mixtures thereof. Examples of amphoteric/zwitterionic surfactants include, but are not limited to alkyl betaines, alkylamido propyl betaines, alkylampho acetates, alkylamphopropionates, alkylamidopropyl hydroxysultaines and the like and mixtures thereof. In an exemplary embodiment, the foaming agent is an olefinic sulfate, olefinic sulfonate, ethoxylated sulfate, cocoamidopropyl dimethyl ammmonium acetate (betaine), coco betaine, butoxyethanol and the like, or a combination comprising at least one of the foregoing. In another embodiment, the foaming agent comprises a blend of surfactants, or at least one surfactant and at least one co-surfactant. Examples of the co-surfactant are organic solvents such as ethylene glycol monobutyl ether, isopropyl alcohol, methanol, glycerol, ethylene glycol, mineral oil, and the like, or a combination comprising at least one of the foregoing.

[0045] The casing flush composition can further include a breaker in some embodiments. The breaker contacts the SAP to break the SAP after the particulates at the bottom of the casing are removed. In an embodiment, the breaker contacts the SAP and breaks a bond in the backbone of the polymer chains of the SAP, a bond in the crosslinker, a bond between the crosslinker and a polymer chain of the SAP, or a combination thereof. That is, breaking the SAP includes disintegrating, decomposing, or dissociating the SAP such as by breaking bonds in the backbone of the SAP, breaking crosslinks among chains of the SAP, changing a geometrical conformation of the superabsorbent polymer, or a combination thereof. In this way, the viscosity of the casing flush composition decreases. In some embodiments, the breaker breaks the SAP to form a decomposed polymer such as a plurality of fragments that have a lower molecular weight than the SAP.

[0046] The breaker includes an oxidizer such as a peroxide, a persulfate, a perphosphate, a perborate, a percarbonate, a persilicate, an oxyacid of a halogen, an oxyanion of halogen, a peracid, a derivative thereof, or a combination thereof.

[0047] The breaker is optionally encapsulated in an encapsulating material to prevent the breaker from contacting the SAP. The encapsulating material is configured to release the breaker in response to the breaking condition. The breaker is a solid or liquid. As a solid, the breaker is, e.g., a crystalline or granular material. In an embodiment, the solid is encapsulated or provided with a coating to delay its release or contact with the SAP. Encapsulating materials are known in the art and are not particularly limited. In an embodiment, a liquid breaker is dissolved in an aqueous solution or another suitable solvent.

[0048] The breaker can be present in the casing flush composition in a mass concentration from 0.1 ppt to 20 ppt, specifically 0.2 ppt to 15 ppt, and more specifically, 0.25 ppt to 10 ppt, based on the total volume of the fluid.

[0049] Other additives can be used in the flush and cleanout fluids. However, it is appreciated that the flush and cleanout fluids can be free of proppants, which are typically used in fracturing applications.

[0050] Set forth below are various embodiments of the disclosure.

[0051] Embodiment 1. A method of removing residual proppant in a horizontal or deviated wellbore from a bottom surface of a casing or tubing string after a fracturing operation, the method comprises: circulating a casing flush fluid comprising a carrier and a superabsorbent polymer in the casing or tubing; and transporting the residual proppant from the bottom surface of the casing or tubing to a fracture created by a hydraulic fracturing operation.

[0052] Embodiment 2. The method of claim 1, further comprising breaking the superabsorbent polymer after the residual proppant is transported from the bottom surface of the casing to the fracture.

[0053] Embodiment 3. The method of claim 1, further comprising setting up a bridge plug after the casing is treated with the casing flush fluid.

[0054] Embodiment 4. The method of claim 1, wherein the carrier comprises water or brine; and the superabsorbent polymer comprises repeating units derived from an acrylic acid or a salt thereof, an acrylate, an acrylamide, a vinylpyrrolidone, a vinyl acetate, a vinyl alcohol, a 2-acrylamide-2-methylpropanesulfonic acid, a derivative thereof, or a combination thereof; and the superabsorbent polymer comprises a plurality of crosslinks.

[0055] Embodiment 5. The method of claim 4, wherein the crosslinks of the superabsorbent polymer are formed prior to combining the superabsorbent polymer with the carrier.

[0056] Embodiment 6. The method of claim 1, wherein the casing flush fluid comprises about 30 to about 60 pounds of the superabsorbent polymer per one thousand gallons of the casing flush fluid.

[0057] Embodiment 7. The method of claim 1, wherein the casing flush fluid further comprises a gas constituent and the sum of the volumes of the gas constituent and the superabsorbent polymer is greater than about 50%, based on the total volume of the casing flush fluid.

[0058] Embodiment 8. The method of claim 1, wherein the casing flush fluid further comprises about 2 pounds to about 25 pounds of a polysaccharide per one thousand gallons of the casing flush fluid.

[0059] Embodiment 9. A method for cleaning out a wellbore, the method comprising: introducing a cleanout fluid through a conduit inserted into the wellbore, the cleanout fluid comprising a carrier fluid and a superabsorbent polymer present in amount effective to suspend and carry debris in the wellbore to a surface of the wellbore; and receiving a returning fluid comprising debris at the surface of the wellbore from an annular space between the conduit and a wall of the wellbore.

[0060] Embodiment 10. The method of claim 9, wherein the conduit comprises a drilling string, casing string, tubing string, joined tubing, or coiled tubing.

[0061] Embodiment 11. The method of claim 9, further comprising: adding water to the returning fluid to provide a thinned out composition comprising a slurry of hydrated particles of the superabsorbent polymer and debris settled out of the thinned out composition; separating the debris from the slurry; and filtering the slurry through a mesh filter to provide recycled hydrated particles of the superabsorbent polymer, the mesh filter having a mesh size smaller than a predetermined average size of the hydrated particles of the superabsorbent polymer.

[0062] Embodiment 12. The method of claim 11, further comprising combining the recycled hydrated particles of the superabsorbent polymer with a carrier and optionally with an unhydrated superabsorbent polymer to provide a treatment fluid, and introducing the treatment fluid into a subterranean formation.

[0063] Embodiment 13. The method of claim 9, wherein the cleanout fluid is a foamed fluid further comprising a foaming agent and a gas constituent.

[0064] Embodiment 14. The method of claim 13, wherein the gas constituent is nitrogen, carbon dioxide, air, argon, helium, natural gas, or a combination comprising at least one of the foregoing.

[0065] Embodiment 15. The method of claim 13, wherein the sum of the volumes of the gas constituent and the superabsorbent polymer is greater than about 50%, based on the total volume of the foamed cleanout fluid.

[0066] Embodiment 16. The method of claim 9, wherein the carrier comprises water or brine; and the superabsorbent polymer comprises repeating units derived from an acrylic acid or a salt thereof, an acrylate, an acrylamide, a vinylpyrrolidone, a vinyl acetate, a vinyl

alcohol, a 2-acrylamide-2-methylpropanesulfonic acid, a derivative thereof, or a combination thereof; and the superabsorbent polymer comprises a plurality of crosslinks.

[0067] Embodiment 17. The method of claim 16, wherein the crosslinks of the superabsorbent polymer are formed prior to combining the superabsorbent polymer with the carrier.

[0068] Embodiment 18. The method of claim 9, wherein the cleanout fluid comprises about 30 to about 60 pounds of the superabsorbent polymer per one thousand gallons of the cleanout fluid.

[0069] Embodiment 19. The method of claim 9, wherein the cleanout fluid further comprises about 2 pounds to about 25 pounds of a polysaccharide per one thousand gallons of the cleanout fluid.

[0070] Embodiment 20. A method of recycling a superabsorbent polymer, the method comprising: adding water to a fluid containing hydrated particles of the superabsorbent polymer and a plurality of suspended particles that are not the same as the hydrated particles of the superabsorbent polymer; precipitating the suspended particles to form precipitated particles and a slurry comprising hydrated particles of the superabsorbent polymer; removing the precipitated particles; and filtering the slurry through a mesh filter to provide recycled hydrated particles of the superabsorbent polymer; the mesh filter having a mesh size smaller than a predetermined average size of the hydrated particles of the superabsorbent polymer

[0071] Embodiment 21. The method of claim 19, wherein the suspended particles have at least a size or a density greater than the hydrated particles of the superabsorbent polymer.

[0072] Embodiment 22. The method of claim 19, further comprising combining the recycled hydrated particles of the superabsorbent polymer with a carrier to provide a treatment fluid, and introducing the treatment fluid into a subterranean formation.

[0073] Embodiment 23. The method of claim 19, further comprising combining the recycled hydrated particles of the superabsorbent polymer with an unhydrated superabsorbent polymer to provide a treatment fluid; and introducing the treatment fluid into a subterranean formation.

[0074] All ranges disclosed herein are inclusive of the endpoints, and the endpoints are independently combinable with each other. "Or" means "and/or." As used herein, "combination" is inclusive of blends, mixtures, alloys, reaction products, and the like. All references are incorporated herein by reference.

[0075] The use of the terms "a" and "an" and "the" and similar referents in the context of describing the invention (especially in the context of the following claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. Further, it should further be noted that the terms "first," "second," and the like herein do not denote any order, quantity, or importance, but rather are used to distinguish one element from another. The modifier "about" used in connection with a quantity is inclusive of the stated value and has the meaning dictated by the context (e.g., it includes the degree of error associated with measurement of the particular quantity).

[0076] While typical embodiments have been set forth for the purpose of illustration, the foregoing descriptions should not be deemed to be a limitation on the scope herein. Accordingly, various modifications, adaptations, and alternatives can occur to one skilled in the art without departing from the spirit and scope herein.

CLAIMS

What is claimed is:

1. A method of removing residual proppant in a horizontal or deviated wellbore from a bottom surface of a casing or tubing string after a fracturing operation, the method characterized by:

circulating a casing flush fluid comprising a carrier and a superabsorbent polymer in the casing or tubing; and

transporting the residual proppant from the bottom surface of the casing or tubing to a fracture created by a hydraulic fracturing operation.

2. The method of claim 1, further characterized by setting up a bridge plug after the casing is treated with the casing flush fluid.

3. A method for cleaning out a wellbore, the method characterized by:

introducing a cleanout fluid through a conduit inserted into the wellbore, the cleanout fluid comprising a carrier fluid and a superabsorbent polymer present in amount effective to suspend and carry debris in the wellbore to a surface of the wellbore; and

receiving a returning fluid comprising debris at the surface of the wellbore from an annular space between the conduit and a wall of the wellbore.

4. The method of claim 3, wherein the conduit comprises a drilling string, casing string, tubing string, joined tubing, or coiled tubing.

5. The method of claim 3, further characterized by:

adding water to the returning fluid to provide a thinned out composition comprising a slurry of hydrated particles of the superabsorbent polymer and debris settled out of the thinned out composition;

separating the debris from the slurry; and

filtering the slurry through a mesh filter to provide recycled hydrated particles of the superabsorbent polymer, the mesh filter having a mesh size smaller than a predetermined average size of the hydrated particles of the superabsorbent polymer.

6. The method of claim 3, further characterized by

combining the recycled hydrated particles of the superabsorbent polymer with a carrier and optionally with an unhydrated superabsorbent polymer to provide a treatment fluid, and

introducing the treatment fluid into a subterranean formation.

7. The method of any one of claims 1 to 6, wherein the cleanout fluid or the casing flush fluid is a foamed fluid further comprising a foaming agent and a gas constituent.

8. The method of claim 7, wherein the sum of the volumes of the gas constituent and the superabsorbent polymer is greater than about 50%, based on the total volume of the foamed fluid.

9. The method of any one of claims 1 to 6, wherein

the carrier comprises water or brine; and

the superabsorbent polymer comprises repeating units derived from an acrylic acid or a salt thereof, an acrylate, an acrylamide, a vinylpyrrolidone, a vinyl acetate, a vinyl alcohol, a 2-acrylamide-2-methylpropanesulfonic acid, a derivative thereof, or a combination thereof; and the superabsorbent polymer comprises a plurality of crosslinks formed prior to combining the superabsorbent polymer with the carrier.

10. The method of any one of claims 1 to 6, wherein the cleanout fluid or the casing flush fluid comprises about 30 to about 60 pounds of the superabsorbent polymer per one thousand gallons of the cleanout fluid or the casing flush fluid.

11. The method of any one of claims 1 to 6, wherein the cleanout fluid or the casing flush fluid further comprises about 2 pounds to about 25 pounds of a polysaccharide per one thousand gallons of the cleanout fluid or the casing flush fluid.

12. A method of recycling a superabsorbent polymer, the method characterized by:

adding water to a fluid containing hydrated particles of the superabsorbent polymer and a plurality of suspended particles that are not the same as the hydrated particles of the superabsorbent polymer;

precipitating the suspended particles to form precipitated particles and a slurry comprising hydrated particles of the superabsorbent polymer;

removing the precipitated particles; and

filtering the slurry through a mesh filter to provide recycled hydrated particles of the superabsorbent polymer; the mesh filter having a mesh size smaller than a predetermined average size of the hydrated particles of the superabsorbent polymer

13. The method of claim 12, wherein the suspended particles have at least a size or a density greater than the hydrated particles of the superabsorbent polymer.

14. The method of claim 12, further characterized by

combining the recycled hydrated particles of the superabsorbent polymer with a carrier to provide a treatment fluid, and

introducing the treatment fluid into a subterranean formation.

15. The method of any one of claims 12 to 14, further characterized by

combining the recycled hydrated particles of the superabsorbent polymer with an unhydrated superabsorbent polymer to provide a treatment fluid; and

introducing the treatment fluid into a subterranean formation.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/024861

A. CLASSIFICATION OF SUBJECT MATTER

C09K 8/80(2006.01)i, C09K 8/52(2006.01)i

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 8/80; C08J 11/04; C08J 11/16; E21B 37/00; E21B 21/06; B08B 9/032; B01D 17/02; C09K 8/52

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: superabsorbent polymer, cleanout fluid, casing flush, recycling

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6164380 A (DAVIS, LLOYD KEITH) 26 December 2000 See abstract and claims 1-32.	1-15
A	US 2010-0099781 A1 (TIAN, GONGLU et al.) 22 April 2010 See abstract and claims 1-12.	1-15
A	US 8839859 B2 (IVAN, CATALIN et al.) 23 September 2014 See abstract and claims 1-23.	1-15
A	US 2009-0095324 A1 (CROWTHER, NICHOLAS JOHN et al.) 16 April 2009 See abstract and claims 1-26.	1-15
A	US 6419019 B1 (PALMER, BENTLEY J. et al.) 16 July 2002 See abstract and claims 1-18.	1-15

☐ 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
08 July 2016 (08.07.2016)	**11 July 2016 (11.07.2016)**

Name and mailing address of the ISA/KR
International Application Division
Korean Intellectual Property Office
189 Cheongsa-ro, Seo-gu, Daejeon, 35208, Republic of Korea
Facsimile No. +82-42-481-8578

Authorized officer
KIM, Dong Seok
Telephone No. +82-42-481-5405

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/024861

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:
See an extra sheet.

1. ☐ As all required addtional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☒ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of any additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
☐ No protest accompanied the payment of additional search fees.

Invention group I (Claims 1-11) is directed to a method of removing residual proppant in a horizontal or deviated wellbore from a bottom surface of a casing or tubing string after a fracturing operation using a casing flush fluid comprising a superabsorbent polymer (claims 1 and 2), or a method of cleaning out a wellbore using a cleanout fluid comprising a superabsorbent polymer (claims 3-11).

Invention group II (Claims 12-15) is directed to a method of recycling a superabsorbent polymer, the method characterized by: adding water to a fluid containing hydrated particles of the superabsorbent polymer and a plurality of suspended particles that are not the same as the hydrated particles of the superabsorbent polymer; precipitating the suspended particles to form precipitated particles and a slurry comprising hydrated particles of the superabsorbent polymer; removing the precipitated particles; and filtering the slurry through a mesh filter to provide recycled hydrated particles of the superabsorbent polymer; the mesh filter having a mesh size smaller than a predetermined average size of the hydrated particles of the superabsorbent polymer.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2016/024861

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 6164380 A	26/12/2000	CA 2232092 A1	17/09/1998
		CA 2232092 C	31/12/2002
		EP 0867495 A2	30/09/1998
		EP 0867495 A3	03/02/1999
		EP 0867495 B1	04/06/2003
		US 6016872 A	25/01/2000
US 2010-0099781 A1	22/04/2010	BR PI0920200 A2	15/12/2015
		CN 102197057 A	21/09/2011
		CN 102197057 B	15/04/2015
		EP 2340265 A1	06/07/2011
		EP 2340265 B1	21/01/2015
		JP 2012-506462 A	15/03/2012
		JP 5548210 B2	16/07/2014
		KR 10-2011-0087293 A	02/08/2011
		RU 2011120237 A	27/11/2012
		RU 2518063 C2	10/06/2014
		TW 201022294 A	16/06/2010
		TW I466900 B	01/01/2015
		US 2011-0121231 A1	26/05/2011
		US 2012-292566 A1	22/11/2012
		US 2013-079221 A1	28/03/2013
		US 7910688 B2	22/03/2011
		US 8309682 B2	13/11/2012
		US 8318895 B1	27/11/2012
		US 8487049 B2	16/07/2013
		WO 2010-046267 A1	29/04/2010
US 8839859 B2	23/09/2014	BR PI0706394 A2	22/03/2011
		CA 2600856 A1	19/07/2007
		CA 2600856 C	21/06/2011
		EA 010800 B1	30/12/2008
		EA 200701531 A1	28/02/2008
		EP 1971636 A1	24/09/2008
		EP 1971636 A4	28/01/2009
		MX 2007009884 A	26/09/2007
		NO 20074031 A	14/03/2008
		US 2010-0204066 A1	12/08/2010
		WO 2007-082207 A1	19/07/2007
US 2009-0095324 A1	16/04/2009	EP 2026914 A1	25/02/2009
		GB 0608342 D0	07/06/2006
		GB 0707947 D0	30/05/2007
		GB 2437640 A	31/10/2007
		JP 2009-534187 A	24/09/2009
		WO 2007-125309 A1	08/11/2007
US 6419019 B1	16/07/2002	None	