Title: PILL BREAKERS COMPRISING THERMALLY GENERATED ACIDS

Abstract: A pill breaker comprising an acid-generating fluid comprising a thermally activated strong acid precursor and associated methods.


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PILL BREAKERS COMPRISING THERMALLY GENERATED ACIDS

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application No. 62/295,338, February 15, 2016, which is incorporated herein by reference.

BACKGROUND

[0002] The present disclosure relates generally to pill breakers comprising thermally generated acids. More specifically, in certain embodiments, the present disclosure relates to methods of breaking a fluid loss pill with a pill breaker comprising a viscosified or solids free weighted thermally generated acid.

[0003] Oil and gas wells are typically completed by placing casing within the wellbore, cementing the casing, and then perforating the casing to provide communication between the formation and the inside of the casing. When the well is located in a poorly consolidated formation, the perforating may be followed by insertion of a wire-wrapped screen and gravel packing between the screen and the inside of the casing. Production tubing may then be inserted along with packers, pumps or other artificial lift devices as required to produce fluids from the well.

[0004] Temporarily controlling permeability at wellbore surfaces may be critical during this completion process. While drilling is proceeding, and throughout the completion process, the hydrostatic pressure of the fluids within the borehole are often maintained above the formation pressures. This may prevent formation fluids from entering the borehole, thereby minimizing the chance of a "kick" or a blowout. The loss of completion fluids into the formation is commonly controlled by the use of fluid loss pills.

[0005] When the casing is perforated, the perforations serve as conduits for formation fluids to flow into the borehole when production commences. Until the well completion is finished, fluid loss into these perforations must be minimized in order to prevent damage to formation permeability. The fluid loss into these perforations is also commonly controlled by the use of fluid loss pills.

[0006] The breaking of fluid loss pills has been identified as a high risk area to well operations, especially in deep water applications. Current technology on breaking fluid loss pills for deepwater applications is limited due to the high reservoir temperatures and the dense fluids required.

[0007] One approach in deepwater wells is to use a fluid loss pill that comprises
internal neutral components that when thermally activated produce strong alpha hydroxy sulfinic acids. Examples of such fluid loss pills are described in WO 2015/069681, the entirety of which is hereby incorporated by reference. However, the use of these pills may be problematic. Once the pill is placed in the reservoir, the "clock" starts ticking on when the stop loss pill will degrade to a point where it becomes ineffective for its intended use. If the completion time is longer than expected, then the fluid loss pill will become ineffective too soon. On the other hand, if the work is complete and the internal breaker has not finished breaking the pill, an operational delay will also follow. As it is often difficult to accurately estimate how long it will take to complete the work, stop loss pills are often designed to degrade longer than necessary and operational delays often take place.

[0008] It is desirable to develop a method of a fast breaking fluid loss control pill in the event that the designated break time is after the work is completed.

**SUMMARY**

[0009] The present disclosure relates generally to pill breakers comprising thermally generated acids. More specifically, in certain embodiments, the present disclosure relates to methods of breaking a fluid loss pill with a pill breaker comprising a viscosified or solids free weighted thermally generated acid.

[0010] In one embodiment the present disclosure provides a pill breaker comprising an acid-generating fluid comprising a thermally activated strong acid precursor.

[0011] In another embodiment, the present invention provides a method comprising: providing a pill breaker comprising an acid-generating fluid comprising a thermally activated strong acid precursor, placing the pill breaker into a subterranean formation, and allowing the pill breaker to generate a thermally activated strong acid.

[0012] In another embodiment, the present invention provides a method comprising: providing a pill breaker comprising an acid-generating fluid comprising a thermally activated strong acid precursor; placing the pill breaker into a subterranean formation; and allowing the pill breaker to break a fluid loss control pill.

**BRIEF DESCRIPTION OF THE DRAWINGS**

[0013] A more complete and thorough understanding of the present embodiments and advantages thereof may be acquired by referring to the following description taken in conjunction with the accompanying drawings.

[0014] Figure 1 illustrates a flow chart for a method in accordance with certain
embodiments of the present disclosure.

[0015] The features and advantages of the present disclosure will be readily apparent to those skilled in the art. While numerous changes may be made by those skilled in the art, such changes are within the spirit of the disclosure.

DETAILED DESCRIPTION

[0016] The description that follows includes exemplary apparatuses, methods, techniques, and/or instruction sequences that embody techniques of the inventive subject matter. However, it is understood that the described embodiments may be practiced without these specific details.

[0017] The present disclosure relates generally to pill breakers comprising thermally generated acids. More specifically, in certain embodiments, the present disclosure relates to methods of breaking a fluid loss pill with a pill breaker comprising a viscosified or solids free weighted thermally generated acid.

[0018] Some desirable attributes of the methods and compositions discussed herein are that they may comprise similar material make up and/or density of fluid loss pills comprising internal neutral components that when thermally activated produce strong alpha hydroxy sulfonic acids. This is particularly advantageous because it allows for the fast breaking of the fluid loss control pill in the event that the designated break time is after the work is completed. Another desirable attribute is that the pill breakers may be much less corrosive to tubing, casing, and other equipment both on the surface and downhole than conventional systems. Another desirable attribute is the pill breakers may be capable of achieving more uniform penetration into the subterranean formation from the well bore than conventional pill breakers.

[0019] In certain embodiments, the present disclosure provides a pill breaker comprising an acid-generating fluid comprising a thermally activated strong acid precursor. As used herein, the term thermally activated strong acid refers to a strong acid that has been generated by heating an essentially pH neutral aqueous solution containing a thermally activated strong acid precursor from a stable temperature. As used herein, the term strong acid refers to an acid having a having a pH value of less than 1 and/or one that is capable of complete ionization.

[0020] In certain embodiments, the thermally activated strong acid precursor may comprise one or more compounds, and/or one or more precursors of such compounds, that react together to form thermally activated strong acids. In certain embodiments, the
compounds capable of reacting together to form thermally activated strong acids may be SO₂ and/or carbonyls. In certain embodiments, the thermally activated strong acid precursors may comprise SO₂ precursors (or SO₂) and/or organic carbonyl precursors (or organic carbonyls).

[0021] Examples of suitable SO₂ precursors include sulfones and sulfites. Examples of suitable sulfones include sulfone adducts of butadiene, sulfone adducts of piperylene, and sulfone adducts of isoprene. Examples of suitable sulfites include sulfite esters such as ethylene sulfite, dimethyl sulfite, diethyl sulfite, 1,2-propylene sulfite, and 1,3-propylene sulfite.

[0022] Examples of suitable carbonyl precursors or carbonyls include any carbonyl (or precursor that generates a carbonyl) capable of reacting with SO₂ to form an alpha-hydroxy sulfonic acid. In certain embodiments, the carbonyls may comprise from 1 to 7 carbon atoms. Examples of suitable carbonyls (or precursors thereof) include aldehydes, metaldehyde, trioxane, formaldehyde, acetaldehyde, propionaldehyde, n-butyraldehyde, i-butyraldehyde, glycolaldehyde, glyceraldehyde, glyoxal, benzaldehyde, cyclohexanone, acetone, chloroacetone, paraformaldehyde, polyoxymethylene, and any precursor or combination thereof. Other examples of suitable carbonyls (or precursors thereof) include ketones, acetone, acetal, ketal, cyclic acetalts, methyl ethyl ketone, mesityl oxide, methyl i-butyl ketone, and any precursors or combination thereof. In certain embodiments, the carbonyl may include a mixture of ketones and/or aldehydes (or precursors thereof) with or without alcohols that may be converted to ketones and/or aldehydes.

[0023] In certain embodiments, the acid-generating fluid may have an essentially neutral pH. In certain embodiments, the acid-generating fluid may have a pH in the range of from 6.5 to 7.5. In other embodiments, the acid-generating fluid may have a pH in the range of from 6 to 8. In other embodiments, the acid-generating fluid may have a pH of in the range of from 3 to 9.

[0024] In certain embodiments, the thermally activated strong acid precursors may be activated to produce an alpha hydroxy sulfonic acid. In certain embodiments, the thermally activated strong acid precursors may be activated to produce a blend of alpha hydroxyl sulfonic acids. In certain embodiments, the alpha hydroxyl sulfonic acid may be of the general formula:
where \( R_1 \) and \( R_2 \) are individually hydrogen or hydrocarbyl with up to about 9 carbon atoms that may or may not contain oxygen. In certain embodiments, the alpha hydroxyl sulfonic acid may comprise hydroxy methyl sulfonic acid and/or hydroxy ethyl sulfonic acid. In certain embodiments, the alpha hydroxyl sulfonic acid, or blend thereof, may have a pH of less than 1. In other embodiments, the alpha hydroxyl sulfonic acid, or blend thereof, may a pH of between 1 and 2.

[0025] As used herein, the term “activated” refers to the process in which the one or more thermally activated strong acid precursors releases strong acid components and then those strong acid components reacts with another component and water to form a thermally activated strong acid. Additionally, the term activated also refers to the process in which the one or more components of the thermally activated strong acid react with each another and water to form the thermally activated strong acid.

[0026] In certain embodiments, the one or more precursors of the components of the thermally activated strong acid may release the components when exposed to a certain temperature. In certain embodiments, the one or more precursors of the components of the thermally activated strong acid may release the components when hydrolyzing in water. For example, trioxane is readily soluble in water and stable at ordinary temperatures, but when warmed to approximately 80°C this compound hydrolyzes or decomposes to generate formaldehyde. Similarly, when aqueous formaldehyde solutions are warmed they may generate acetaldehyde. If the aqueous solutions contained SO\(_2\) or a precursor thereof, the warmed solution may immediately form an alpha hydroxyl sulfonic acid. In certain embodiments, the one or more precursors of the components of the thermally activated strong acid may release the components at room temperature.

[0027] In another example, an aqueous solution of ethylene sulfite and formaldehyde, which is essentially pH neutral is warmed, the ethylene sulfite may hydrolyze with water present to make SO\(_2\) and ethylene glycol, and SO\(_2\) and formaldehyde may combine with water to make alpha hydroxyl methane sulfonic acid.

[0028] In certain embodiments, the thermally activated strong acid precursor may comprise a sulfone adduct of butadiene and/or an aldehyde. In certain embodiments, the amount of sulfolene adduct of butadiene present in the acid-generating fluid may be an
amount sufficient to generate a strong acid in the fluid with a concentration of from 0.05% to 20%, from 0.1% to 10%, or from 0.5% to 5% by weight of the acid-generating fluid. In certain embodiments, the amount of aldehyde present in the acid-generating fluid may be an amount sufficient to generate a strong acid in the fluid at a concentration of from 0.05% to 20%, from 0.1% to 10%, or from 0.5% to 5% by weight of the acid-generating fluid. In certain embodiments, the ratio of sulfolene adduct of butadiene to aldehyde present in the acid-generating fluid may be from 10:1 to 1:10.

[0029] In certain embodiments, for example when thermally activated strong acid precursors comprises a sulfone adduct, the acid-generating fluid may comprise a dieneophile. The dieneophile may be capable of reacting with a generated diene from the sulfone adduct to from a Diels-Alder adduct. Prudent selection of the dieneophile may result in a di-acid chelating agent. Examples of such suitable dieneophiles include dimethylmaleate. In certain embodiments, the amount of dieneophile present in the acid-generating fluid may be in the range of from fractional to excess molar amounts to the amount of the sulfone adduct employed. In certain embodiments, the dieneophile may be present in an equal molar concentration of the sulfone adduct.

[0030] In certain embodiments, the thermally activated strong acid may comprise a sulfite ester and/or a carbonyl. In certain embodiments, the amount of sulfite ester present in the acid-generating fluid may be an amount sufficient to generate a strong acid in the fluid with a concentration of from 0.05% to 20%, from 0.1% to 10%, or from 0.5% to 5% by weight of the acid-generating fluid. In certain embodiments, the amount of aldehyde present in the acid-generating fluid may be an amount sufficient to generate a strong acid in the fluid with a concentration of from 0.05% to 20%, from 0.1% to 10%, or from 0.5% to 5% by weight of the acid-generating fluid. In certain embodiments, the ratio of sulfite ester to carbonyl present in the acid-generating fluid may be from 10:1 to 1:10.

[0031] In certain embodiments, the acid-generating fluid may comprise a base fluid. Examples of suitable base fluids include water. In certain embodiments, the base fluid may be present in the acid-generating fluid in an amount in the range of from 0.01% to 99% by weight of the acid-generating fluid.

[0032] In certain embodiments, the acid-generating fluid may be present in the pill breaker in an amount in the range of from 0.01% to 99% by weight of the pill breaker.

[0033] In certain embodiments, the acid-generating fluid may comprise a viscosity fluid. In certain embodiments, the acid-generating fluid may comprise any
conventional viscosifying additive and/or gelling agent. Examples of conventional viscosifying additives and/or gelling agents are described in U.S. Patent No. 8,017,563, 7,795,186, and 8,927,466, the entireties of which are hereby incorporated by reference.

[0034] In certain embodiments, the acid-generating fluid may comprise a solids free weighted fluid. Examples of solids free weighted fluids are described in U.S. Patent Nos. 6,632,779 and 6,489,270, the entireties of which are hereby incorporated by reference. In certain embodiments, the acid-generating fluids may be weighted up to a weight in the range of from 12 ppg to 20 ppg with a salt. In certain embodiments, the acid-generating fluids may be weighted up to a weight in the range of from 13 ppg to 15 ppg with a salt.

[0035] In certain embodiments, the pill breaker may be designed to match the chemical makeup of a fluid loss control pill. In certain embodiments, the pill breaker may be designed to match the chemical makeup of a fluid loss control pill that comprises an acid-generating fluid comprising a thermally activated strong acid precursor. Examples of such fluid loss pills are described in WO 2015/069681, the entirety of which is hereby incorporated by reference. In certain embodiments, the pill breaker may comprise the same thermally activated strong acid precursors as the fluid loss control pill in a fluid loss control pill.

[0036] In certain embodiments, the acid-generating fluid in the pill breaker may comprise a higher concentration of thermally activated strong acid precursors than the acid-generating fluid in the fluid loss control pill. For example, in certain embodiments, the fluid loss control pill may comprise a sufficient concentration of thermally activated strong acid precursors to generate thermally activated generated acid over the course of 2 weeks.

[0037] In certain embodiments, the pill breaker may comprise a sufficient concentration of thermally activated strong acid precursor to generate an amount of thermally activated acid as quickly as possible, for example in the range of from 0.1 hours to 5 hours.

[0038] In certain embodiments, the pill breaker may comprise 1 to 2 times the concentration of thermally activated strong acid precursors than the fluid loss control pill. In certain embodiments, the pill breaker may comprise 2 to 5 times the concentration of thermally activated strong acid precursors than the fluid loss control pill. In certain embodiments, the pill breaker may comprise 5 to 10 times the concentration of thermally activated strong acid precursors than the fluid loss control pill. In certain embodiments,
the pill breaker may comprise 10 to 50 times the concentration of thermally activated strong acid precursors than the fluid loss control pill. In certain embodiments, the pill breaker may comprise 50 to 200 times the concentration of thermally activated strong acid precursors than the fluid loss control pill.

[0039] In certain embodiments, the pill breaker may have a density designed to match or be higher than a fluid loss control pill. In certain embodiments, the pill breaker may have a density in the range of from 5 pounds per gallon to 20 pounds per gallon. In certain embodiments, the pill breaker may have a density in the range of from 10 pounds per gallon to 15 pounds per gallon.

[0040] In certain embodiments, the present invention provides a method comprising: providing a pill breaker comprising an acid-generating fluid comprising a thermally activated strong acid precursor, placing the pill breaker into a subterranean formation, and allowing the pill breaker to generate a thermally activated strong acid.

[0041] In certain embodiments, the pill breaker may comprise any pill breaker discussed above. In certain embodiments, the pill breaker may be placed into the subterranean formation by any conventional means. Examples of suitable subterranean formations include any subterranean formation with a temperature high enough to activate the thermally activated strong acid. In certain embodiments, the subterranean formation temperature may at room temperature or above 40°C, above 50°C, above 60°C, above 70°C, above 80°C, above 90°C, above 100°C, above 110°C, or above 120°C. Alternatively the localized temperature of the formation can be raised by known methods, such as steam assisted, resistance heaters, or by chemical means to activate the thermally generated acids.

[0042] In certain embodiments, a fluid loss control pill comprising a thermally activated strong acid may be present in the subterranean formation before the pill breaker is introduced into the subterranean formation. In certain embodiments, a fluid loss control pill comprising a thermally activated strong acid may be placed introduced into the subterranean formation before the pill breaker is introduced into the subterranean formation. In certain embodiments, the pill breaker may be designed match the chemical composition and/or density of the fluid loss control pill.

[0043] In certain embodiments, one or more thermally activated strong acid precursors may be present in the subterranean formation before the pill breaker and/or the fluid loss control pill is introduced into the subterranean formation. In certain
embodiments, water may be present in the subterranean formation before the pill breaker and/or the fluid loss control pill is introduced into the subterranean formation.

[0044] In certain embodiments, the method may further comprise generating a thermally activated strong acid. In certain embodiments, generating a thermally activated strong acid may comprise activating the thermally activated strong acid precursors in the pill breaker to form the thermally activated strong acid. In certain embodiments, generating a thermally activated strong acid may comprise activating the thermally activated strong acid precursors in the fluid loss control pill to form the thermally activated strong acid. In certain embodiments, generating a thermally activated strong acid may comprise activating the thermally activated strong acid precursors in the fluid loss control pill and the pill breaker to form the thermally activated strong acid.

[0045] In certain embodiments, a thermally activated strong acid precursor present in the pill breaker and/or the fluid loss control pill may react with a thermally activated strong acid precursor previously in the subterranean formation and water to form the thermally activated strong acid. In certain embodiments, the thermally activated strong acid precursor present in the pill breaker and/or the fluid loss control pill may release a component of the thermally activated strong acid due to the temperature in the subterranean formation. For example, a fluid loss control pill and/or pill breaker comprising an SO₂ precursor such as a sulfone or sulfite and a carbonyl is introduced into a subterranean formation at a temperature above 80°C, the SO₂ precursor may release the SO₂ and the SO₂ may react with the carbonyl to form an alpha hydroxy sulfonic acid. Alternatively, when a fluid loss control pill and/or pill breaker comprising a carbonyl precursor and SO₂ is introduced into a subterranean formation containing at a temperature above 80°C, the carbonyl precursor may release the carbonyl and the carbonyl may react with the SO₂ form an alpha hydroxy sulfonic acid.

[0046] In certain embodiments, two thermally activated strong acid precursors present in the fluid loss control pill and/or pill breaker may release components of the thermally activated strong acid and those components may then react with each other and water in the subterranean formation to form the thermally activated strong acid. In certain embodiments, the two thermally activated strong acid precursors present in the fluid loss control pill and/or pill breaker may release a component of the thermally activated strong acid due to the temperature in the subterranean formation. For example, when a fluid loss control pill and/or pill breaker comprising an SO₂ precursor such as a sulfone or sulfite and
a carbonyl precursor is introduced into a subterranean formation at a temperature above 80°C, the SO₂ precursor may release the SO₂, the carbonyl precursors may release the carbonyl, and the SO₂ may react with the carbonyl to form an alpha hydroxy sulfonic acid.

[0047] In embodiments, where the fluid loss control pill and/or pill breaker comprises a sulfone addict of butadiene, the sulfone addict of butadiene may release butadiene when activated. In such embodiments, a dienophile present in the fluid loss control pill and/or pill breaker or the subterranean formation may react with butadiene to form a diacid. In certain embodiments, where the fluid loss control pill and/or pill breaker comprises a sulfite ester, an alcohol such as ethylene glycol may be released when the sulfite ester is activated.

[0048] In certain embodiments, the formation of the thermally activated strong acid may be an autocatalytic reaction. In certain embodiments, calcium carbonate or other base, such as KOH, NaOH, NH₃OH, MgO may be added to the reaction as part of the fluid loss control pill and/or pill breaker or be present in the subterranean formation to slow the reaction. In certain embodiments, the base may be present in the fluid loss control pill and/or pill breaker in an amount in the range of from 0% to 5% by weight of the acid-generating fluid.

[0049] In certain embodiments, the present invention provides a method comprising: providing a pill breaker comprising an acid-generating fluid comprising a thermally activated strong acid precursor, placing the pill breaker into a subterranean formation, and allowing the pill breaker to break a fluid loss control pill present in the subterranean formation.

[0050] In certain embodiments, the pill breaker may comprise any pill breaker discussed above. In certain embodiments, the fluid loss control pill may comprise any fluid loss pill discussed above. In certain embodiments, allowing the pill breaker to break a fluid loss control pill comprises, allowing the pill breaker to mix with the fluid loss control pill. In certain embodiments, the fluid loss control pill and the pill breaker may have similar densities and/or chemical make-ups allowing them to mix. In certain embodiments, allowing the pill breaker to break the fluid loss control pill may further comprise allowing the fluid loss control pill and/or the pill breaker to generate a thermally activated strong acid. In certain embodiments, allowing the pill breaker to break the fluid loss control pill may further comprise allowing the thermally activated strong acid to break the fluid loss control pill.
[0051] In certain embodiments, the present disclosure provides a method for performing a completion operation comprising: providing a wellbore, introducing a fluid loss control pill into the wellbore, performing a completion operation, introducing a pill breaker into the wellbore, and allowing the pill break to break the fluid loss control pill. A flow chart for such a method is illustrated in Figure 1. In certain embodiments, the wellbore may comprise any type of wellbore penetrating a subterranean formation. In certain embodiments, the wellbore may be an onshore wellbore or an offshore wellbore. In certain embodiments, the fluid loss control pill may comprise any fluid loss control pill discussed above. In certain embodiments, the pill breaker may comprise any pill breaker discussed above.

[0052] To facilitate a better understanding of the present invention, the following examples of certain aspects of some embodiments are given. In no way should the following examples be read to limit, or define, the scope of the invention.

**Examples**

[0053] **Example 1**

[0054] Two samples were prepared to test the effectiveness of breaking a fluid loss control pill comprising an acid-generating fluid with a pill breaker comprising acid-generating fluid comprising. Sample 1 comprised 15 ml of a blank Kmax fluid loss control pill weighted up to 14.3 ppg with CaBr_2. Sample 2 comprised 15 ml of a Kmax fluid loss control pill weighted up to 14.3 ppg with CaBr_2 and an internal breaker comprising sulfolene (0.158 %w of pill) and paraformaldehyde (0.04 %w of pill). Both samples 1 and 2 were held at 105°C for approximately 84 hours.

[0055] An equal amount (15 ml) of Kmax pill weighted to 14.3 ppg with CaBr2 comprising 3%w sulfolene and 0.76 %w paraformaldehyde was added after 84 hours to both samples. Samples 1 and 2 were then held at 105°C for approximately 7 hours. It was observed that sample 2 was cleanly broken while sample 1 remained intact.

[0056] **Example 2**

[0057] Two samples were prepared to test the effectiveness of breaking a fluid loss control pill comprising an acid-generating fluid with a pill breaker comprising acid-generating fluid comprising. Samples 1 and 2 comprised 15 ml of a kmax fluid loss control pill weighted up to 14.3 ppg with CaBr_2 and an internal breaker comprising sulfolene (0.158 %w of pill) and paraformaldehyde (0.04 %w of pill). Samples 1 and 2 were held at 90°C for approximately 96 hours.
[0058] 15 ml of 5 %w HCl was added to sample 1 after 96 hours. 15 ml of Kmax pill weighted to 14.3 ppg with CaBr₂ comprising 4.82 %w ethylene sulfite and 1.34 %w was added to sample 2 after 96 hours. It was observed that sample 1 took over 21 hours at 90°C to fully break the original kmax pill. Sample 2 was fully and cleanly broken within 3 hours.

[0059] While the embodiments are described with reference to various implementations and exploitations, it will be understood that these embodiments are illustrative and that the scope of the inventive subject matter is not limited to them. Many variations, modifications, additions and improvements are possible.

[0060] Plural instances may be provided for components, operations or structures described herein as a single instance. In general, structures and functionality presented as separate components in the exemplary configurations may be implemented as a combined structure or component. Similarly, structures and functionality presented as a single component may be implemented as separate components. These and other variations, modifications, additions, and improvements may fall within the scope of the inventive subject matter.
CLAIMS

1. A method comprising:
   providing a pill breaker comprising an acid-generating fluid comprising a
   thermally activated strong acid precursor;
   placing the pill breaker into a subterranean formation; and
   allowing the pill breaker to generate a thermally activated strong acid.

2. The method of claim 1, wherein the thermally active strong acid precursor
   comprises an SO₂ precursor.

3. The method of claim 1, wherein the thermally activated strong acid
   precursor comprises a sulfone adduct of butadiene, a sulfone adduct of piperylene, a
   sulfone adduct of isoprene, a sulfite ester, or any combination thereof.

4. The method of claim 1, wherein the thermally activated strong acid
   precursor comprises ethylene sulfite or dimethyl sulfite.

5. The method of claim 1, wherein the thermally activated strong acid
   precursor comprises an aldehyde or ketone precursor.

6. The method of claim 1, wherein the thermally activated strong acid
   precursor comprises paraformaldehyde, polyoxymethylene, metaldehyde, trioxane,
   formaldehyde, acetaldehyde, or any combination thereof.

7. The method of claim 1, wherein the thermally activated strong acid
   precursor comprises SO₂ and an aldehyde or ketone precursor in a ratio of 1:1.

8. A method comprising:
   providing a pill breaker comprising an acid-generating fluid comprising a
   thermally activated strong acid precursor;
   placing the pill breaker into a subterranean formation; and
   allowing the pill breaker to break a fluid loss control pill.

9. The method of claim 8, wherein the fluid loss control pill comprises an
   acid-generating fluid comprising a thermally activated strong acid precursor.

10. The method of claim 8, wherein the acid-generating fluid in the pill breaker
    comprises a higher concentration of thermally activated strong acid precursor than the acid-
    generating fluid in the fluid loss control pill.
FIGURE 1

Provide a wellbore

Introduce a fluid loss control pill into the wellbore

Perform a completion operation

Introduce a pill breaker into the wellbore

Allow the pill breaker to break the fluid loss control pill
A. CLASSIFICATION OF SUBJECT MATTER

INV. C09K/50 C09K/52 C09K/76

ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09K

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 database and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>US 2010/270017 A1 (PRASEK BETHICIA B [US] ET AL) 28 October 2010 (2010-10-28) claim 1; example 1</td>
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<td>US 2007/049501 A1 (SAINI RAJESH K [US] ET AL) 1 March 2007 (2007-03-01) cited in the application claim 1; example 1</td>
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<td>X</td>
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* 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
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Date of the actual completion of the international search
6 April 2017

Date of mailing of the international search report
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Name and mailing address of the ISA/
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Authorized officer
Redecker, Michael
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<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
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<td>X</td>
<td>US 2005/252659 A1 (SULLIVAN PHILIP F [US] ET AL) 17 November 2005 (2005-11-17) claim 1; example 3</td>
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