Abstract: A quick-setting plugging composition that allows for plugging a region of a subterranean formation, and in particular for plugging a region of a subterranean formation in a near wellbore area.
QUICK-SETTING ELASTOMER PLUGGING COMPOSITION

FIELD OF THE INVENTION

The present invention relates to a quick-setting plugging composition that allows for plugging a region of a subterranean formation, and in particular for plugging a region of a subterranean formation in a near wellbore area.

BACKGROUND OF THE INVENTION

In oil recovery there are many factors, such as voids, fractures etc. which may lead to a fluid loss and complicate the recovery of the oil. Thus the recovery of oil will be largely affected by the heterogeneity of rock such a high permeability channels, voids and fractures. In case of cavities in the near wellbore there is a risk of back-flow and uncontrolled delivery of substances to the far wellbore areas.

CN104109514 discloses a plugging agent system for permanently plugging multilayer low-pressure large-tunnel oil reservoir and technology using the same.

CN104119847 discloses an acid-soluble composite plugging agent and application thereof.

CN105131294 discloses an organosilicone microsphere with reverse wetting property and polymerization process thereof.

CN105567190 discloses a gel plugging agent and preparation method thereof.

CN105567191 discloses a weak-gel micro-silicon suspension, and preparation method and application thereof.

CN105567195 discloses a well cementing slurry free liquid control agent, preparation method and application thereof.

CN105885819 discloses an ultra-low-density spherical silicone oil to support its preparation method.

CN106082807 discloses an oil (water) system of channeling, plugging the well preparation and application method.
US2009205824 discloses polymeric microspheres as degradable fluid loss additives in oilfield applications.


US2011048715 discloses radiation-induced thickening for set-on-command sealant compositions and methods of use.

US2011315383 discloses a method for gelation acceleration.

US2015308221 discloses a method of providing a barrier in a fracture-containing system.

US2015376492 discloses a plugging composition using swellable glass additives.

US6196316 discloses compositions for use in well construction, repair and/or abandonment.

It would be desirable to be able to shutting off back-flow and allowing controlled delivery of substances to the intended place of action. It would also be desirable to be able to ensure good stabilization of oil recovery equipment inside an injection well, when offshore oil recovery treatments are applied. It would also be desirable to be able to provide a composition that is easily pumpable at lower temperatures and rapidly solidifies at higher temperatures to provide an elastomer plug.

OBJECT OF THE INVENTION

It is an object of embodiments of the invention to provide a composition that allows for pumping to a desired place of action and upon activation allows setting of a plug in a controlled manner.

It is a further object of embodiments of the invention to provide a composition that allows for pumping to a desired place of action and upon thermal activation rapidly gels and therefore allows setting of a plug in a controlled manner.

It is a further object of embodiments of the invention to provide a composition that allows for efficient water injection into a pre-treated rock formation in order to achieve enhanced oil recovery.
SUMMARY OF THE INVENTION

It has been found by the present inventors that by providing a plugging composition which is readily pumpable at working temperatures and quickly creates a solid network at higher temperatures, it is possible to obtain good stabilization of a wellbore.

So, in a first aspect the present invention relates to a plugging composition for servicing a wellbore, comprising:

a) A base fluid;

b) Functionalised polyalkysiloxane microspheres;

c) A crosslinker suitable for covalent inter-microsphere crosslinking of said functionalised polyalkysiloxane microspheres;

d) A catalyst for said crosslinking reaction; and

e) An inhibitor for said catalyst.

In a second aspect the present invention relates to a method for servicing a wellbore comprising:

i) providing a plugging composition according to any of the preceding claims;

ii) introducing the plugging composition into a wellbore;

iii) Heating the plugging composition to at least 100 °C and allowing the plugging composition to form a plug.

In a third aspect the present invention relates to a use of a plugging composition according to the invention for providing a plug around a wellbore.

DETAILED DISCLOSURE OF THE INVENTION

Definitions

In the present context the term "microsphere" refers to spherical microparticles without membrane or any distinct outer layer and with dimensions between $1 \times 10^{-7}$ and $1 \times 10^{-4}$ m.
In the present context the terms "crosslinker" and "crosslinking agent" are used interchangeably to denote a chemical substance capable of providing bonds between polymer chains.

In the present context the term "polyalkylsiloxane" refers to a compound of the form $R_b$-[Si($R_a$)$R_b$]$_n$Si$R_2$, wherein each of $R_1$, $R_2$, $R_b$ and $R_b$ is alkyl, and $n$ is the number of repeating units.

In the present context the term "alkyl" means a linear, cyclic or branched hydrocarbon group having 1 to 24 carbon atoms, such as methyl, ethyl, propyl, iso-propyl, cyclopropyl, butyl, iso-butyl, tert-butyl, cyclobutyl, pentyl, cyclopentyl, hexyl, and cyclohexyl.

In the present context the term "functionalised polyalkylsiloxane" refers to a polyalkylsiloxane having functional groups at the side chains or at the ends of the polyalkylsiloxane chain, wherein the term "functional groups" in the present context refers to chemical groups selected to impart a desired characteristic at the side chains or at the ends of the polyalkylsiloxane chain. Suitable non-limiting examples of functional groups are vinyl and hydride groups.

In the present context the term "polydimethylsiloxane", abbreviated "PDMS", refers to a compound of the formula $\text{CH}_3[\text{Si}(\text{CH}_3)_{20}]_n\text{Si}(\text{CH}_3)_{13}$, where $n$ is the number of repeating units.

In the present context the term "silicone oil" refers to a non-reactive polyalkylsiloxane composition, i.e. a polyalkylsiloxane composition which does not react with other components of the plugging composition.

The term "curing" in the present context refers to the process of cross-linking of polymer chains, more particularly to the process of cross-linking of functionalised polyalkylsiloxane polymer chains at the microsphere surface with a cross-linker.

In the present context the term "wellbore" refers to a borehole, i.e. a narrow shaft bored in the ground, such as for extraction of oil or petroleum, water, natural gas etc.

Specific embodiments of the invention

In an embodiment of the plugging composition according to the invention the base fluid is selected from the group consisting of an aqueous fluid and an oleaginous fluid, preferably water or a hydrocarbon or silicone fluid, more preferably a silicone oil. The base fluid for use
in the plugging composition according to the invention should be non-reactive with the other components of the plugging composition in order not to interfere with the crosslinking reaction. The base fluid acts as a suspension medium for the microspheres and controls the initial viscosity of the plugging composition so as to make the plugging composition pumpable at the desired working temperature, such as temperatures in the range 0-60 °C. A preferred base fluid is a silicone oil. Non-limiting examples of suitable silicone oils for use in the invention include a silicone oil commercially available from Sigma-Aldrich as 'Silicone oil viscosity 20 cSt'.

In an embodiment of the plugging composition according to the invention the functionalised polyalkylsiloxane microspheres are functionalised polydimethylsiloxane (PDMS) microspheres.

Suitable functionalised polyalkylsiloxane microspheres for use according to the invention are vinyl-functionalised polydimethylsiloxane (PDMS) microspheres or hydride-functionalised polydimethylsiloxane (PDMS) microspheres. Non-limiting examples of vinyl-functionalised polydimethylsiloxane include vinyl-terminated poly(dimethylsiloxane) commercially available from Gelest as DMS-V22 (M_w=9400 g/mol, viscosity 200 cSt).

Vinyl-functionalised polyalkylsiloxane microspheres may be produced from an excess of telechelic vinyl functionalised polydimethylsiloxane (PDMS) which are crosslinked in the presence of a crosslinker in emulsion to yield microspheres with an excess of vinyl groups such as the technology disclosed in


Alternatively the functionalised polyalkylsiloxane microspheres may be produced from an excess of telechelic hydride functionalised polydimethylsiloxane (PDMS) which are crosslinked in the presence of a crosslinker in emulsion to yield microspheres with an excess of hydride groups. A suitable system would be telechelic hydride functionalised PDMS (e.g. DMS-H31 from Gelest) crosslinked by Vinylmethylsiloxane - Dimethylsiloxane Copolymers, trimethylsiloxy terminated (e.g. VDT-131 from Gelest), preferably with a 5-30, such as 10-20% molar excess of PDMS.

Alternatively both vinyl and hydride-functionalised microspheres may be achieved by using the respective crosslinker in excess, preferably with a 5-30, such as 10-20% molar excess, such that the microspheres bear the functionality of the crosslinker rather than that of the polymer.
In an embodiment of the plugging composition according to the invention the crosslinker is a liquid at temperatures in the range 0-60 °C. The provision of a crosslinker in liquid form allows efficient mixing of the crosslinker and the functionalised polyalkylsiloxane microspheres. A crosslinking reaction between the crosslinker and the functionalised polyalkylsiloxane microspheres takes place rapidly creating a solid network at about 100-140 °C, such as 110-120 °C.

A suitable crosslinker for use in the plugging composition according to the invention is a crosslinker suitable for covalent inter-microsphere crosslinking, i.e. a crosslinker which is suitable for forming covalent bonds between the microspheres via bonding of the functional groups of the microspheres. Thus a suitable coupling pair is the vinyl-hydride coupling pair. Thus in the case of vinyl-functionalised microspheres a suitable crosslinker would be a hydride-functionalised crosslinker, whereas in the case of hydride-functionalised microspheres a suitable crosslinker would be a vinyl-functionalised crosslinker.

Suitable, non-limiting examples of a crosslinker for use in the plugging composition according to the invention is a crosslinker selected from the group consisting of hydride functional polysiloxanes, such as methylhydrosiloxane - dimethylsiloxane copolymers, such as HMS-301 commercially available from Gelest. A non-limiting example of a vinyl-functionalised crosslinker is vinylmethylsiloxane - dimethylsiloxane copolymers, trimethylsiloxy terminated commercially available as VDT-131 from Gelest Inc.

The plugging composition according to the invention comprises a catalyst for the crosslinking reaction between the crosslinker and the functionalised polyalkylsiloxane microspheres.

In an embodiment of the invention the catalyst is selected from the group consisting of Pt, Rh, Ru, Re and Pd based catalysts, preferably the catalyst is a Pt based catalyst. A commercially available Pt based catalyst is Catalyst 511 from Evonik. A suitable Rh based catalyst is commercially available from Sigma Aldrich as Product no 334987. Suitable Ru, Re and Pd based catalysts are commercially available from Gelest as OMRE47, OMRE47 and INPD024, respectively.

In an embodiment of the invention the plugging composition furthermore comprises an inhibitor for said catalyst. The inhibitor is preferably a liquid at temperatures in the range 0-60 °C and complexes with the catalyst at room temperature to deactivate the catalyst at lower temperatures therefore preventing the crosslinking reaction to occur. At higher temperatures the inhibitor either thermally degrades or evaporates so as to restore the activity of the catalyst and facilitate solidification of the plug. Addition of an inhibitor extends the pumpability time of the plugging composition according to the invention while
maintaining the required high curing speed at elevated temperatures, such as in the range 100-140 °C, such as 110-120 °C, and allowing the preparation of compositions which are stable during transport of said composition until the desired point of activation.

5 In an embodiment of the invention the inhibitor is selected from the group consisting of 1,3-divinyltetramethyldisiloxane, 1,3,5,7-tetra vinyl-1,3,5,7-tetra methylcyclosiloxane, methylvinylcyclosiloxane (MVC), divinylsulfone (DVS) and an alkynyl type compound such as acetylene or methylacetylene, preferably the inhibitor is MVC. Non-limiting examples of commercially available inhibitors include 1,3-divinyltetramethyldisiloxane inhibitor from Sigma Aldrich, 1,3,5,7-tetra vinyl-1,3,5,7-tetra methylcyclosiloxane from Gelest, methylvinylcyclosiloxane (MVC) from Evonik, divinylsulfone (DVS) from Evonik and an alkynyl type compound "Inhibitor 600" from Evonik.

10 In an embodiment of the invention the reaction time, i.e. the time until storage modulus (G') becomes constant, is in the range 40-180 seconds, such as about 90-120 seconds. The reaction time may be controlled by means of the amount of catalyst added, the ratio between silicone oil and microspheres, the amount of type of crosslinker, the amount and type of inhibitor added, and the reaction temperature.

20 In the method for servicing a wellbore according to the invention the functionalised polyalkylsiloxane microspheres may be prepared by mixing functionalised polyalkylsiloxane with a catalyst and optionally an inhibitor at room temperature at a speed in the range 1500-3500 rpm, such as 2000-3000 rpm. Subsequently a crosslinker is added, followed by mixing at 1500-3500 rpm, such as 2000-3000 rpm. The mixture is mixed with a surfactant solution and stirred first at a speed in the range 1500-3500 rpm, such as 2000-3000 rpm, and subsequently at a lower speed, such as 300-1000 rpm, such as about 500 rpm, and cured at a temperature in the range 70-90 °C, such as about 80 °C.

25 In the method for servicing a wellbore according to the invention the plugging composition may be provided by first providing the functionalised polyalkylsiloxane microspheres, for instance as described above. A silicone premix may be prepared by mixing silicone oil and a catalyst followed by addition of the functionalised polyalkylsiloxane microspheres, the crosslinker and any inhibitor and curing at elevated temperature, such as 100-140 °C, such as about 110-120 °C.

30 The plugging composition according to the invention may be used for providing a plug around a wellbore, such as an oilfield wellbore in order to stabilise the oil field equipment inside the injection well when offshore oil recovery treatments are applied. In order to facilitate proper
stabilization of the equipment an easily pumpable plugging composition that solidifies in a short time needs to be injected into the well.

In another embodiment of the invention the well is a soil remediation wellbore.

In another embodiment of the invention the well contains gas.

The invention is disclosed in more detail via the below non-limiting examples.

EXAMPLE 1

Preparation of PDMS microspheres
5 g of vinyl-terminated poly(dimethylsiloxane) DMS-V22 (M_w=9400 g/mol, viscosity 200 cSt, Gelest), 0.05 g of a PT88 inhibitor (Wacker Chemie) and 0.005 g of a Catalyst 511 (Evonik) were mixed for 2 minutes at 2000 rounds per minute (rpm) using a SpeedMixer. Subsequently, 0.24 g of hydride functional cross-linker HMS-301 (M_w=2000 g/mol, viscosity 25-35 cSt, Gelest) was added, followed by another mixing of the mixture for 2 minutes at 2000 rpm. The mixture was then poured into a conical flask with 150 mL of aqueous surfactant solution, which contained 3% (by weight) sodium dodecyl sulfate (SDS, M_w=288 g/mol, Sigma Aldrich) and 1% (by weight) poly(vinyl alcohol) (PVA, M_w=22000 g/mol, Sigma Aldrich). Initially, the aqueous surfactant solution was stirred mechanically at 2000 rpm for 2 minutes to form an oil-in-water emulsion. Upon the formation of the emulsion, the stirring speed was reduced to 500 rpm and the system was cured at 80°C for 2 h in the water bath. The obtained PDMS microspheres were filtered with 1 L of deionized water and dried at room temperature for one day.

Preparation of the plugging composition with PDMS microspheres and liquid cross-linker
Firstly, non-reactive silicone oil commercially available from Sigma-Aldrich as 'Silicone oil viscosity 20 cSt' and a Catalyst 511 (Evonik) were mixed using a SpeedMixer in order to prepare a silicone premix containing 50 ppm of the catalyst. Subsequently, 1 g of the PDMS microspheres, 0.05 g of the liquid cross-linker HMS-301 from Gelest (chemical name (25-35% methylhydrosiloxane) - dimethylsiloxane copolymer, trimethylsiloxane terminated) and 0.02 g of a PT88 inhibitor and 1 g of the silicone oil premix were added to a beaker and mixed by spatula. Such prepared plugging composition was cured at 120°C. Fully cross-linked plug was obtained after 95 s. Values of the storage and the loss moduli of the cross-linked plugging composition reached 60000 Pa and 330 Pa, respectively.
In order to decrease the reaction time, a plugging composition with silicone oil containing 100 ppm of the catalyst was prepared analogously to the sample containing 50 ppm of the catalyst; with the difference that double amount of the catalyst was added to the silicone oil in order to prepare the silicone oil premix. Such prepared plugging composition was cured at 120°C. Fully cross-linked plug was obtained after 40 s. Values of the storage and the loss moduli of the cross-linked plugging composition reached 50500 Pa and 450 Pa, respectively.

**EXAMPLE 2**

*Preparation of the plugging compositions with various amount of silicone oil*

Firstly, non-reactive silicone oil commercially available from Sigma-Aldrich as 'Silicone oil viscosity 20 cSt' and a Catalyst 511 (Evonik) were mixed using a SpeedMixer in order to obtain a silicone oil premix containing 100 ppm of the catalyst. Subsequently, 0.2 g of the PDMS microspheres, 0.05 g of the liquid cross-linker HMS-301 and 0.02 g of a PT88 inhibitor and 0.2 g of the silicone oil premix were added to a beaker and mixed by spatula. Then, 0.2 g of silicone oil, 'Silicone oil viscosity 20 cSt', was added in portions until a mixture capable of flowing was obtained. Before the cross-linking reaction, a sample with mass ratio 1:4 (PDMS microspheres to silicone oil) was capable to flow. At 120°C values of the G' and G" of the cross-linked plugging composition reached 18000 Pa and 700 Pa, respectively, in 150 s meaning that the cross-linked network was formed.

**EXAMPLE 3**

*Preparation of plugging compositions with different inhibitors*

Firstly, non-reactive silicone oil, "Silicone oil viscosity 20 cSt", and a Catalyst 511 were mixed using a SpeedMixer in order to obtain a silicone oil premix containing 100 ppm of the catalyst. Subsequently, 0.2 g of the PDMS microspheres, 0.05 g of the liquid cross-linker HMS-301, 0.2 g of the silicone oil premix and 0.6 g of silicone oil, "Silicone oil viscosity 20 cSt", were added to a beaker and mixed by spatula. Then, certain amount of an inhibitor was added. Four commercially available inhibitors were tested - PT88 (Wacker Chemie), MVC (Evonik), DVS (Evonik) and Inhibitor 600 (Evonik). Recommended concentrations of the inhibitors were used and the mass of the inhibitor was calculated regarding the mass of the PDMS microspheres. The plugging compositions were tested at 60°C and at 120°C for 3 hours at each temperature.

The plugging composition with MVC inhibitor was fully stable for first 2 hours at 60°C. The storage modulus did not increase over this time, and only minor changes were observed afterwards. The cross-linking reaction took place mainly at 120°C as the G' rapidly reached constant, high values (43000 Pa).
The plugging composition with Pt88 inhibitor was not fully stable at 60°C since the G’ was constantly increasing during first 3 hours. At 120°C the G’ slightly increased and did not reach constant value at 120°C, which testified that the reaction was still occurring during the measurement. After 3 hours at 120°C, the storage modulus value was 14000 Pa.

At 60°C the storage modulus of plugging compositions with DVS inhibitor and Inhibitor 600 increased notably reaching constant value after 90 min (1200 Pa) and 30 minutes (1300 Pa), respectively. When the temperature was increased to 120°C the storage modulus increased, however in both cases the increase was not significant. Moreover, the G’ was constantly increasing during 3 hours at 120°C indicating that the cross-linking reaction was not completed. After 3 hours at 120°C, the G’ values for plugging compositions with DVS and Inhibitor 600 reached 10500 Pa and 13000 Pa, respectively.
CLAIMS

1. A plugging composition for servicing a wellbore, comprising:
   a) A base fluid;
   b) Functionalised polyalkylsiloxane microspheres;
   c) A crosslinker suitable for covalent inter-microsphere crosslinking of said functionalised polyalkylsiloxane microspheres;
   d) A catalyst for said crosslinking reaction; and
   e) An inhibitor for said catalyst.

2. The plugging composition according to claim 1, wherein the base fluid is selected from the group consisting of an aqueous fluid and an oleaginous fluid, preferably water or a hydrocarbon or silicone fluid, more preferably a silicone oil.

3. The plugging composition according to claim 1 or 2, wherein the functionalised polyalkylsiloxane microspheres are functionalised polydimethylsiloxane (PDMS) microspheres.

4. The plugging composition according to any one of the preceding claims, wherein the functionalised polyalkylsiloxane microspheres are vinyl- or hydride-functionalised polydimethylsiloxane (PDMS) microspheres.

5. The plugging composition according to any one of the preceding claims, wherein the crosslinker is a liquid at temperatures in the range 0-60 °C.

6. The plugging composition according to claim 5, wherein, when the functionalised microspheres are vinyl-functionalised microspheres, the crosslinker is selected from the group consisting of hydride functional polysiloxanes, such as methylhydrosiloxane-dimethylsiloxane copolymers, and when the functionalised microspheres are hydride-functionalised microspheres, the crosslinker is selected from the group consisting of vinyl functionalised polysiloxanes, such as vinylmethylsiloxane-dimethylsiloxane copolymers.

7. The plugging composition according to any one of the preceding claims, wherein the catalyst is selected from the group consisting of Pt, Rh, Ru, Re and Pd based catalyst, preferably the catalyst is a Pt based catalyst.
8. The plugging composition according to any one of the preceding claims, wherein the inhibitor is selected from the group consisting of 1,3-divinyltetramethyldisiloxane, 1,3,5,7-tetravinyl-1,3,5,7-tetramethyldisiloxane, methylvinylcyclotetrasiloxane (MVC), divinylsulfone (DVS) and an alkynyl type compound such as acetylene or methylacetylene, preferably the inhibitor is MVC.

9. A method for servicing a wellbore comprising:
   i) providing a plugging composition according to any of the preceding claims;
   ii) introducing the plugging composition into a wellbore;
   iii) heating the plugging composition to at least 120 °C and allowing the plugging composition to form a plug.

10. A use of a plugging composition according to any one of claims 1-8 for providing a plug around a wellbore.

11. The use according to claim 10, wherein the wellbore is an oilfield wellbore.

12. The use according to claim 10, wherein the wellbore is a soil remediation wellbore.
A. CLASSIFICATION OF SUBJECT MATTER

INV. B01J13/02 C04B26/32 C09K8/42 C09K8/44 C08G77/20

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 C08G B01J E21B C04B

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Date of the actual completion of the international search

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Name and mailing address of the ISA

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