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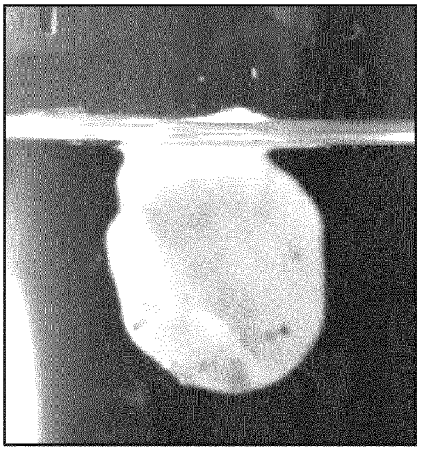
(54) **Title**: PROPPANT COMPOSITE

Fig.1



(57) **Abstract**: The present invention relates to process to prepare a proppant composite comprising a wax, the process comprises the steps of: (a) addition of a wax to a heated proppant to obtain a blend with a temperature above the congealing point of wax; (b) mixing of the blend of step (a) until a homogeneous fluid mixture with well dispersed proppant is obtained; (c) forming a particulate matter of the homogeneous fluid mixture of step (b) with a forming technique to obtain a proppant composite comprising a wax.

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PROPPANT COMPOSITE

Field of the Invention

The present invention relates to a process to prepare a proppant composite comprising a wax and said proppant composite. The present invention also relates to the use of said the composite proppant for hydraulic fraccing to keep fractures open after releasing the pressure during hydraulic stimulation for the production of unconventional resources such as tight oil and/or gas.

Background of the Invention

It is known in the art to use low-density proppants for hydraulic fraccing. Typically hydraulic fraccing induces and opens fractures for hydrocarbon flow, such as gas and oil. Proppants are then placed in these fractures to keep them open after releasing the hydraulic pressure. One way to place the proppants in these fractures is with water. A conventional proppant is sand or ceramic with a density layer larger than 2 g/mL. However, placement with water results in fast sedimentation and limited penetration into the frack. Another mode of placement is with gel formulations.

US2014/0144635 discloses the use of a cement slurry comprising an expandable cementitious material as proppant and a breakable gel fluid. The proppant will be suspended by a gel formulation, which gel will induce the sedimentation upon chemical breaking of the gel. Said chemical breaking will be temperature activated. Although the placement with the gel formulation will lead to faster penetration into the fracture and delayed sedimentation, complicated and costly chemistry is needed for gelling and breaking of the gel used for proppant placement.

US 20150083418 discloses a proppant particle including a core of swellable material and a dissolvable layer encapsulating the core. However, the release of the proppant is dependent on the solubility of the dissolvable layer in water.

It is an object of the invention to provide a simple process which allows the proppants to be carried far into the fracture before sedimentation.

It is a further object of the present invention to provide a low density proppant.

Another object of the present invention is to provide a simple and controlled process for hydraulic fraccing to keep fractures open after releasing the hydraulic pressure.

Yet another object of the present invention is to provide a carrier containing the proppant which may control the release of the proppant in such a way that the release is not entirely dependent on the solubility of the carrier.

Summary of the invention

From a first aspect, above and other objects may be achieved according to the present invention by providing a process to prepare a proppant composite comprising a wax, the process comprises the steps of:

(a) addition of a wax to a heated proppant to obtain a blend with a temperature above the congealing point of wax;

(b) mixing of the blend of step (a) until a homogeneous fluid mixture with well dispersed proppant is obtained;

(c) forming a particulate matter of the homogeneous fluid mixture of step (b) with a forming technique to obtain a proppant composite comprising a wax.

It has been found that the process according to the present invention provides a proppant composite allowing the proppant be carried far into the fracture before sedimentation.

An advantage of the process according to the present invention to provide a proppant composite is that the wax used to prepare the proppant composite undergoes a sharp melting transition. Due to this sharp melting transition of the wax the composite may disintegrate and the proppant particles may be released when the downhole temperature exceeds the wax melting temperature.

Also, a wax will be chosen in such a way that the congealing point of the wax will match the temperature downhole.

From a second aspect, the invention embraces a proppant composite. An advantage of the proppant composite is the low density of said composite which is achieved by formulating fine grained proppant with a low density wax. In this way the composite may be carried far into the fracture before sedimentation.

From a third aspect, the invention resides in the use of a proppant composite for hydraulic fraccing to keep fractures open after releasing the pressure during hydraulic stimulation for the production of unconventional resources such as tight oil and/or gas.

The advantage of said use is that the proppant composite withstands the closure stress, allows the hydrocarbon flow through the proppants, the proppants fit into natural fractures, the proppants are carried far into the fracture before sedimentation and the composite allows ease of placement.

From a fourth aspect, the invention embraces a the use of Fischer-Tropsch derived wax in a composite proppant.

An advantage of the use of Fischer-Tropsch derived wax is that the Fischer-Tropsch derived wax has very low levels of aromatics, sulphur, napthenics and impurities.

Detailed description of the invention

In step (a) according to the process of the present invention, a wax is added to a heated proppant to obtain a blend with a temperature above the congealing point of the wax. The proppant is preferably heated at a temperature in a range of from 50 to 105°C, more preferably from 70 to 100°C, most preferably in range of from 70 to 90°C. The person skilled in the art will understand that the temperature used is dependent on the wax to be used. In addition, the blend of step (a) comprises a wax in the range of from 5 to 30 wt.% based on the total amount of the blend.

In another embodiment of the process according to the present invention the proppant is heated together is the wax to a temperature above the congealing point of the wax.

The wax preferably has a congealing point of at least 50°C. Also, preferably the wax has a congealing point of at least 70°C. In addition, the wax has a congealing point of at least 105°C and at most 130°C. Suitably, the wax in step (a) is a natural wax, such as beeswax, a petroleum derived wax or a synthetic derived wax. Suitable natural waxes are for example disclosed in the "International Journal for Applied Science, 4-2011, Natural waxes-Properties, Compositions and Applications, E. Endlein, K Peleikis; Natural Waxes-Properties, Compositions and Applications".

Preferably, the wax in step (a) is a paraffin wax. Paraffin wax may be obtained by various processes. US 2,692,835 discloses a method for deriving paraffin wax from crude oil. Also, paraffin wax may be obtained using the so called Fischer-Tropsch process. An example of such process is disclosed in WO 2002/102941, EP 1 498 469, and WO 2004/009739. In addition, the wax is preferably a Fischer-Tropsch derived wax.

Preferably, the proppant is sand or ceramics. In addition, the size of the proppant in step (a) is less than 30 Mesh, preferably less than 50 Mesh and most preferably less than 80 Mesh.

The blend of step (a) preferably comprises wax in a range of from 15 to 50 wt.%, preferably 20 to 35 wt.% based on the total amount of the blend.

In step (b) according to the process of the present invention the blend of step (a) is mixed until a homogeneous fluid mixture with well dispersed proppants is obtained. In other words, in step (b) according to the process of the present invention the blend of step (a) is mixed to obtain a homogeneous fluid mixture with well dispersed proppants. The person skilled in the art will understand that the blend of step (a) is mixed until a homogeneous fluid mixture with well dispersed proppants is obtained. Preferably, the amount of wax is such that a homogeneous fluid mixture with well dispersed proppants is obtained. In addition, an extra amount of wax may be added to step (b) in order to obtain the homogenous fluid mixture.

In step (c) of the process according to the present invention a particulate matter of the fluid mixture of step (b) is formed by a forming technique to obtain a proppant composite comprising a wax. Typically, depending

on the forming technique the fluid is first cooled before being formed into a particulate matter. Also, the particulate form of the particulate matter is preferably a pellet, flake, sphere, granule or pill. Formation techniques and particulate forms formed by these formation techniques are known by the skilled person in the art and can for example be found in the presentation of J. d'Aquin, titled "Airborne Sulfur Dust: Composition and Control" published for Mespon 2015, 20 October 2015 in Abu Dabi.

Suitably, the size of the composite as obtained in step (c) of the process according to the present invention is less than 10 Mesh, preferably less than 30 Mesh, most preferably less than 40 Mesh.

In addition, the density of the composite is in range of from 0.8 to 2.0 g/mL, preferably in a range of from 1.1 to 1.6 g/mL.

In a further aspect, the present invention provides a proppant composite.

Preferably, the wax in the proppant composite according to the present invention is a Fischer-Tropsch derived wax. In addition, the Fischer-Tropsch derived wax has a congealing point of at least 50 and at most 130°C. Also, the amount of Fischer-Tropsch derived wax in the proppant composite is in a range between 15 to 50 wt.%, preferably 20 to 35 wt.% based on the amount of the proppant composite.

In another aspect, the present invention provides the use of proppant composite for hydraulic fraccing to keep fractures open after releasing the pressure during hydraulic stimulation for the production of unconventional recources such as tight oil and/or gas. The process for using proppants for hydraulic fraccing

is a known process and is for example described in US2014/014463.

In a further aspect the present invention provides the use of the Fischer-Trospch derived wax in a composite proppant.

An advantage of the use of a Fischer-Tropsch derived wax in the composite proppant is that the Fischer-Tropsch derived wax is compatible with tight oil because of its paraffinic nature and the absence of heterogeneous molecules such as nitrogen and sulphur.

The present invention is described below with reference to the following Examples, which are not intended to limit the scope of the present invention in any way.

Examples

Example 1

Preparation of a proppant composite comprising a wax with a congealing point of 50°C.

Sand was mixed with a Fischer-Tropsch wax having a congealing point of 50°C. The obtained mixture was heated to 60°C to obtain a melted mixture comprising melted wax and sand. The melted mixture wax cooled to room temperature and a proppant composite was obtained. Table 1 shows the density of the different proppant compositions obtained with above method.

Table 1

Proppant Composite	Sand (wt.%)	FT wax (wt.%)	Density composite (g/mL)[a]
1	0	100	0.85
2	10	90	0.91
3	20	80	0.98
4	30	70	1.05
5	40	60	1.15
6	50	50	1.26
7	60	40	1.39
8	70	30	1.55
9	75	25	1.65
10	80	20	1.76
11	90	10	2.03
12	100	0	2.40

[a]density composite ρ is calculated with formula $1/\rho_{composite} = (wt.\%sand/\rho sand) + (wt.\% wax/\rho wax)$

Example 2

Sand sedimentation

The proppant composite 3 of Example 1 was released in water. Initially, the composite was floating on the surface of the water (see Figure 1). The wax started melting (see Figure 2), followed by sand sedimentation (Figure 3).

Discussion

Figures 1 to 3 show that the Fischer-Tropsch wax forms a stable proppant wax in water and upon heating to a temperature to or above the congealing point of the wax the sand sedimentation occurred. These observations indicate that Fischer-Tropsch wax can be used to form

stable low density proppant composites and that the proppant matter can be released upon a temperature above the wax congealing point which in practice should be matched to formation temperature downhole.

C L A I M S

1. Process to prepare a proppant composite comprising a wax, the process comprises the steps of:
   (a) addition of a wax to a heated proppant to obtain a blend with a temperature above the congealing point of wax;
   (b) mixing of the blend of step (a) to obtain a homogeneous fluid mixture with well dispersed proppant ;
   (c) forming a particulate matter of the homogeneous fluid mixture of step (b) with a forming technique to obtain a proppant composite comprising a wax.
2. Process according to claim 1, wherein the wax has a congealing point of at least 50°C.
3. Process according to claim 1 or 2, wherein the wax has a congealing point of at least 70°C.
4. Process according to any one of claims 1 to 3, wherein the wax has a congealing point of at least 105°C and at most 130°C.
5. Process according to any one of claims 1 to 4, wherein the wax of step (a) is a Fischer-Tropsch derived wax.
6. Process according to any one of claims 1 to 5, wherein the proppant is sand or ceramics.
7. Process according to any one of claims 1 to 6, wherein the size of the proppant is less than 30 Mesh, preferably less than 50 Mesh and most preferably less than 80 Mesh.
8. Process according to any one of claims 1 to 7, wherein the blend of step (a) comprises wax in a range of from 15 to 50 wt.%, preferably 20 to 35 wt.% based on the amount of the blend.
9. Process according to any one of claims 1 to 8, wherein prior to forming in step (c) the homogeneous fluid mixture of step (b) is cooled.
10. Process according to any one of claims 1 to 9, wherein the size of the composite of step (c) is less than 10 Mesh,

preferably less than 30 Mesh, and most preferably less than 40 Mesh.

11. Process according to any one of claims 1 to 10, wherein the density of the composite is in range of from 0.8 to 2.0 g/mL, preferably in a range of from 1.1 to 1.6 g/mL.

12. Proppant composite obtainable by the process according to one of the preceding claims.

13. Use of a proppant composite of claim 12, for hydraulic fraccing to keep fractures open after releasing the pressure during hydraulic stimulation for the production of unconventional recources such as tight oil and/or gas.

14. Use of Fischer-Tropsch derived wax in a composite proppant.

Fig.1

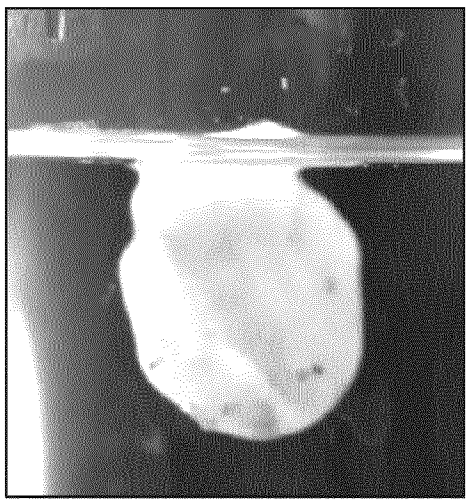


Fig.2

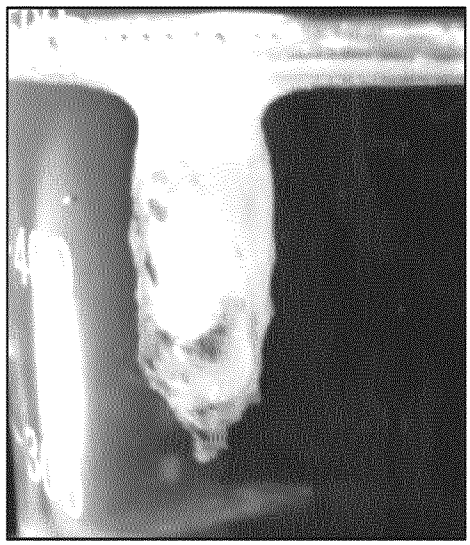
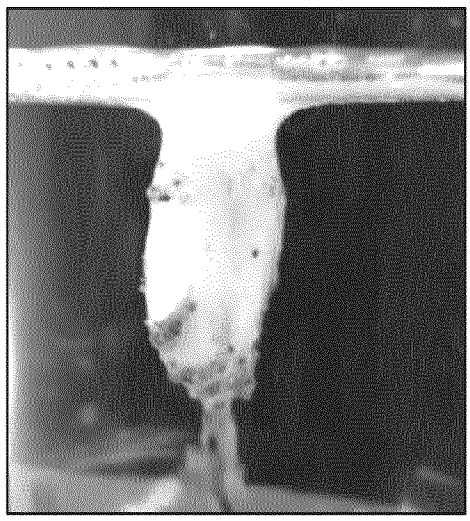


Fig.3



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/082339

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K8/62 C09K8/80
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 E21B

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 875 525 A (MANA MICHAEL L [US]) 24 October 1989 (1989-10-24) column 4, lines 11-18; claims 1,11 column 1, lines 52-57 column 3, lines 44-55; claim 9	1,4,6-8, 11,12
X	US 2011/036577 A1 (BARMATOV EVGENY [GB] ET AL) 17 February 2011 (2011-02-17) paragraph [0065]; claim 22; examples 12,13	1,2,6,7, 12
X	EP 2 899 172 A1 (CARL UNGEWITTER TRINIDAD LAKE ASPHALT GMBH & CO KG [DE]) 29 July 2015 (2015-07-29) claim 1; example 1	1,5,9, 12,14
X	CN 1 124 755 A (LIU QINGSHAN [CN]) 19 June 1996 (1996-06-19) abstract; claims 1,2; example 1	1,6,9, 10,12

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

[X] See patent family annex.

* Special categories of cited documents :

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
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Name and mailing address of the ISA/	Authorized officer
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Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2012/196969 A1 (ADAMS LAWTON [US] ET AL) 2 August 2012 (2012-08-02) paragraphs [0030], [0091] - [0093]; claim 1	1-3,6,9, 12
X	US 3 173 484 A (HUITT JIMMIE L ET AL) 16 March 1965 (1965-03-16) column 3, line 67 - column 4, line 5; claims 1,2 column 4, line 46 - column 5, line 10; table 1 column 3, lines 18-36	13
A	US 7 178 596 B2 (BLAUCH MATTHEW E [US] ET AL) 20 February 2007 (2007-02-20) column 1, lines 60-66	13
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A	US 2006/113078 A1 (NGUYEN PHILIP D [US] ET AL) 1 June 2006 (2006-06-01) paragraphs [0026] - [0028], [0031], [0032], [0035], [0052], [0057], [0064], [0068], [0069]; claims 1,16,21; examples 3,4	1-14

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2016/082339

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