Abstract: A proppant particle 1 comprises a proppant core 2 and a resin coating 3, and the coating 3 comprises an oligonucleotide-based tracer. A method of making a proppant 1 comprises: providing a proppant core 2; and forming a resin coating 3 on the proppant core 2, and the method comprises providing an oligonucleotide-based tracer on the proppant. A method of manufacturing traced proppant comprises: generating an oligonucleotide sequence of between 60 and 90 bases; checking that the sequence is unique; checking that the melting temperature is 70°C or above; synthesising the sequence to form a tracer; and applying the tracer to proppant particles destined for a first production region.
CROSS-REFERENCE TO RELATED APPLICATION

This application claims the benefit of UK Application No. 1410723.9 filed 16 June 2014.

BACKGROUND OF THE INVENTION

The present invention relates to proppants, and in particular to proppants which include a tracer, the tracer comprising an oligonucleotide-based sequence, e.g., a DNA sequence. It also relates to methods of making such a proppant and to methods of monitoring well production using the proppant and tracer.

Proppants are small particles of solid material, typically treated sand or man-made ceramic particles, which are normally less than 1mm in diameter. Proppants are also often referred to as "frac sand" or "propping agents". They are used during a fracturing treatment ("fracking") to prop open cracks that are formed by the hydraulic pressure of the fracturing fluid ("fracking fluid") fracturing the rock. In this way, after the injection pressure of the fracturing treatment is released, the proppants can hold open these passageways and so be used to aid production of the oil and gas trapped within the subterranean formations.

Proppants generally come in three forms: graded sand particles, resin coated sand and man-made ceramic particles (e.g., sintered bauxite or quartz, etc.) which may also be resin coated. The advantage of sand is that it is inexpensive; however it suffers from lower strength compared to man-made ceramic particles, leading to the particles becoming crushed in use. The natural spread of particle size in sand can also reduce permeability to the oil and gas (production fluid) released from the formation. Sintered ceramic particles, on the other hand, can be much more crush-resistant and can be made to a more uniform size, improving the permeability. However, they are more expensive and can cause high wear in the pumps and lines.

A resin coating may be applied to either sand or the sintered ceramic particles (which form the proppant core), and this may serve several functions. As well as improving strength, the resin coating can be used to fuse particles together when certain levels of pressure and temperature are reached. This causes bridging of the proppant particles which can help to keep them in place within the cracks for longer. Additionally, the resin coating provides a
"pack" which encapsulates the proppant core, such that if the proppant is crushed, the resultant particulates (referred to as "fines") remain enclosed within the resin pack.

It is known to incorporate tracers into proppants to be able to monitor the flow of the production fluids. These are typically in the form of chemical or radioactive tracers. However, the use of such tracers, particularly radioactive tracers, is considered undesirable in view of environmental concerns, such as the risk of the radioactive traced fracturing fluid contaminating water sources.

It is also known to use DNA tracers for tracing fluid pumped into or extracted from oil wells. WO-A-20 14/005031 of BaseTrace, LLC, for example, describes using DNA tracers to label wells in order establish liability in the event that there is an escape of fracturing fluid into a water course. In this document the DNA tracer, which has a hairpin structure with a pair of dangling ends, is added as a liquid into the fracturing fluid. Each well can be given a unique tracer to identify the source of any contamination.

BRIEF SUMMARY OF THE INVENTION

Viewed from a first aspect, the present invention can be seen to provide a proppant particle comprising: a proppant core; and a resin coating, wherein the coating comprises an oligonucleotide-based tracer.

In this way the tracer may be encapsulated in resin which is serving additional benefits in terms of particle strength, encapsulation of fines, or bridging.

An oligonucleotide-based tracer provides many advantages over existing tracers. For example, it may be selected so that it is not harmful to the environment in the event that there is an escape of the fracturing fluid into an aquifer or other water source. It can be chemically synthesized and checked against records to ensure that it presents a nucleotide sequence which would not usually be present in the well environment, or more preferably, is not present in nature at all. The use of nucleotide sequences, and in particular DNA sequences, to provide the set of unique codes for the tracers also offers the possibility of almost unlimited codes for the tracer. A DNA traced particle is also going to require fewer handling considerations compared to the prior art radio-active tracers or the like.
An additional layer or layers of resin may be provided to seal in the tracer. In this way, the additional resin layer can help to protect the oligonucleotide-based tracer from the temperatures and harmful chemical environment within the well.

Two or more different oligonucleotide-based tracers may be provided in the proppant.

Viewed from a second aspect, the present invention can be seen to provide a method of making a proppant comprising: providing a proppant core; and forming a resin coating on the proppant core, wherein the method comprises adding an oligonucleotide-based tracer to the coating.

The core of the proppant, for example, may comprise a crystalline silica particle in the form of quartz, which may make up over 95wt% of the particle. A polymer coating, for example comprising phenol-formaldehyde resin may make up the remainder, typically less than 5wt%, and this may be applied to the core as one layer or as two layers. Clearly additional resin layers may be added as desired.

The oligonucleotide-based tracer may be added to the coating in a number of ways. For example, the oligonucleotide-based tracer may be mixed into the resin prior to forming a layer on the core from that resin. The oligonucleotide-based tracer may be incorporated into a single layer. Where more than one layer is provided, the oligonucleotide-based tracer may be incorporated into an outer layer, or an inner layer, or both.

Alternatively, a first layer of resin may be formed (without any oligonucleotide-based tracer), and the oligonucleotide-based tracer may then be deposited (by spraying, for example) onto the surface of the resin. A further layer of resin (which does not include any oligonucleotide-based tracer) may then be deposited to encapsulate the oligonucleotide-based tracer. Such a second layer may not be necessary, however.

Two or more different oligonucleotide-based tracers may be provided in the proppant.

Viewed from a third aspect, the present invention can be seen to provide a method of monitoring production levels in a plurality of production regions comprising: introducing a first proppant into a first production region, the first proppant being labelled with a first tracer; introducing a second proppant into a second production region, the second proppant being labelled with a second tracer; collecting a sample of production fluid extracted from a third region downstream of the first and second regions; and analysing the sample to determine
relative proportions of the first and second tracer, wherein the first and second tracer each comprise an oligonucleotide-based tracer which is different to the other.

Either through erosion or through a leaching mechanism, the oligonucleotide-based tracer may be allowed to enter the production fluid (for example, hydrocarbon oil or gas) thereby providing a label in the fluid to indicate the source of the production. The proppants, which are lodged in the fissures, may release the site-specific tracers from known regions for up to several years, up to several months, or alternatively up to several weeks.

Two or more different oligonucleotide-based tracers may be provided in the proppant.

In embodiments where the oligonucleotide-based tracer is covered by a layer of resin which does not include any of the oligonucleotide-based tracer, the release of the tracer may be delayed, compared to the embodiments in which the oligonucleotide-based tracer is provided on the surface of the proppant (either incorporated into an outer layer, or on the outer surface of the proppant).

In addition to, or as an alternative to the leaching of the oligonucleotide-based tracer from the proppant, the proppant particles with the oligonucleotide-based tracer may break free of a fracture in a subterranean formation, and the flow of such traced particles may also be used to monitor the rate of production.

This tracer information can assist with well-to-well tracing as well as the optimisation of the production fluid output. For example, if it is discovered that the majority of the production fluid is produced from a first production region, then efforts can be focused on this region.

The following considerations regarding the choice of the oligonucleotide-based tracer apply equally to each of the first to third aspects of the present invention.

 Preferably the oligonucleotide-based tracer comprises a DNA sequence. It may comprise single stranded DNA sequence (ssDNA) or a double stranded DNA sequence (dsDNA).

Thus the tracer may be added to the proppant as a single stranded DNA that will spontaneously form a secondary structure with itself as predicted, or it may be added as a mixture of two complementary DNA strands that will spontaneously form a DNA double helix.
An important consideration for the selection of the oligonucleotide sequence is that the synthesis of the sequence should be accurate. If there are too many errors in a sample which has been synthesised, then the certainty of knowing that a specific tracer has been identified may be put into doubt. While it is possible to purify samples which have achieved a low yield, this can add to the costs of production. In general, the longer a sequence, the lower the accuracy of synthesis of the sequence. For example, at base pair lengths of 100, samples of synthesised DNA in certain situations might only achieve a yield of 20% or so. This accuracy can be improved significantly by choosing sequences which are 80 base pairs or fewer. This improves the reliability of the tracer as well as making it much cheaper to produce.

Thus, preferably the oligonucleotide-based tracer comprises fewer than 100 nucleobases (nitrogenous bases, referred to subsequently as "bases") more preferably 90 or fewer bases, and most preferably 80 or fewer bases. This enables efficient real-time PCR to be achieved, reduces inaccuracies in the synthesis and detection and provides a more cost-effective solution.

Though shorter sequences may be synthesized more accurately, they are disadvantageous because of the reduced stability of the oligonucleotide sequence at high temperatures.

Generally, increased sequence length will lead to increased stability but it can come at the expense of accuracy in the synthesis of the sequence and in the identification. Also a longer sequence can take longer to analyse using identification techniques such as polymerase chain reaction (PCR), and in particular real-time PCR. A balance therefore needs to be struck between the stability of the sequence, the accuracy of the synthesized tracer, and the ability to perform real-time monitoring of the traced production fluids.

The DNA sequence may comprise three nucleotide sequences that are selected as binding sites for each of a forward primer, a probe and a reverse primer, as is standard practice for polymerase chain reaction (PCR). The primers and probe are preferably selected to give the most probable success for real-time PCR. The DNA sequence should also be relatively stable, and/or compatible with the resin-based coating of the proppant.

The real-time PCR assay also needs to be accurate and for this primer and probe lengths of 16 to 25 base pairs are generally required. A minimum sequence length comprising binding sites for each of a forward primer, a probe and a reverse primer might be between 50 to 70 base pairs. Preferably the sequence chosen is close to this limit, in order to achieve good
accuracy during synthesis, good reliability during amplification, while at the same time keeping the production costs to a minimum.

In preferred embodiments, the sequence may additionally include a set of two, three, four or more bases or base pairs at the ends of the sequence to provide nuclease precautions.

Thus, in preferred embodiments, the total sequence length may be the length of the binding sites for the primers and probe plus the nuclease precautions (e.g., up to 10 extra bases or base pairs) plus up to fifteen further bases or base pairs, more preferably less than ten further bases or base pairs. In other words, preferably the sequence includes less than 20 bases or base pairs beyond those selected for the binding sites for the primers and probe.

Thus, preferably the oligonucleotide-based tracer comprises a strand of 50 or more bases, more preferably greater than 60 bases and most preferably 70 or more bases of nucleotides.

The probe oligonucleotide sequence may be labelled with a reporter and a quencher at the ends of the probe sequence. The reporter might be, for example, a chemical which fluoresces and the quencher may quench that fluorescence. During the polymerase reaction, the probe may become separated from the quencher to allow the fluorescence intensity to significantly increase. The brightness of this fluorescence can be used to monitor the progress of the real-time PCR amplification.

Stability of the oligonucleotide sequence may be quantified in terms of the melting temperature. Melting is when the double stranded molecules separate into their respective single stranded molecules, and the melting temperature is defined as the temperature at which 50% of the double stranded molecules are converted to single stranded molecules.

The resin coating stage of the production process takes place at temperatures which will exceed the melting temperature of the oligonucleotide sequence, for example, temperatures of about 150°C or more. Temperatures in the well could be higher still (for example, 300°C or more). In order to provide the sequence with greater stability to resist such high temperatures, sequences which have higher melting temperatures are generally selected.

Accordingly, preferably the melting temperature of the sequence is at least 60°C, more preferably greater than 65°C, and yet more preferably greater than 70°C.
Preferably a nucleotide sequence is chosen which has a melting temperature which also suits a real-time PCR assay. For example, preferably it has a melting temperature of between 70 and 90°C. While the melting temperature may be towards the top end of the real-time PCR assay range, the extra stability this provides is considered advantageous.

More preferably the melting temperature is above 75°C and less than 85°C. In one example it was 75°C and in another it was 81°C.

However, rather than looking to longer base sequences to achieve these higher melting temperatures, which would reduce the accuracy of the synthesis, preferably other aspects of the sequence are optimised and the oligonucleotide sequence is kept below one hundred base pairs in length, more preferably than 90 base pairs, still more preferably less than 85 base pairs, and yet more preferably less than 80 base pairs in length.

In particular, higher melting temperatures may be achieved by providing a high GC content in the sequence. It is known that higher GC content, because of the additional hydrogen bond, can lead to more stable DNA structures. Thus, preferably the GC content is higher than 60% as this would be expected to have greater temperature resistance.

Efficient real-time PCR would be expected to be seen for 50-60% GC content.

Alternatively the oligonucleotide-based tracer may have a GC content of less than 50%, since this may offer advantages in terms of its compatibility with the resin-based coating.

The oligonucleotide sequence’s stability can also be gauged in terms of the free energy or dG value. Preferably the sequence has a negative free energy value (dG) of greater than -5 kcal/mol (e.g., -6 kcal/mol or greater). Preferably the free energy is as low as possible without the formation of significant additional secondary structures.

BRIEF DESCRIPTION OF THE DRAWINGS

Certain preferred embodiments of the present invention will now be described in greater detail by way of example only and with reference to the accompanying drawings in which:

Figure 1 shows a schematic cross-section of a preferred embodiment of a proppant particle having a core and resin coating;

Figure 2 shows a further embodiment where the proppant particle comprises a core, a first layer of resin and a second layer of resin to make up the resin coating;
Figure 3 shows a flow diagram of a preferred method used during the manufacture of a proppant particle;
Figure 4 shows a representation of the structure for a first example DNA sequence; and
Figure 5 shows a representation of the structure for a second example DNA sequence.

DETAILED DESCRIPTION OF THE INVENTION

Figure 1 shows a schematic cross-section of a proppant particle 1 having a core 2 and resin coating 3. Figure 2 shows a further embodiment where the proppant particle comprises a core 2, a first resin layer 3 and a second resin layer 4 making up the resin coating.

In Figure 1, the oligonucleotide-based tracer is incorporated into the resin coating. In Figure 2, the oligonucleotide-based tracer may be incorporated into the first resin layer 3, and/or the second resin layer 4. In addition or alternatively, the oligonucleotide-based tracer may be deposited between the first resin layer 3 and the second resin layer 4.

Figure 3 shows a flow diagram of a preferred method used during the manufacture of a proppant particle. The method comprises the steps of:

- Generating an oligonucleotide sequence having binding sites for a forward primer, probe and reverse primer, the sequence comprising preferably between 60 and 90 bases and having a GC content of between 40 and 70% (step 301).

- Checking that the sequence is unique and not found in nature, or at least is not normally present in an oil reservoir, and discarding the sequence if it occurs naturally and/or is present in an oil reservoir (step 302).

- Determining the melting temperature of the sequence, and discarding the sequence if the melting temperature is below 70 °C (step 303).

- Determining the dG of the sequence, and discarding the sequence if the dG has a negative value of greater than 5 kcal/mol (step 304).

- Synthesizing the sequence (step 305).
• Applying the sequence to proppant particles (step 306).

EXAMPLE 1

Figure 4 shows a representation of the structure for a first example DNA sequence, which is a preferred embodiment. The DNA sequence is preferably as follows:

[Seq. ID 1]
TGAAAACCAGTTGGTGTAAAGGAATTCTTCTGCTCCiAGGiACiAiACiACiACGLAGTGAAAGT TACATGTTCGTTGGTCTCC

or an identity of 95% or more thereto, for example 96%, 97%, 98% or 99%.

The group of nucleotides highlighted in bold in the example sequence are the binding sites for the forward and reverse primers respectively; the central group of nucleotides highlighted in bold and italics is the binding site for the probe; and the 2x four base pair segments at the 5’ and 3’ ends are the nuclease precautions.

As shown in Figure 4, this structure is expected to have a secondary structure including up to three hairpins.

This example sequence has the following properties:

- GC-content of 45%
- Free energy: \( \Delta G = -6 \text{ kcal/mol} \)
- Melting temperature: \( T_m = 75^\circ C \)
- Sequence length: 78 base pairs
- Sequence is not present in nature

In this example, the forward primer was selected to be between 21 and 25 base pairs long, for example 23 base pairs.

Preferably the binding site for the forward primer comprises nucleotides 5 to 27 of seq. ID 1, i.e. AACCAGTTGGTGTAAAGGAATGC (seq. ID 5), or a sequence with greater than 95% identity thereto.
The reverse primer was selected to be between 22 and 26 base pairs long, for example 24 base pairs.

Preferably the binding site for the reverse primer comprises nucleotides 51 to 74 of seq. ID 1, i.e. TGAAAGTTACATGTTGTTGGGT (seq. ID 6), or a sequence with greater than 95% identity thereto.

The binding site for the probe may be between 16 and 20 base pairs long, for example 18 base pairs.

Preferably the binding site for the probe comprises nucleotides 32 to 49 of seq. ID 1, i.e. TCCAGGACAACACACGTA (seq. ID 7), or a sequence with greater than 95% identity thereto.

Preferably the sequence includes an initial four base pair sequence of TGAA closest to the 5’ end of the tracer sequence and preferably a final four base pair sequence of CTCC at the 3’ end of the tracer sequence.

Preferably the sequence TCTG appears between the binding site for the forward primer and the binding site for the probe.

Preferably a G nucleotide is positioned between the binding site for the probe and the binding site for the reverse primer.

Thus in this first example, there are just five additional bases on either side of the binding site of the probe between the binding sites for the forward and reverse primers.

A complimentary sequence could comprise:

[Seq. ID 2]

5-
GGAGAACCACGAACTGAACTTTTCACTACGTTGTTGTCCGCTGGACGACGACTCTCT
TAACACCAACTGGTTTCA-3.
EXAMPLE 2

Figure 5 shows a representation of the structure for a second example DNA sequence, which is a preferred embodiment. The DNA sequence is preferably as follows:

[Seq. ID 3]

TGGCGCGCGTGCGCCTTAATC7CCGCTCCGAC7,AGGGTGCTGGCTGCATGCTACGT

TGACACACCCACG

or an identity of 95% or more thereto, for example 96%, 97%, 98% or 99%.

The group of nucleotides highlighted in bold in the example sequence are the binding sites for the forward and reverse primers respectively; the central group of nucleotides highlighted in bold and italics is the binding site for the probe; and the 2x four base pair segments at the 5' and 3' ends are the nuclease precautions.

Figure 5 illustrates the structure for this example. It is expected to form up to three hairpins.

This example sequence has the following properties:

- GC-content of 63%
- Free energy: dG= -10.46 kcal/mol
- Melting temperature: Tm=81°C
- Sequence length: 70 base pairs
- Sequence not present in nature

The forward primer may be between 14 and 18 base pairs long, for example 16 base pairs.

Preferably the binding site for the forward primer comprises nucleotides 5 to 20 of seq. ID 3, i.e. GCGCGTGCCTTAAT (seq. ID 8), or a sequence with greater than 95% identity thereto.

The reverse primer may be between 19 and 23 base pairs long, for example 21 base pairs.

Preferably the binding site for the reverse primer comprises nucleotides 46 to 66 of seq. ID 3, i.e. TGCATGCTACGTGACACACC (seq. ID 9), or a sequence with greater than 95% identity thereto.
The probe may be between 16 and 20 base pairs long, for example 18 base pairs.

Preferably the binding site for the probe comprises nucleotides 22 to 37 of seq. ID 3, i.e. TCCGCTCCATGCTAGG (seq. ID 10), or a sequence with greater than 95% identity thereto.

Preferably the sequence includes an initial four base pair sequence of TGGC closest to the 5' end of the tracer sequence and preferably a final four base pair sequence of CACG at the 3' end of the tracer sequence.

Preferably a C nucleotide appears between the binding site for the forward primer and the binding site for the probe.

Preferably a sequence comprising GGTCTGGC is positioned between the binding site for the probe and the binding site for the reverse primer.

Thus in this first example, there are just nine additional bases on either side of the binding site of the probe between the binding sites for the forward and reverse primers.

A complimentary sequence could comprise

[Seq. ID 4]

5-
CGTGGGTGTGTCACGCATGCAACCGAGCCACCCCCTAGCATGGGAGGAGGATTAAGG
CGACCGCGCCCA-3.

The following is a set of clauses that may or may not form the basis of the appended claims but which may also provide basis for future divisional applications:

1. A proppant particle for an oil or gas well, wherein the proppant comprises an oligonucleotide-based tracer, for example a tracer as described above.

2. A proppant as recited in clause 1, further comprising a resin-based coating.

3. A proppant as recited in clause 2, wherein the oligonucleotide-based tracer is provided in the resin-based coating.

4. A proppant as recited in any preceding clause, wherein the oligonucleotide-based tracer comprises a DNA sequence.
CLAIMS

1. A proppant particle comprising:
   a proppant core; and
   a resin coating,
wherein the coating comprises an oligonucleotide-based tracer.

2. A proppant particle according to claim 1, wherein the oligonucleotide-based tracer is provided within the resin of the resin coating.

3. A proppant particle according to claim 1, wherein the oligonucleotide-based tracer is provided beneath a resin layer of the resin coating.

4. A proppant particle according to claim 1, wherein the oligonucleotide-based tracer is deposited on the proppant core, or deposited on a resin layer of the resin coating.

5. A proppant particle according to any preceding claim, wherein the oligonucleotide-based tracer has been chemically synthesized and comprises a unique sequence.

6. A proppant particle according to any preceding claim, wherein the oligonucleotide-based tracer comprises single stranded or double stranded DNA.

7. A proppant particle according to any preceding claim wherein the GC content of the sequence for the oligonucleotide-based tracer is greater than 60%.

8. A proppant particle according to any preceding claim, wherein the oligonucleotide-based tracer comprises a strand of less than 90 bases, and preferably less than 80 bases.

9. A proppant particle according to any preceding claim, wherein the oligonucleotide-based tracer comprises a strand of more than 50 bases, and preferably more than 60 bases.

10. A proppant particle according to any preceding claim, wherein the oligonucleotide-based tracer comprises separate sequences of between 16 and 25 bases of the oligonucleotide sequence to provide binding sites for each of a forward primer, a probe and a reverse primer, preferably wherein the probe binding site is separated from each of the primer binding sites by less than 10 bases.
11. A proppant particle according to any preceding claim, wherein the oligonucleotide sequence of the oligonucleotide-based tracer has a melting temperature of 70°C or more.

12. A proppant particle according to any preceding claim, wherein the oligonucleotide sequence of the oligonucleotide-based tracer has a negative free energy value (dG) of greater than -5 kcal/mol.

13. A proppant particle according to any preceding claim, wherein the proppant core comprises a sintered ceramic particle.

14. A proppant particle according to any of claims 1 to 12, wherein the proppant core comprises a sand particle.

15. A proppant particle according to any preceding claim, wherein the oligonucleotide-based tracer is able to leach from the resin coating over time when immersed in production fluids.

16. A proppant particle according to any preceding claim, wherein the resin coating is able to erode over time to release the oligonucleotide-based tracer.

17. A proppant particle according to any preceding claim, wherein the coating comprises two or more different oligonucleotide-based tracers.

18. A method of making a proppant comprising:

   providing a proppant core; and

   forming a resin coating on the proppant core,

wherein the method comprises providing an oligonucleotide-based tracer on the proppant.

19. A method according to claim 18, wherein the oligonucleotide-based tracer is added to the resin prior to forming the resin coating on the proppant core, so as to provide the oligonucleotide-based tracer within the resin of the resin coating.

20. A method according to claim 18, wherein the oligonucleotide-based tracer is provided beneath a resin layer of the resin coating.

21. A method according to claim 18, wherein the oligonucleotide-based tracer is deposited on top of a resin layer of the resin coating, or is deposited on top of the proppant core.
22. A method according to any of claims 18 to 21, wherein the method includes the step of chemically synthesizing the oligonucleotide-based tracer, wherein the tracer comprises a unique sequence.

23. A method according to any of claims 18 to 22, wherein the oligonucleotide-based tracer is formed from single stranded or double stranded DNA.

24. A method according to any of claims 18 to 23, wherein the method includes the step of synthesizing a sequence of bases to form the oligonucleotide-based tracer, preferably wherein the sequence contains less than 90 bases, and more preferably less than 80 bases.

25. A method according to claim 24, wherein the synthesizing of the sequence comprises assembling more than 50 bases, and preferably more than 60 bases.

26. A method according to claim 24 or 25, wherein the synthesizing of the sequence comprises providing a sequence with a GC content of greater than 60%.

27. A method according to claim 24, 25 or 26, wherein the oligonucleotide-based tracer comprises separated sequences of between 16 and 25 bases of the oligonucleotide sequence to provide binding sites for each of a forward primer, a probe and a reverse primer, preferably wherein the binding site for the probe is separated from the binding site for each of the primers by less than 10 bases.

28. A method according to any of claims 24 to 27, wherein the synthesizing of the sequence comprises providing a sequence with a melting temperature of 70°C or more.

29. A method according to any of claims 24 to 28, wherein the synthesizing of the sequence comprises providing a sequence with a negative free energy value (dG) of greater than -5 kcal/mol.

30. A method according to any of claims 18 to 29, comprising providing two or more different oligonucleotide-based tracers on the proppant.

31. A method of monitoring production levels in a plurality of production regions comprising: introducing a first proppant into a first production region, the first proppant being labelled with a first tracer;
introducing a second proppant into a second production region, the second proppant being labelled with a second tracer;
collecting a sample of production fluid extracted a region downstream of the first and second regions; and
analysing the sample to determine relative proportions of the first and second tracer, wherein the first and second tracer each comprise an oligonucleotide-based tracer, each different to the other.

32. A method according to claim 31, wherein the analysing comprises a real-time PCR assay.

33. A method of manufacturing traced proppant comprising:
generating an oligonucleotide sequence of between 60 and 90 bases;
checking that the sequence is unique;
checking that the melting temperature is 70°C or above;
synthesising the sequence to form a tracer; and
applying the tracer to proppant particles destined for a first production region.

34. A method according to claim 33, wherein the method further comprises:
checking the sequence has a negative free energy value (dG) of greater than -5 kcal/mol.

35. A method according to claim 33 or 34, wherein the method further comprises:
checking the sequence has a GC content of greater than 60%.

36. A method according to claim 33, 34 or 35, wherein the oligonucleotide sequence is of between 65 and 85 bases in the generating step, more preferably 80 or less bases.

37. A method according to any of claims 33 to 36, wherein the generating step includes selecting three separated sequences of between 16 to 25 bases of the oligonucleotide sequence to provide binding sites for a forward primer, a probe and a reverse primer respectively for a real-time PCR assay.

38. A method according to any of claims 33 to 37, wherein the method further comprises:
generating a second oligonucleotide sequence of between 60 and 90 bases;
checking that the sequence is unique;
checking that the melting temperature is 70°C or above;
synthesising the sequence to form a second tracer; and
applying the second tracer to proppant particles destined for a second production region.

39. A proppant particle as claimed in any of claims 1 to 17, wherein the oligonucleotide-based tracer comprises an oligonucleotide molecule as recited in Seq. ID 1, Seq. ID 2, Seq. ID 3 and/or Seq. ID 4.

40. A method of making a proppant as claimed in any of claims 18 to 30, wherein the oligonucleotide-based tracer comprises an oligonucleotide molecule as recited in Seq. ID 1, Seq. ID 2, Seq. ID 3 and/or Seq. ID 4.

41. A method of monitoring production levels in a plurality of production regions as claimed in claim 31 or 32, wherein the oligonucleotide-based tracer comprises an oligonucleotide molecule as recited in Seq. ID 1, Seq. ID 2, Seq. ID 3 and/or Seq. ID 4.

42. A method of manufacturing traced proppant as claimed in any of claims 33 to 38, wherein the oligonucleotide-based tracer comprises an oligonucleotide molecule as recited in Seq. ID 1, Seq. ID 2, Seq. ID 3 and/or Seq. ID 4.
Generate an oligonucleotide sequence having binding sites for a forward primer, probe and reverse primer, the sequence comprising between 60 and 90 bases and having a GC content of between 40 and 70%.

Check that the sequence is unique and not found in nature, or at least is not normally present in an oil reservoir. Discard the sequence if it occurs naturally and/or is present in an oil reservoir.

Determine the melting temperature of the sequence. Discard the sequence if the melting temperature is below 70 °C.

Determine the dG of the sequence. Discard the sequence if the dG has a value above -5 kcal/mol.

Synthesize the sequence.

Apply the sequence to proppant particles.

Fig. 3
INTERNATIONAL SEARCH REPORT

INTERNATIONAL APPLICATION No
PCT/EP2015/063447

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K8/80 E21B47/10 C12Q1/68
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09K E21B C12Q

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

<table>
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<tr>
<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<tr>
<td>X</td>
<td>GB 2 489 714 A (TRACESA LTD [GB]) 10 October 2012 (2012-10-10) claims page 1 - page 6</td>
<td>1-38</td>
</tr>
<tr>
<td>X,P</td>
<td>WO 2014/144464 A2 (CARB0 CERAMICS INC [US]) 18 September 2014 (2014-09-18) claims 1, 8-10, 31-37</td>
<td>1-6, 13, 18-23, 31</td>
</tr>
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Further documents are listed in the continuation of Box C. See patent family annex.

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