Methods and apparatus for using a fluid within a subterranean formation including forming a fluid comprising an oil-soluble resin acid and an organosilicon compound and introducing the fluid to the formation, wherein the relative permeability of the formation increases, and wherein the production of water is reduced more than if no fluid was introduced to the formation. Methods and apparatus for reducing water production within a subterranean formation including forming a fluid comprising an oil-soluble resin acid and an organosilicon compound and introducing the fluid to the formation, wherein the production of water is reduced more than if no fluid was introduced to the formation.

Treatment fluid (15 wt% calcium resinate in DPM) (middle top) diluted with either oil (left) or brine (right).
Figure 1. Treatment fluid (15 wt% calcium resinate in DPM) (middle top) diluted with either oil (left) or brine (right).
SELECTIVE FLUID WITH ANCHORING AGENT FOR WATER CONTROL

FIELD

[0001] Embodiments of the invention relate to fluids for use in oilfield applications for subterranean formations. More particularly, embodiments of the invention relate to methods and compositions for enhanced water control.

BACKGROUND

[0002] The statements in this section merely provide background information related to the present disclosure and may not constitute prior art.

[0003] It has been increasingly challenging to develop a suitable solution to reduce water production without reducing oil and gas production, especially for mature reservoirs. Worldwide, on average, water production is three times as much as the oil production, the impact is significant on the operating cost. Water production also limits the oil production substantially from the oil-rich zones in the reservoir. In the treatment of oil and gas wells including hydraulic fracturing treatments, viscosifiers such as polymer systems are commonly used in carrier fluids. A fluid loss additive is often used with such carrier fluids to inhibit excessive fluid loss from the carrier fluid. The fluid loss additive helps form a filter cake on the surface of the formation.

[0004] In a fracturing operation, the fluid efficiency is directly related to the amount of fluid loss. High fluid efficiency minimizes the amount of fluid needed to generate a given length of fracture and limits the amount of filter cake that is generated. Fluid loss additives can be used to decrease fluid loss and increase fluid efficiency. The filter cake formed by the fluid loss additives reduces permeability at the fluid-rock interface. Conventional fluid loss additives usually contain fine particles such as mica or silica flour with a broad distribution of particle sizes designed to effectively plug the pore throats of the rock matrix. Starches or other polymers can be added to help fill in the spaces and further reduce the flow.

[0005] Often, fluid loss additives are injected into a fracture with the initial pad volume used to initiate hydraulic fracturing. After the pad is injected, proppant slurry which may also contain a fluid loss additive is pumped into the fracture in various stages depending on job design. The proppant is designed to hold the fracture open and allow reservoir fluid to flow through the proppant pack. The proppant slurry generally includes a viscous carrier fluid to keep the proppant from prematurely dropping out of the slurry. After the proppant has been placed in the fracture, the pressure is released and the fracture closes on the proppant. After the treatment, it is necessary to remove or break both the viscous carrier in the carrier fluid and the filter cake (that may contain viscous carrier polymer) so that reservoir fluids can thereafter flow into the fracture and through the proppant pack to the wellbore and the production string.

[0006] Fracture clean-up issues are a problem. Although other systems such as viscoelastic surfactants, gelled oil, slick water, etc. are used, the majority of fluids used to create the fracture and carry the proppants are polymer-based. In most reservoirs with lower permeability, the polymer concentrates as carrier fluid leaks off during the fracturing process. The concentrated polymer hinders fluid flow in the fracture and often results in underperforming fractures. Typical remedies include use of breakers, including encapsulated breakers that allow a significant increase of the breaker loading. The breaker is added to the fluid/slurry and is intended to reduce the viscosity of the polymer-based carrier fluid and facilitate fracture clean-up. Despite high breaker loading, in such breaker systems the retained permeability of the proppant pack is still only a fraction of the initial permeability. In certain cases, the encapsulated breakers may have a large particle size (e.g. 1 mm) that prevent the solid breaker material from entering small natural fractures of the formation so that the polymer that enters these small fractures remains unbroken. And soluble breaker materials are only used in limited concentrations as the base fluid rheology must be maintained for some time. If too much soluble breaker is used, the viscosity of the fluid may drop prematurely. Soluble breaker materials may also tend to leak off into the formation, where they are no longer effective.

[0007] Historically, the industry has used a method for selectively reducing the water production from a hydrocarbon reservoir. The treatment fluid is comprised of 5-40 weight percent of a water-immiscible dissolved compound based on a cyclic carboxylic acid such as abietic acid and capable of forming a precipitate that is substantially soluble in hydrocarbon and substantially insoluble in water. This system, however, does not impart long-lasting effectiveness in higher permeability rocks.

Another historical approach uses a chemical treatment that selectively reduces water production. Such treatments employ polymeric relative permeability modifier and an organosilicon compound. Although the relative permeability modifiers are effective in reducing the water, they also reduce oil production to some extent.

[0008] Embodiments of the present invention provide further approaches and methods to improve the clean-up of hydraulic fracturing treatments.

SUMMARY

[0009] Embodiments of the invention provide methods and apparatus for using a fluid within a subterranean formation including forming a fluid comprising an oil-soluble resin acid and an organosilicon compound and introducing the fluid to the formation, wherein the relative permeability of the formation increases, and wherein the production of water is reduced more than if no fluid was introduced to the formation. Embodiments of the invention provide methods and apparatus for reducing water production within a subterranean formation including forming a fluid comprising an oil-soluble resin acid and an organosilicon compound and introducing the fluid to the formation, wherein the production of water is reduced more than if no fluid was introduced to the formation.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] FIG. 1 is a photograph series comparing treatment fluid (15 wt % calcium resinate) (middle top) diluted with either oil (left) or brine (right).

DETAILED DESCRIPTION

[0011] The procedural techniques for pumping fluids down a wellbore to fracture a subterranean formation or to perform other well services treatments are well known. The person that designs such treatments is the person of ordinary skill to whom this disclosure is directed. That person has available
many useful tools to help design and implement the treatments, including computer programs for simulation of treatments.

In the summary of the invention and this description, each numerical value should be read once as modified by the term “about” (unless already expressly so modified), and then read again as not so modified unless otherwise indicated in context. Also, in the summary of the invention and this detailed description, it should be understood that a concentration range listed or described as being useful, suitable, or the like, is intended that any and every concentration within the range, including the end points, is to be considered as having been stated. For example, “a range of from 1 to 10” is to be read as indicating each and every possible number along the continuum between about 1 and about 10. Thus, even if specific data points within the range, or even no data points within the range, are explicitly identified or refer to only a few specific numbers, it is to be understood that inventors appreciate and understand that any and all data points within the range are to be considered to have been specified, and that inventors have disclosed and enabled the entire range and all points within the range. All percents, parts, and ratios herein are by weight unless specifically noted otherwise.

A selective fluid system based on a waxy solid resin soluble in oil but insoluble in brine with organosilica for water control problems is needed. Embodiments of the invention provide a fluid that effectively reduces the water flow for an extended period of time without causing any damage to the oil zone by blocking the water zone selectively.

The fluid system as a solution for water control contains two different components: 1) oil-soluble, water-insoluble resin acids (example: calcium salt of abietic acid, commercially known as DERTOCAL 140™ which is commercially available from DRT DAX of Cedex, France) and 2) an organosilica compound, such as an organosilane halide or an organosilane alkoxide. The waxy solid will selectively precipitate in the water zone causing damage to the water zone and the organosilicon compound will act as an anchoring agent of the precipitate by anchoring to the formation surface or surfaces for long-term efficacy. The acids are soluble in mutual solvents and oil. The reaction is faster if the organosilicone compound is soluble in the same solvents. Some embodiments will benefit if the chemicals are in mutual solvent or oil. Some embodiments will benefit if there is a spacer before water/brine is pumped to prevent precipitation in the wellbore. In some embodiments, cleanup can be done with oil easily. Some embodiments of the composition are best for sandstone formation. Temperatures as high as 300 deg F. and pressures as high as 1000 psi have been tested successfully for some embodiments. Embodiments of the invention may benefit a formation when the temperature of the formation is 300 deg F. or lower. Water control processes, formation of water-insoluble plugs, and diversion may benefit from embodiments of the invention.

The selective fluid includes a mixture of a waxy solid or salt of a resin acids, such as (but not limited to) DERTOCAL 140™ and an organosilicon compound. DERTOCAL 140™ is the calcium salt of abietic acid as shown below. Abietic acid is a natural product derived from pine tree resin.

[0016] This resin acid salt is highly soluble in oil and in a mutual solvent (which is miscible with both water and oil), such as dipropylene glycol methylether (DPM, shown below).

Dipropylene glycol methylether (DPM).

[0017] Resin acids and their Na, K, Ca salts that would work with the aforementioned organosilica compounds to form insoluble waxy material as water control agents:

1. The most prevalent resin acids are:
   - Abietic-type acids
   - Abietic acid
   - abiet-7,13-dien-18-oic acid
   - 13-isopropylpodocarpa-7,13-dien-15-oic acid
   - neoabietic acid
   - dehydroabietic acid
   - palustic acid
   - levopimaric acid
   - simplified formula C_{29}H_{49}O_2 or C_{15}H_{25}COOH
   - represents the majority 85-90% of typical tall oil.
   - structurally shown as (CTl_2)_{C_{13}H_{17}}COOH
   - molecular weight 302.

Abietic acid
Pimaric-type acids

Pimaric acid

-continued

[0031] pimaric acid
[0032] pimara-8(14),15-dien-18-oic acid
[0033] isopimaric acids
[0034] simplified formula $C_{20}H_{30}O_2$ or $C_{19}H_{29}COOH$
[0035] structurally represented as $(CH_3)$$_2$$(CH_2)_3$ $C_{15}H_{11}$COOH
[0036] molecular weight 302
[0037] 2. Other long chain (including unsaturated bonds) water-insoluble fatty acids also should work.
[0038] A long-term effect in blocking the water zone requires a strategy by which the waxy, solid precipitate can be retained in the core. For this purpose, an organosilicon compound capable of forming a water soluble silanol by hydrolisis will be particularly useful. The organosilicon compound increases flow resistance and can attach to the resin such as calcium resinate as well as to the mineral surface of the formation. As a result, retention of the calcium resinate precipitate in the formation can be extended significantly producing a much longer water control treatment.
[0039] Additional organosilicon compounds to form products with the resin acids include the following.

1. With organosilanol:

[0040] a) Silanol

R² R³ R⁴ S-OH + R-C-OH $\rightarrow$ R² S-OH $\rightarrow$ R² R³ R⁴

[0041] b) Silanediol

R² R³ R⁴ S-OH + 3 (R-C-OH) $\rightarrow$

[0042] c) Silanetriol

R² R³ R⁴ S-OH + 3 (R-C-OH) $\rightarrow$

2. Other organosilicon compounds that form silanol:

[0043] a) Organosilane halide: These compounds form organosilanol upon hydrolisis with water (this can provide controlled delay in the process to form the desired water control agent). The reaction with acid would then be the same as in scheme L

[0044] b) Silanes: same as in (a)

[0045] c) Alkoxysilanes: same as in (a)

[0046] d) Organosilazane compounds:

R₂Si$\equiv$NH₂ + R-C-OH $\rightarrow$ HN-C-R

Organosilazane

$\&$

R₂Si + NH + R-C-OH $\rightarrow$ N-C-R

Organosilazane

R, R¹, R², R³, R⁴, R⁵ can be alkyl, allyl, ary groups (both aliphatic and aromatic). Cyclic siloxanes and linear chains may be selected for some embodiments. More hydrophobic groups are desirable for plugging water.

[0047] b) Silanediol

R² R³ R⁴ S-OH + 2 (R-C-OH) $\rightarrow$
[0047] e) Any polymeric silicon compounds with a Si—OH, or Si—H, or Si—X (X=halogen), or Si—OR, or Si—OCOR group:

\[ \text{HO-Si-O-Si-O-Si-OH} \]

Silines (Si—C compounds) and silynes (Si-triplebonded to C) are also options that may be selected for some embodiments, but these are less stable compared to the more common Si—C compounds.

**EXAMPLES**

[0048] The following examples are presented to illustrate the preparation and properties of fluid systems, and should not be construed to limit the scope of the invention, unless otherwise expressly indicated in the appended claims. All percentages, concentrations, ratios, parts, etc. are by weight unless otherwise noted or apparent from the context of their use.

[0049] When injected in the oil zone, this fluid causes no damage to the oil permeability. On the other hand, when water or brine is added to the solution, the solid starts precipitating out and forms a yellow flocculent solid, as shown in FIG. 1.

[0050] When a fluid containing 20 or 30 weight percent DERTOCAL 140™ in oil or DPM is injected in a brine saturated core, it damages the brine permeability significantly (up to 80%, from available core data). However, this damage is not long-lasting. With the continuing flow of brine through the core (5-10 pore volume) the precipitate slowly starts to come out of the core resulting in an increase in the brine perm, eventually gaining the initial value. This is observed because the particle size of the waxy solid precipitate is not large enough to block the pores of the formation permanently.

[0051] The particular embodiments disclosed above are illustrative only, as the invention may be modified and practiced in different but equivalent manners apparent to those skilled in the art having the benefit of the teachings herein. Furthermore, no limitations are intended to the details herein shown, other than as described in the claims below. It is therefore evident that the particular embodiments disclosed above may be altered or modified and all such variations are considered within the scope and spirit of the invention. Accordingly, the protection sought herein is as set forth in the claims below.

What is claimed is:

1. A method of using a fluid within a subterranean formation, comprising:
   - forming a fluid comprising an oil-soluble resin acid and an organosilicon compound; and
   - introducing the fluid to the formation;
   - wherein the relative permeability of the formation increases, and
   - wherein the production of water is reduced more than if no fluid was introduced to the formation.

2. The method of claim 1, wherein the organosilica compound anchors the relative permeability modifier to the formation surfaces.

3. The method of claim 1, wherein the oil-soluble resin acid is abietic acid, abiet-7,13-dien-18-oic acid, 13-isopropyloctodocarva-7,13-dien-15-oic acid, neoabietic acid, dehydroabietic acid, palustic acid, levopimaric acid, or a combination thereof.

4. The method of claim 1, wherein the oil-soluble resin acid comprises a calcium salt of abietic acid.

5. The method of claim 1, wherein the oil-soluble resin acid is pimamic acid, pimara-8(14),15-dien-18-oic acid, isopimamic acids, or a combination thereof.

6. The method of claim 1, wherein the organosilicon compound is an organosilane halide or an organosilane alkoxide.

7. The method of claim 1, wherein organosilicon compound is silanol, silanediol, and/or silanetriol.

8. The method of claim 1, wherein the organosilicon compound is organosilane halide, silanes, alkoxylysilanes, organosilazane compounds, and/or polymeric silicon compounds.

9. The method of claim 1, wherein the organosilicon compound comprises silanol.

10. The method of claim 1, wherein a temperature of the formation is 300 deg F. or lower.

11. The method of claim 1, wherein a pressure of the formation is 1000 psi or lower.

12. A method of reducing water production within a subterranean formation, comprising:
   - forming a fluid comprising an oil-soluble resin acid and an organosilicon compound; and
   - introducing the fluid to the formation;
   - wherein the production of water is reduced more than if no fluid was introduced to the formation.

13. The method of claim 12, wherein the oil-soluble resin acid is abietic acid, abiet-7,13-dien-18-oic acid, 13-isopropyloctodocarva-7,13-dien-15-oic acid, neoabietic acid, dehydroabietic acid, palustic acid, levopimaric acid, or a combination thereof.

14. The method of claim 12, wherein the oil-soluble resin acid comprises a calcium salt of abietic acid.

15. The method of claim 12, wherein the oil-soluble resin acid is pimamic acid, pimara-8(14),15-dien-18-oic acid, isopimamic acids, or a combination thereof.

16. The method of claim 12, wherein the organosilicon compound is an organosilane halide or an organosilane alkoxide.

17. The method of claim 12, wherein organosilicon compound is silanol, silanediol, and/or silanetriol.

18. The method of claim 12, wherein the organosilicon compound is organosilane halide, silanes, alkoxylysilanes, organosilazane compounds, and/or polymeric silicon compounds.

19. The method of claim 12, wherein the organosilicon compound comprises silanol.

20. The method of claim 1, wherein a temperature of the formation is 300 deg F. or lower and wherein a pressure of the formation is 1000 psi or lower.

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