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(54) **Title:** COMPOSITIONS AND METHODS FOR REMOVAL OF ASPHALTENES FROM A PORTION OF A WELLBORE OR SUBTERRANEAN FORMATION

(57) **Abstract:** Compositions are provided for removing an organic material, especially asphaltenes, from a portion of a wellbore or a subterranean formation. The composition comprises: (A) water, wherein the water is greater than 50% by volume of the composition; (B) an organic solvent blend that is immiscible with water, wherein the organic solvent comprises: (i) a non-polar organic solvent; and (ii) a polar organic solvent; and (C) a surfactant adapted for forming an emulsion of the organic solvent blend and the water. Methods are provided for removing an organic material from a portion of a wellbore or a subterranean formation. The method comprises the steps of: (A) forming a composition according to the invention; and (B) introducing the composition to the portion from which the organic material is to be removed.

COMPOSITIONS AND METHODS FOR REMOVAL OF ASPHALTENES FROM A PORTION OF A WELLBORE OR SUBTERRANEAN FORMATION

Technical Field

[0001] The invention relates to the problem of removing oil-soluble materials such as asphaltenes from a wellbore or subterranean formation.

Background

[0002] Asphaltenes are a problem in crude oil production in many areas around the world. Asphaltenes may precipitate in the matrix of the formation, in a previously-created fracture in the formation, in the wellbore, or in production tubing. Asphaltenes that precipitate in the formation can result in plugging of the pores in the matrix subterranean formation. Because asphaltenes have a higher affinity to adsorb on surfaces with a similar structure, that is, on surfaces already with adsorbed asphaltenes, clean up should be as thorough as possible.

[0003] Asphaltenes are negligibly soluble in water. Solvents such as toluene and xylene generally dissolve only about 50% of a typical downhole sample of asphaltenes, which has poor solubility parameters in these solvents.

[0004] Asphaltenes are known to possess hereto-elements such as N, S, and O in some asphaltene molecules. Such polar sites contribute to asphaltenes adsorbing on rock surfaces.

[0005] Both van der Waals forces and polar-polar interactions play a role in the adsorption of asphaltenes onto minerals and rock. The presence of water also affects adsorption of asphaltenes. Water-wet rock exhibits considerable reduction in adsorbed asphaltenes, but the polar constitutions of asphaltenes can penetrate the water film and compete for active sites on the rock surface.

[0006] It may not be possible to achieve full desorption of asphaltenes. At best, the rock surface may be changed from oil wet to the range of water wet to intermediate wet. Further, desorption of asphaltenes requires more time than the dissolution of precipitated asphaltenes. However, a full water-wet formation may not be necessary because an intermediate to slightly water-wet formation may be optimum for oil production.

[0007] Clean up with pure toluene may remove the majority of the asphaltenes, but the surface on which the asphaltenes are adsorbed will still be covered with a layer of asphaltenes. This layer is likely to be the most polar and highest molecular weight layer, so the rock surface will still be intermediate wet to oil wet. Further, the wettability of a formation can be changed from water wet to oil wet because the toluene can strip water off the rock surface, as the solubility of water in toluene at 100°C is about 8 times higher than at ambient temperature.

[0008] Surfactants can facilitate the dispersion of an organic phase in water. However, a surfactant will not dissolve asphaltenes in water.

Summary of the Invention

[0009] Compositions are provided for removing an organic material from a portion of a wellbore, wellbore tubular, fracture system, or matrix of a subterranean formation. The compositions comprise: (A) water, wherein the water is greater than 50% by volume of the composition; (B) an organic solvent blend that is immiscible with water, wherein the organic solvent comprises: (i) a non-polar organic solvent; and (ii) a polar organic solvent; and (C) a surfactant adapted for forming an emulsion of the organic solvent blend and the water. Methods are provided for removing an organic material from a portion of a wellbore, wellbore tubular, fracture system, or matrix of a subterranean formation. The methods comprise the steps of: (A) forming a composition according to the invention; and (B) introducing the composition to the portion from which the organic material is to be removed.

Detailed Description

[0010] As used herein, the words "comprise," "has," and "include" and all grammatical variations thereof are each intended to have an open, non-limiting meaning that does not exclude additional elements or steps.

[0011] A purpose of the invention is to remove asphaltene scales and deposits and leave the formation in a water wet condition to help delay the plugging caused by further asphaltene or paraffin deposition.

[0012] Initially, the absorption or dissolution of organic solvent into the asphaltene coating causes the coating to swell and reduces the effective pore diameter, which may cause an increase in pressure required to push fluid through the matrix of a formation. At the point where the organic layer/solvent becomes mobile, the higher viscosity of the mixture can also contribute to an increase in pressure. A pressure effect can, therefore, be anticipated when cleanup commences. As the initial mixture is diluted with more solvent, the viscosity will decrease and the fluid will become more mobile as the cleanup proceeds.

[0013] To remove the strongly-adsorbed asphaltenes layer requires an effective solvent blend. The adsorption/desorption is an equilibrium process that requires a considerable amount of time to reach. But the application of a solvent alone will only partly remove the asphaltenes.

[0014] To improve the desorption process, components such as water that compete with the asphaltenes for polar sites on the surface are expected to be helpful. The wetting behavior of this component improves the wettability of the formation towards water wet. The stability of the water wetting film depends, for example, on the pH, salinity, and composition of the brine solution. A water-based fluid containing an organic solvent blend with good solvency for asphaltenes should provide a long-lasting effect.

[0015] According to this invention, a high proportion of water is used in the composition for removing the asphaltenes. This reduces the amount of solvent needed to remove the scale from the wellbore or formation. This greatly reduces the cost of the treatment relative to prior approaches.

[0016] The composition is preferably applied as a single fluid treatment without need for pre-treatment or post-treatment of other fluids for asphaltenes removal.

[0017] Purposes of making the composition an emulsion include: keeping the formulation together, preventing other emulsions to be formed downhole when the water-containing fluid contacts crude oil, and aiding in the removal of polar components of asphaltenes from a surface, particularly a rock surface.

[0018] The compositions and methods of this invention provide the synergy of the combination of the water, non-polar organic solvent, polar organic co-solvent, and surfactant in the action of dissolving the asphaltene scale as quickly as possible and leaving less asphaltene residue.

[0019] Preferably, the water further comprises a water-soluble salt.

[0020] The organic solvent blend is selected for being effective to substantially dissolve asphaltenes. The organic solvent blend comprises a non-polar organic solvent and a polar organic solvent. Preferably, the organic solvent blend comprises the non-polar organic solvent and the polar organic solvent in the ratio of: (a) from about 99.9% to about 90% by volume of the non-polar organic solvent; and (b) from about 0.1% to about 10% by volume of the polar organic solvent. Most preferably, the organic solvent blend comprises the non-polar organic solvent and the polar organic solvent in the ratio of: (a) from about 99% to about 95% by volume of the non-polar organic solvent; and (b) from about 1% to about 5% by volume of the polar organic solvent.

[0021] Another important consideration in selecting the organic solvent blend is that the components should not be incompatible with the formation fluids to avoid the formation of undesirable precipitates or residues. Other considerations include that the solvent blend should not tend to poison any catalysts used in the refining of the hydrocarbon produced from the well.

[0022] The non-polar organic solvent is preferably selected from the group consisting of: aromatic solvents, terpenes, kerosene, diesel, and any combination thereof.

[0023] The flash point of the organic solvent blend is an important safety concern, and preferably should be greater than 50°C (122°F). The flash point of xylene, for example, is only 27°C (80°F). The non-polar organic solvent can comprise, for example, a mixture of D-limonene and dipentene, for which some mixtures have a flash point of about 47°C (117°F). A more preferable non-polar solvent is a terpene blend that has a flash point of greater than 50°C (122°F). Preferably a "heavy aromatic solvent" is used, which is a distillation cut of a crude oil from which light aromatic solvents, such as xylene and toluene, have been previously distilled out.

[0024] The polar organic solvent is preferably selected for its ability to enhance the solubility of asphaltenes in the organic solvent blend relative to the solubility of the asphaltenes in the non-polar organic solvent alone. A suitable polar organic solvent is N-methyl pyrolidone, which has a high flash point of 92°C (199°F).

[0025] The surfactant preferably comprises a water-soluble surfactant. "Baraklean" is a suitable example of a blend of water-soluble surfactants and has a flash point above 93°C (200°F), which is commercially available from Baroid Fluid Services. "Baraklean NS" is also suitable, being a blend of water-soluble surfactants with a complexing agent. Further, a suitable surfactant can be selected from the group consisting of: ethoxylated alcohols, ethoxylated nonylphenol, and any combination thereof.

[0026] The composition can be a weak emulsion or a dispersion. The composition is preferably a water-external emulsion.

[0027] Preferably, the step of forming the composition further comprises the step of: prior to mixing with the solvent blend, mixing the water with the surfactant.

[0028] In a batch, the method preferably includes the step of slowly mixing the solvent blend with the mixture of the water and the surfactant under sufficient shear conditions to form an emulsion. In a continuous process, sometimes referred to as being "on the fly," the method preferably includes the step of mixing a stream of the solvent blend with a stream of the mixture of the water and the surfactant under sufficient shear conditions to form an emulsion.

[0029] Preferably, the step of introducing the composition further comprises the step of: placing the composition in the portion of the well to be treated for a sufficient contact time for the organic solvent blend to dissolve a substantial amount of the organic material. More preferably, the method further comprises the step of: after placing the composition, flowing back the composition through the wellbore.

[0030] When a composition according to the invention was tested in the laboratory, a 60% water-phase emulsion was more effective for removing asphaltenes from a rock core sample than a solvent only approach.

[0031] The asphaltene treatment fluid was also tested in a well. About 440 m^3 of a composition according to the invention was injected into the well. There was an increase in the injection pressure much higher than expected immediately after the composition started to enter the formation. This is believed to be caused by the initial swelling of the asphaltenes by the organic solvent blend. It is also possible that the increase in the injection pressure is due to a fluid viscosity effect. In any case, this effect is expected to be a useful self-diverting effect. Following the treatment and displacement with nitrogen, the well flowed without pumping and initially produced a very heavy viscous fluid. The final production of the well was almost 400 m^3/day. The performance of the composition confirmed the exceptional results seen in the laboratory, and the initial performance of the well after the test treatment with the new treatment fluid exceeded expectations.

CLAIMS

1. A composition for removing an organic material from a portion of a wellbore, wellbore tubular, fracture system, or matrix of a subterranean formation, the composition comprising:

(A) water, wherein the water is greater than 50% by volume of the composition;

(B) an organic solvent blend that is immiscible with water, wherein the organic solvent comprises:

(i) a non-polar organic solvent; and

(ii) a polar organic solvent; and

(C) a surfactant adapted for forming an emulsion of the organic solvent blend and the water.

2. The composition according to Claim 1, wherein the organic material to be removed comprises asphaltenes.

3. The composition according to Claim 1, wherein the water further comprises a water-soluble salt.

4. The composition according to Claim 1, wherein the organic solvent blend is further selected for being effective to substantially dissolve asphaltenes.

5. The composition according to Claim 1, wherein the organic solvent blend comprises the non-polar organic solvent and the polar organic solvent in the ratio of:

(a) from about 99.9% to about 90% by volume of the non-polar organic solvent; and

(b) from about 0.1% to about 10% by volume of the polar organic solvent.

6. The composition according to Claim 1, wherein the non-polar organic solvent is selected from the group consisting of: aromatic solvents, terpenes, kerosene, diesel, and any combination thereof.

7. The composition according to Claim 1, wherein the non-polar organic solvent has a flash point of greater than greater than 50°C (122°F).

8. The composition according to Claim 1, wherein the polar organic solvent enhances the solubility of asphaltenes in the organic solvent blend relative to the solubility of the asphaltenes in the non-polar organic solvent.

9. The composition according to Claim 1, wherein the polar organic solvent has a flash point of greater than greater than 50°C (122°F).

10. The composition according to Claim 1, wherein the polar organic solvent

comprises N-methyl pyrolidone.

11. The composition according to Claim 1, wherein the surfactant comprises a water-soluble surfactant.

12. The composition according to Claim 1, wherein the water-soluble surfactant has a flash point of greater than greater than 50°C (122°F).

13. The composition according to Claim 1, wherein the surfactant is selected from the group consisting of: ethoxylated alcohols, ethoxylated nonylphenol, and any combination thereof.

14. The composition according to Claim 1, wherein the composition is a water-external emulsion.

15. A method for removing an organic material from a portion of a wellbore, wellbore tubular, fracture system, or matrix of a subterranean formation, the method comprising the steps of:

(A) forming a composition comprising:

(i) water, wherein the water is greater than 50% by volume of the composition;

(ii) an organic solvent blend that is immiscible with water, wherein the organic solvent comprises:

(a) a non-polar organic solvent; and

(b) a polar organic solvent; and

(iii) a surfactant adapted for forming an emulsion of the organic solvent blend and the water; and

(B) introducing the composition to the portion from which the organic material is to be removed.

16. The method according to Claim 15, wherein the organic material to be removed comprises asphaltenes.

17. The method according to Claim 15, wherein the composition further comprises a water-soluble salt.

18. The method according to Claim 15, wherein the organic solvent blend is further selected for being effective to substantially dissolve asphaltenes.

19. The method according to Claim 15, wherein the polar organic solvent enhances the solubility of asphaltenes in the organic solvent blend relative to the solubility of the asphaltenes in the non-polar organic solvent.

20. The method according to Claim 19, wherein the polar organic solvent comprises N-methyl pyrolidone.

INTERNATIONAL SEARCH REPORT

International application No
PCT/IT2006/000316

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K8/524

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 practical, 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 4 775 489 A (WATKINS DAVID R [US] ET AL) 4 October 1988 (1988-10-04) column 4, line 20 - line 25 column 6, line 5 - column 7, line 49 column 5, line 15 - line 61	1-20
A	US 6 051 535 A (BILDEN DEAN M [US] ET AL) 18 April 2000 (2000-04-18) column 6, line 20 - column 7, line 30	1-20
A	WO 01/46553 A (BP EXPLORATION OPERATING [GB]; COLLINS IAN RALPH [GB]) 28 June 2001 (2001-06-28) the whole document	1-20

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

[X] See patent family annex.

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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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INTERNATIONAL SEARCH REPORT

International application No
PCT/IT2006/000316

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	DATABASE WPI Week 198516 Derwent Publications Ltd., London, GB; AN 1985-097204 XP002406298 & SU 1 114 687 A (PETRO GAS RES INST) 23 September 1984 (1984-09-23) abstract	1-20

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
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