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Froning et al.

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[54] METHOD OF MOBILITY CONTROL IN MISCIBLE DISPLACEMENT PROCESS

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[52] **U.S. Cl.**.....**166/273,** 166/274

[51] **Int. Cl.** **E21b 43/22**

[58] **Field of Search**.....166/273, 274, 305, 309, 275

[56] **References Cited**

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[57] **ABSTRACT**

In displacement by water of a solvent substantially miscible with both water and petroleum through a petroleum-containing reservoir, the mobility of the drive agent is controlled by generating a weak, mobile foam at or near the trailing edge of the solvent slug. Foams found to be suitable for this purpose, and which do not result in plugging the reservoir, are characterized by the fact that they have a maximum viscosity of not more than about 1,000 cps and when confined in a column over a 20-minute period decrease in volume to not more than one-third of the foam present at the beginning of said period.

12 Claims, No Drawings

METHOD OF MOBILITY CONTROL IN MISCIBLE DISPLACEMENT PROCESS

SUMMARY OF THE INVENTION

The present invention relates to an improved process for the recovery of petroleum from an underground deposit thereof by means of a miscible flooding technique. More particularly, it is concerned with a miscible flood displacement process employing a foam between the solvent and the drive agent as a mobility control agent.

BACKGROUND OF THE INVENTION

Miscible waterflooding processes such as are described in U.S. Pat. Nos. 3,254,714; 3,354,953 and 3,406,754 require the use of an oil solvent slug which is in turn driven by water through the reservoir. In the process, there exists an unfavorable mobility ratio at the trailing edge between the solvent and the drive water. The fingering and channeling of the drive water into the more viscous solvent slug eventually causes it to break down. This condition can be avoided, however, if a mobility control agent is added, creating a mobility buffer zone behind the solvent slug. In the aforesaid zone the viscosity changes gradually from that of the water to that of the solvent.

Those active in this field have suggested as mobility control agents certain water-external emulsions, polysaccharide polymers and polyacrylamide polymers which, because of high viscosity and/or surface adsorption, have a mobility equal to or lower than the solvent slug. A major drawback of these polymeric materials as mobility control agents, however, is their cost and the amount that must be used to obtain the desired results. At costs of the order of a dollar per pound for the polymer and a 50 percent pore volume (PV) bank of polymer solution necessary, the economics of such a flooding operation can begin to look questionable from the standpoint of the mobility control agent alone.

DESCRIPTION OF THE INVENTION

We have now discovered a means for providing a very low-cost but effective mobility control agent in miscible waterflooding processes employing solvents such as micellar solutions, systems having a low surface tension, i.e., less than about 0.1 dyne/cm, or a water soluble alcohol such as, for example, isopropyl alcohol. At this point it should be mentioned that the micellar systems contemplated herein usually consist of combinations of a surfactant, a cosurfactant, such as an alcohol, oil, water, and an electrolyte. In carrying out the processes of our invention a bank of mobile foam is generated behind the displacing solvent slug. In the case where a solubilized oil or micellar solution is used as the solvent, the surface-active agent therein can be employed to generate the necessary amount of foam. Such foam can be formed from the surface-active agent that has been left behind the micellar slug as it passes through the formation, or in the case in which isopropyl alcohol is used as a solvent and a slug of a suitable surface-active agent may be incorporated in or injected behind the solvent and the foam formed in the manner described herein. Other solvent systems are those which create a low interfacial tension (IFT) at the solvent-oil interface such as are described in copending

application U.S. Ser. No. 848,681, filed Aug. 8, 1969. Such systems are capable of reducing the interfacial tension to values less than 0.1 dyne per cm.

Once the foaming agent is made available, the foam is generated by injecting the drive agent, e.g., gas followed by water, water followed by gas or a gas-water mixture, which agitates the surface-active agent at or near the trailing edge of the solvent slug, thereby forming a foam having the desired characteristics. The drive agent pushes the resulting semi-stable foam which in turn drives the displacing solvent through the formation. This process continues until the displacing solvent slug reaches the producing well. In this way a continuously moving buffer zone consisting essentially of a weak or mobile foam is provided between the solvent slug and the drive agent. This ensures the movement of the displacing slug from the injection well to the producing well without deterioration.

Injection of a gas such as nitrogen, natural gas, air, inert gas, etc., for example, behind a bank of micellar solvent slug produces the semi-stable foam in place. While it is generally thought that the foam itself does not move through the rock to any appreciable extent, the conditions provided by the process of our invention make possible continuous generation of the desired quantity of foam at the trailing edge of the solvent slug. This in turn results in an effective reduction in drive agent velocity, thereby reducing the overall mobility ratio and increasing the area contacted by the slug. Under these conditions it is contemplated that a high degree of miscibility exists between the drive water and the trailing edge of the solvent slug.

The procedure used for forcing the solvent slug through the formation and continuously generating a weak or semi-stable foam thereof is subject to some variation. For example, a finite volume of gas may be followed injected behind the solvent bank containing a surface-active agent followed by water injection. Water and gas are thus flowing behind the solvent to regenerate the foam and lower the overall mobility ratio of the system. On the other hand, it may be desirable initially to alternately inject gas and water behind the solvent slug. The gas causes the formation of a semi-stable foam at the trailing edge of the slug as previously stated. Injection of water behind the gas favorably affects the overall system mobility ratio. With alternate injection of gas and water the gas zone pushing the solvent slug remains nearly constant in size. This procedure may, or course, be reversed, i.e., water is injected first, followed by gas. Once the stability is achieved the slug is pushed uniformly through the reservoir, resulting in improved sweep efficiency.

The foam employed in the process of our invention should have an apparent or effective viscosity of not more than about 1,000 cps. In this connection it is to be understood that the expression "semi-stable foam" as used in the present description and claims is intended to mean a foam whose effective viscosity is not in excess of about 1,000 cps. We have found that with a mobility buffer zone consisting essentially of a foam having a viscosity not greater than about 1,000 cps we are still able to drive the oil through the reservoir at an essentially increased sweep efficiency with in situ semi-stable foam forming and collapsing. Ideally, foam is always present owing to the face that it is continuously

forming at the trailing edge of the solvent slug, while previously formed foam downstream is collapsing.

In generating foam as used in the present invention, precautions should be taken to avoid foams having viscosity in excess of about 1,000 cps. Foams having higher viscosities can cause blocking within the flow path, resulting in high pressure drop and little or no production. Another important property characterizing the semi-stable or weak mobile foams used in the process of our invention is that they form rather substantial volumes of foam initially, but over a 20-minute period under the test conditions described herein they decrease in volume to not more than one-third of that originally produced.

The amount of solvent slug injected into the formation in accordance with our invention may vary widely. In most instances, however, it may be employed in quantities ranging from about 2 to about 20 percent of the reservoir pore volume contacted and preferably from about 3 to 7 or 8 percent thereof. If the foaming agent (surfactant) is incorporated in the solvent it may be present in a concentration of from about 1 to about 20 weight percent. Foaming agents may also be injected as a separate slug in the form of an aqueous or aqueous alcoholic solution. In such case, the volume of the solution may range from about 2 to about 10 percent of the reservoir pore volume contacted.

In addition to the specific surfactants mentioned herein, straight chain sulfonates of the type described in copending U. S. application Ser. No. 848,748, filed Aug. 8, 1969, by H R. Froning et al., may be used. Also, surfactants of the type commonly employed in the preparation of micellar solutions are contemplated.

Suitable foams for driving solvent slugs in accordance with our invention may be produced through the use of a modifying agent of suitable nature in the micellar solution. For example, micellar solutions usually contain a substantial amount of salt to enhance their ability to solubilize the crude oil through a lowering of the interfacial tension between the oil and the micellar solution. The presence of appreciable salt concentration, particularly at room temperature (75°F) or thereabout, has been found to reduce foam formation, especially in the case of producing the weak, mobile foams for use in accordance with our invention. At elevated temperatures, e.g., 150°F, systems having an appreciable salt concentration no longer present a serious problem insofar as concerns the formation of satisfactory foams for use in our process Salt-containing micellar solutions for use at lower temperatures may also be improved by dilution with water. Other micellar systems tending to foam can be modified to produce foams suitable for use in our process by the addition of a water soluble alcohol.

In our study to determine the various factors affecting satisfactory foam formation we tested a number of surfactant compositions in solution form, the test fluids were:

Surfactant	Water Content
(1) Ammonium alkylpolyol oxyethylene sulfonate	99% distilled water
(2) 82% alkyl aryl sulfonate and 18% 6 mol ethylene oxide adduct of 1 hexanol	90% Madison water + 2 N NaCl*
(3) 62.5% alkyl aryl sulfonate and 37.5% isopropyl alcohol	92Madison water + 2 N NaCl*
(4) 30% petroleum sulfonate (average MW 425) and 70% isopropyl alcohol	90% .25 N NaCl
(5) 70% kerosene, 25% alkyl aryl sulfonate, 5% 6 mol ethylene oxide adduct of 1 hexanol	50% 9000 ppm NaCl brine

*Water from the Madison formation plus enough NaCl to make the resulting solution .2 N in NaCl.

The above compositions were separately diluted 1:1 and 1:3 with either distilled water or 0.25 N NaCl brine with the exception of surfactant No. 5 which was separately diluted to 50, 90, and 95 percent with distilled water and 0.25 N NaCl brine. Each test was carried out by introducing 20 ml of the test solution into a 100 ml stoppered, graduated cylinder and thereafter shaking vigorously for 30 seconds. The volume of foam produced was then measured after 1, 5, 10, and 20 minute intervals. The work was done at room temperature (75°F) and at 150°F. The results obtained appear in the tables below.

TABLE 1

Room Temperature Tests

Foam Volume After Shaking, ml.

Time, minutes	No dilution							
	Surfactant #1		Surfactant #2		Surfactant #3		Surfactant #4	
1	95		6		2		32	
5	95		5		1		5	
10	95		5		1		5	
20	95		4		½		5	
	1:1 surfactant to water							
	Surfactant #1		Surfactant #2		Surfactant #3		Surfactant #4	
	Distilled H_2O	0.25 N NaCl brine	Distilled H_2O	0.25 N NaCl brine	Distilled H_2O	0.25 N NaCl brine	Distilled H_2O	0.25 N NaCl brine
1	83	100	50	2	23	5	53	40
5	80	100	45	2	20	4	45	35
10	80	100	40	½	20	4	45	32
20	80	100	28	½	20	4	45	27
	1:3 surfactant to water							
1	75	70	41	4	47	10	59	43
5	75	70	35	2	45	8	59	40
10	75	70	35	2	45	8	59	32
20	75	65	32	1	43	6	59	32

TABLE 2

150° F. Tests

Foam Volume After Shaking, ml.

Time, minutes	No dilution			
	Surfactant #1	Surfactant #2	Surfactant #3	Surfactant #4
1	90	4	40	50
5	90	4	9	2
10	90	4	5	2
20	90	4	2	1

	1:1 surfactant to water							
	Surfactant #1		Surfactant #2		Surfactant #3		Surfactant #4	
	Distilled H_2O	0.25 N NaCl brine	Distilled H_2O	0.25 N NaCl brine	Distilled H_2O	0.25 N NaCl brine	Distilled H_2O	0.25 N NaCl brine
1	90	93	65	25	45	20	80	55
5	90	83	33	17	25	10	50	28
10	90	82	12	5	12	8	20	10
20	90	82	6	3	5	5	10	4
	1:3 surfactant to water							
1	100	90	85	23	90	30	100	50
5	100	85	30	12	75	20	80	25
10	100	85	15	7	17	16	20	20
20	100	85	10	3	14	10	20	10

TABLE 3

Surfactant #5

Foam volume after shaking, ml.

Time, minutes	Room temperature					
	50% distilled	90% distilled	95% distilled	50% 0.25 N NaCl	90% 0.25 N NaCl	95% 0.25 N NaCl
1	51	70	70	1	1	2
5	10	33	38	0	½	½
10	8	21	25	0	0	0
20	6	20	22	0	0	0
	150° F.					
1	60	70	90	0	0	0
5	8	18	25	0	0	0
10	4	10	18	0	0	0
20	0	2	8	0	0	0

TABLE 4

Test	Liquid composition and volume, cc.			Foam volume after 30 sec. shaking, cc.			
	Sodium petroleum sulfonate avg. MW 425	0.25 N brine	Isopropyl alcohol	1 min.	2 min.	5 min.	20 min.
1	0.5	18.0	0	9.5	9.0	8.0	6.5
2	0.5	18.0	1	5.0	5.0	2.2	2.0
3	0.5	18.0	2	4.5	3.0	2.0	1.0
4	Same as 1 with 1 cc. Slaughter crude added			0.75	----------	0.25	0.25
5	Same as 3 with 1 cc. Slaughter crude* added			0.0	----------	0.0	----------

*Slaughter Field, Texas.

The effect of alcohol on the volume and stability of a typical foam suitable for use in the process of our invention is shown in Table 4 below. In these tests, after all components were dissolved the solution was shaken in a 50 cc, graduated cylinder for 30 seconds, after which the amount of foam was measured at intervals over a 20-minute period.

From the data in the above Table it is seen that the surfactant employed in the presence of 0.25 N brine only, gave a relatively stable foam over the 20-minute test period; however, weak foams were formed in the presence of isopropyl alcohol.

The ability of such foams to break or degenerate over the 20-minute test period renders them suitable for use in the process of our invention. It is also seen that addition of crude oil tends to break foams rapidly. This is a favorable factor in our process since the presence of foam at the oil-solvent interface tends to reduce the contacting efficiency of the solvent with the oil in the displacement mechanism. Thus, it is apparent that our invention provides conditions in which the leading edge of the solvent slug maintains maximum solvent power for crude oil while at the trailing edge thereof a bank of weak, mobile foam is created which breaks and regenerates as the fluids progress through the formation. This foam, because of its relatively low viscosity and its ability to decay and re-form, serves as a highly satisfactory mobility control agent for the water or other drive fluid employed in the miscible water-flooding process of our invention.

The compositions used as solvents in carrying out the process of our invention may be any of the well known materials having a high degree of solubility in both crude oil and water. One class of such solvents is represented by the lower molecular weight oxygenated organic compounds such as isopropyl alcohol, acetone, butyl Cellosolve, butyl Carbitol, n-propyl alcohol, etc. The other class of solvents is composed of a solubilized oil or micellar solution which has a surface-active agent incorporated therein. The various methods of preparing these compositions, both in the oil-external and water-external forms, is well known, such methods

being described, for example, in U. S. Pat. Nos. 3,254,714, 3,470,958 and 3,500,919.

SPECIFIC EMBODIMENTS OF THE INVENTION

The process of our invention may be further illustrated by reference to the series of experimental runs referred to below. In all tests an 8-foot Berea sandstone core 2 inches in diameter was used at 150°F and 125 psi. An alternate gas-water drive was employed to force the solvent through the core. The fluid injection sequence was as follows:

1. The core was first saturated with Salt Creek* brine.
2. Reduction to connate water saturation with Salt Creek crude oil.
3. Secondary waterflood with synthetic Madison* brine.
4. Preflush the core with synthetic Madison brine plus 11,700 ppm NaCl solution.
5. Inject solubilized oil-water solution.
6. 7.6 percent PV nitrogen at 125 psi, 18.4 percent PV synthetic Madison brine plus 11,700 ppm NaCl.
7. 10.9 percent PV nitrogen at 125 psi.
8. Inject synthetic Madison brine to flood out.

*Salt Creek field, Wyoming

**Comparable to brine obtained from the Madison formation, Salt Creek field, Wyoming.

The results appearing in the Table below show that in both Tests 2 and 3 employing the process of the present invention, the percent recovery of oil was substantially improved over that obtained when a polymer was used for mobility control (Test No. 1).

TABLE 5

	Test		
	1	2	3
Percent Recovery, Total Oil in Place	85.5	95.8	91.3
Percent Recovery Tertiary Oil	76.8	93.0	86.0
Percent PV Slug((1) Injected	10.1	23.5	11.4
ml Slug Injected	104.0	242.2	109.8
ml Polymer Injected (2)	500.5	0	0
ml Tertiary Oil Recovered	273.1	325.5	285.5

(1) Micellar solution containing 90% .03N brine, 8.2% petroleum sulfonate (average molecular weight 425), 1.8% cosurfactant (6 mol ethylene oxide adduct of n-hexanol)
(2) Polysaccharide polymer

In comparing the results of Test No. 1 — using polymer for mobility control — and Test No. 3 — employing a mobile foam — it is evident that the gas drive and foam generation for mobility control in place of polymer solution produced a higher overall recovery (91.3 percent vs. 85.5 percent) and higher tertiary recovery (86.0 percent vs. 76.8 percent). In the case of Tests Nos. 2 and 3 it is seen that by decreasing the slug size from 23.5 percent PV to 11.4 percent PV the overall oil recovery was reduced only by 4.5 percent and recovery of tertiary oil decreased from 93.0% to 86.0 percent. In Test No. 2 the slug was deliberately oversized to prevent premature gas breakthrough.

On the basis of the results obtained we have calculated that a field test currently planned and using polymer for mobility control would cost about 20 percent more than would be the case if the means of effecting mobility control in accordance with our invention were used. Test No. 3 proves that the use of gas drive and foam generation will effect the mobility control needed in the process of miscible waterflooding. Moreover, higher recovery performance and better economics are indicated using gas drive in place of the polymer solution. The foregoing data show that our process is definitely superior to the presently used polymer solutions for mobility control. Accordingly, the potential application of the miscible waterflooding process is much greater because of the lower initial chemical investment and improved economics provided by our invention.

We claim:

1. In a method for recovering oil from an underground formation penetrated by an injection well and a producing well, the improvement which comprises the steps of:

injecting into said formation via said injection well a liquid solvent for said oil, said solvent being present in an amount sufficient to form a bank thereof,

forming substantially at the trailing edge of said solvent as a mobility buffer a weak, mobile foam bank having an apparent viscosity not in excess of about 1,000 cp,

thereafter displacing said oil, solvent bank and said foam bank through said formation towards said producing well, and

recovering displaced oil from said producing well.

2. In a method for recovering oil from an underground formation penetrated by an injection well and a producing well, the improvement which comprises the steps of:

injecting into said formation via said injection well a liquid solvent for said oil, said solvent being present in an amount sufficient to form a bank thereof,

forming substantially at the trailing edge of said solvent as a mobility buffer a weak, mobile foam which when confined in a column over a 20-minute period decreases in volume to not more than about one-third of its original volume at the beginning of said period,

thereafter displacing said oil, solvent bank and said foam bank through said formation towards said producing well, and recovering displaced oil from said producing well.

3. The method of claim **1** wherein said solvent is a salt containing micellar solution.

4. The method of claim **1** wherein said foam is generated by injecting a gas followed by water.

5. The method of claim **4** wherein said foam bank is characterized by its deterioration and regeneration as it is displaced through said formation.

6. The method of claim **1** wherein said solvent is capable of producing an interfacial tension between it and the oil of less than 0.1 dyne per cm.

7. The method of claim **3** wherein said micellar solution contains a petroleum sulfonate surfactant having a molecular weight ranging from about 400 to about 470.

8. The method of claim **1** wherein an aqueous slug of surfactant is injected behind and is in close proximity with said solvent and forms said foam bank by agitating said surfactant slug with a fluid, said foam bank continuously forming at the trailing edge of said solvent slug while previously formed foam is collapsing.

9. The method of claim **1** wherein the liquid solvent employed is miscibly displaced by water.

10. The method of claim **1** wherein said foam bank is

brought into contact with an alcoholic brine solution.

11. The method of claim 1 wherein said solvent is a micellar solution containing a water soluble alcohol.

12. The method of claim 1 wherein said foam bank is formed from an aqueous brine solution of surfactant in which the surfactant and brine solution are employed in a ratio of about 1:3.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,722,590 Dated March 27, 1973

Inventor(s) H R. Froning, Syed H. Raza and Warren S. Askew

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 37, "followed" should be deleted
line 68, "face" should be --fact--

Column 4, the test result tabulations beginning line 18, for (2) and (3) under "Water Content", "+ 2N" should be --+.2N--

Signed and sealed this 20th day of November 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

RENE D. TEGTMEYER
Acting Commissioner of Patents