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SECONDARY RECOVERY PROCESS USING GAS-LIQUID DRIVE FLUIDS

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This invention relates to the recovery of petroleum from underground reservoirs, and is more particularly concerned with a flooding process for recovering petroleum in greater amounts than is possible by conventional flooding techniques.

It is well known in the secondary recovery art to inject a slug of solvent which is miscible with both the petroleum oil in the reservoir and with water, and to drive this slug of fluid through the reservoir by injecting floodwater behind it. Typical of the solvents used in such secondary recovery processes are lower alcohols. It has also been proposed to inject a slug of hydrocarbon solvent, usually of low molecular weight, and then inject a slug of solvent which is miscible with both the petroleum oil and with water. Finally, floodwater is injected. The presence of large volumes of water in the reservoir hinders the removal of petroleum by such miscible phase displacement processes. Where alcohol alone is used as the solvent, the alcohol dissolves in the reservoir water, deteriorating the alcohol bank. Because of the high solubility of the injected solvent in the reservoir water, the leading edge of the solvent zone becomes diluted with water, and the solvent zone may break down entirely, with the result that the oil-to-solvent-to-water miscible displacement is lost.

When a first slug of hydrocarbon solvent is used prior to the alcohol, the presence of large volumes of water in the reservoir still strongly hinders oil recovery, although the reason is obscure, since the first injected hydrocarbon would be expected to drive formation water ahead of it and prevent contamination of the alcohol bank.

It has now been found that an improvement of the dual slug type miscible displacement process can be obtained in treating reservoirs containing high concentrations of reservoir water by first injecting a slug of a gas into the reservoir, before the injection of the hydrocarbon solvent. It has been found that still greater improvement in recovery of petroleum from reservoirs having high water-to-oil ratios can be obtained if a foam is injected through the input well and into the formation or produced downhole, prior to the injection of solvent.

Briefly, this invention teaches a process for the recovery of oil from reservoirs containing high concentrations of reservoir water comprising the steps of first injecting a small slug of an aqueous solution of high foaming surfactant into the formation, then injecting a slug of gas which is substantially insoluble in the petroleum contained in the reservoir and has only limited solubility in water, then injecting a quantity of hydrocarbon solvent, followed by a solvent such as an alcohol which is soluble in both petroleum and floodwater, and finally injecting floodwater to drive the gas and solvent through the formation to a producing well. Alternatively, the injection of aqueous surfactant solution can be omitted. The function of the aqueous surfactant solution and gas injected prior to the solvent is to produce a stable foam in the formation, which foam is effective in reducing the water saturation ahead of the solvent bank and thereby preventing deterioration of the solvent bank.

It is an object of this invention to provide an improved method for the secondary recovery of oil from underground reservoirs.

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Another object of this invention is to provide a method for recovering higher percentages of petroleum in reservoirs which contain high concentrations of water.

The injection of aqueous surfactant solution and gas having low solubility in petroleum, prior to the injection of liquid hydrocarbon solvent and a second solvent which is soluble in both the petroleum oil and the subsequently injected floodwater, is contrary to principles taught in the prior art. The prior art considers the injection of a highly mobile gas before the injection of a miscible solvent disadvantageous in that it results in disruption of continuity in the oil phase in the reservoir, and tends to cause fingering and by-passing of oil-containing zones, and thereby reduces flood efficiency. It has nevertheless been found that where the reservoir to be treated contains water in amount of about 0.5 pore volume or more, the disrupting effects of the gas injected prior to the miscible solvent is minimized, and the efficiency of the process is enhanced. Accordingly, it has been found that by injecting a small amount of aqueous surfactant solution and a larger amount of gas prior to the injection of miscible solvents, when treating reservoirs having a water concentration of not less than about 0.5 pore volume, the efficiency of recovery is raised far above that possible by conventional solvent flooding.

In carrying out the process of this invention, a small slug of water having a volume in the range of about 0.005 to 0.05 reservoir pore volume, preferably about 0.02 reservoir pore volume, containing a small amount of surfactant of the high-foaming type, sufficient in amount to produce a stable foam when the water slug is contacted by a gas, is injected. The concentration of surfactant is ordinarily in the range of 0.1 to 5.0% by weight of the water slug. Following the injection of the aqueous surfactant solution, a slug of gas having low solubility in petroleum and a volume of about 0.1 to 0.5 reservoir pore volume is injected through the input well and into the petroleum reservoir. The volume of gas injected must be sufficient to form a foam bank which will substantially displace the formation water and maintain an effective buffer between the formation water and the later-injected solvent. In general, the lowest effective amounts of gas will be most suitable, since the injection of a gas slug larger than is required could have an adverse effect upon the sweep efficiency of the process, thereby preventing maximum oil recovery. While quantities of gas in the range of 0.1 to 0.5 pore volume may be employed, in most instances it will be preferred to use not more than about 0.2 pore volume of gas measured at injection temperature and pressure. Next, a slug of liquid hydrocarbon solvent is injected. The amount of hydrocarbon will be in the range of 0.03 to 0.20 reservoir pore volume, and preferably about 0.10 pore volume.

A slug of a suitable solvent which is soluble in both petroleum oil and water, and preferably is miscible with both oil and water, is injected into the reservoir behind the hydrocarbon slug. The volume of that solvent injected is not critical, but quantities less than 0.03 pore volume are seldom effective, and quantities in excess of about 0.2 reservoir pore volume increase the expense of the process without producing a proportionate increase in the oil ultimately recovered. Finally, floodwater is injected in a conventional manner to drive the previously injected gas and solvent slugs towards the producing well. This final water injection is continued until the water-to-oil ratio at the producing well rises to such a level that further oil recovery becomes uneconomical, at which time injection is terminated. This process is applicable to any of the standard flooding patterns, such as the line drive, five-spot, or nine-spot systems.

A wide variety of gases are available which may be

used in carrying out the process of this invention. The gas chosen must have a solubility in petroleum not greater than about 10% by weight at reservoir temperature and pressure, and should be substantially inert, that is, chemically non-reactive under reservoir conditions. It is also desirable, but not essential, that the gas have a solubility not greater than about 10% by weight in the water. Suitable gases include, but are not limited to nitrogen, flue gas, air and natural gas which is substantially free of components heavier than ethane.

The injected solvent can consist of a hydrocarbon fraction of the C₃ to C₁₀ range. Exemplary materials are LPG, propane and naphtha. Especially preferred are materials such as catalytic reformat, which contain more than 50 percent aromatics and/or olefins.

Similarly, a wide variety of materials are available which may be used as the second injected solvent, it being required only that the solvent be liquid in physical state, capable of dissolving at least 10% of its weight of petroleum, and soluble in water to the extent of at least 10% of the weight of the water. Preferably, the solvent will be miscible with both petroleum oil and water, and still more preferably will have a partition coefficient favoring solution in oil when in the presence of both oil and water. Typical suitable solvents are partially oxidized hydrocarbons such as alcohols, including tertiary butanol, secondary butanol, n-butanol, isopropanol, n-propanol, and pentanols. Other suitable materials include ketones, such as methylethyl ketone, diethyl ketone, and di-n-propyl ketone; aldehydes such as acetaldehyde, propionaldehyde and butyraldehyde, and organic acids such as acetic acid, propionic acid, butyric acid, and isobutyric acid. Mixtures of the aforementioned liquids may also be used in the process of this invention. Mixtures of partially oxidized hydrocarbons produced by hydrocarbon oxidation processes comprising a wide variety of alcohols, aldehydes, ketones and acids, and other constituents, in mixture, may be used provided the weighted average of the solubilities of the constituents of the mixture in petroleum is suitably high. Such mixtures may contain minor amounts of material having a low solubility in petroleum, such as methyl and ethyl alcohols, provided the quantities of such constituents are not excessive and other more soluble constituents are present in quantity. Mixtures of C₃ and C₇ alcohols, ketones, aldehydes, and organic acids are suitable.

The foaming surfactant employed in the aqueous surfactant slug must be water-soluble at least to the extent in which it is incorporated. Suitable water-soluble surfactants include iso-octyl phenyl polyethoxy ethanolols, having about 9 to 10 ethoxy groups per molecule, sulfonated alkyl esters, and sodium lauryl ether sulfate. These materials are merely exemplary of a wide variety of high-foaming, water soluble surfactants which are reasonably compatible with reservoir water and capable of producing large quantities of stable foam when contacted by a gas. Other suitable surfactants can be selected from published lists describing numerous surfactants and their properties.

The term "high-foaming surfactant" as used in this specification and the appended claims denotes a surfactant which, when placed in solution in water in the amount of 5% by weight or less, is capable of producing large quantities of stable foam. The suitability of surfactants for use in the method of this invention may be experimentally determined by incorporating 5% or less, by weight, of the selected surfactant in water, which is preferably typical in salt content to the water to be injected. About 500 milliliters of the aqueous surfactant solution is placed in a graduated cylinder to form a liquid column 50 centimeters in height. Gas is then introduced from the bottom of the column through a fritted glass disc, at substantially atmospheric pressure; and permitted to bubble upward through the column, at a rate of 500 milliliters of gas per minute, per square centimeter of column cross-

sectional area. After the gas has bubbled through the column of liquid for a period of about 15 minutes, the height of the column of foam produced above the liquid is measured, and should be not less than about 150 centimeters. High-foaming surfactants, in accordance with this specification, are those which will meet the aforedefined test. It is preferred to employ surfactants capable of meeting the aforedescribed test with respect to foam quantity when the amount of surfactant employed is substantially less than 5% by weight of water. In general, it is preferred to maintain the amount of surfactant added at a minimum, both for reasons of economics, and to avoid the production in the formation of a foam of excessive thickness which may tend to plug the formation. It will be understood that the quantity of surfactant to be added may vary depending upon the salt content of the water employed, but that the weight of surfactant will be in the range of 0.5 to 5% and that the best amount may be readily determined by the aforedescribed experiment.

The effectiveness of the method of this invention has been established by comparative experiments. The experiments were conducted in 3½ inch diameter, 8 foot long Berea sandstone cores using water-driven solvents, at 120° F. and 1400 p.s.i.g. The tabulation below reports the experimental results.

Exp.	Oil in Place (Percent PV)	Gas (Percent PV) Injected Nitrogen	Solvents (Percent PV) Injected		Oil Recovered (Percent OIP)	Cat. Rec'd (Percent of Injected)
			1st (Cat. Ref.)	2d (Isopropanol)		
1-----	27.5	none	none	26.5	66.1	-----
2-----	28.2	120	none	26.0	94.5	-----
3-----	29.4	none	15.5	10.5	96.0	0
4-----	28.9	114	15.5	10.5	100.0	15.5

¹ Measured at 1400 p.s.i.g. and room temperature.

Experiment 4 establishes the effectiveness of the method of this invention over similar processes in which the injection of hydrocarbon, or gas, or both, are omitted. In Experiment 4, although no aqueous surfactant was injected, all of the oil in place and 15.5% of the catalytic reformat (hydrocarbon) injected was recovered.

In long systems, as exist in actual field operations, an increase in the amount of oil and/or hydrocarbon solvent recovered is obtained by injecting a slug of aqueous surfactant solution before the injection of gas.

As a specific example of the method of this invention a petroleum reservoir penetrated by wells in five-spot pattern, which has been subjected to waterflood and now contains 0.60 pore volume of water, 0.30 of oil, and 0.10 of gas, is treated as follows: Through the central well of the pattern are injected in sequence 0.15 pore volume of air, 0.05 pore volume of liquid propane, 0.05 pore volume of isopropyl alcohol, and floodwater. Petroleum oil is recovered from the other four wells of the pattern. The foregoing procedure may be modified to the extent of shutting in the production wells while the air is being injected into the injection well of the well pattern.

As another example of the method of this invention, the foregoing example is modified to the extent of first injecting 0.03 reservoir pore volume of an aqueous solution containing 3% by weight of sodium lauryl ether sulfate. Oil recoveries slightly higher than those obtained in the foregoing example are realized.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. The method for the recovery of petroleum oil from reservoirs containing water in excess of about 0.5 pore volume and petroleum comprising first injecting through an input well and into said reservoir about 0.1 to 0.5 pore volume of a gas having a solubility in petro-

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leum not greater than about 2% by weight, then injecting 0.03 to 0.20 pore volume of liquid C₃ to C₁₀ hydrocarbon, thereafter injecting about 0.03 to 0.20 pore volume of a liquid solvent capable of dissolving at least 10% its weight of petroleum and soluble in water to at least 10% of the weight of the water, driving the injected material through said reservoir by the injection of floodwater and producing petroleum from an output well.

2. The method in accordance with claim 1 in which the principal constituent of said gas is nitrogen.

3. The method in accordance with claim 2 in which said gas is air.

4. The method in accordance with claim 3 in which said producing well is shut in while air is injected through the input well.

5. The method in accordance with claim 3 in which said liquid solvent consists essentially of oxygenated hydrocarbons having 3 to 7 carbon atoms per molecule.

6. The method in accordance with claim 5 in which a major proportion of the C₃-C₁₀ hydrocarbons are selected from the group consisting of olefins and aromatics.

7. The method in accordance with claim 6 in which the volume of solvent injected is about 0.1 pore volume.

8. The method in accordance with claim 7 in which the volume of hydrocarbons injected is about 0.1 reservoir pore volume.

9. The method in accordance with claim 8 in which the volume of air injected is about 0.1 to 0.5 reservoir pore volume.

10. The method in accordance with claim 1 including

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the step of injecting through said input well about 0.005 to 0.05 reservoir pore volume of an aqueous solution of a high foaming surfactant, said surfactant being present in sufficient quantity to produce a stable foam when said solution is contacted by gas, said solution being injected prior to the injection of said gas.

11. The method in accordance with claim 10 in which the principal constituent of said gas is nitrogen.

12. The method in accordance with claim 11 in which said gas is air.

13. The method in accordance with claim 12 in which said liquid solvent consists essentially of oxygenated hydrocarbons having 3 to 7 carbon atoms per molecule.

14. The method in accordance with claim 13 in which a major proportion of the C₃-C₁₀ hydrocarbons are selected from the group consisting of olefins and aromatics.

15. The method in accordance with claim 14 in which the volume of air injected is about 0.1 to 0.5 reservoir pore volume.

16. The method in accordance with claim 15 in which said solution contains 0.1 to 5.0 percent by weight of surfactant.

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