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OLEFIN AND/OR AROMATIC MISCIBLE SLUG SECONDARY RECOVERY PROCESS

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This invention relates to an improved method for recovering oil from subterranean reservoirs. More particularly, this invention relates to an improved miscible displacement process whereby improved oil recoveries can be obtained. In another aspect, this invention relates to a secondary recovery process wherein oil recoveries equivalent to those obtained by prior art process may be achieved by the use of smaller amounts of injected solvents.

It is conventional to treat depleted petroleum reservoirs by the injection of a driving fluid, typically water, through an injection well to force migration of oil toward surrounding producing wells. The prior art recognizes that the efficiency of such waterfloods is low, in that only a small portion of the petroleum contained in the reservoir is usually produced. The prior art further recognizes that the quantities of oil recovered by waterflood may be increased by injecting a petroleum miscible solvent into the reservoir before the floodwater. Where the petroleum miscible solvent is also miscible with floodwater, or where a second solvent bank which is miscible with the petroleum and first injected solvent, and also with the floodwater, is injected, the occurrence of well defined interfaces between differing liquids is avoided, and a single phase displacement is said to be achieved. It is recognized that such single phase displacement processes are extremely efficient, and are capable of recovering a major portion of the oil in place in the reservoir. Morse et al., 2,742,089, teaches a miscible displacement process wherein a quantity of oil-viscosity reducing liquid hydrocarbon is first injected into the reservoir, a quantity of an amphipathic solvent which is preferablly miscible with both the petroleum and floodwater is then injected, and the solvents are driven towards producing wells by the injection of floodwater.

It has now been found that an improvement over the prior art miscible flood process, such as that of Morse et al., can be obtained. It has been found that the partition coefficient of the amphipathic solvent employed has a critical effect upon the efficiency of the process. By employing an amphipathic solvent having a partition coefficient favoring solution in the hydrocarbon phase, when in the presence of both hydrocarbon and water, substantially improved oil recoveries can be obtained; and also equivalent oil recoveries can be obtained, as compared to the processes of the prior art, by employing proportionately smaller quantities of amphipathic solvent. Thus, it has been demonstrated that in a process such as that disclosed by Morse, wherein the ampliphathic solvent is miscible with both the petroleum and the subsequently injected floodwater, the partition coefficient of the amphipathic solvent has a dramatic effect on the quantity of oil which can be recovered by the process, and also upon the quantity of solvent which must be employed.

While a number of solvents are available which are miscible with, or highly soluble in, both oil and water, it has been found that solvents which have a sufficiently high solubility in water to be useful as amplipathic solvents, almost invariably display a partition coefficient which favors solution in water when the solvent is in the presence of both oil and water. Few solvents are available which are miscible with water, and have a partition coefficient favoring solution in oil when in the presence

of oil and water, and the costs of such materials makes their use as secondary recovery solvents unattractive. For example, isopropyl alcohol and ethyl alcohol, two moderately priced amphipathic solvents stated to be preferred by Morse et al., display partition coefficients strongly favoring solution in water. When isopropyl alcohol, which is miscible with both oil and water, is placed in admixture with water and Dollarhide crude oil in the amounts of 65% isopropyl alcohol, 23% water, and 12% oil, the water phase is found to comprise 91% of the volume of the mixture, and the oil phase only 9%. Corresponding figures are 12% oil phase and 88% water phase for either acetone or ethyl alcohol.

It has been found that the partition coefficient of partially oxidized hydrocarbon solvents, such as isopropyl alcohol, depends to a large extent upon the nature of the hydrocarbon. Thus, while isopropyl alcohol shows a partition coefficient strongly favoring solution in the aqueous phase, rather than in an oil phase where the oil is a typical petroleum, naphtha, paraffinic hydrocarbon, polynuclear aromatic hydrocarbon, or long-chain olefin, the partition coefficient is to a marked degree displaced towards solubility with the oil phase where the oil phase comprises a predominantly shortchain olefinic or monoculear aromatic material. In accordance with this invention, a slug of low molecular weight olefinic or mononuclear aromatic hydrocarbon is first injected into the subterranean formation to be treated. Then a quantity of amphipathic solvent, such as isopropyl alcohol, is injected. Finally, floodwater is injected to drive the petroleum towards the producing wells. Because the first injected hydrocarbon is miscible with the petroleum in the reservoir, and the amphipathic solvent displays a more favorable partition coefficient in the presence of the olefin or aromatic hydrocarbon, the efficiency of oil recovery is substantially enhanced.

In accordance with this invention, a slug of liquid hydrocarbon amounting to 0.02 to 0.20, and preferably about 0.05 reservoir pore volume, is first injected through an input well into the formation. The selected hydrocarbon slug must be at least 60% olefin and/or monnuclear aromatic hydrocarbon. Suitable olefins are branched or straight chain mono- or polyolefins having about 3 to 10 carbon atoms per molecule. Suitable aromatic materials are benzene and alkyl substituted benzenes where the total number of carbon atoms per molecule does not exceed about 10. Thus benzene, toluene, xylene, and other alkyl substituted benzenes may be employed. It is preferred that the alkyl groups contain no more than about 2 carbon atoms. While pure olefins or aromatic materials may be employed, it is preferred to use predominantly olefinic and/or aromatic refinery streams as a source of the injected hydrocarbon material. Fractions boiling within the range of about 100 to 300° F. are preferred. Examples of such fractions are catalytic polymer gasoline (predominantly olefinic), catalytically cracked light cycle stock (predominantly aromatic), butylene polymers (olefinic) and catalytic reformate (predominantly aromatic). The selected fraction should contain at least about 60% olefins and/or aromatics as afore-defined. The amphiphatic solvent next injected can be in the amount of about 0.02 to 0.20, and preferably 0.05, reservoir pore volume. The amphiphatic solvent must be completely miscible with water, have a solubility in the first injected hydrocarbon fraction to the extent of at least one volume of amphiphatic solvent to one volume of hydrocarbon, and display a partition coefficient favoring solution with the oil phase when in the presence of water and olefin or aromatic hydrocarbons. Suitable amphipathic solvents for use in the method of this invention are the numerous water miscible oxygenated hydrocarbons, such as ethyl alcohol,

isopropyl alcohol, tertiary butyl alcohol, acetone, dioxane, acetic acid, and propionic acid. Of these, isopropyl alcohol and ethanol, and especially isopropyl alcohol, are preferred because they are available in quantity at reasonable cost. Mixtures of the aforenamed and other partially oxygenated hydrocarbons may be employed, such as the product streams from thermal or catalytic hydrocarbon oxidation processes. Such product streams comprise a wide variety of partially oxidized hydrocarbons, the great bulk of which are water miscible, have a substantial solubility in low molecular weight olefins and aromatics, and display the desired shift in partition coefficent towards solution in the olefin or aromatic.

Floodwater is then injected to drive the selected hydrocarbon fraction and the amphipathic solvent to the producing wells, from which petroleum is produced until the water-to-oil ratio rises to an excessively high value.

The following block diagram graphically illustrates the aforedescribed invention:

Inject 0.02–0.20 reservoir pore volume of a liquid hydrocarbon comprised of at least 60% C_3–C_{10} olefins, C_6–C_{10} mono-nuclear aromatics and mixtures thereof

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Inject 0.02–0.20 reservoir pore volume of a water miscible solvent having a solubility ratio of at least 1:1 with the first injected fluid

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Inject flood water

The effectiveness of the method of this invention has been demonstrated by laboratory core experiments. The experiments were conducted on a 5 ft. long Berea sandstone which was saturated with a refined oil (Kensol 50) and 1.5% NaCl water solution. The sandstone was 2" wide and 2" thick. In the first experiment, the oil was displaced by a slug of n-heptane followed by a slug of isopropyl alcohol, and then followed by brine. In the second experiment a similar flood was made using a slug of catalytic reformate (octane rating of 95 O.N.), followed by a slug of isopropyl alcohol, followed by brine. The results show the improved oil recovery obtained using the catalytic reformate over the heptane at corresponding total fluid throughputs.

In Experiment 1 the oil initially in place in the core amounted to 39.3 pore volume percent prior to solvent flood, and 30 pore volume percent of n-heptane, followed by 23 pore volume percent of IPA, followed by brine, were injected. The results were as follows:

Table I

Fluid Injected Pore Volumes	Oil Received, Percent Originally In Place	Oil Received, Percent of Total Hydrocarbon (includes heptane)	Residual Hydrocarbon, Percent PV
0.280	35.7	19.1	----------
0.505	90.1	48.1	----------
0.825	100	61.3	----------
1.30	100	67.2	25.2

In Experiment 2 the oil initially in place in the core amounted to 37.2 pore volume percent prior to solvent flood, and 30 pore volume percent of 95 O.N. catalytic reformate, followed by 23 pore volume percent of IPA, followed by brine, were injected. The results were as follows:

Table II

Fluid Injected Pore Volumes	Oil Received, Percent Originally In Place	Oil Received, Percent of Total Hydrocarbon (includes Reformate)	Residual Hydrocarbon, Percent PV
0.284	39.2	21.3	----------
0.51	97.1	52.8	----------
0.82	100.0	66.2	----------
1.3	100.0	72.3	18.9

The 95 O.N. catalytic reformate was a mixture of 62 percent by volume of aromatics and 38 percent by volume of saturated hydrocarbons having an average boiling point of 250° F. (complete range 130 to 400°F.). N-heptane is a C_7 saturated hydrocarbon having a boiling point of 210° F. The physical characteristics of n-heptane (other than partition coefficient) are generally similar to those of the catalytic reformate. Conditions of the experiments were maintained as uniform as possible. Where undiluted aromatic and/or olefinic fractions are employed, more dramatic improvement over this use of comparable paraffinic materials is obtained.

As a specific example of the method of the invention, a subterranean reservoir having an initial oil saturation of 35% and a brine saturation of 65%, which is penetrated by 5 wells arranged in 5-spot pattern, is produced by injecting 0.05 pore volume of benzene through the injection well and into the formation, and then injecting 0.05 pore volume of isopropyl alcohol, and finally driving the solvents towards the producing wells by the injection of floodwater in the usual manner. Petroleum is recovered from the four producing wells until the water-to-oil ratio reaches a ratio of 5 to 1. At this point, the injection and production is terminated. The injection pressures are maintained in the order of 100 p.s.i., and the rate of flood advance through the formation is about 1 to 2 feet per day.

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

1. A method of recovering petroleum from subterranean reservoirs penetrated by an input well and a producing well comprising injecting through said input well and into said formation 0.02 to 0.20 reservoir pore volume of liquid hydrocarbon, at least 60% of said liquid hydrocarbon being of the group consisting of C_3 to C_{10} olefins, C_6 to C_{10} mononuclear aromatics and mixtures thereof, then injecting 0.02 to 0.20 reservoir pore volume of a solvent which is miscible with water, soluble in said hydrocarbon to the extent of at least 1 volume of solvent per volume of hydrocarbon, and displays a partition coefficient favoring solution in said hydrocarbon when in the presence of said hydrocarbon and water, injecting floodwater to drive said hydrocarbon and solvent toward a producing well, and recovering petroleum from said producing well.

2. A method in accordance with claim **1** in which said liquid hydrocarbon has a boiling range of about 100 to 300° F.

3. A method in accordance with claim **1** in which said liquid hydrocarbon is a catalytic reformate.

4. A method in accordance with claim **1** in which said liquid hydrocarbon is catalytically cracked light cycle stock.

5. A method in accordance with claim **1** in which said hydrocarbon consists essentially of butylene polymers.

6. A method of recovering petroleum from subterranean reservoirs penetrated by an input well in a producing well comprising injecting from said input well and into said formation 0.02 to 0.20 reservoir pore volume of liquid hydrocarbon, at least 60% of said liquid hydrocarbon being of the group consisting of C_3 to C_{10} olefins, C_6 to C_{10} mononuclear aromatic hydrocarbons and mixtures thereof, then injecting 0.02 to 0.20 reser-

voir pore volume of water miscible partially oxygenated hydrocarbons which are soluble in said first injected hydrocarbons to the extent of at least one volume of oxygenated hydrocarbon to one volume of said first injected hydrocarbon, injecting floodwater to drive said hydrocarbon and solvent toward a producing well, and recovering petroleum from said producing well.

7. A method in accordance with claim **6** in which said partially oxygenated hydrocarbon is a C_2 to C_4 alcohol.

8. A method in accordance with claim **7** in which said alcohol is isopropyl alcohol.

9. A method in accordance with claim **7** in which said alcohol is ethanol.

10. The method in accordance with claim **7** in which said hydrocarbons have a boiling range of about 100 to 400° F.

11. A method in accordance with claim **7** in which said hydrocarbon is a catalytic polymer gasoline.

12. A method in accordance with claim **7** in which said hydrocarbon is a catalytically cracked light cycle stock.

13. A method in accordance with claim **7** in which said hydrocarbon consists essentially of butylene polymers.

14. A method in accordance with claim **1** in which said liquid hydrocarbon consists essentially of C_3–C_{10} olefins.

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