FIP7912 OR 3,236,303

United States Patent Office

3,236,303

Patented Feb. 22, 1966

3,236,303

WATER-FLOODING METHOD USING AN ALCOHOL-SURFACTANT MIXTURE

Albert K. Csaszar, Dundee, Ill., assignor, by mesne assignments, to Union Oil Company of California, Los Angeles, Calif., a corporation of California

No Drawing. Filed Nov. 9, 1961, Ser. No. 151,160

6 Claims. (Cl. 166—9)

This invention relates to an improved method for recovering petroleum 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 secondary-recovery processes wherein oil recoveries equivalent to those obtained by prior art processes 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 obtained 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 waterflood. Where the petroleum-miscible solvent is also miscible with floodwater, or where a second solvent bank which is miscible with petroleum and with the first injected solvent, and also with the floodwater, is injected, the occurrence of well-defined interfaces between different liquids is avoided, and a single-phase displacement process is said to be achieved. It is recognized that such single-phase displacement processes are very efficient, and capable of recovering, in most instances, more than half of the oil in place of the reservoir.

Morse et al., U.S. 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 preferably missible with both petroleum and flood water is then injected, and the solvents are driven towards producing wells by the injection of flood water. Morse also discloses that the step of injecting the liquid hydrocarbon may be omitted, in which case the amphipathic solvent directly contacts petroleum in the reservoir.

Prior art processes employing an amphipathic solvent, which by definition is mutually soluble in both oil and water, and which preferably is miscible in both oil and water, are effective for treating reservoirs which have been produced by primary-depletion techniques, and also are effective for treating reservoirs which have been subjected to a prior waterflood carried to the limits of economical oil recovery. The process of this invention is similarly adapted to the treatment of reservoirs previously subjected to primary depletion, and is particularly adapted to the recovery of additional quantities of oil from reservoirs which have been subjected to waterflood to the point at which further production by this method becomes economically unattractive.

It is an object of this invention to provide a secondary-recovery process by which a greater percentage of the residual oil in a subterranean reservoir can be recovered. Another object of this invention is to provide a secondary-recovery process by which recoveries equivalent to those obtainable by prior art miscible floods can be achieved by the use of smaller quantities of injected materials. Other objects of the invention will become apparent from the following description.

This invention is based upon the finding that the quantity of oil recovered by a miscible-drive process is substantially increased by incorporating in the solvent injected a minor proportion of a surface-active material. While the use of surfactants in secondary-recovery processes is not new, the use of such agents in a miscible-flood process has not before been proposed, apparently for the reason that the miscible solvent is by definition miscible with, or highly soluble in, both the petroleum and the injected floodwater. For this reason it is entirely unexpected that the incorporation of a surface-active agent in the miscible solvent should have any effect on the process.

Contrary to expectation, the dramatic effect of surface-active agents incorporated in the miscible solvent has been demonstrated by laboratory experiments conducted upon unconsolidated sand cores having a diameter of 1.25 inches and a length of 1 foot. The cores were saturated with a six-centipoise oil, then driven by floodwater to residual oil saturation. (Residual oil saturation is a condition which exists when the injection of additional quantities of floodwater into the core results in the production of no additional oil therefrom. Under this condition, the oil and water phases of the core have reached equilibrium. This is the approximate condition of a reservoir which has been subjected to waterflood over a long period of time.)

TABLE I

Run No.	Type of Slug	Oil Saturation After Waterflood (cm.³)	Volume of Slug Inserted (Pore Vol. percent)	Net Oil Produced by Slug (cm.³)	Percent of Oil in Place Recovered
1	IPA	30	50	19.5	65.0
2	IPA	35	46	23.0	65.7
3	98% IPA, 0.3% Potassium oleate, 1.7% Sodium sulfonate.	29	50	28.0	96.7
4	95% IPA, 5% Triton X-45.	27	50	24.0	89.0

In Runs 1 and 2, cores driven to residual oil saturation, and having oil contents of 30 and 35 cubic centimeters, respectively, were treated in accordance with the prior art miscible-flood processes by injecting isopropyl alcohol, followed by additional quantities of floodwater through the core. In each case, the isopropyl alcohol flood was capable of recovering about 65% of the residual oil in the core. In Run No. 3, a core similarly reduced to residual oil saturation was treated in accordance with the method of this invention by injecting a slug comprising 98% isopropyl alcohol, and 2% surface-active agent, followed by floodwater. In this experiment, 96.7% of the oil in place in the core prior to solvent flooding was recovered. Isopropyl alcohol alone is, of course, miscible with both water and with the oil recovered. While no certain explanation for the unexpected increase in oil recovery has been established, it is believed that the presence of the surface-active agent displaces the partition coefficient of the miscible solvent towards greater solubility in oil, when the solvent is in the presence of both oil and water.

The quantity of surfactant-containing solvent injected in accordance with the method of this invention will vary depending upon the nature of the reservoir treated, but generally will be within the range of about 0.03 to 0.10 reservoir pore volume, and preferably about 0.05 reservoir pore volume. The surface-active agent will be incorporated in the solvent-sufactant mixture in the amount of about 0.1 to 2.0 percent by volume.

The method of this invention is not limited to the use

of solvents which, in the pure state, are completely miscible with both oil and water; solvents which merely have high solubilities in both oil and water may also be used. Solvents which are truly miscible are nevertheless preferred. Examples of suitable materials are relatively low-molecular-weight, partially oxygenated hydrocarbons, such as tertiary butyl alcohol, isopropyl alcohol, ethyl alcohol, propanaldehyde, acetic acid, propionic acid, acetone, methyl ethyl ketone, 1,2 propylene oxide, 1,4 butylene oxide, dioxane, and ethylene glycol monobutyl ether. Also usable are the raw oxidation products of various thermal and catalytic methods for producing partially oxidized hydrocarbons from low-molecular-weight hydrocarbon starting materials. Such raw products comprise a wide variety of low-molecular-weight, partially oxygenated materials, most of which have substantial solubility in both oil and water. Ethyl alcohol and isopropyl alcohol are especially preferred because they are economical, abundant, and effective.

Any of a wide variety of oil-soluble surface-active agents may be incorporated in the solvent, providing only that the solvent and surface-active agents are compatible, i.e., nonreactive, and providing further that the surface-agent is compatible with reservoir constituents. Thus, under appropriate circumstances, anionic, cationic, and nonionic surface-active agents may be employed. Especially preferred, however, is the use of nonionic, predominantly oil-soluble surface-active agents. Exemplary of such preferred materials are isooctyl phenol polyethoxy ethanols, wherein the compounds contain about 3 to 5 ethylene oxide groups per molecule, on the average, sold for example under the name of Triton X–45. Numerous other surface-active agents may be selected from published tables listing the chemical, physical, and surface-active properties of various surfactants.

As a specific example of the method of this invention, a petroleum reservoir is penetrated by five wells in a five-spot pattern. This reservoir has been subjected to primary depletion and secondary-recovery waterflood until the water-to-oil ratios at the producing wells have risen to a value of about 2 to 1. Isopropyl alcohol in the amount of 0.05 reservoir pore volume is admixed with 1% by volume of a commercial mixed isooctyl phenol polyethoxy ethanol surfactant having an average of about five ethylene oxide groups per molecule. The mixture is injected into the formation through the central well of the five-spot pattern, and driven by the injection of floodwater towards the producing wells. The water-to-oil ratio at the producing wells initially continues to rise, and then drops abruptly to a value less than unity. The water-to-oil ratio then slowly rises to a value of about 5 to 1, at which point injection of floodwater and production of well fluids is discontinued. About 85% of the petroleum existing in the reservoir at the start of solvent injection has then been recovered.

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

1. The method of recovering petroleum from subterranean reservoirs penetrated by an injection well and a producing well comprising injecting through said injection well and into said reservoir about 0.03 to 0.10 reservoir pore volume of a mixture consisting essentially of a partially oxygenated hydrocarbon solvent which is mutually soluble in oil and water, and about 0.01 to 2.0% by volume of a surfactant, said surfactant being chemically nonreactive with said partially oxygenated hydrocarbon solvent driving said mixture towards said producing well by the injection of floodwater, and recovering petroleum from said producing well.

2. A method in accordance with claim 1 in which said partially oxygenated hydrocarbon is miscible with both oil and water.

3. The method in accordance with claim 1 in which said partially oxygenated hydrocarbon is a low-molecular-weight alcohol.

4. The method in accordance with claim 1 in which said partially oxygenated hydrocarbon is isopropyl alcohol.

5. The method in accordance with claim 4 in which said surfactant is an oil-soluble, non-ionic surfactant.

6. The method in accordance with claim 5 in which said surfactant is included in the amount of about 1% by volume.

References Cited by the Examiner

UNITED STATES PATENTS

2,800,962	7/1957	Garst	166—9
2,875,831	3/1959	Martin et al.	166—9
2,885,003	5/1959	Lindauer	166—9
2,910,123	10/1959	Elkins et al.	166—9
3,102,587	9/1963	Holbrook et al.	166—9

OTHER REFERENCES

Muscat, Morris: "Principles of Oil Production," 1st Edition, McGraw-Hill Book Company, Inc. (1949). Pages 99–105.

McCutcheon, John W.: "Surfactants Listed," reprinted from Soap and Chemical Specialties, December 1957, January through April 1958, MacNair-Dorland Co., Inc. (1958).

BENJAMIN HERSH, *Primary Examiner.*

CHARLES E. O'CONNELL, *Examiner.*