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MISCIBLE-DISPLACEMENT PROCESS

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This invention relates to the recovery of petroleum from subterranean reservoirs. It is more specifically concerned with improving the efficiency of gas-drive, secondary-recovery operations.

Secondary recovery of petroleum by the injection of a gas through an input well and withdrawal of reservoir fluids from a producing well has long been known and practiced. It was later discovered, in laboratory core experiments, that the recovery of petroleum by gas-drive could be greatly increased by first injecting a liquid hydrocarbon of low viscosity through the injection well, and following this slug of liquid hydrocarbon with a gas which is miscible with or highly soluble in the liquid hydrocarbon. Thus, it was found, for example, that when a petroleum-containing core was treated by the injection of a small amount of low-molecular-weight hydrocarbon, such as liquid propane, and then driven by a gas which is miscible with the propane, such as natural gas or methane, a highly efficient process was obtained.

Oil recoveries achieved in applying such miscible-displacement gas-drive processes to actual reservoirs were disappointing, in that the total oil recovery fell far short of that anticipated from predictions based on core experiments. It was found that while the process in fact succeeds in recovering practically all of the petroleum in the reservoir which is contacted by the injected liquid hydrocarbon, large quantities of petroleum are still by-passed and left in the reservoir when the process is carried out. This unfortunate result is due to the unfavorable mobility relationships of the reservoir fluids and injected fluids, which results in unsatisfactory areal sweep efficiencies and a corresponding decrease in the over-all efficiency of the process.

It is an object of this invention to provide an improved miscible-displacement, gas-drive, secondary-recovery process by which greater quantities of oil can be produced. Another object of this invention is to provide a miscible-displacement, gas-drive process in which greatly enhanced areal sweep efficiencies are obtained.

It has been found that the areal sweep efficiency of miscible-displacement, gas-drive, secondary-recovery processes can be greatly improved, and the over-all efficiency of the processes thereby enhanced, by incorporating in the low-viscosity liquid hydrocarbon injected a small amount of a high-foaming surfactant. The surfactant must be oil-soluble, and of the high-foaming type as hereinafter defined. It has been found that the injected driving gas coacts with the surfactant-containing liquid hydrocarbon to produce a stable foam which appears as a bank at the trailing edge of the bank of injected liquid hydrocarbon.

In carrying out the process of this invention, about 0.03 to 0.20 reservoir pore volume of a low-viscosity liquid hydrocarbon is first injected through the input well and into the reservoir. The liquid hydrocarbon is preferably a liquefied, normally gaseous, low-molecular-weight material, such as L.P.G., propane, or butane. However, other low-molecular-weight, normally liquid hydrocarbon fractions may be used. In general, hydrocarbon fractions consisting predominantly of C_3 and lower hydrocarbons are satisfactory. The gas injected to provide a gas drive must be inert, and miscible with, or highly soluble in, the injected hydrocarbon. Gases such as methane, ethane, and natural gas are preferred. The oil-soluble, high-foaming surfactant should be incorporated in the

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first-injected liquid hydrocarbon in the amount of about 0.1 to 5% by weight. The exact amount will vary depending upon the nature of the surfactant injected, but should be sufficient to produce a substantial quantity of stable foam upon contact of the surfactant-containing liquid hydrocarbon with natural gas. The exact amount of surfactant to be used can be determined by experiment, as hereinafter described.

The term high-foaming surfactant, as used in this specification and the appended claims, denotes a surfactant which, when incorporated in a liquid hydrocarbon in an amount not in excess of 5% by weight, meets the following test. The surfactant is dissolved in a hydrocarbon, such as hexane, and 500 ml. of the solution is placed in a graduated cylinder to form a column having a height of 50 centimeters. Natural gas at low pressure is passed into the bottom of the column through a fritted-glass disc at substantially atmospheric pressure, so that the gas bubbles through the column of liquid and passes out of the top of the cylinder. The gas rate is maintained at about 500 ml. of gas per minute, per square inch of column cross-sectional area. The flow of gas is continued for a period of 15 minutes, after which time the flow of gas is discontinued. A column of foam will then be found to exist at the top of the column of liquid hydrocarbon. A high-foaming surfactant, as defined in this specification, must be capable of producing a column of foam not less than 180 centimeters in height under the conditions aforedescribed.

With some high-foaming surfactants, the afore-described test requirements will be met by incorporating quantities of surfactant far less than 5% by weight, in the liquid hydrocarbon. Thus, where it is found that 2% by weight of a given surfactant is capable of meeting the requirements of the afore-defined experiment, it is preferred, for reasons of economy, that this amount be used. The use of excess quantities of surfactant should be avoided for reasons of economy, and to prevent the production of an excessively thick and viscous foam bank, which results in the necessity for employing excessive gas-injection pressures. While the use of various commercial high-foaming surfactants is contemplated, an example of a satisfactory foaming agent is a 1-to-1 mixture of di-coco dimethyl ammonium chloride and decyl trimethyl ammonium chloride. This mixture can be used in the amount of about 2% by weight, with excellent results. High-foaming surfactants can be selected from published tables describing the properties of commercially available surfactants.

As a specific example of the method of this invention, a petroleum-containing reservoir is subjected to secondary recovery by injecting through an input well a slug of liquid propane in which is incorporated 2% by weight of a 1-to-1 mixture of di-coco dimethyl ammonium chloride and decyl trimethyl ammonium chloride. Natural gas is then injected at sufficient pressure to maintain the propane as a liquid, to drive the propane bank toward four producing wells which surround the injection well. Petroleum is produced from the producing wells until the gas-to-oil ratio reaches an unattractively high value. At this point, the injection of gas is terminated and production continued under conditions of pressure depletion.

While all of the injected liquid hydrocarbon may contain a high-foaming surfactant, and such is preferred where small amounts of liquid hydrocarbon are injected, when larger banks of liquid hydrocarbon are used, it is preferred that the surfactant be incorporated only in the last-injected portion of the liquid hydrocarbon. Thus, where the quantity of liquid hydrocarbon injected is not more than about 0.05 reservoir pore volume, surfactant will generally be incorporated in the entire quantity of liquid hydrocarbon, or at least in most of it. Where a larger bank of propane is employed, such

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as 0.15 reservoir pore volume, it is preferred that the surfactant be incorporated only in the last-injected portion of the liquid hydrocarbon. The amount of liquid hydrocarbon in which the surfactant is placed should be not less than about 0.03 reservoir pore volume, and ordinarily will be about 0.05 reservoir pore volume. Where the reservoir is known to contain substantial quantities of free gas dispersed in a substantially homogeneous distribution throughout the reservoir, it is especially preferred that the first-injected liquid hydrocarbon contain no surfactant in order to avoid the production of a bank of foam at the leading edge of the liquid hydrocarbon bank, thereby encouraging the liquid hydrocarbon to bypass a portion of the reservoir. On the other hand, where the reservoir is known to contain free gas which is localized in a gas cap above the petroleum-containing portions of the reservoir, it is advantageous to distribute the surfactant throughout the entire liquid hydrocarbon bank, so that the production of a foam bank at the interface with the gas cap will occur, thus retarding the entry of the liquid hydrocarbon bank into the gas cap, and avoiding consequent bypassing of the petroleum-containing portions of the formation.

The objects of this invention cannot be achieved by incorporating the surfactant in the injected gas, rather than in the liquid hydrocarbon, for the reason that any foam produced will lag behind the liquid hydrocarbon-gas interface, and the presence of the foam at this interface is essential.

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

1. The method for recovering petroleum from underground reservoirs penetrated by an injection well and a producing well comprising injecting through said injection well and into said formation 0.03 to 0.20 reservoir pore volume of a low-molecular-weight liquid hydrocarbon, at least the last-injected 0.03 reservoir pore volume of which contains in solution a high-foaming, oil-soluble surfactant in an amount sufficient to produce a foam on contact in the reservoir with a hydrocarbon gas, then injecting hydrocarbon gas, substantially free of a surfactant, to form a foam bank at least between said injected liquid hydrocarbon and said hydrocarbon gas and to drive said injected liquid hydrocarbon toward said producing well, and recovering petroleum therefrom.

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2. The method in accordance with claim 1 in which the amount of liquid hydrocarbon injected is in excess of 0.05 reservoir pore volume, and the portion of said liquid hydrocarbon in which the high-foaming surfactant is incorporated is not in excess of 0.05 reservoir pore volume.

3. The method in accordance with claim 1 in which the high-foaming surfactant is in hydrocarbon solution in the amount of about 0.1 to 5.0% by weight.

4. The method in accordance with claim 1 in which the liquid hydrocarbon is liquefied propane, and the hydrocarbon gas is injected under sufficient pressure to maintain said propane as a liquid in the reservoir.

5. The method in accordance with claim 4 in which the concentration of high-foaming surfactant in said propane is about 0.1 to 5.0% by weight.

6. The method in accordance with claim 5 in which the quantity of propane injected is in excess of 0.05 reservoir pore volume, and the last-injected portion of said bank in which high-foaming surfactant is incorporated amounts to about 0.05 reservoir per volume.

7. The method in accordance with claim 6 in which said high-foaming surfactant is a 1-to-1 mixture of dicoco dimethyl ammonium chloride and decyl trimethyl ammonium chloride, and the mixture is incorporated in the propane in the amount of about 2% by weight.

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