

March 19, 1968

C. E. COOKE, JR

3,373,809

MICROEMULSION OIL RECOVERY PROCESS

Filed Nov. 15, 1965

2 Sheets-Sheet 1

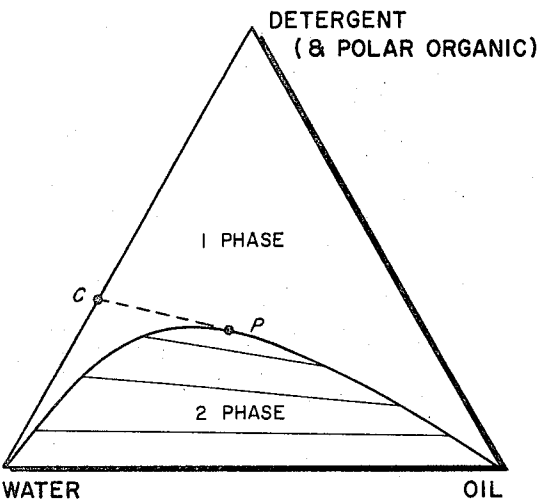


FIG.-1

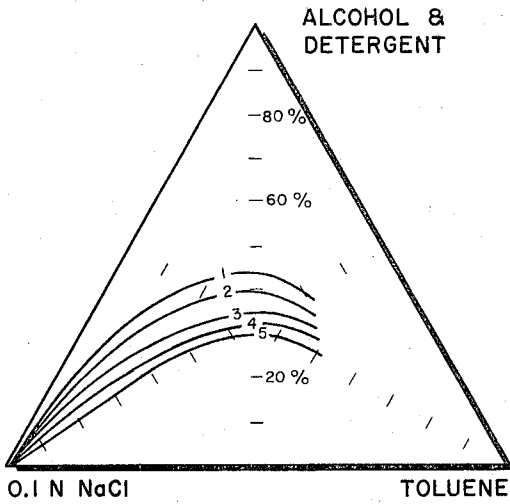


FIG.-2

102
X102
X102

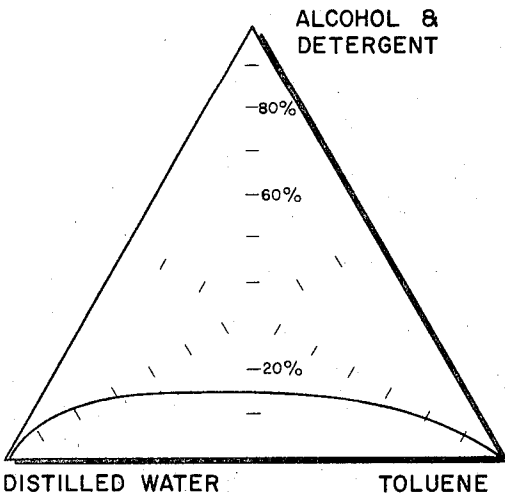


FIG.-3

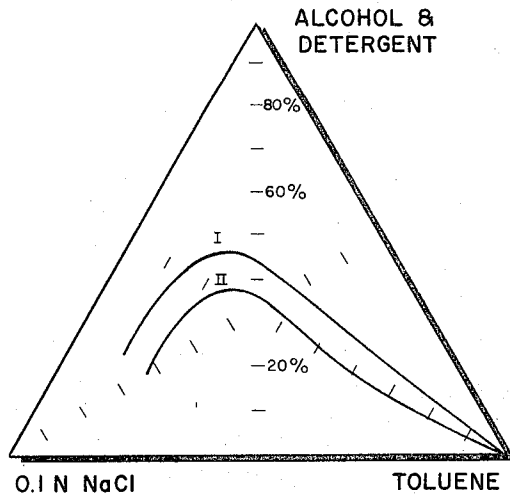


FIG.-4

CLAUDE E. COOKE, JR. INVENTOR.

BY *Gary C. Honeycutt*
ATTORNEY

March 19, 1968

C. E. COOKE, JR

3,373,809

MICROEMULSION OIL RECOVERY PROCESS

Filed Nov. 15, 1965

2 Sheets-Sheet 2

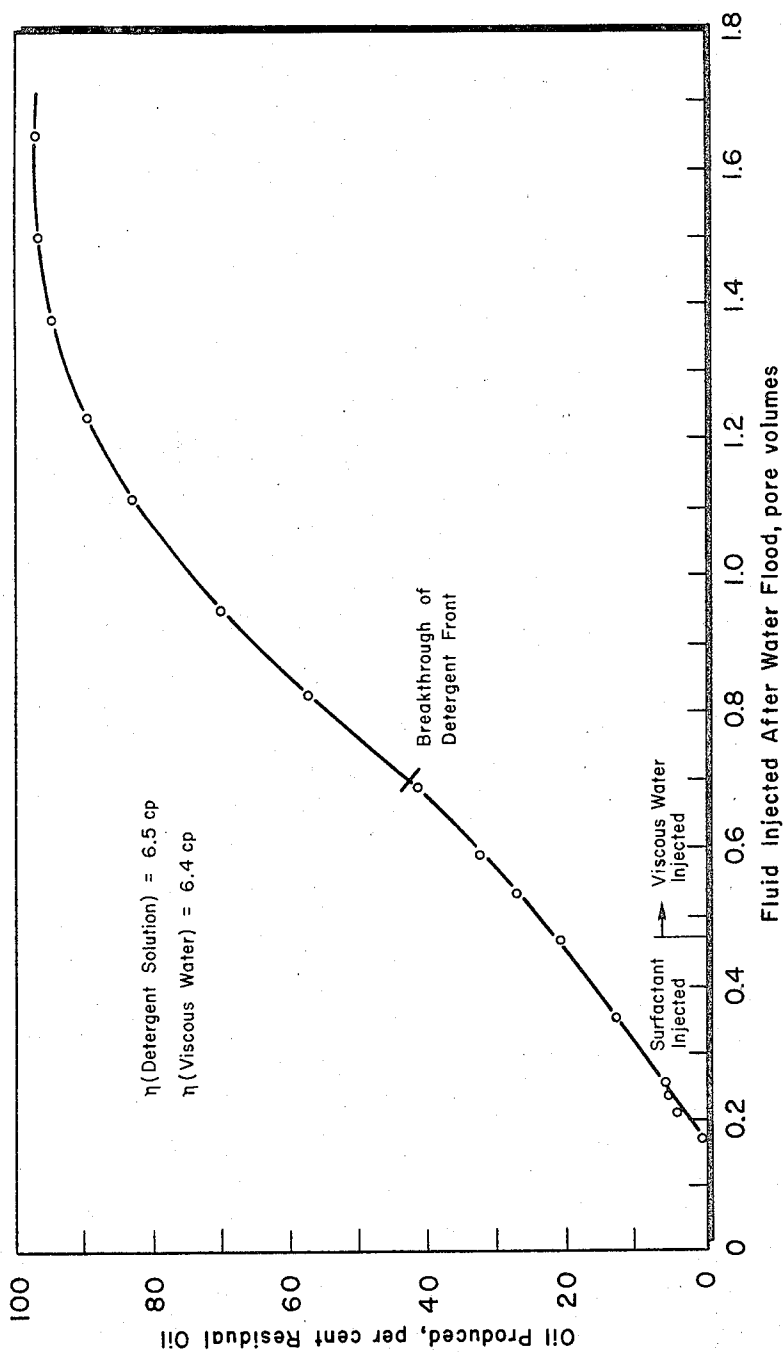


FIG-5

CLAUDE E. COOKE, JR. INVENTOR.

BY *Gary C. Honigsmitt*

ATTORNEY

1

3,373,809

MICROEMULSION OIL RECOVERY PROCESS
Claude E. Cooke, Jr., Houston, Tex., assignor to Esso
Production Research Company, a corporation of
Delaware

Filed Nov. 15, 1965, Ser. No. 507,836
10 Claims. (Cl. 166-9)

ABSTRACT OF THE DISCLOSURE

In the recovery of oil from subterranean oil-bearing formations, an aqueous detergent solution is injected for the in situ formation of a water external microemulsion on contacting the reservoir oil. The concentration of surfactant in the injected solution is greater than the minimum miscibility concentration.

This invention relates to the recovery of additional oil from porous subterranean reservoirs. A method is provided which involves a displacement of the reservoir oil by a concentrated aqueous detergent solution. The detergent is selected from a limited class of materials which have the unique ability to solubilize unusually large amounts of oil, forming microemulsions. In accordance with a more limited embodiment, the addition of a polar organic compound, an alcohol for example, is essential to the formation of a microemulsion. Such polar materials may be introduced with the detergent solution, or as a separate bank.

Numerous prior disclosures have proposed the recovery of oil by displacement with an aqueous detergent solution. It has been a general premise of such prior disclosures that the essential function of a detergent is to lower the interfacial tension between the aqueous and oil phases. It is well known that surfactant concentrations in excess of the critical micelle concentration have a negligible effect on interfacial tension. Accordingly, since the critical micelle concentration of a detergent rarely exceeds 1 to 2 percent, the investigation of more concentrated detergent solutions may have appeared to hold little promise.

Of course, the solubilization of oil in aqueous solutions can occur, to an appreciable extent, in any aqueous solution of a surface-active chemical, to an appreciable extent, in any aqueous solution of a surface-active chemical, whenever micelles are formed. But the amount of oil solubilized by a surfactant solution is usually small, because the micelles are very small, consisting of about seventy molecules of surfactant, for example. In most instances, an increased concentration of surfactant is ineffective to increase the size of individual micelles. Thus, increased concentrations of surface-active agents are usually ineffective to improve the efficiency with which residual oil is displaced from a porous reservoir.

Under certain conditions, however, with selected surfactants, the micelles can be caused to grow to much larger dimensions, with a consequent increase in the amount of oil solubilized by a given amount of detergent. These systems, which include unusually large micelles and large amounts of solubilized oil in aqueous media, are transparent, and are known as microemulsions. It has now been found that an aqueous detergent solution capable of forming a microemulsion with oil has an unusually high displacement efficiency in the recovery of reservoir oil.

SUMMARY OF THE INVENTION

This invention is a method for miscibly displacing the oil contained in subterranean reservoir by injecting a solution capable of forming a water external microemul-

2

sion with the reservoir oil upon injection. The solution capable of forming a water external microemulsion which will maintain miscibility with the resident oil and following flood water consists of an aqueous solution of detergent and in most instances an organic polar compound. The concentration of detergent and organic polar compound in the aqueous solution is at or above the minimum miscibility concentration. The minimum miscibility concentration is discussed in greater detail hereinafter.

With few exceptions, the formation of a microemulsion requires the presence of an organic polar material, such as an alcohol, phenol, amine, acid, etc., in addition to the surfactant or detergent itself. It is known to displace reservoir oil with a bank of an oil-miscible liquid, for example, with alcohol alone, whereby a true molecular solution of the reservoir oil is formed. The microemulsion-forming solutions of the present invention are as effective as alcohol alone in their ability to recover oil, while possessing the distinct advantage of being far less expensive. Frequently, the solutions of the present invention are even more effective than an oil-miscible solvent, for example, an alcohol bank injected by itself, because relatively small volumes of connate water are sufficient to cause a separation of phases when flooding with an alcohol alone, whereas the solutions of the present invention retain their oil-miscible character despite substantial dilution by connate water or brine.

In accordance with one embodiment of the invention, the detergent solution consists essentially of detergent plus water, and is injected into the petroleum reservoir as the sole flooding medium. However, this will be recognized by those skilled in the art as an uneconomic alternative compared with the injection of a detergent solution in a limited amount, sufficient to form a bank of 3 to 20 percent of the reservoir pore volume, followed by the injection of a propelling medium, usually water.

In accordance with a further embodiment of the invention, a bank of concentrated microemulsion-forming detergent solution is injected, followed by the injection of water containing a thickening agent such as polyacrylamide or sulfonated polystyrene. The use of water thickened to a viscosity at least as great as the viscosity of the detergent solution as a propelling medium is particularly preferred. The thickened water permits the use of a minimum detergent solution bank size, since the viscous propelling medium does not finger through the detergent bank with a consequent disruption and dissipation of the detergent bank.

In accordance with a further embodiment of the invention, the microemulsion-forming detergent solution is preceded by a bank of oil. In some instances, a leading bank of oil is essential to the economic success of the process, particularly where the reservoir oil is highly resistant to the formation of a microemulsion. Thus, the injected bank of oil is selected for the ease with which it forms a microemulsion, thereby permitting the detergent bank to achieve a miscible-like displacement. As before, the detergent bank may be followed by thickened water as a propelling medium.

In accordance with a further embodiment of the invention, the microemulsion-forming detergent bank consists essentially of water, a detergent, and an organic polar compound. The aqueous detergent bank containing a polar additive is injected as a leading bank, or is preceded by a bank of oil as before. The detergent bank is then followed by water as a propelling medium, which preferably is thickened to a viscosity at least as great as that of the detergent solution.

In accordance with a still further embodiment of the invention, the organic polar material may be injected as a separate bank, either before or after the injection of the aqueous detergent solution. This embodiment may

therefore involve the successive injection of four materials; that is, a leading bank of oil selected for the ease with which it forms a microemulsion, followed by a bank of organic polar solvent, followed by the aqueous microemulsion-forming detergent solution, followed by thickened water to propel the system through the reservoir.

FIGURE 1 is a ternary phase diagram illustrating the phase behavior required to obtain a miscible displacement of reservoir oil.

FIGURE 2 is a ternary phase diagram showing the two-phase envelopes for various alcoholic detergent-brine-toluene systems.

FIGURE 3 is a ternary phase diagram showing the two-phase envelope of the alcoholic sodium dodecylbenzene sulfonate-water-toluene system.

FIGURE 4 is a ternary phase diagram showing the two-phase envelopes of two alcoholic sodium dodecylbenzene sulfonate-brine-toluene systems having different ratios of detergent to alcohol.

FIGURE 5 is a recovery curve obtained by displacing waterflood residual oil from a Berea sandstone core with a microemulsion-forming alcohol detergent solution in distilled water.

The flow behavior in a porous reservoir during a microemulsion flood is similar to the flow behavior obtained in the displacement of oil with an oil-water mutual solvent, alone, such as butyl alcohol. The flow behavior is similar, in that the microemulsion-forming flood medium contains in aqueous solution certain materials which, by mass transfer, pass into the oil phase thereby swelling the residual oil, such as occurs during an alcohol flood. In addition, some oil will become mobile because of a lowering of interfacial tension; and this oil is pushed ahead of the microemulsion-forming solution. The oil phase left immobile in the rock is finally dissolved in or becomes miscible with the injected fluid and begins moving at the same velocity as the injected fluid.

It is preferred that a microemulsion flood behave as a miscible displacement, in order that on a pore volume basis much smaller, more economical banks of injected solution can be employed to obtain high oil recovery, than would otherwise be possible. The required conditions for a miscible displacement are illustrated by the ternary phase diagram of FIGURE 1. It can be shown that a miscible displacement will occur if the injected aqueous detergent solution is richer in detergent than the composition denoted by point C. The point C is defined by the intersection of a line drawn tangent to the two-phase envelope, at the plait point, with the water-detergent side of the diagram. This detergent-polar organic compound concentration is referred to herein, for the purpose of convenience in nomenclature, as the Minimum Miscibility Concentration.

In those embodiments wherein the aqueous detergent solution also contains a polar organic compound, such as an alcohol, it has been found convenient to approximate the phase behavior of the resulting four-component system in a ternary diagram, by treating the polar solvent and detergent as a single component. This representation is exact only when the ratio of polar compound to detergent is the same in both phases of any two-phase composition. The error introduced by this assumption is relatively slight, however, and can readily be tolerated in preference to the complexity of a three dimensional four-component phase model. Thus, in FIGURE 1, the vertex designated "detergent" may represent a certain fixed ratio of detergent to polar additive. In such instances, the point C as defined above represents the minimum concentration of detergent plus polar additive, in water, required to achieve miscible displacement of the oil.

Accordingly, for the purposes of the present invention, the preferred embodiments are those characterized by a ternary-phase diagram having a large one-phase region. Systems having a large one-phase region are preferred, since the point C for such system falls closer to the water

vertex of the ternary diagram, which means that miscible displacement may be achieved with lower concentrations of detergent, or detergent plus polar additive. It is essential that the two-phase envelope fall entirely below that level of the ternary diagram which corresponds to 70% detergent, or 70% detergent plus polar organic compound. Preferably, the two-phase region should not include any compositions which contain more than 50% detergent, or 50% detergent plus polar organic.

In accordance with a more limited aspect of the invention, the two-phase region may be further reduced in size, not only by the selection of various preferred species of detergent and polar additive, but also by first injecting an oil component characterized by the formation of microemulsion solutions with unusual ease. This is accomplished, for example, by injecting a small bank of toluene or other light aromatic or paraffinic oil; or any material which is miscible with the crude and more readily capable of forming microemulsion solutions than is the reservoir crude.

Suitable examples of polar organic compounds for use in accordance with the invention include the n-, cyclo- and iso-alcohols having 4-16 carbon atoms per molecule; the n-, cyclo- and iso-amines having 5-12 carbon atoms per molecule; phenol and phenols having side chains with 1-10 carbon atoms per molecule; n-, cyclo- and isomercaptans having 2-10 carbon atoms per molecule; glycols having 2-12 carbon atoms per molecule; fatty acids having 6-22 carbon atoms per molecule; glycerols having 3-18 carbon atoms per molecule; ketones having 5-18 carbon atoms per molecule; ethers having 4-18 carbon atoms per molecule; aldehydes having 4-18 carbon atoms per molecule; and mixtures of two or more of the above. All these molecules may contain saturated or unsaturated carbon-carbon bonds.

Suitable concentrations of polar organic compound, in those embodiments of the invention which comprise the injection of both detergent and polar organic in the same bank, range from about 15% to 60% by weight, preferably from 20% to 40% by weight, depending primarily upon the selection of detergent, and the relative ease with which the reservoir oil or injected oil forms microemulsions. As noted earlier, the polar organic may be injected in a separate bank, or in highly concentrated banks. The stated range of concentrations would apply, in that event, to the "effective concentration" of polar organic, when considering the combination of the detergent bank plus the polar organic-comprising bank.

Suitable detergents or surfactants include anionic and nonionic compounds, for example, sulfonated aromatic hydrocarbons, ethylene oxide condensates of aliphatic acids, alkyl aryl polyalkylene glycol ethers, esters of sulfosuccinic acid, mono- and dibasic carboxylic acids, alkyl and aryl sulfates; specific examples of which include isopropyl naphthalene sodium sulfonate, sulfonated petroleum distillates, ethylene oxide condensates of coco fatty acids, octylphenyl polyoxyethylene ether, diisooctyl sodium sulfosuccinate, perfluorocaprylic acid, diisohexyl succinic acid, dodecyl sulfate and amylphenyl sulfate.

The concentrations of detergent(s) useful in accordance with the present invention range from about 5% by weight up to about 40% by weight, and preferably from 10% to 30% by weight, based on the total weight of the injected detergent solution, which usually includes the polar organic compound. It will be apparent that these concentrations are much greater than the concentrations proposed in the prior art for the use of surfactants as waterflood additives in oil recovery processes. The greater concentrations are essential in accordance with the present invention, since the present mechanism involves microemulsion formation and miscible displacement, whereas the prior art use of detergents has been to lower interfacial tension, without achieving miscibility.

Specific combinations of a polar organic compound and a soap or detergent for use in the present invention in-

clude phenol and sodium oleate; phenol and sodium abietate; phenol and ethanolamine oleate; pine oil and sodium oleate; glycerol and turkey red oil; diethylene glycol and turkey red oil; octyl alcohol and potassium myristate; octylamine and potassium myristate; octylamine and potassium myristate; octyl mercaptan and potassium myristate; cetyl alcohol and oleic acid; p-methyl cyclohexanol and oleic acid; oleic acid and sodium oleate; n-amyl alcohol and an octylphenyl polyoxyethylene ether obtained by reacting 13 mols ethylene oxide with octylphenol (Triton X-102).

It will be apparent that some of the above-named detergents are sensitive to divalent ions, such as calcium and magnesium, frequently encountered in petroleum reservoirs. It is contemplated in such instances that the detrimental effect of these ions can be avoided by the addition of a chelating agent to the flood water, or by preflooding the reservoir to displace divalent salt-containing brines and thereby eliminate the problem.

In FIGURE 2, each two-phase envelope was obtained with a different alcohol. Envelope 1 was obtained with tertiary amyl alcohol; envelope 2 was obtained with normal butyl alcohol; envelope 3 was obtained with cresol; envelope 4 was obtained with normal amyl alcohol; and envelope 5 was obtained with normal hexyl alcohol. The detergent in each instance was sodium dodecyl benzene sulfonate. The ratio of sulfonate to alcohol was 2:1 by weight in each system. In the order named, these polar additives have a decreasing solubility in water. It is significant that for these materials, the lower the water solubility of the polar additive, the larger is the one-phase region of the diagram; and consequently, the greater is the solubilizing power of the microemulsion-forming solution. For example, miscible displacement can be achieved with a lower concentration of the normal hexyl alcohol-detergent combination, than with similar combinations of detergent and the lower molecular weight alcohols or cresol.

In certain instances, gel formation may tend to occur when concentrated solutions of detergent are prepared, with or without the presence of polar organic solvent and/or oil. Therefore, it is generally advisable to test a proposed detergent solution, in contact with the reservoir oil, prior to injection, in order to determine its suitability as a displacing medium. A viscosity in excess of 200 cps. is considered too great for most flooding operations, due to low injectivities at the input wells, and the consequently excessive periods of time required to complete the recovery of oil. Ordinarily, the solutions injected in accordance with the invention have a viscosity of about 10 cps., and preferably should not exceed 100 cps.

In FIG. 3, the detergent is sodium dodecylbenzene sulfonate, and the alcohol is normal butanol. A weight ratio of sulfonate to butanol of 1:1 has been found to give essentially the same two-phase envelope as obtained with a sulfonate-to-butanol ratio of 0.838:1. The two-phase region for this system is unusually small, indicating that a successful miscible displacement can be obtained with an unusually high proportion of water in the microemulsion-forming flood bank.

The system of FIGURE 4 differs from that of FIGURE 3 only in the substitution of 0.1 N sodium chloride for distilled water. Curve I is the two-phase envelope for a sulfonate-to-butanol ratio of 0.838:1, whereas curve II is the two-phase envelope obtained for a weight ratio of sulfonate-to-butanol of 1:1. Thus, the presence of salt decreases the amount of solubilized toluene; and the amount solubilized increases with an increasing ratio of sulfonate to alcohol.

The recovery curve of FIGURE 5 illustrates the results of Example I below.

Example I

A 3-ft.-long, 2-in.-diameter Berea sandstone core was prepared to contain water and 32% pore volume of residual oil after a waterflood. A solution consisting of

16.1% dodecylbenzene sulfonic acid neutralized with NaOH, and 27.3% n-butyl alcohol in distilled water was then injected into the core. A total of 46.7% pore volume of solution was injected, at a linear flow rate of one foot per day. This solution was followed by a water solution of polyacrylamide, a polymer used to increase the viscosity of the flood water to approximately the viscosity of the microemulsion-forming sulfonate-alcohol water solution (6.5 cps.). This was done to prevent fingering or channeling of water through the microemulsion solution. The effluent from the column was collected in several steps, and the microemulsion was broken by the addition of methanol so that the oil content could be measured. About 40% of the residual oil was produced before breakthrough of the detergent. The total recovery was 97% of the residual oil after the injection of about 1.5 pore volumes of fluid.

Example II

A petroleum reservoir is waterflooded to a residual crude oil saturation of about 30% pore volume. In accordance with the present invention, flood water is then injected which contains 20% by weight petroleum sulfonates, and 30% by weight oxygenated olefinic hydrocarbons. The petroleum sulfonates are obtained, for example, by treating a heavy aromatic naphtha (average mol. weight of 230) with 20% oleum, separating the acid layer which contains water-soluble sulfonates, and neutralizing with NaOH to obtain the corresponding sodium salts. The oxygenated hydrocarbons are obtained, for example, by the partial oxidation or oxygenation of unsaturated hydrocarbon fractions, in accordance with known methods. The olefins present in such fractions are thereby converted to aldehydes, alcohols, ethers, ketones, and minor amounts of other oxygen compounds. Such reaction product mixtures are particularly suited for use in accordance with the invention, without the need for separation or refinement, which affords an attractive economy with respect to sources of relatively pure compounds.

The solution of petroleum sulfonates and oxygenated hydrocarbons is injected until about 0.05 pore volume of the reservoir is flooded. Thereafter, a 0.2 pore volume bank of thickened water is injected, containing 0.05% by weight of partially hydrolyzed polyacrylamide as the thickener. The thickened bank is then followed with water or brine until a total of about 1.5 pore volumes of flooding medium is injected, counting the detergent-polar organic bank and the thickened water. Oil recovery is essentially complete, indicating miscible displacement.

Example III

A series of aqueous solutions containing 1.5 parts by weight of petroleum sulfonate detergent, and one part by weight of n-pentanol, were prepared. The ability of each solution to solubilize oil was determined by slowly adding a petroleum crude oil, while stirring the mixture, until the first appearance of turbidity was noted. The following data were obtained:

Wt. percent detergent plus alcohol in total system:	Wt. percent oil solubilized
24.0	4.9
28.0	5.5
42.5	14.6
45.0	27.2

It is readily seen from the data that this combination of detergent and alcohol falls within the preferred scope of the invention, since the system containing 45% detergent plus alcohol and substantially equal weights of water and oil was on the boundary between the one-phase and the two-phase parts of the phase diagram. The two-phase envelope falls entirely below that part of the phase diagram which corresponds to 45.0% detergent plus polar organic.

What is claimed is:

1. A method for the recovery of oil from a porous reservoir having an input well and an output well which comprises injecting through said input well a detergent solution capable of forming a water-external microemulsion with oil, forming a water-external microemulsion within the reservoir, and withdrawing displaced reservoir oil from said output well, wherein the concentration of the detergent is at least the minimum miscibility concentration which is a detergent concentration denoted on a water and detergent side of a water, oil, and detergent ternary phase diagram by an intersection of the water and detergent side with a line tangent to a phase envelope at a plait point.

2. The method as defined by claim 1 wherein the amount of detergent solution injected is 3 percent to 20 percent of the pore volume of the reservoir flooded.

3. The method as defined by claim 1 wherein the detergent is selected from the group consisting of sulfonated aromatic hydrocarbons, ethylene oxide condensates of aliphatic acids, alkyl aryl polyalkylene glycol ethers, esters of sulfosuccinic acid, mono- and dibasic carboxylic acids, alkyl and aryl sulfates.

4. The method as defined by claim 1 further including injecting a light hydrocarbon solvent, miscible with the reservoir oil prior to injection of the detergent solution.

5. The method as defined by claim 1 further including injecting a polar organic material as a separate bank.

6. A method for the recovery of oil from a porous subterranean reservoir having an input well and an output well which comprises injecting through said input well a solution capable of forming a water-external microemulsion on contacting oil, forming a water-external microemulsion in the reservoir, and withdrawing displaced reservoir oil from said output well wherein the solution comprises detergent and polar organic material in aqueous solution, the concentration of detergent and polar organic material being at least the minimum miscibility concentration which is a detergent-polar organic material concentration denoted on a water and detergent-polar organic material side of a water, oil, and detergent-polar organic material ternary phase diagram by an intersection of the water and detergent-polar organic ma-

terial side with a line tangent to a phase envelope at a plait point.

7. The method as defined in claim 4 wherein the amount of the aqueous solution of detergent and polar organic material injected is 3 percent to 20 percent of the pore volume of the reservoir flooded.

8. The method as defined in claim 4 wherein the detergent is selected from the group consisting of sulfonated aromatic hydrocarbons, ethylene oxide condensates of aliphatic acids, alkyl aryl polyalkylene glycol ethers, esters of sulfosuccinic acid, mono- and dibasic carboxylic acids, alkyl and aryl sulfates.

9. The method as defined in claim 4 wherein the polar organic compound is selected from the group consisting of normal, cyclo- and iso-alcohols having 4-16 carbon atoms per molecule; the n-, cyclo- and iso-amines having 5-12 carbon atoms per molecule; phenol and phenols having side chains with 1-10 carbon atoms per molecule; n-, cyclo- and iso-mercaptans having 2-10 carbon atoms per molecule; glycols having 2-12 carbon atoms per molecule; fatty acids having 6-22 carbon atoms per molecule; glycerols having 3-18 carbon atoms per molecule; ketones having 5-18 carbon atoms per molecule; ethers having 4-18 carbon atoms per molecule; aldehydes having 4-18 carbon atoms per molecule.

10. The method as defined by claim 5 further including injecting a light hydrocarbon solvent, miscible with the reservoir oil prior to injection of the microemulsion forming solution.

References Cited

UNITED STATES PATENTS

3,330,344	7/1967	Reisberg	166—9
2,742,089	4/1956	Morse et al.	166—9
3,131,759	5/1964	Susser et al.	166—9
3,163,214	12/1964	Csaszar	166—9
3,254,714	6/1966	Gogarty et al.	166—9
3,266,570	8/1966	Gogarty	166—9
3,275,075	9/1966	Gogarty	166—9
3,301,325	1/1967	Gogarty	166—9
3,307,628	3/1967	Sena	166—9

JAMES A. LEPPINK, *Primary Examiner.*