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2,846,012

RECOVERY OF OIL FROM PARTIALLY DEPLETED RESERVOIRS BY SECONDARY RECOVERY

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This invention is concerned with increasing the efficiency of secondary recovery methods employed in producing petroleum oil from partially depleted subterranean reservoirs. It more specifically relates to modifying the wettability of a formation reservoir in controlling the movement of a water injection fluid through the openings of an oil-containing reservoir.

The phenomena of capillarity and surface tension and their application in petroleum production have been extensively studied. It is well known that these phenomena influence the efficiency of processes employed in the production of petroleum oils from subterranean reservoirs by so-called secondary recovery methods wherein the residual oil is flushed or driven from the rock reservoir by injecting into the reservoir by means of an injection well a drive fluid such as water or gas. The produced fluids are recovered for further processing by means of a recovery well or wells. In facilitating the use of water as a drive fluid in the treatment of oil sands, a number of expedients have been employed to complement the effect of the drive fluid. Surface-active agents have been used to induce the preferential wetting of the sand by the water flood rather than by the reservoir oil in order to permit the oil to be more readily driven out by the water-flooding. However, it is an object of the instant invention to employ the opposite approach and facilitate reservoir drainage in secondary recovery operations by making the formation preferentially oil-wettable in a peripheral zone immediately adjacent the well bore. This and other objects will become more apparent from the following detailed description of the instant invention.

In the water-flooding of depleted or partially depleted subterranean oil-bearing reservoirs to recover the residual oil, the initial flow of water into the formation openings is controlled by a number of factors. From a geometrical standpoint, considerable flow resistance is encountered due to the limited access provided by the small amount of area of rock face which is exposed by a traversing bore hole of relatively small diameter. Limitations in the size of the formation openings directly entering into the bore hole can be overcome by the use of formation penetrators, such as acidizing media or hydraulic fracturing fluids. The function of these processes is to increase the size of the interstitial openings which channel out in a radial, horizontal direction from the bore hole, thereby increasing the porosity and permeability of the formation in an area near the bore hole. The use of these expedients involves special equipment, the use of which can greatly add to the expense entailed in producing oil from subterranean reservoirs. These techniques improve the fluid distribution by increasing the size of the interstitial openings, thereby reducing the resistance to the flow of fluids therethrough. The fluid distribution can also be influenced by modifying the effective permeability characteristics of the formation without in fact increasing the diameter of the interstitial openings. This change in effective permeability is effected by

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controlling the wetting characteristics of the injection fluid. From a wettability standpoint, formations are encountered which are oil-wet, or water-wet. While most reservoirs are considered preferentially water-wet, it is possible to have reservoirs which are intermediate in wettability, being on a borderline between oil-wet and water-wet. A number of procedures have been used to change the characteristics of the formation from water-wet to oil-wet in order to avoid the loss in mobility of a fluid which will wet the formation reservoir surfaces and thereby adhere thereto. In a water-wet formation the water is distributed in the finer capillaries, and in a more or less thin layer over the entire surface accessible to fluid contact. Because the water is restricted to the smaller interstitial passageways and is spread out over a large solid surface, its mobility is not as great as that of the oil which is located in the larger interstitial passageways and is spread out over a water surface. Thus if the water is to move it must overcome the resistance of the solid-water interface and the oil-water interface, while the oil has only to overcome the resistance offered by the oil-water interface. Furthermore, the oil, occupying the larger interstitial passageways, has larger channels available to flow through than does the water. From this it is evident that if two fluids are present in a rock, the non-wetting fluid should find less resistance to flow.

In water injection wells two fluids, oil and water, are present in the surrounding formation. After a relatively short injection period, most of the recoverable oil will have been flushed from the area immediately surrounding the well bore to a radius of about 10-20 feet. If the formation is water-wet, as is the more common case, the water passing through the flooded-out section of 10 feet radius will meet the resistance to flow of a water-wet system which is higher than would be the case of an oil-wet system. Therefore, according to this invention the introduction of water into a partially depleted oil-bearing reservoir is facilitated by modifying the characteristics of this substantially oil-free, circumambient zone immediately adjacent the bore hole, which is serving as the injection well, to make the formation surfaces in this zone preferentially oil-wettable. This change in wettability is effected in the instant invention by coating the formation surfaces in this circumambient zone with a monomolecular silicone coating. In the prior art, a number of expedients have been described for treating formations with silicones. In U. S. Patents 2,469,354 and 2,633,919 silicone coatings have been provided on the formation reservoir surfaces by treating the formation with a silicon halide, such as methyl dichlorosilane, which is subsequently hydrolyzed to form a silicone polymer which is adsorbed on the surfaces of the formation. In employing silicon halides it is necessary that the formation be dried by the use of heating and/or solvent washing in order to prepare the reservoir surfaces preparatory to coating them with the silicone polymer. Such preliminary treatment requires the use of auxiliary equipment and frequently, in spite of the efficiency of this equipment, complete drying is not always effected, which influences the efficacy of the treat. In U. S. Patent 2,614,635 this disadvantage is overcome in the treating of subterranean formations by employing an oil solution containing a small amount of a liquid silicone polymer. To be effective, the silicone solution must be heated to a temperature of at least about 500° F. While in this instance it is unnecessary to employ a dehydrating step, it is necessary to provide heating means to heat the treating agent. Also, this method entails the introduction of substantial amounts of oil into the formation in order to provide the desired coating of the reservoir surfaces. This, of course, requires that in order that the process be

conducted economically it is necessary that this oil, or at least a substantial amount of it, be recovered. This, however, is not always possible because the irreducible minimum saturation of formation areas with this oil may occur, preventing its recovery. In practicing the instant invention these disadvantages are overcome by the use of water-soluble salts of esters of silicic acids as the silicone-forming agents. Such materials, because of their water-solubility, may be readily introduced directly into the water flood and injected into the formation whereby a silicone coating is formed on the reservoir surfaces without the need for dehydrating the formation or using oil solutions of silicone-forming agents. The silicone-forming substances which may be employed in the instant invention are those water-soluble salts of esters of silicic acid which decompose and precipitate a silicone when contacted with a weakly acidic solution. Examples of suitable siliconates for use in carrying out the invention include the water-soluble alkyl, aryl, and alkaryl derivatives of the silicic acid salts or mixtures thereof. Specific metal siliconates include sodium methyl siliconate, potassium ethyl siliconate, calcium phenyl siliconate, barium benzyl siliconate, lithium propyl siliconate. Although only alkali metal and alkaline earth metal siliconates are specifically illustrated, other cationic substituents may be employed. Other suitable salts include aluminum, zinc, copper, etc., as well as the substituted ammonia salts. The preferred salts are the alkali metal and substituted ammonia salts because of their excellent water-solubility which prevents any deleterious precipitates from forming within the formation due to the presence of cations which may react to form water- and oil-insoluble products. The silicic acids which are utilized in preparing the salts of this invention may be formed by hydrolyzing alkyl trichlorosilanes to form a hydrolyzate which then is neutralized with aqueous sodium hydroxide according to conventional neutralization techniques. Methods of preparing metal organic siliconates are described in detail in U. S. Patents 2,438,055, 2,441,422, and 2,441,423. If alkyl siliconates are dried, free-flowing water-soluble powders can be produced. One suitable water-soluble alkyl siliconate, sodium methyl siliconate, is commercially available and may be purchased from the General Electric Company under the mark "SC-50."

In employing the silicone-forming solutions of this invention, dilute solutions of the metal organic siliconate are employed. Satisfactory results can be obtained using solutions containing .01 to 10% of the silicone-forming agents of this invention, although amounts outside this range may be employed. The siliconate is introduced directly into the flood water and pumped into the subterranean reservoir. The siliconate solution is then contacted within the formation interstices with an acidic solution. On mixing, the siliconate reacts with the acid to form a silicone polymer which coats the sand surface and makes it preferentially oil-wettable. Solutions of acids, especially weak acids such as carbon dioxide, phenol, acetic acid, low concentrations of hydrochloric acid and nitric acid, etc., are especially suitable for producing silicone polymer coatings.

In the practice of the instant invention a water injection well, having a ten ft. thick injection zone, is treated using conventional flooding apparatus by adding sodium methyl siliconate to the injection water at the well head in sufficient amount to provide approximately 10,000 gals. This volume is sufficient to fill half of the pore volume within a 20 ft. radius of the well bore with a 0.5% solution of sodium methyl siliconate. After all of this solution has been injected into the well (in the course of normal water injection operations), the injection of 10,000 gals. of an aqueous 5% HCl solution is started (after first flushing the sodium methyl siliconate solution from the well bore with water). After the HCl injection, normal water injection is again started. As the HCl

solution is pushed out into the formation it mixes and reacts with the sodium methyl siliconate solution and thereby renders the formation, preferentially oil-wet, for a radius around the well bore of approximately 20 or more feet.

The foregoing example is only illustrative in that the treatment may effectively be carried out in either siliceous or calcareous formations. In treating either type of formation care must be taken in the selection of the acidic reagent employed to avoid using an acidic substance that would spend itself by reacting with the formation constituents and become ineffective. For example, hydrochloric acid should not be employed in treating calcareous formations. The amount of siliconate solution which is initially introduced into the formation will depend, of course, upon the extent and structural characteristics of the formation. Porosity, which may be readily determined by standard procedures (Vide Elements of Oil Reservoir Engineering, Pirson, McGraw-Hill, 1950 at p. 20 et seq.), is a convenient criterion. Accordingly, a volume of siliconate solution equal to 25 to 75% of the pore volume of a circumambient section of formation having a radius of about 10-20 feet should be used, and preferably about 50% of said pore volume. Amounts outside this range may also be employed. However, maximum benefits are obtained by facilitating the flow through that section of formation adjacent to the injection well bore. In forming the silicone coating the amount of acidic reagent which is introduced into the formation will depend upon the amount of siliconate which is employed because the neutralization reaction proceeds stoichiometrically and requires an equivalent amount of acid solution. In order to insure complete precipitation of the silicone coating an amount of acidic reagent in excess of the stoichiometric amount should be used.

Thus, by treating a circumambient section of the oil-containing reservoir in order to make it oil-wet by means of the invention, the resistance to water flow is lowered, thereby decreasing the pumping cost and expediting the water flood. Conventional water-flooding equipment can be employed without substantial modification. No significant amounts of oil are lost because the section treated has already been water flooded and no additional amounts of oil are introduced into the formation.

Therefore, we claim as our invention:

1. In a secondary recovery process employing a water drive to facilitate the drainage of residual petroleum oil from a partially depleted, subterranean oil-bearing normally water-wettable reservoir, traversed by a water injection well and a recovery well, a method for minimizing the resistance of said reservoir to the flow of said water drive through a circumambient zone immediately adjacent said injection well which comprise forcing into said reservoir through said injection well an aqueous solution containing about 0.1-10% by weight of a water-soluble metal salt of an organic silicic acid into a circumambient zone immediately adjacent the injection bore hole and having a radius not greater than about 20 feet, in a volume equal to about 25-75% of said zone, contacting the aqueous salt-containing solution while in said circumambient zone with an acidic solution whereby a silicone polymer is precipitated to form an oil-wettable coating on the mineral surfaces of said circumambient zone without deleteriously affecting the specific permeability of said zone, and injecting a water injection fluid into said reservoir through said zone to force said residual oil therefrom.

2. In a secondary recovery process employing a water drive to facilitate the drainage of residual petroleum oil from a partially depleted, subterranean oil-bearing normally water-wettable reservoir, traversed by a water injection well and a recovery well, a method for minimizing the resistance of said reservoir to the flow of said water drive through a circumambient zone immediately adjacent said injection well which comprise forcing into said reservoir through said injection well an aqueous solution con-

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taining about 0.01–10% by weight of a water-soluble metal salt of an organic silicic acid into a circumambient zone immediately adjacent the injection bore hole and having a radius within the range of about 10–20 feet, in a volume equal to about 25–75% of the pore volume of said zone, contacting the aqueous salt-containing solution while in said circumambient zone with an acidic solution whereby a silicone polymer is precipitated to form an oil-wettable coating on the mineral surfaces of said circumambient zone without deleteriously affecting the specific permeability of said zone, and thereafter injecting a water injection fluid into said reservoir through said zone to force said residual oil therefrom.

3. A method in accordance with claim 2 in which the salt is an alkali metal alkyl silicate.

4. A method in accordance with claim 3 in which the silicate is sodium methyl silicate.

5. A method in accordance with claim 2 in which the acidic solution is a solution of a weak acid selected from the group consisting of aqueous solutions of carbon dioxide, phenol, and acetic acid.

6. A method for recovering oil from partially depleted normally water-wettable oil-containing subterranean formation by employing a water injection well and a recovery well, which comprises introducing a first water injection fluid from said injection well into said formation until a

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circumambient zone having a radius not greater than about 20 feet adjacent the water injection well is substantially free of oil, introducing into the injection water 0.01–10% by weight of a water-soluble metal salt of an organic silicic acid, forcing the salt-containing water in a volume equal to about 25–75% of the pore volume of said circumambient zone into said formation, contacting the salt-containing injection water while in said circumambient zone with an acidic solution whereby a silicone polymer is precipitated to form an oil-wettable coating on the mineral surfaces of said circumambient zone, without deleteriously affecting the specific permeability of said zone, and thereafter continuing the injection of said first, water injection fluid into said formation.

7. A method in accordance with claim 6 in which the salt is an alkali metal alkyl silicate.

8. A method in accordance with claim 7 in which the silicate is sodium methyl silicate.

9. A method in accordance with claim 6 in which the acidic solution is a solution of a weak acid.

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