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## TREATMENT OF OIL WELLS

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7 Claims. (Cl. 166—21)

This invention relates to the treatment of an oil well, and more particularly to the chemical treatment of the sand adjacent a producing well in order to render the sand preferentially wettable by oil to thereby increase the proportion of oil and decrease the proportion of water produced by that well.

It is recognized that ordinary sand is more easily wet by water than by oil. It is further recognized that oil producing sands are predominantly water-wet. When the pore spaces of an oil producing sand contain both water and oil the fact that the sand surfaces are water-wet will cause the water to occupy the smaller capillaries and crevices to the exclusion of the oil, thereby limiting the flow of the oil to the larger capillaries only, this flow of oil through these capillaries being retarded because the pore spaces of the capillaries are substantially reduced in cross section by the presence of the relatively immobile water film on the sand grains. The oil flow into and through the smaller capillaries and crevices is opposed by the interfacial tension between the oil and the water. My invention resides in a method of causing oil to flow through all of the capillaries and crevices of an oil producing sand by removing the water film from the walls of the capillaries and crevices and rendering the surfaces oil-wettable. In this manner the flow of water into the well is retarded by the same force which obstructs the flow of oil through the average water-wet oil producing sand.

In Patent No. 2,024,119 issued to William V. Vietti and Allen D. Garrison, there is disclosed and claimed a method of treating a producing sand of this character which is wet with water, by the depositing of a water and oil insoluble precipitate on the sand grains, which precipitate is of such character that it does not fill or block the pore space of the sand and is preferentially wettable by oil. In accordance with the method of the patent, an aqueous solution of an alkali metal salt of a sulfonated oil, fat or fatty acid is introduced into the well and into the producing sand, and is either reacted in situ with calcium and magnesium salts of naturally occurring brines therein, or is reacted with a subsequently introduced aqueous solution of a water soluble salt of an alkaline earth or heavy metal, so as to form a film coating about the sand grains of a precipitate of an alkaline earth or heavy metal sulfonate.

The present invention relates to a different method of producing a film coating upon the sand grains which is preferentially wettable by oil, and which in some respects constitutes an improvement over the method of said patent. As distinguished from the aqueous solutions employed in accordance with the method of the patent, the present invention involves the use of mineral oil solutions to carry the film forming chemicals to the zone of reaction in the producing sand, which possesses an advantage in freeing the pore space of the sand from water. Further, in accordance with the present invention, a film coating about the sand grains which is preferentially wettable by oil is formed by depositing thereon a water and oil insoluble metallic sulfide.

A very satisfactory coating for this purpose is represented by a sulfide of a heavy metal which does not hydrolyze in slightly acid water, such for example as sulfide of lead, copper, cadmium, cobalt, iron, mercury, molybdenum, nickel, tin, silver, zinc, arsenic, antimony and the like. This coating is conveniently formed by introducing into the well a mineral oil solution of a heavy metal compound which is soluble in the oil, and following this by the introduction of a mineral oil solution of a sulfide compound which reacts within the producing sand with the heavy metal compound to produce a precipitate of a heavy metal sulfide. Various heavy metal soaps which are sufficiently oil soluble to be employed in this manner are satisfactory for this purpose, such as heavy metal salts of oleic, stearic, palmitic, and other fatty acids as well as the heavy metal salts of naphthenic acids. Various mineral oil fractions can be employed as the solvent, such as kerosene, naphtha, gas oil, lubricating oil, or crude oil.

Following the introduction of the oil solution of the heavy metal soap, there is then charged into the well an oil solution of an oil soluble sulfide compound, such as hydrogen sulfide. The same mineral oil fractions as specified above may be employed as solvents for the sulfide compound used.

Prior to the depositing of the oil wettable film coating upon the sand grains, the producing sand may be pretreated as disclosed and claimed in my co-pending application Serial No. 212,972, filed of even date herewith, by flushing to remove fine clay particles and silt from the interstices of the sand and increase the pore space of the sand. This may be accomplished by introducing a charge of an aqueous alkaline solution of a metaphosphate, such as sodium hexametaphosphate which also preferably contains a buffer salt or salt mixture and a clay dispersing colloidal agent

of the character of alkali metal salts of organic acids such as tannic acid, gallic acid and the like.

In addition to the flushing treatment specified above, or in lieu thereof, the sand may be pretreated by dehydrating the same to remove water from the pore space thereof as disclosed and claimed in my co-pending application Serial No. 212,974, filed of even date herewith. This may be accomplished by blowing with a heated gas under pressure, by electrical heaters or heated bodies lowered into the well opposite the producing sand, by a combination of the electrical heaters or heated bodies with a flow of gas under pressure, or by the use of chemical dehydrating agents. A suitable method of chemically dehydrating the producing sand is that disclosed and claimed in my co-pending application Serial No. 212,976, filed of even date herewith, in which the sand is first flushed with oil, then with a mixture of oil and an aliphatic ketone such as acetone, and finally with a solution of an acid anhydride such as acetic anhydride in oil preferably containing a small amount of a suitable catalyst such as sulfuric acid.

Following the depositing of the preferentially oil wettable coating upon the sand grains, a charge of crude oil is preferably introduced into the well to force the solutions farther out into the sand and to render the sand immediately about the well wet by oil. Excess solution may be removed from the well by pumping or bailing. The well is then ready to be placed on production.

As a specific example of the present invention, there is introduced into a well which may have been pretreated by one or more of the methods described above a kerosene solution of lead oleate, which is forced into the producing sand under pressure. Following this, a kerosene solution of hydrogen sulfide, formed by bubbling hydrogen sulfide through the oil until substantially saturated, is introduced into the well and into the pore space of the sand to react with the lead oleate and form a film coating of lead sulfide about the sand grains. This is followed by a charge of crude oil, the excess solutions then removed by pumping or bailing, and the well placed in production.

As illustrative of the effectiveness of the sulfide coating of the present invention in repelling the flow of water or brine while facilitating the flow of oil through the sand, the following experiment was performed. A sample of oil well producing sand was treated to deposit about the sand grains a film coating of lead sulfide in the manner described above. This sand was placed in a Buchner funnel mounted in an inclined position, so that the upper surface of the sand is arranged on an inclined plane. There was then introduced onto the sand in the funnel a quantity of oil field brine which only partially covered the exposed inclined surface of the sand. The treated sand resisted the passage of the brine through the filter. There was then introduced into the funnel a quantity of crude oil so as to form an upper layer over the brine layer, which upper oil layer had substantially equal access to the surface of the sand as the brine. Under these conditions, it was found that the oil passed readily through the filter with only a very small proportion of brine so that the oil produced was of pipeline quality, and the greater part of the brine was left upon the filter after the oil had passed therethrough. This shows an unusual effectiveness of the sulfide coating of this invention, inasmuch as I have found that it is more difficult to shut off brine flow in a well than it is to shut off flow of pure water. This is due in part to the fact that the interfacial tension between oil field brines and crude oil is less than the interfacial tension between pure water and crude oil. Consequently, the treatment of the present invention is particularly effective in connection with those oil wells tending to produce substantial quantities of brine.

Obviously many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. The method of treating an oil well to convert a water wet producing sand to one which is preferentially wettable by oil, which comprises depositing on the sand grains of said sand without blocking the sand a film coating of a water and oil insoluble metallic sulfide which is preferentially wettable by oil, to thereby increase the proportion of oil relative to water produced from said sand.

2. The method as defined in claim 1 in which the film coating is a sulfide of a heavy metal selected from the group consisting of lead, copper, cadmium, cobalt, iron, mercury, molybdenum, nickel, tin, silver, zinc, arsenic and antimony.

3. The method as defined in claim 1 in which the film coating is lead sulfide.

4. The method of treating an oil well to convert a water wet producing sand to one which is preferentially wettable by oil, which comprises introducing into the said sand an oil solution of a soap of a metal whose sulfide resists hydrolysis in slightly acid water, is water and oil insoluble and is preferentially wettable by oil, and then introducing into the sand to react therewith an oil solution of hydrogen sulfide.

5. The method of treating an oil well to convert a water wet sand to one which is preferentially wettable by oil, which comprises introducing into the said sand an oil solution of a lead soap, and then introducing into the sand to react therewith an oil solution of hydrogen sulfide.

6. The method of treating an oil well to convert a water wet sand to one which is preferentially wettable by oil, which comprises introducing into the said sand a kerosene solution of lead oleate, and then introducing into the sand to react therewith a kerosene solution of hydrogen sulfide.

7. The method of treating an oil well to convert a water wet producing sand to one which is preferentially wettable by oil, which comprises introducing into the said sand a mineral oil solution of an oil soluble heavy metal compound capable of reacting to form a water and oil insoluble film coating upon the sand grains which is preferentially wettable by oil, and then introducing into the sand a second mineral oil solution of a sulfide compound which reacts with the first mentioned solution to produce the said water and oil insoluble film coating of a heavy metal sulfide on the sand grains, to thereby increase the proportion of oil relative to water produced from said sand.

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