Patented May 6, 1941 2,241,253

# UNITED STATES PATENT OFFICE

2,241,253

## METHOD OF TREATING OIL WELLS

Allen D. Garrison, Houston, Tex., assignor to The Texas Company, New York, N. Y., a corporation of Delaware

No Drawing. Application June 10, 1938, Serial No. 212,974

11 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 said 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 so that the sand becomes wet with oil, whereby the proportion of oil produced by the well is increased while the proportion of water so produced is decreased. In accordance with the method of said patent, a water solution of a water soluble alkali metal salt of a sulfonated fat, fatty acid or oil is introduced into the well and into the sand adjacent the well, and this solution either reacted with the calcium and magnesium salts of the brine naturally occurring in the well, or else reacted with a subsequently introduced water solution of a soluble alkaline earth or heavy metal salt, to cause precipitation of an alkaline earth or heavy metal sulfonate within the sand to form the said water and oil insoluble film coating upon the sand grains.

The present invention contitutes an improvement over the method of said patent, and involves the pretreatment of the producing sand so that the pore space of the sand is enlarged or increased and the sand rendered in more suitable condition to receive the preferentially oil wettable precipitate which is then deposited upon the sand grains. This invention is further distinguished from the method of said patent by introducing into the sand, after the pretreatment thereof as above described, an oil miscible solution of a water and oil insoluble compound, which compound is precipitated upon contact by and dilution with oil in the pore space of the sand.

In accordance with the present invention, the producing sand is preferably first treated by washing back the sand with a flushing liquid to remove clay and fine silt therefrom and increase the pore space thereof. This may be accomplished by pumping in a charge of an aqueous alkaline solution of the type disclosed and claimed in my co-pending application Serial No. 212,972 filed of even date herewith, comprising a metaphosphate, such as sodium hexametaphosphate, preferably containing a buffer salt or salt mixture, and preferably also containing a clay dispersing colloidal agent such as a water soluble alkali metal salt of an organic acid of the character of tannic acid.

Irrespective of whether or not this flushing treatment is first employed, an important feature of the present invention involves the drying or dehydrating of the oil sand to remove water from the pore space thereof prior to the application of the film coating upon the sand grains. This may be accomplished by introducing into the well under pressure a quantity of oil followed by a heated gas, so that this gas is blown through the pore space of the producing sand adjacent the well to take up and remove moisture therefrom. Any suitable gas may be employed for this purpose, such as air, flue gas, natural gas and the like.

This dehydration of the sand may also be accomplished by the application of heat, such as by lowering electrical heaters into the well opposite the producing area and applying a high degree of heat thereto for a period of time. Electrical heaters or other heated bodies may be employed in conjunction with a stream of gas under pressure, so that this gas passes over the heater or heated body and then flows through the pore space of the sand.

Still another method of dehydrating the sand is that more particularly disclosed and claimed in my co-pending application Serial No. 212,976 filed of even date herewith, which involves the use of dehydrating chemicals. For example, a mixture of oil and an aliphatic ketone such as acetone is first introduced into the well and through the producing sand. While acetone is soluble in the mineral oil when dry, it separates and mixes with the water in the formation; and

by applying pressure on this charge, the water now in solution in the acetone is flushed out of the sand. This charge may be followed with a charge of a solution of an acid anhydride such as acetic anhydride in oil to remove the last traces of water from the sand. A small proportion of a catalyst such as sulfuric acid may be added to this latter charge to assist and speed this final drying treatment.

After dehydrating the pore space of the sand by one or a combination of the methods above described, the treating solutions are preferably flushed from the well outwardly into the surrounding sand by a following charge of oil. There is then introduced an oil miscible solution of the water and oil insoluble compound which is to be deposited upon the sand grains to form the preferentially oil wettable film. This is accomplished by forming a solution in a suitable aromatic or other strong solvent of the water and oil insoluble compound or material which is to be deposited upon the sand grains. For example, the alkaline earth or heavy metal salts of sulfonated oil, fats or fatty acids of the above mentioned Patent No. 2,024,119 may be employed for this purpose. These include the calcium, barium, iron, manganese, zinc, tin, lead and other heavy metal salts of sulfonated oils, fats or fatty acids. Natural fats such as tallow, oleum, stearin and the like, which have been sulfonated by treatment with sulfuric acid, are suitable. Likewise, sulfonated fatty acids formed by sulfonating stearic, palmitic, oleic and the like, are included. A very satisfactory and comparatively cheap material, which is a byproduct of the petroleum industry, is the sulfonic sludge acid derived from the treatment of petroleum oil with sulfuric acid, and termed herein a petroleum oil sulfonate. Another very satisfactory material is prepared by sulfonating a mixture of a petroleum oil, such as a lubricating distillate or a solvent extract of a petroleum oil, and an aromatic of the character of benzol, toluol and diphenyl. The sulfonated materials described above are first preferably prepared in the form of a solution of their alkali metal salts, by neutralizing the sulfonated products with an excess of a water solution of the alkaline material, such as caustic soda. Then the alkaline earth or heavy metal sulfonate is prepared by a double decomposition reaction by mixing with the alkali metal sulfonate solution a water solution of a water soluble salt of an alkaline earth or heavy metal, such as a chloride or nitrate. The heavy metal salt so precipitated is separated as by filtration from the reaction mixture, washed, and is then in condition to be employed for purposes of the present invention.

While these alkaline earth and heavy metal salts described above are practically insoluble in crude petroleum oil, they are sufficiently soluble in an aromatic solvent of the character of xylene, toluol, benzol and coal tar oils or other strong solvents of the character of nitrobenzene, carbon tetrachloride, carbon disulfide and the like, that a solution thereof in sufficient concentration for purposes of this invention may be produced. The solvent selected is preferably one which is miscible with crude oil, so that when the solvent solution of a compound is introduced into the well and brought into contact with the crude oil within the pore space of the producing sand, the solvent will be diluted by the oil, and the solute will be precipitated to form a strongly adherent film coating upon the sand grains. I have found xylene to be an unusually effective solvent for this purpose.

In addition to the alkaline earth and heavy metal salts specified above, I have found that petroleum acid sludge resulting from the treatment of petroleum oil with sulfuric acid can be employed for purposes of the present invention by first forming an extract thereof with a suitable solvent of the type mentioned above. For example, when acid sludge resulting from the treatment of mineral lubricating oil with sulfuric acid is extracted with xylene, a solution of the sulfonated tarry or asphaltic bodies present is formed. When this solution is introduced into the well and brought into contact with the crude oil present therein, a portion of the bodies present in the solution will be precipitated out and form the desired water and oil insoluble film coating upon the sand grains which is preferentially wettable by oil.

While I have particularly mentioned certain types of compounds or materials which can be dissolved in an oil miscible solvent of the character specified above, and which will precipitate upon dilution with mineral oil to form the desired film coating upon the sand grains having preferential oil wettability, it is to be understood that any other suitable water and oil insoluble material which will function in this manner can be employed in accordance with the present invention. For example, an oil insoluble asphalt of the type disclosed and claimed in my co-pending application Serial No. 212,976 filed of even date herewith, which is prepared by sulfurizing or highly oxidizing asphaltic materials at high temperatures, can be used with eminently satisfactory results.

As a specific example of the present invention, the following is mentioned. The water wet sand of a producing well making both oil and water is treated by forcing into the well a charge of crude oil sufficient to flush the sand to remove clay and silt and also force out part of the water therefrom. It is found, however, that this oil flushing treatment is inadequate to free the pore space from water and that as much as about 15 to 20% or more of the pore space will still be occupied by water after this treatment. The sand is then dehydrated by blowing with heated flue gas for a period of about 6–12 hours or more. The time for dehydration may be shortened by combining the gas blowing with electrical heating, or by passing the gas over a suitable heated body and thence through the sand. Following the drying of the sand, a charge of a xylene extract of the aluminum salt of the mixed sulfonates prepared by sulfonating a mixture of petroleum distillate lubricating oil and benzol, is introduced into the well. This is then followed by a charge of crude oil. The application of the xylene extract may be repeated one or more times with alternate slugs of oil, until the desired thickness and extent of coating has been built up on the sand grains. Following the last application of oil, the excess solutions in the well may be removed by pumping or bailing, and the well then placed in production.

As illustrative of the efficacy of the coating process of the present invention in rendering a producing sand oil wettable and water repellent, the following experiments were performed. A sand of the character found in producing wells in the Gulf Coast area was coated with a xylene extract of the aluminum sulfonates formed from a sulfonated mixture of petroleum distillate lubricating oil and benzol. This coated sand was then

placed in a Buchner funnel and some water poured on top of the layer of coated sand. The material was sufficiently water repellent to prevent the passage of any water through the sand bed. The water was then poured off of the top of the bed, and a quantity of kerosine poured onto the sand, and it was found that all of the kerosene passed quickly through the filter. A layer of water was then poured on top of the sand and a layer of kerosene carefully added on top of the water layer. The sand bed was sufficiently water repellent to prevent the passage of the water therethrough, but as soon as the liquid layers had been agitated as by thrusting a stirring rod through the kerosene and water layers so as to break the water layer and allow the kerosene access to the filter bed, the kerosene flowed quickly through the filter, leaving substantially all of the water remaining on top of the coated sand bed.

The coating materials described herein are not effected by moderate heat such as may be encountered in deep producing wells, and sand particles coated with these materials have successfully withstood long continued boiling in water without impairing the film coating.

While in the preferred process as described above, the precipitation of the film coating material from an aromatic or other suitable solution thereof is facilitated by dilution with oil in the producing formation, it is to be understood that the invention is not limited to this method of depositing the coating. I have found that a sufficiently thick and durable coating of these materials can be formed by one or more applications of the aromatic or other solution of these materials to the dry producing sand in the absence of any appreciable quantity of oil. Apparently a film of the solute remains on the sand grains after each application, and after the excess of the solution has been forced farther out into the sand or removed from the well by pumping or bailing, the solute film, held by the forces of adsorption, forms a durable coating upon the sand grains which is satisfactory for purposes of the present invention.

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 introducing into the said sand an oil miscible solution of a water and oil insoluble material which is preferentially wettable by oil as opposed to water, which material is precipitated upon contact by and dilution with oil in the pore space of the sand to form a strongly adherent film coating upon the sand grains of a character which renders them preferentially wettable by oil.

2. The method as defined in claim 1 in which the oil miscible solution is formed with an aromatic solvent.

3. The method as defined in claim 1, in which the oil miscible solution is formed with xylene as the solvent.

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 aromatic solution of an oil and water insoluble material selected from the group consisting of alkaline earth and heavy metal salts of sulfonated fats, fatty acids and oils, and petroleum acid sludge.

5. 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 flushing liquid to wash back the sand and remove clay and silt therefrom and increase the pore space thereof, then blowing a heated gas through the sand to dry the same, and finally introducing into the dried sand an oil miscible solution of a water and oil insoluble material which is precipitated upon contact and dilution with oil in the pore space of the sand to form a strongly adherent film coating upon the sand grains which is preferentially wettable by oil.

6. The method of treating an oil well to convert a water wet producing sand to one which is preferentially wettable by oil, which comprises first dehydrating the sand to remove water from the pore space thereof throughout a substantial volume of the producing sand surrounding the bore hole of the well, and then coating the sand grains with a film coating which is preferentially wettable by oil without blocking the said sand, to thereby increase the proportion of oil relative to water produced from the said sand.

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 flushing liquid to wash back the sand and remove clay and silt therefrom and increase the pore space thereof, then dehydrating the sand to remove water from the pore space thereof, and finally coating the sand grains with a film coating which is preferentially wettable by oil.

8. In the method of treating an oil well to convert a water wet producing sand to one which is preferentially wettable by oil, the step which comprises introducing into the said sand a non-aqueous solution of an oil and water insoluble material which is preferentially wettable by oil as opposed to water to form a film coating about the sand grains which is preferentially wettable by oil without blocking the said sand, to thereby increase the proportion of oil relative to water produced by the said sand.

9. The method as defined in claim 8, in which the non-aqueous solution is formed with xylene as the solvent.

10. The method according to claim 6, in which the dried sand is film coated by introducing into the said sand a non-aqueous solution of an oil and water insoluble material which forms a preferentially oil-wettable film coating about the sand grains without water-wetting the said sand.

11. The method according to claim 7, in which the flushed and dried sand is film coated by introducing into the said sand a non-aqueous solution of an oil and water insoluble material which forms a preferentially oil-wettable film coating about the sand grains without water-wetting the said sand.

ALLEN D. GARRISON.

# DISCLAIMER

2,241,253.—*Allen D. Garrison*, Houston, Tex. METHOD OF TREATING OIL WELLS. Patent dated May 6, 1941. Disclaimer filed September 22, 1943, by the assignee, *The Texas Company*.

Hereby disclaims claim 6 of said patent.

[*Official Gazette October 19, 1943.*]