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TREATMENT OF OIL WELLS

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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.

This is a continuation-in-part of my copending application, Serial No. 212,972, filed June 10, 1938.

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 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. The present invention constitutes 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 coating which is then deposited upon the sand grains.

In accordance with the present invention, the producing sand is first flushed with an aqueous alkaline solution which is effective to disperse fine clay particles and silt from the interstices of the sand and which may also dissolve certain calcium and magnesium salts present in the formation, as well as remove oil from the pore space. This flushing treatment is then followed by a treatment to coat the sand grains with a water and oil insoluble precipitate which is preferentially oil-wettable.

A satisfactory aqueous flushing medium for carrying out the first step of this process is an aqueous alkaline solution of an alkali metal hexametaphosphate such as sodium hexametaphosphate, potassium hexametaphosphate, lithium hexametaphosphate and ammonium hexametaphosphate. The chemical formula usually ascribed to the hexametaphosphates is exemplified by that of the sodium salt $(NaPO_3)_6$. The latter is available commercially in a form which upon solution in water gives an alkaline reaction. The presence of the metaphosphate compound in the aqueous flushing medium prevents precipitation of calcium and magnesium compounds or salts which may be dissolved from the formation, by rendering these calcium and magnesium compounds immune to reaction by repressing ionization thereof. It is believed that the hexametaphosphate compound reacts with calcium and magnesium ions, forming complex compounds which are only slightly ionized and which remain in the aqueous alkaline solution. The aqueous flushing medium is thereby rendered capable of dissolving and holding in solution increased quantities of such salts, so that an effective removal of such sparingly water soluble salts from the pore space is obtained. Sodium hexametaphosphate has the property of segregating the calcium and magnesium ions in substantially non-ionized but water soluble form. Amounts of from $\frac{1}{10}$% to 1% by weight on the basis of the aqueous flushing medium are usually sufficient, although larger quantities may be employed if desired.

It is desirable to maintain the aqueous flushing medium in a slightly alkaline state, for example of a pH from 8.0 to 11.5. In order to insure this, a buffer salt or a buffer salt mixture may be used in conjunction with the metaphosphate. Examples of the former are alkali metal salts such as sodium carbonate, sodium pyrophosphate and the like, or balanced mixtures of alkali metal hydroxides with alkali metal salts of such acids as boric, phosphoric, carbonic, oxalic,

silicic and similar weak acids. Sufficient buffer salt or salt mixture is added to the aqueous flushing medium to adjust the alkalinity thereof within the desired limits as outlined above.

There is also preferably added to the aqueous flushing medium a clay dispersing colloidal agent which is effective to take up and hold in colloidal suspension the fine silt and clay present in the pore space of the sand, so that this material is ultimately removed from the sand upon discharge of the flushing medium from the treated zone. Examples of suitable clay dispersing colloidal agents of this character are the water soluble alkali metal salts of such organic acids as tannic acid, gallic acid, humic acid, pyrogallic acid and the like. A small proportion of such colloidal agent is satisfactory, for example a proportion of .01% to .5% on the basis of the aqueous flushing medium.

In place of the metaphosphates mentioned above, other suitable calcium sequestering agents may be employed. For example, various molecularly dehydrated phosphates, such as the triphosphates, tetraphosphates and higher condensed nuclei phosphates of this character, as well as the sulfur containing derivatives thereof, such as the trithiophosphates, tetrathiophosphates, etc., may be employed. In addition, the nitrogen-bearing complexes of the molecularly dehydrated phosphoric acids which possess calcium sequestering action can be used. Examples of such nitrogen-bearing complexes are imidophosphoric acids, diamidophosphoric acids, phosphimic acids and the like.

These calcium sequestering agents are employed in aqueous solution, preferably in the presence of a suitable buffer salt or buffer salt mixture of the character described above to maintain the aqueous flushing medium in a slightly alkaline state, for example of a pH from 8.0 to 11.5. A suitable clay dispersing colloidal agent of the character of the water soluble alkali metal salts of the organic acids specified above may also be used in conjunction with the calcium sequestering agent. Such solutions are employed when there is indication that some of the obstruction to the flow through the pore space of the producing sand is due to clogging precipitates of calcium and magnesium compounds, or when the water content of the producing sand contains dissolved calcium and magnesium salts which would result in such clogging precipitates in the absence of a suitable calcium sequestering agent.

However, it is not necessary in all cases to employ a calcium sequestering agent, and good results may be obtained by initial flushing of the water-wet producing sand with any suitable aqueous alkaline solution which is effective to flush out the pore space of the sand prior to the coating of the flushed sand with the preferentially oil-wettable material. For example, aqueous alkaline solutions containing alkali metal carbonates, oxalates, citrates, borates, phosphates, and silicates, either alone or in suitable admixture, may be employed, either with or without the presence of a suitable colloidal agent of the character of the water-soluble alkali metal salts of the organic acids specified above. Where the clogging is due primarily to clay, very satisfactory results are secured by initial flushing with a water solution of an alkali metal pyrophosphate or alkali metal silicate or other suitable agent having strong deflocculating properties. Moreover, any of the above mentioned aqueous alkaline solutions or solutions containing a clay deflocculating agent can be combined with any of the calcium sequestering compounds capable of solvent action on the alkaline earth salts. This preliminary flushing step preceding the depositing of the preferentially oil-wettable coating is of particular advantage in the case of old wells where the production rate has declined due to the clogging of the pores of the producing formation, as well as where the ratio of water to oil produced from the formation may have substantially increased.

In accordance with the process of the present invention, a suitable aqueous alkaline solution of the character set out above is first forced into the well and into the sand adjacent the well to clean the pore space of the sand by removing the fine silt and clay and dissolving the soluble salts. This treatment is also effective to flush out oil from the pore space, so that the sand grains will be left in freely exposed and suitable condition for the subsequent treatment of depositing the preferentially oil-wettable precipitate thereon. This first treatment may be followed directly with solutions producing the desired oil-wettable precipitate, or an intermediate slug of water can be forced into the well between the first flushing treatment and the subsequent coating of the sands with the desired precipitate, or the flushing liquid can be first removed from the sand and the well bore by pumping or bailing.

Following this initial treatment, the prepared sand bed is then treated to coat the sand grains with a thin adhering film of a water and oil insoluble precipitate which is preferentially wettable by oil. This may be accomplished in the manner disclosed in the above mentioned Patent No. 2,024,119. As set forth therein, there is forced into the well and into the sand adjacent the well a solution of a precipitatable compound of the preferential wetting character described. This is followed by a solution of a compound which is active to react with the first mentioned compound to produce the desired precipitate when these two solutions are brought into contact with each other within the producing sand being treated, whereby the precipitate so produced is effectively distributed and deposited throughout the treated sand zone. The procedure described above may be repeated one or more times, so as to secure the desired effective deposit and coating of the sand grains throughout the water-wet sand. Preferably, this is then followed by forcing a charge of oil into the well in order to force the chemicals farther out into the sands to increase the zone of treatment and to immediately create a zone of sand around the well which is wet by oil.

Suitable materials which possess the preferential wetting property include various water and oil insoluble salts of sulfonated oils, fats or fatty acids. For example, the alkaline earth and heavy metal salts, including those of calcium, barium, iron, manganese, zinc, tin, lead, and the like of sulfonated oils, fats or fatty acids may be employed. Natural fats such as tallow, olein, stearine 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 by-product 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. These various materials may conveniently be used in the form of their alkali metal salts, whereby a water solution of the soluble salt may first be forced into the bore of the well and into the sand immediately surrounding the well. Then a water solution of a water soluble salt of calcium, barium, or other alkaline earth or heavy metal, such as a chloride or nitrate, is forced into the well and into the sand to react with the first mentioned solution to produce a precipitate of the water and oil insoluble metal salt of the sulfonated oil, fat or fatty acid, upon the sand grains.

These particular salts are highly dispersed when formed in dilute solutions, and have the characteristic of not flocculating or cohering with themselves so that they do not block or cement the sand being treated; rather, they have strong adherence for the sand grains and deposit in the form of a thin permanently adhering film about these grains without materially reducing the porosity of the sand. These films are preferentially wettable by oil, as opposed to water, so that after the treating solutions are removed from the well bore, which may be accomplished by flushing with oil or pumping, the sand grains become wet with oil. The net result is that the oil in flowing through the pores and capillaries of the producing sand does not have to overcome the interfacial tension between oil and water, so that the rate of production of oil from the treated sand is increased. Moreover, the sand has been converted to a state in which it is water repellent, so that at the same time the proportion of water produced by that well is substantially decreased.

As a specific example of the present invention, the following is mentioned. A dilute water solution of sodium hexametaphosphate buffered with sodium carbonate and also containing sodium tannate is forced into the well and the producing sand. This is followed by a water wash to remove the first flushing liquid, then a dilute water solution of the sodium salt of petroleum sulfonate is introduced into the sand, and this is followed by a wash with a dilute solution of calcium chloride. Another charge of the sodium salt of petroleum sulfonate is then forced into the well, followed by another charge of the calcium chloride solution. This may be repeated still a third time, or even more, depending upon the extent of sand to be treated. Finally a quantity of oil is pumped into the well which will force the chemicals farther out into the sand and will render the sand in the immediate vicinity of the well wet by oil.

As a further example of the present invention, the following is mentioned as particularly suitable in the case of an old well where the formation is particularly low in calcium and magnesium salts but has become clogged with deposits of clay or silt. A dilute water solution of sodium pyrophosphate is first forced into the well and agitated in the hole for a period of time with a spudder. This is followed by bailing to remove the first flushing liquid together with the deflocculated clay and loosened sand carried in suspension therein. The producing sand may then be dried to remove water from the pore space thereof, as by suitable chemical or other dehydrating treatment, although this step may be omitted and good results obtained in many cases. A coating of the preferentially oil-wettable material is then applied to the producing sand and finally a quantity of oil pumped into the sand, following which the well is placed back on production.

Another suitable type of aqueous alkaline flushing medium, particularly for cleaning out old wells for application of the preferentially oil-wettable coating, comprises a clay deflocculating agent or a calcium sequestering agent of the character set forth above together with a suitable wetting agent or surface tension depressant, which latter functions to enable the fluid to be forced into the sand with greater ease, and assists in wetting the clay and sand more rapidly so that it can be loosened. Any suitable wetting agent or surface tension depressant which is water soluble and non-reactive with the fluid, and does not form clogging precipitates with constituents of the formation can be employed, such as various alcohols, ketones, sulfonated organic detergents, and the like. Highly effective for this purpose are the alkali metal salts of sulfated long chain fatty alcohols, such as sodium oleyl sulfate, the alkali metal salts of long chain fatty acid-taurine condensation products, and other synthetic organic detergents of this general type whose calcium salts are water soluble.

By way of example, a well in Duval County, Texas, in which the sand was clogged with clay, was treated by introducing an aqueous solution of sodium hexametaphosphate containing an organic detergent known in the trade as "Nacconol." The fluid was agitated in the hole for about an hour with a spudder, and then the loosened sand and the deflocculated clay and shale were bailed out of the well. The cleaning effect was unusually effective in that the sand caved in so fast that the bailer was difficult to empty, and the shale and clay were well deflocculated. This treatment obviously enlarged the hole and exposed fresh formation walls which were then in an excellent condition to receive a preferentially oil-wettable coating.

While in the preferential oil-wetting treatment described herein, mention has been made of the use of the particular treatment set forth and claimed in Patent No. 2,024,119 mentioned above, it is to be understood that any other suitable treatment which will render the sand grains preferentially wettable by oil can be employed in accordance with the present invention, which relates to a combination of such preferential oil-wetting treatment with a preliminary flushing of the sand bed such as to render the latter in more suitable condition to receive the preferential oil-wetting treatment.

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 a water-wet producing sand of an oil well to improve the production of oil relative to the production of water from the well, which comprises flushing the well and the said water-wet producing sand with an aqueous alkaline solution substantially free from added dispersed solids and containing a clay-dispersing agent which disperses fine clay particles from the pore space of the sand grains to thereby flush out the pores of the formation, and then distributing in the treated sand a chemical material which acts as a preferential oil-wetting agent to render the sand more permeable to oil and less permeable to water.

2. The method of claim 1, in which the aqueous alkaline solution contains a calcium sequestering agent having solvent action on calcium and magnesium salts.

3. The method of claim 1, in which the aqueous alkaline solution contains a metaphosphate.

4. The method of claim 1 in which the aqueous alkaline solution contains a metaphosphate and a clay dispersing agent and has a pH of about 8.0–11.5.

5. The method of claim 1 in which the aqueous alkaline solution contains a clay dispersing agent selected from the group consisting of the alkali metal salts of tannic, gallic, humic, pyrogallic, pyrophosphoric and silicic acids.

6. The method of treating a water-wet producing sand of an oil well to improve the production of oil relative to the production of water from the well, which comprises flushing the well and the said water-wet producing sand with an aqueous alkaline solution substantially free from added dispersed solids and containing a strong clay deflocculating agent, and then coating the flushed sand with a preferentially oil-wettable material to render the sand more permeable to oil and less permeable to water.

7. The method of claim 6, in which the clay deflocculating agent is selected from the group consisting of the alkali metal salts of pyrophosphoric and silicic acids.

8. The method of treating an oil well to improve the production of oil from the well, which comprises flushing the well with an aqueous alkaline solution containing a hexametaphosphate and a clay dispersing colloidal agent selected from the group consisting of the alkali metal salts of tannic, gallic, humic and pyrogallic acids, and then depositing in the sand a water and oil insoluble metal salt of a petroleum sulfonate which is preferentially oil-wettable.

9. In the method of treating an oil well to convert a water-wet producing sand to one which is preferentially wettable by oil by coating the sand grains with an oil-wettable precipitate, the step of pretreating the sand to receive the oil-wettable coating which comprises flushing the sand with an aqueous alkaline solution containing a hexametaphosphate.

10. The method of treating a water-wet producing sand of an oil well to improve the production of oil relative to the production of water from the well, which comprises flushing the well and the said water-wet producing sand with an aqueous alkaline solution substantially free from added dispersed solids and containing a clay-deflocculating agent and having a pH of about 8.0 to 11.5 to flush out the pores of the producing sand, and then coating the treated producing sand with a chemical material which acts as a preferential oil-wetting agent to render the sand more permeable to oil and less permeable to water.

11. The method of treating a water-wet producing sand of an oil well to improve the production of oil relative to the production of water from the well, which comprises flushing the well and the said water-wet producing sand with an aqueous solution of a calcium sequestering agent having solvent action on calcium and magnesium salts, and then coating the flushed sand with a preferentially oil-wettable material to render the sand more permeable to oil and less permeable to water.

12. The method as defined in claim 11, in which the calcium sequestering agent is selected from the group consisting of the alkali metal salts of molecularly dehydrated phosphoric acids and sulfur containing derivatives thereof and alkali metal salts of nitrogen-bearing complexes of the molecularly dehydrated phosphoric acids which have solvent action on calcium and magnesium salts.

13. The method of treating a water-wet producing sand of an oil well to improve the production of oil relative to the production of water from the well, which comprises treating the well and the said water-wet producing sand with an aqueous alkaline solution substantially free from added dispersed solids and containing a clay deflocculating agent and a wetting agent, and then coating the treated sand with a preferentially oil-wettable material to render the sand more permeable to oil and less permeable to water.

14. The method according to claim 13, in which the wetting agent is a synthetic organic detergent of the type of an alkali metal salt of a sulfated long chain aliphatic organic compound whose calcium salt is water soluble.

15. The method according to claim 13, in which the aqueous alkaline solution is agitated within the hole of the well, and the resulting loosened sand and deflocculated clay and shale are removed by bailing prior to application of the preferentially oil-wettable coating.

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