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PROCESS FOR TREATING OIL WELL FORMATIONS

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7 Claims. (Cl. 166—38)

The present invention relates to a process for treating oil wells by heating a subterranean oil-bearing formation pierced by a bore hole to remove from portions of the formation adjacent the bore hole deposits or accumulations of substances which interfere with the production of petroleum from it. More particularly, this invention relates to a process for introducing into and about the formation an alkali metal which has been conditioned to spread over the exposed areas and to penetrate within the pore spaces and interstices of the formation so that the heat liberated upon reaction of the alkali metal with formation water, or water introduced into the formation, will be effective both at the exposed surface in the bore hole and in depth into the formation to accomplish the desired removal of the deleterious substances.

It is known in the art of producing petroleum from subterranean formations that various substances may precipitate or otherwise separate from the petroleum as it flows from the formation to the well bore and gradually accumulate in the portions of the formation adjacent the well bore and on the surface of the formation exposed in the well bore. Such accumulations act to block off and continuously reduce the flow of petroleum into the well until, eventually, the production from the well is so seriously affected it may be uneconomical to continue its operation. Deposits of waxes, paraffins, bitumens, asphalts, and miscellaneous resins in well bores are familiar problems for their unfavorable effects in this regard, and various processes and devices have been employed to remove them, some with more or less success. For convenience and simplicity, the types of deposits in which we are interested, of which the foregoing are cited only by way of example, will hereafter be termed "waxes," and the method of the invention will be described in relation to such waxes.

It has been proposed heretofore to introduce sodium metal and water into a well bore in a manner to cause the sodium to be reacted in the region of an oil-bearing formation with the water so that the heat produced by the reaction would melt the waxy deposits that were blocking the formation. Such proposals also contemplated a beneficial action from the hot sodium hydroxide produced by the reaction acting on the formation and also some benefit from a scrubbing action which would occur incident to the evolution of hydrogen gas to agitate the hot reaction products across the exposed face of the formation to remove deposits therefrom. In the prior art, sodium metal was used in a mass of appreciable size, such as in pellet or brick form, and was placed in the bore hole approximately at the position of the oil-bearing formation where it was reacted with water. Necessarily under such conditions, the reaction would take place in a localized portion of the bore hole, and the heat generated would, in effect, be concentrated primarily in the immediate vicinity of the sodium metal mass. The heat would be diffused from this locus along the well bore and over the exposed face of the formation by the agitation of the water and reaction products generated by the

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liberation of gases resulting from the reaction, as well as by heat conduction through the elements of the formation.

It is an object of this invention to provide a novel method for treating a subterranean formation to free it of waxy deposits which have a deleterious effect on the production of oil from it.

Another object of the present invention is to treat a subterranean formation with an alkali metal or an alloy of alkali metals which has been conditioned before introducing it into the bore hole to place it in a form that will enable it to be spread over the exposed face of the formation and be forced into the interstices and pore spaces of the formation for an appreciable depth beyond the exposed face so that the exothermal effects of the reaction of the metal with water will be pronounced both in area and in volume.

It is a further object of this invention to treat a subterranean formation to remove waxes from it by introducing into the formation a wax solvent in which has been dispersed an agent which will react exothermally with water in the formation to heat up the wax solvent above the formation temperature to enable it more effectively to dissolve the waxes and assist the removal of them from the formation.

Other objects and advantages of this invention will become apparent as the description of it proceeds hereinafter.

As one illustrative embodiment of a reactive agent useful in this invention, a dispersion of sodium metal is made in a carrier which is inert to it. Preferably, although not necessarily, the carrier is a wax solvent and may be, for example, a crude oil, a highly aromatic petroleum fraction, or a refined petroleum product. SO₂ extracts of diesel fuel and SO₂ extracts of kerosene have been found to be especially effective as solvents of waxes found in oil wells and are suitable for the purpose of this invention. The sodium dispersion may be made by violently mixing the metal into the carrier by a mechanical agitator until the sodium is reduced to particle sizes which will remain dispersed. Particles ranging in size from sub-micron to 5 microns are desirable because this size range is advantageous for migrating into a subterranean formation. A particle size of less than 1 micron is preferable for this purpose. Dispersing aids or stabilizers, such as long-chain fatty acids, silicone oil or other suitable surface-active agents, may be added and the carrier and metal may be heated to aid the formation of the dispersion. Dispersing aids may be selected which also will affect the rate of reaction of the sodium with water, to control the rate at which heat is liberated by the reaction.

Instead of sodium metal, an alloy of sodium and potassium metals may be used. The proportions of metals in the alloy may be selected so that the alloy is a liquid at ordinary temperatures and the dispersion will be that of the liquid alloy in the liquid carrier. Under these circumstances, there is obviously no criticality of particle size of the liquid alloy for the best effect on the formation. Lithium, potassium, rubidium and cesium also may be used separately or in combination as the reactive agent.

In carrying out the steps of the present invention, the dispersion of alkali metal in its inert wax-solvent carrier may be introduced into the bore hole by one of several means. Care must be taken to remove all traces of water from the conduits through which the alkali metal dispersion is to be introduced, including the well tubing or casing down to the location of the oil-bearing formation. If, for example, the dispersion is to be introduced into the well through tubing, a slug of the water-free carrier for the dispersion is introduced into the tubing prior to plac-

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ing the dispersion in it, and the slug of carrier is forced down to the location of the formation to clear all water from the path to be taken by the dispersion. A quantity of alkali metal dispersion is then placed in the tubing, followed by another slug of the carrier alone. If it is necessary to do so, the final slug of carrier is placed under pressure to force the quantity of sodium dispersion down to the elevation of the formation. Sufficient pressure is placed on the quantity of dispersion to cause it to migrate into the formation a predetermined distance. In some cases, the hydrostatic head of the products in the tube may be sufficient for this purpose.

As the alkali metal distributes itself over the exposed face of and into the formation, it will contact the connate water therein and react with it to produce heat. The initial quantities of alkali metal will react with the water nearest the exposed face of the formation, causing that portion of the formation to be heated first. Subsequent particles of alkali metal migrating through the heated zone may become melted before they reach additional water with which to react. The melting of the alkali metal will aid it in progressing into the formation. Hence, the process of heating the formation in volume will continue until all of the alkali metal or water is used up. When it is desired to produce more heat than the available water in the formation will permit, additional water may be added from the surface, as required.

Another way of introducing the dispersion into the well is by the use of a proportioning pump. In this procedure, a liquid carrier is continuously pumped into the well and predetermined proportions of a concentrated dispersion automatically are added to it from an appropriate tank to give the desired proportion of alkali metal at the location of the formation.

It is also within the concept of this invention that the alkali metal dispersion or a liquid alloy of alkali metals may be introduced into the bore hole in a sealed container which can be transported down to the elevation of the subterranean formation to be treated and then ruptured to release the reactive material. In this latter case, care must be taken to make sure the bore hole is substantially free from water at the location of the formation so that the reactive material will not all react in the bore hole before it can be forced into the formation.

Preferably, after the dispersion of sodium or other alkali metal or alkali metal alloy has been introduced into the formation, the well is shut-in for a time to insure reaction of the alkali metal with formation waters and the proper distribution of heat throughout the formation. For example, the well may be shut-in from 1 to 4 hours to produce the desired result. While the formation and the reaction products are still warm, the well is placed on production, and the waxes dissolved in the carrier, as well as the reaction products of the alkali metal with the formation water, will be produced out of the well to free the formation for the subsequent production of petroleum.

As an illustrative example of some of the conditions which apply to the practice of this invention, the relationships which follow from the use of a dispersion of sodium metal in a wax solvent liquid hydrocarbon carrier, as described hereinbefore, will be set forth. It will be apparent that such a dispersion will have many of the physical characteristics of a liquid.

The volume of solution required per linear foot of treated formation for injection to a distance r_1 feet from the center of a well radius r_w feet may be obtained from the formula

$$\text{Gallons solution per foot of formation} = 0.24 (r_1^2 - r_w^2) \times f \quad (\text{I})$$

where f is the percent porosity of the formation.

The concentration of sodium that must be used to ap-

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proach quantitative reaction with the connate water in the formation will be given by the equation

$$\text{Pounds sodium per gallon of solvent} = \frac{13 S_w}{100 - S_w} \quad (\text{II})$$

where S_w is the percent of pore space filled with water.

The theoretical temperature increase in degree F. from the reaction under adiabatic conditions may be determined from the relationship

$$^{\circ}\text{F. temperature rise} = 0.066 f (100 - S_w) \times (\text{lb. Na per gal. solvent}) \quad (\text{III})$$

where it is assumed the density of the rock formation and contained fluids is about 2.5 gm./cc. and the heat capacity of the rock and contained fluids is about 0.25 cal./gm./ $^{\circ}\text{C.}$, and the reaction between sodium and water will produce 900,000 gram calories per pound of sodium. This formula assumes there is sufficient water for quantitative reaction, and there is no heat loss to surrounding rocks or fluids.

The temperature rise in degrees F., if just enough sodium is used for quantitative reaction with the water present, is given by the equation

$$^{\circ}\text{F.} = 0.85 f S_w \quad (\text{IV})$$

again assuming no heat loss to surrounding rock or fluids.

The following calculations illustrate for a hypothetical case the values that result from the above relationships: Let

$$\begin{aligned} r_1 &= 2 \text{ ft.} \\ r_w &= \frac{1}{2} \\ f &= 20\% \\ S_w &= 20\% \end{aligned}$$

By substituting the numerical values in the equations set forth above, it can be determined from Equation I that it will require 18 gallons of dispersion per foot of formation to fill it to a distance 2 feet from the center of the hole.

From Equation II above, it can be determined that there will be required 3.25 pounds of sodium per gallon of carrier to achieve quantitative reaction with the connate water in the formation under the conditions specified.

From Equation III it can be determined that the theoretical temperature rise of the treated portion of the formation when a dispersion of one pound of sodium metal per gallon of dispersion is used will be 105°F. maximum.

From Equation IV, it can be determined that the temperature rise resulting from using enough sodium for quantitative reaction with the water present will be 340°F. maximum.

The above temperature increases are theoretical and are not obtained in practice since some heat transfer must exist in the formation. Also, there is the possibility that not all of the dispersed sodium will penetrate into the formation or be reacted with water therein. Therefore, it is desirable to adopt a factor which will depend on the particular formation and hole conditions to decrease the theoretical calculated amount to a value which will be encountered practically in the field. This factor will be between 0.1 and 0.5, depending on specific conditions indicated above. However, even the 0.1 factor indicates there will be an appreciable temperature rise in the subterranean formation following the practice of this invention.

It will be apparent that heating the formation in the manner set forth herein will have several beneficial effects in freeing it from deleterious waxy deposits. The heat of reaction of the alkali metal with the formation water will, in itself, cause melting of some such deposits and the subsequent freeing of the formation. Just as important as this effect, however, is that created by raising the temperature of the wax solvent which is a car-

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rier for the dispersed reactive metal. As the temperature of the solvent is raised, it becomes increasingly more effective to dissolve the waxes from the formation and thereby free it for production of oil. Since the dispersion, including both the wax solvent and the reactive agent, has been caused to migrate into the formation in depth, there will take place more than a heating and cleaning of merely the exposed surface of the formation, but the effect of heat and solvent will reach beyond the exposed surface to remove the waxes that have been deposited in the pore spaces and interstices at some distance from the face.

It will be obvious that the method of this invention can be practiced by other specific apparatus and agents than those set forth above as exemplary embodiments without departing from the inventive concept, and it is intended to include all modifications and variations which fall within the scope of the appended claims.

I claim:

1. The method of treating an oil well which comprises introducing into said well a dispersion of alkali metals in a liquid wax solvent carrier which is inert to said metals, placing said dispersion under pressure to force a portion of said alkali metals and said liquid wax solvent carrier into an oil-bearing formation to allow said alkali metal to react with the water contained within said formation to raise the temperature of said wax solvent, reacting the remaining portion of said alkali metals with water in said oil well, and removing the reaction products and wax solvent carrier and dissolved waxes from said well while the temperature of said products and carrier is above the normal temperature of said well.

2. The process of treating an oil well which comprises introducing into said well a particulated alkali metal having particles ranging in size from sub-micron to 5 microns and contained in a wax solvent fluid carrier which is inert to it, placing said carrier and particulated alkali metal under pressure in the well to force some of said particles and wax solvent to migrate into an oil-bearing formation to allow said alkali metal to react with the water contained therein and heat said formation and said wax solvent, and removing the products of reaction and dissolved waxes from said oil well.

3. The process for treating an oil-bearing formation penetrated by a well bore to free said formation of waxy deposits which comprises introducing into said well bore a dispersion of sodium in a liquid wax solvent carrier for it, positioning said dispersion in said carrier at the location of said oil-bearing formation and placing said dispersion and carrier under a pressure greater than the pressure existing in said formation to force said dispersion and carrier into said formation to allow said sodium to react with the water contained within said formation, and thereafter removing the products of reaction and the wax solvent and dissolve the waxes from said formation.

4. The process for treating an oil-bearing formation in an oil well to free it of waxy deposits comprising introducing a quantity of a liquid which is inert to sodium into the well bore, immediately thereafter introducing a

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predetermined amount of a dispersion of sodium in said liquid into said well bore, immediately thereafter introducing a further quantity of said liquid into said well bore, transporting said quantities of liquid and the included amount of said dispersion of sodium to a position where said dispersion of sodium is at the location of said formation, and at said location placing said dispersion of sodium under a pressure greater than the pressure in said formation to cause particles of the dispersed sodium and a portion of said liquid to enter said formation to allow said sodium to react with the water contained therein and subsequently removing said liquid and the reaction products of said sodium from the well bore.

5. The process for treating an oil well which comprises introducing into said well a dispersion of sodium metal in a liquid solvent for wax, placing said dispersion under pressure to force particles of the sodium metal and portions of said solvent into an oil-bearing formation, to allow said sodium metal to react with water in said well and within said formation, and thereafter removing the products of the reaction together with the wax solvent and dissolved waxes from said oil well.

6. A method for treating an oil well which comprises introducing a liquid alloy consisting essentially of sodium metal and potassium metal into said oil well, placing said liquid alloy under pressure to force said alloy into an oil-bearing formation, to allow said alloy to react with water within said formation, and removing the products of reaction from said oil well.

7. A method of treating an oil-bearing formation penetrated by a well bore to free said formation of waxy deposits and water which comprises removing substantially all the water from the portion of said well bore adjacent the formation to be treated, introducing into said substantially water-free portion of said well bore an aromatic wax solvent inert to alkali metal and containing dispersed therein alkali metal particulated into sizes ranging from submicron to five micron, placing said wax solvent dispersion under pressure sufficiently greater than the pressure in said formation to force said solvent dispersion substantially into said formation to allow said alkali metal to react with the water in said formation and to raise substantially the temperature of the wax solvent within said formation, whereby the solvent power of the solvent wax is greatly increased, and removing the reaction products of alkali metal with water in the solvent and dissolved waxes from said formation and said well bore while the temperature of said products, solvent and dissolved waxes is appreciably above the normal temperature of said formation.

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UNITED STATES PATENT OFFICE
Certificate of Correction

Patent No. 2,799,342

July 16, 1957

Irving Fatt

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 68, after "well" and before "radius" insert —of—; same column, lines 71 and 72, the formula should read as shown below instead of as in the patent—

Gallons solution per foot of formation $= 0.24(r_1^2 - r_w^2) \times f$ (I)

Signed and sealed this 24th day of September 1957.

[SEAL]

Attest:

KARL H. AXLINE,
Attesting Officer.

ROBERT C. WATSON,
Commissioner of Patents.