METHOD FOR REMOVING PARAFFINIC AND ASPHALTIC RESIDUES FROM WELLS

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Fig. 3.

DIESEL OIL DIPEN'TENE CALCIUM CHLORIDE

Fig. 4.

WATER CALCIUM CHLORIDE SURFACTANT (EMULSIFIER)
METHOD FOR REMOVING PARAFFINIC AND ASPHALTIC RESIDUES FROM WELLS

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This application is a continuation-in-part of application Serial No. 191,713, filed May 2, 1962, now abandoned.

This invention relates to a new and improved method of treating wells for the removal of paraffinic and asphaltic residues, and more particularly to a method encompassing a novel means of heating a paraffin solvent, increasing the effective specific gravity of the solvent, and removing the paraffin dissolved or loosened thereby.

One of the problems frequently encountered in the production of crude petroleum is the accumulation and deposition of paraffin in the producing string, flow lines, tank batteries, and in some instances on the faces of the formation sand. These waxes, gums, resins, and asphaltic materials or paraffins which compose the deposits were originally in solution in the crude oil as it originally existed in the reservoir. Often times in the production or transporting of crude petroleum, the equilibrium of the solution is altered or destroyed and these paraffins being the less soluble constituents separate and accumulate on the string, pipe or tank as the case may be. The accumulation of these paraffins progressively decreases the rate of movement of the petroleum and must therefore be periodically removed.

The cleaning of wax or paraffin deposits from wells, flow lines, separators, tanks and the like, is expensive and raises the overall cost of producing or transporting operations. Numerous methods of removing paraffin have been tried with varying degrees of success. Such methods include the use of mechanical scrapers, solvents for dissolving the wax and the use of heat. As the temperature is one of the most important factors affecting the stability of the solution of paraffin constituents in crude oil or petroleum, various means of heating the paraffin and/or petroleum have been proposed. Among these means are the use of alkali metals such as sodium and potassium, and steam.

One particular method of removing paraffin from a formation penetrated by a well bore, utilizes a metal such as sodium or potassium in an inert non-aqueous carrier, preferably a wax solvent, which metal upon injection into the well formation reacts with the connate water to liberate heat, thus heating the well formation.

An extensive discussion of the causes of paraffin build-up and remedies therefor, may be found in Bulletin 348 of the U.S. Department of Commerce, Bureau of Mines, entitled "Paraffin and Congealing-oil Problems" by C. E. Redifer, Jr. It is therefore an important object of the present invention to provide a new and improved and economical means of removing paraffin or the deposits or accumulations from wells, lines, tanks or the like.

It is another object of the present invention to provide a new and improved method of heating a paraffin solvent for a more effective removal of paraffin and the like.

Still another object of the present invention is to provide a new and improved method of removing paraffin deposits or accumulations from producing well strings or the like wherein such deposits or accumulations may be readily removed from the well after the deposits have been dissolved or loosened.

A further object of the present invention is to provide a new and improved method of removing paraffin and the like from well strings or tubing, wherein the effective specific gravity of a paraffin solvent is increased thereby enabling the solvent to be more efficiently used.

Other objects and advantages of the present invention will be readily determinable from a reading of the specification and claims hereinafter and by reference to the accompanying drawings.

FIG. 1 is a block flow diagram illustrating broadly a preferred form of the present invention wherein A, a paraffin solvent with a heat generating chemical dispersed therein is introduced into an area or formation to be treated and, B, thereafter followed by water, which may or may not have been preheated, as desired, and which is brought into contact with the paraffin solvent-heat generating chemical mixture at the area or formation to be treated.

FIG. 2 is a block flow diagram illustrating broadly and alternate form of the present invention, wherein, A, the paraffin solvent is first introduced into the area to be treated, and B, water with the heat generating chemical therein is introduced behind the paraffin solvent and brought into contact therewith;

FIG. 3, is a block flow diagram illustrating another form of the present invention, wherein the paraffin solvent is pumped into a well and simultaneously therewith, water with a heat generating chemical and emulsifier therein is pumped through a second pump into the well; and,

FIG. 4 is a block flow diagram illustrating a preferred form of the invention similar to that of FIG. 1, but in more detail.

The present invention is essentially adapted for the removal of paraffinic and asphaltic residues which form in well equipment and/or the bore hole as crude petroleum or oil is produced. It generally comprises, the application of heat to a light paraffin solvent by the simple and inexpensive expedient of dispersing the solvent in a chemical solution which has evolved a large amount of heat, and adding a surface active agent or emulsifier to the solution for enabling the solvent to mix with the solution and to provide a more effective paraffin removal as will be discussed in detail hereinafter.

In the present invention, the use of an inorganic salt or base which evolves a large amount of heat upon the addition to water is preferred as the heat generating solution.

Other chemical solutions which generate heat exothermically upon contact with water or aqueous solutions may be used without departing from the scope of the invention.

Such materials as aluminum chloride, magnesium chloride, calcium chloride, sodium hydroxide and potassium hydroxide are especially preferred in that each produces large amounts of heat upon going into solution, are readily available and relatively inexpensive. Some of the hydrated states of these inorganic salts also produce sufficient heat upon going into solution, and may be used in the present invention. Other inorganic salts and bases which might also be used in the present invention are not presently economical and some undesirable by-products may result from their dissolution in water.

Aluminum chloride, which is the most reactive of the above group, should be handled with special caution, as the amount of heat it generates on being added to water is dangerous to handle and it may also react to form hydrochloric acid and aluminum oxide.

Such oxide, if precipitated in a well formation, could damage production of crude petroleum. By controlling the hydrostatic pressure, the solution can be prevented from entering the producing formation, and its use can then be permitted.

An inorganic salt such as calcium chloride can be added to water in sufficient quantities to cause a rise in the temperature of the water in the range of 200° F. Other salts can be used which give up even larger amounts of heat
under similar conditions. This system can be used to heat a paraffin solvent, which solvent will be discussed more in detail hereinafter, can be mixed intimately with the aqueous salt solution in any desired proportion, and depending upon the quantity of solvent added, the temperature of the solvent can be increased up to about 200° F. above its own ambient temperature.

Another type of heat generating chemicals or compounds which may be used in the present invention are the alkali metal hydrides, the alkaline earth metal hydrides and the alkali metal borohydrides. Some examples of these are calcium hydride, sodium hydride, potassium hydride, lithium borohydride, potassium borohydride and sodium borohydride. These hydrides or borohydrides, as is well known in the art, produce heat when contacted with water or aqueous solutions. Some of the higher hydrides or borohydrides may require a suitable catalyst to achieve sufficient heat to carry out the present invention. The quantities of materials used and amount of heat generated may be varied in accordance with the requirements of the paraffin removal operation all well within the skill of one skilled in the art.

Other methods of producing heated or hot solutions, such as adding a metal to acid or water and adding a hydroxide to water, may also be used without departing from the scope of the invention.

Numerous oil soluble paraffin solvents and combinations thereof may be used in the present invention. Such solvents include saturated and unsaturated hydrocarbons, organic acids, paraffinic hydrocarbons, olefinic hydrocarbons, alkylene compounds, condensed polynuclear aromatic hydrocarbons, nitro paraffins, and the esters, ethers and alcohols thereof. Chlorinated hydrocarbons may also be used, but as many petroleum refiners object to the thereof, they are not recommended. Organic sulphur compounds, such as carbon disulphide, dimethyl sulphide, dimethyl sulfoxide and others may also be used, but these, too, are generally not preferred because of the dangers in handling same. Carbon disulphide, for example, is very dangerous because of its low flash point and auto-ignition point and broad explosion limits.

Some examples of other well-known paraffin solvents are gasoline, kerosene, benzene, xylene, toluene, chloroform, methyl ethyl ketone, cyclohexane and alpha methyl naphthalene. Terpenes and mixtures such as turpentine have been found to be particularly good solvents. Some examples of terpines are dipentene, terpinolene, phellandrene, and pinene.

It can be appreciated that any oil soluble paraffin solvent may be used in the present invention, without departing from the scope thereof. It is preferred, however, that the solvent used be relatively safe to handle, inexpensive and readily available as well as being effective.

In addition to the paraffin solvent and the solution for heating same, a surface active agent which acts as an emulsifier enables the solvent to mix with the solution and thereby receive the maximum benefit from the heat evolved by the solution. The paraffin solvent can be the internal or external phase in the method of the present invention and an appropriate emulsifier can be chosen for the desired type of emulsion. A class of surfactants or surface active agents, a polyoxylethylene ether of a heptan partial ester of a high molecular weight organic carboxylic acid, which also acts to prevent the deposition of paraffin and the like, is described in U.S. Patent No. 2,830,859.

Some specific examples of compounds in this class are: 15 polyoxylethylene sorbitan monolaurate, 20 polyoxylethylene sorbitan monopalmitate, 20 polyoxylethylene sorbitan monostearate, 30 polyoxylethylene sorbitan monoleate, 25 polyoxylethylene sorbitan monopalmitate, 20 polyoxylethylene sorbitan monostearate, di-esters and tri-esters corresponding to the foregoing compounds, 20 polyoxylethylene sorbitan tri-tall oil esters, and mannitol derivatives corresponding to the foregoing, etc. In the names of the compounds set forth above, the numeral designates the average number of ethylene oxide groups per molecule of ester.

Polyoxylethylene ethers containing 4-30 oxyethylene groups per acid radical, or a hexain partial ester of an organic carboxylic acid having 12-22 carbon atoms and selected from the group consisting of fatty, naphthenic and resin acids, are particularly effective in preventing and retarding the deposition of wax or paraffin from crude oils upon the surfaces of well tubing, flow lines or other equipment through which oil is transported.

Other surfactants, which function similarly but may not have the added effect of preventing the repackipation of paraffin, may also be used without departing from the scope of the invention. Non-ionic and cationic materials are preferable.

The emulsifier of the present invention also aids in the removal of the paraffin from the well or lines after it has been dissolved by the solvent.

The emulsion or dispersion of the solvent and the aqueous phase generally becomes separated in the period of time that the solvent is dissolving the paraffin. Some paraffin will be loosened from the well equipment or formation by the solvent, but will not be completely dissolved thereby. By providing a means of agitation, such as pumping or flowing the well, the solvent with the dissolved paraffin as well as the loosened paraffin becomes emulsified with the salt solution and makes it easier to remove. Should agitation not be provided for, there is likelihood that the loosened paraffin would fall to the bottom of the well and damage the formation or plug the pumping equipment. Generally, the reaction of the chemical in the aqueous solution and/or the pumping of the solution will provide sufficient agitation for effective emulsification. Additional agitation can be provided by mechanical or other suitable means, if needed or desired.

In paraffin removal operations it is generally desirable to employ a solvent which is heavier than the paraffin, so that the solvent will easily fall to the bottom of the well or to the area containing the paraffin deposits or accumulations. Both chlorinated solvents and certain sulfur-containing solvents are heavier than either oil or water. Should these solvents not be used, for reasons as explained above or for other reasons, and considering the overall economics of using other solvents, the only solvents remaining are those with a specific gravity lighter than or very near that of crude oil or paraffin, which are referred to herein as light paraffin solvents. By making an emulsion of a relatively light paraffin solvent and an aqueous salt solution, an effective specific gravity higher than either paraffin, crude, and most brines can be obtained. For example, a 30-50 mixture of a light paraffin solvent such as dipentene and a 40 percent solution of calcium chloride will have a specific gravity of 1.1.

For economical reasons, it is generally preferred that an expensive light paraffin solvent be diluted or mixed with a less expensive paraffin solvent such as a mineral oil. Diesel oil is particularly desirable as a diluent. Broadly, the steps of the process or method of the present invention are: adding a heat generating chemical such as an inorganic salt, a metallic hydride or other suitable heat producing chemicals to water or an aqueous solution to provide heat; adding a light paraffin solvent to the water or solution to become heated and the effective specific gravity thereof increased and contact the paraffin to be treated or removed; and, removing the paraffin from the well after it has been contacted, partially or all dissolved, and emulsified in the water or solution.

In the treatment of wells for the removal of paraffin, the method of the present invention may be the variation on the method used to treat the area of the well to be treated, or the heat may be generated in the well bore at or near the area formation to be treated. The latter method is generally preferred as a maximum amount of the heat produced can be utilized.
In the form of the invention illustrated in FIG. 1, the heat generating chemical or inorganic salt is dispersed in the paraffin solvent then pumped or otherwise introduced into the well and subsequently into the formation or other area to be treated. After a suitable quantity of the paraffin solvent with the chemical dispersed therein has been pumped into the well, water is pumped into the well and into the formation, if desired. The water which may be preheated by any suitable means, including chemically heating thereof, when contacting the chemical dispersed in the solvent produces a large quantity of heat at the area to be treated. The paraffin solvent is heated and the paraffin deposits are loosened or dissolved therein.

Alternatively, the paraffin solvent, water and an emulsifier can be mixed together prior to introduction into the well with the heat generating chemical added as the mixture is introduced or pumped into the well.

The heated fluid is preferably circulated and then returned to the surface while still heated where the paraffin can be readily removed therefrom. As the paraffin dissolved in the solvent may come out of solution upon cooling thereof, it is important to get the treating fluid to the surface before cooling sufficiently to cause the paraffin therein to solidify or come out of solution.

In the form of the invention illustrated in FIG. 2, the paraffin solvent is pumped into the oil and into the area to be treated and followed by the aqueous solution or water to which has been added the heat generating chemical. Heating begins when the chemical is added to the water and the water is heated as it is being pumped. The heated solution thus flows through the paraffin solvent thereby heating same at the area to be treated. Some heat is of course dissipated while the solution is being pumped down the well bore to the treating area.

In the form of the invention illustrated in FIG. 3, two separate pumps are required, one to pump the paraffin solvent, and one to pump the heated aqueous solution. The solvent and aqueous solution are mixed together at the well head, with the solvent being heated at this time. The heated paraffin solvent or solution is then introduced into the area to be treated, with circulation, return to surface and removal of paraffin being performed as in the case of the other methods illustrated in FIGS. 1, 2, and 4. FIG. 3 also shows the use of the emulsifier or surfactant which in this instance is added to the aqueous solution after the chemical has been added thereto.

In FIG. 4, which is similar to FIG. 1, but in more detail, dinipentene is added to diesel oil to make an excellent and economical paraffin solvent, with the heat generating chemical of calcium chloride subsequently dispersed therein. This diesel oil dinipentene-calcium chloride mixture is pumped into the well and then into the area to be treated.

The above solution is followed by an aqueous solution or water to which has been added calcium chloride, for pre-heating same, and an emulsifier, preferably in that order. This aqueous solution is then brought into contact with the above oil solution at the area to be treated, thereby heating the paraffin solvent or oil solution. The heated fluid is then circulated, returned to the surface and the paraffin removed therefrom.

It can be appreciated that an emulsifier for producing the required results or surfactant may be added to either the solvent or the aqueous solution. It is generally preferred that the emulsifier be the last to be added in either the oil (solvent) or water (aqueous solution) medium and prior to the mixing of the two mediums.

In an actual field test, an experimental treatment of a well for the removal of paraffin was conducted. The well treated had a total depth of 3276 feet, a bottom hole temperature of 100°F, and no bottom hole pressure as fluid was taken on vacuum. The well was originally completed in 1947 with a 2-inch tubing inside a 5½ inch casing. Several years subsequent to that, a 4½ inch liner had been set several feet in the bottom.

About two months prior to the test treatment, new tubing had been placed in the well and the rods had been steamed. Paraffin buildup in this well was such that the rods were pulled and steamed about every three months to remove the accumulated paraffin. The paraffin had adhered to the rods from top to bottom and was particularly heavily deposited on the section of rods between 1500 and 2100 feet. This section or interval went through a cooling zone, about 60°F, and the paraffin deposited on the rods was very hard.

In the treating procedure employed, one 50 gallon drum of paraffin was mixed with 50 gallons of diesel fuel prior to going on the well site. At the well site, 200 pounds of powdered anhydrous calcium chloride were dumped into the oil solution, while pumping the solution down the well annulus. A sack, 100 pounds, of pelleted anhydrous calcium chloride was also added to the oil tank and the oil was agitated as much as possible during pumping to retain or hold the pellets in suspension.

After this mixture was pumped into the annulus, 120 gallons of fresh water, to which 100 pounds of pelleted anhydrous calcium chloride and 1 gallon of a sulfonated ethylene oxide derivative of polyglycol emulsifier or surfactant had been added, were pumped behind, and the water actually ended up containing about 150 pounds of calcium chloride, as about 50 pounds of calcium chloride had been left in the tank from the oil. A temporary thickening of the oil to aid in suspending the solids therein would aid in inhibiting the leaving of a calcium chloride residue in the tanks, if desired.

After pumping of the aqueous solution was completed, about 10:00 a.m., circulation with the well pump was commenced. After circulating the fluid about three hours, the dipentene was observed to be coming around in the oil. About an hour afterwards, the fluids were very thick and mushy, indicating that the paraffin was beginning to go into solution. Circulation was continued until nightfall, and the following morning the well was pumped off into the line.

In carrying out the method of the present invention, it should be noted that the heat can be generated substantially in situ as illustrated in the above example, or the heat can be generated at the well surface, with the heated fluid then being pumped into the annulus to the area to be treated.

Broadly, the present invention relates to a new and improved method of removing paraffin by inexpensively heating a paraffin solvent-aqueous system, and transmitting the system to the area of the paraffin and removing the system with the paraffin.

The present invention particularly provides an economical, heated, weighted, emulsified, light paraffin solvent-aqueous system for removing paraffinic deposits in a well.

What is claimed is:

1. A method of treating wells for the removal of paraffinic and asphaltic residues, comprising the steps of:
   (a) mixing a light paraffin solvent, an aqueous medium, an emulsifying agent, and a chemical capable of generating heat when contacted with said aqueous medium to provide a heated emulsion having an effective specific gravity greater than the specific gravity of said light paraffin solvent, said heat generating chemical being selected from the group consisting of aluminum chloride, magnesium chloride, calcium chloride, sodium hydroxide, potassium hydroxide and mixtures thereof and the aqueous medium and light paraffin solvent being separately introduced into the well;
   (b) contacting the paraffinic and asphaltic residues with the heated emulsion, thereby loosening and dissolving the residues; and,
   (c) removing the loosened and dissolved residues.
2. The method of claim 1, wherein the paraffin solvent is a terpene.
3. The method of claim 1, wherein the paraffin solvent is dipentene.
4. The method of claim 1, wherein the heat generating chemical is anhydrous calcium chloride.
5. The method of claim 1, wherein the emulsifying agent is a polyoxyethylene ether of a hexitan partial ester of a high molecular weight organic carboxylic acid.
6. The method of claim 1, wherein the paraffin solvent comprises a terpene selected from the group consisting of dipentene, terpinolene, phellandrene, and pinene.
7. The method of claim 1, wherein the paraffin solvent, heat generating chemical and the emulsifying agent are mixed together, introduced into the well and subsequently contacted by the aqueous medium.
8. The method of claim 7, wherein the aqueous medium is heated prior to contacting the solvent-chemical-emulsifying agent mixture.
9. The method of claim 1, wherein the paraffin solvent and heat generating chemical are mixed together and introduced into the well and wherein the aqueous medium and emulsifier are mixed together and subsequently introduced into the well.
10. The method of claim 9, wherein the aqueous medium is heated prior to contacting the solvent-chemical mixture.
11. The method of claim 1, wherein the paraffin solvent is introduced into the well and the aqueous medium, chemical and emulsifier are mixed together and subsequently introduced into the well.
12. The method of claim 1, wherein a predetermined amount of the light paraffin solvent is mixed with a predetermined amount of diesel oil.
13. A method of treating wells for the removal of paraffinic and asphaltic residues, comprising the steps of:
   (a) mixing a light paraffin solvent and diesel oil in about equal amounts by volume;
   (b) pumping the solvent-diesel oil mixture down the well bore;
   (c) adding a quantity of an inorganic compound selected from the group consisting of aluminum chloride, magnesium chloride, calcium chloride, sodium hydroxide and potassium hydroxide to the mixture as the mixture is being pumped down the well bore;
   (d) pumping an aqueous solution of water, the inorganic compound of step (c) and a surfactant behind the solvent-oil mixture, so as to disperse the mixture in the aqueous solution, heat it and bring it into contact with the paraffinic and asphaltic residue in the well bore and thereby loosen and dissolve same; and
   (e) removing the loosened and dissolved paraffin from the well bore.
14. The well treating method of claim 13, including the steps of:
   (a) adding a quantity of said inorganic compound to the solvent-oil mixture prior to pumping the mixture down the well bore rather than adding said inorganic compound to the mixture as the mixture is being pumped down the well bore; and
   (b) agitating the mixture while pumping the mixture down the well bore so as to disperse and suspend said inorganic compound therein.
15. The well treating method of claim 13, including the step of agitating the solvent-oil aqueous solution mixture in the well bore whereby the loosened paraffin and asphaltic residue is emulsified with the solvent-oil aqueous solution mixture.
16. The well treating method of claim 13, wherein the inorganic compound of step (c) is calcium chloride.

References Cited by the Examiner

UNITED STATES PATENTS

47,410 4/1865 Fraser .................................. 166—40
119,883 10/1871 Roberts ................................ 166—44
1,351,945 9/1920 Dulany ................................ 166—38
1,531,371 10/1924 Campbell .......................... 252—8.55
1,963,072 6/1934 Boundy et al. ......................... 252—8.55
2,139,595 12/1938 Lerch et al. ......................... 252—8.55
2,218,306 10/1940 Austerman .......................... 166—38
2,342,656 2/1944 Frye et al. .......................... 252—8.55
2,753,939 7/1956 Carpenter et al. ...................... 252—8.55
2,799,342 7/1957 Patt .................................. 166—41
2,889,884 6/1959 Hendrixson et al. ................ 166—38

FOREIGN PATENTS

778,819 7/1957 Great Britain.

OTHER REFERENCES


CHARLES E. O'CONNELL, Primary Examiner.

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Assistant Examiners.