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[54] METHOD AND APPARATUS FOR REMOVAL OF PETROLIFEROUS ADHERENT SOLIDS FROM AN INACCESSIBLE SURFACE

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[51] **Int. Cl.**.....**E21b 21/00**

[58] **Field of Search** .....175/17, 69; 166/303, 304, 309, 166/312, 57, 62; 134/22 R, 22 C, 23, 24, 34, 36, 40, 42

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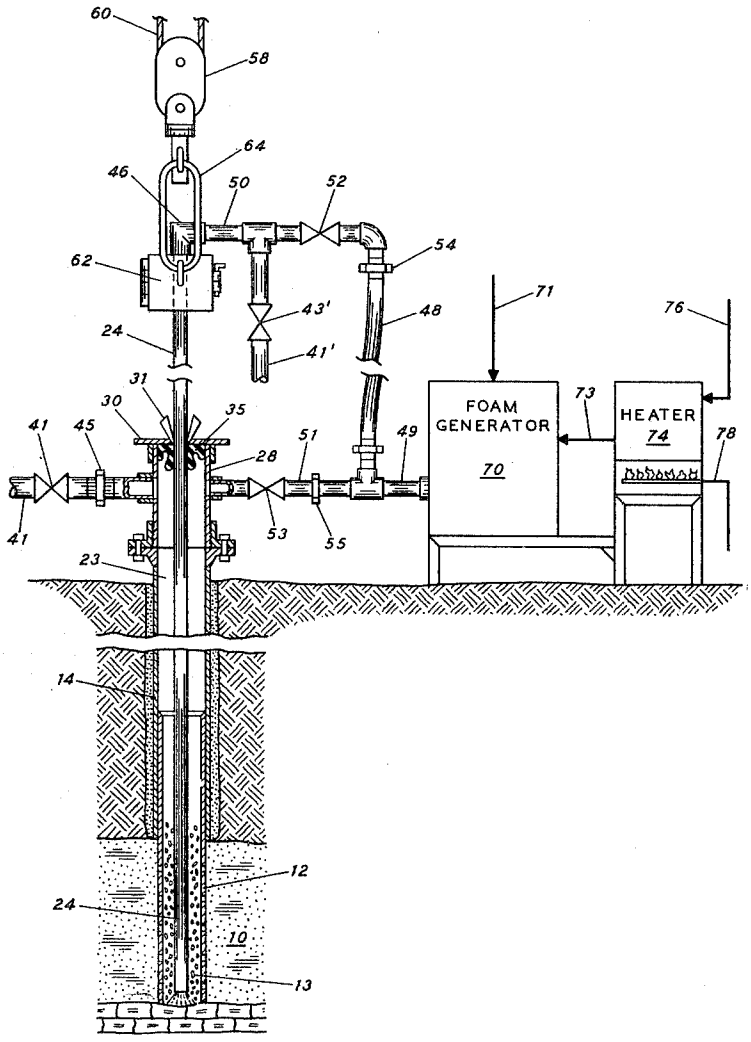
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[57] **ABSTRACT**

Petroliferous solid matter adhering to an inaccessible surface, such as the well bore in the producing zone of an oil well, are removed by contact of the solid with aqueous gas-in-liquid foams having a temperature above 140° F.

9 Claims, 2 Drawing Figures



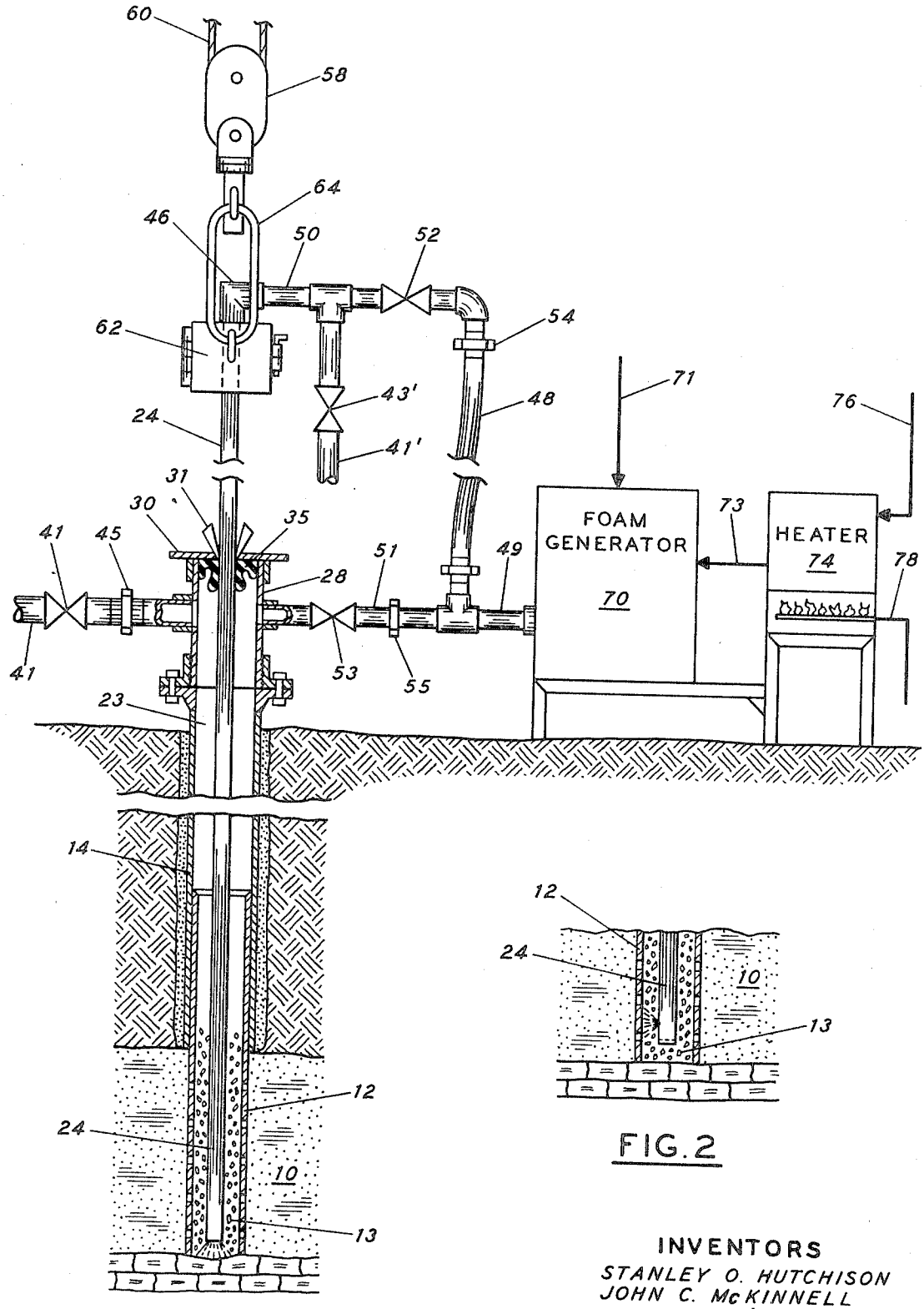


FIG. 1

FIG. 2

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METHOD AND APPARATUS FOR REMOVAL OF PETROLIFEROUS ADHERENT SOLIDS FROM AN INACCESSIBLE SURFACE

BACKGROUND OF THE INVENTION

This invention relates to a method for the removal of petroliferous paraffinic deposits from a surface, and more particularly the removal of such deposits from an inaccessible surface, such as in a well, and the like. Still more particularly, it relates to a method for the removal of petroliferous paraffinic deposits adhering to a surface by means of a hot foam.

It is known to remove loose solids and fluids from a well by means of a cold foam suitable for circulation in a well (see, for example, U.S. Pat. No. 3,463,231). There is still a need, however, for an effective method for the removal of adhering matter such as paraffinic petroliferous depositions on the surface of formations, pipes, pumps, and the like.

It is also known to remove paraffinic deposits from a surface, for example in an oil well by mechanical means and/or by contacting the coated surface with an organic solvent, for example a hydrocarbon mixture, dissolving at least a substantial portion of the deposit in the solvent and removing the resulting solution from the well. This method, while useful, has disadvantages, particularly in the situation where the formation pressure of the well is relatively low, as is often the situation. In such an instance, the paraffinic solution tends to back up into the formation and to deposit the solute, thus aggravating the problem rather than alleviating it. The amount of solvent required for effective paraffin removal can be substantial and in view of the cost factor, this is a further disadvantage.

A further expedient for the removal of paraffinic depositions from a well is to heat crude oil, solvent oils, and the like. In general this means is of limited utility and has many disadvantages including fire hazards, noxious fuming, danger to personnel, and the like.

Petroliferous depositions in wells are often complex mixtures of polar and nonpolar materials. Thus a solvent satisfactory for the nonpolar fraction of the deposit tends to extract out the former and leave the latter converting the deposition to one which can be more difficult to remove or requiring for effective removal treatment of the residue with a second solvent or chemical means.

SUMMARY OF THE INVENTION

It has now been found that petroliferous deposits can be removed from an inaccessible surface by forming an aqueous gas-in-liquid foam having a temperature in excess of about 140° F., contacting the surface bearing the deposit with the hot foam to remove the deposit from the surface, and circulating the foam up and out of the well. Surprisingly, the heat content of a hot aqueous gas-in-liquid foam and the mechanical effect achieved by the contacting of the foam with a petroliferous solid is sufficient for the effective removal of the solid from a surface, particularly such solids which contain a substantial paraffin fraction.

By the term "petroliferous solid" as used herein is meant the substantially organic material which precipitates in a well bore, etc., from crude oil and the like during a recovery operation, such as a producing oil well, or during the storage or passage of these materials. Typical of these deposits are paraffinic deposits containing 55 to 90 percent (weight) of saturated hydrocarbons, 5 to 15 percent of aromatic hydrocarbons, and up to 30 percent of asphaltenes. In addition, inorganic solids such as sand, silt, metal corrosion products and the like can be present in the deposit and bound in a conglomerate matrix which is most difficult to remove.

The term "aqueous gas-in-liquid foam," as used herein, has the meaning that the gas is the discontinuous phase and the liquid is the continuous phase of the system. The preparation and use of these foams as circulation media in wells is substantially disclosed in a patent and an allowed application, U.S. Pat. No. 3,463,231 and U.S. application Ser. No. 720,977, filed Apr. 12, 1968, now U.S. Pat. No. 3,486,560, and the disclosures of each of them is referred to and is incorporated herein by reference.

Petroliferous materials, in general, can be removed from inaccessible surfaces by the method of the present invention. Those deposits resulting from the separation of paraffin from crude oil are, in particular, susceptible to removal by the instant method, especially the adherent mixtures which result in a well in a petroleum producing zone.

For satisfactory solids removal the foam should be above a temperature in the range from about 130°–160° F., preferably at least above about 140° F. Foams having a temperature in the range above about 140° F. and below about 212° F. are in general most satisfactory and conveniently employed in the present method. Provided that the foam is used in a system under a superatmospheric pressure, it may have a temperature in the range above 212° F. and below the critical temperature of water, preferably below about 445° F. and at a pressure at least sufficient to maintain the liquid phase.

The hot foam required herein is preferably preformed, that is, prepared out of contact with the environment in which it is to be used. In situ preparation of a foam, and particularly a hot foam, ordinarily results in one which is an unsatisfactory circulation fluid. Local contaminants generally have an inhibitory effect upon foam formation. Moreover, in addition to furnishing the heat required to free the paraffin from the inaccessible surface, the foam must serve as a carrier for the transport of the material which has loosened from the surface. Useful hot carrier foams in general have a component gas-to-liquid volume ratio, standard cubic feet of air per gallon of liquid in the range below about 50 and above about 1. Best results are obtained where the ratio is below about 20. In situ production of foam ordinarily does not include satisfactory control of foam generation parameters.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is an elevation view partially in section and illustrates the preferred form of apparatus assembled in accordance with the invention, and

FIG. 2 is a partial sectional view showing an alternative embodiment of the apparatus of the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Refer now to the drawings and to FIG. 1 in particular where the preferred embodiment of apparatus assembled in accordance with the present invention is illustrated. FIG. 1 shows an elevation view, partially in section, of a well penetrating an oil-producing formation **10**. The portion of the well adjacent the producing formation **10** contains a perforated or suitably slotted well liner **12**. The well liner **12** is connected by suitable means to a string of casing **14** which extends from the upper portion of the producing formation through the earth to the surface. The well liner is placed during completion of the well and oil from the producing formation **10** enters the well through the slots in well liner **12**. Oil is pumped to the surface by suitable means such as an oil well pump. In the course of such production the well liner tends to accumulate a paraffinic deposit **13** and other occluded materials such as sand, asphaltenes and the like, and often the slots or perforations of the liner and substantial portions of the well bore itself become partially or completely plugged. This results in drastically reducing the amount of oil which can enter the well through the liner. When such plugging occurs, the method of the present invention may be utilized to assist in removing the paraffinic deposit from the liner and well bore in general so that improved production may be obtained from the well.

In accordance with the preferred embodiment of the invention a tubing string is positioned in the well through a suitable wellhead **28**. The particular size and type of tubing string will depend upon the particular well being serviced. Both segmented tubing strings and continuous tubing strings are suitable for use in the present invention. When using a segmented

tubing string, slips **31** are positioned on a slip baseplate **30**, which is connected to the top of the wellhead **28**. The slips are used to hold the tubing string during makeup of the string. Stripper rubber **35** is used in the wellhead **28** to prevent leakage of foam passed the tubing string where it enters the wellhead. The lower end of the tubing string **24** is positioned in the producing zone of the well bore, that is in the area of the well liner **12** which is to be cleaned. The tubing string **24** and the well liner **12** and well casing **14** form a well annulus **23**. Thus a path for circulating foam through the well is provided in the interior or tubing string **24** and well annulus **23**. A blooie line **41** is connected through valve **43** and connection **45** to the well annulus **23** for exhausting foam therefrom. The tubing string may be raised or lowered in the well during foam circulation by hoist means which include a traveling block **58** which is moved by suitable cable **60**. A conventional hoist means or derrick (not shown) is used to move the traveling block up and down. The elbow joint **46**, which is connected to the upper end of the tubing string **24**, is held in an elevator **62** which is connected by suitable links **64** to the traveling block **58**. Thus, when the traveling block **58** moves up or down, the tubing string and the apparatus connected thereto are also raised or lowered.

As an alternative mode, particularly where the fluid level in the well tends to build up, the body of liquid and entrained solids in the well may be driven in slug flow up pipe string **24** by a reverse foam flow procedure. In this case valves **43'** and **53** are opened and valves **52** and **43** are closed. The preformed foam then flows via lines **49** and **51** into and down annulus **23** and up the string **24** exiting at the surface via line **41'**. The foam and well fluids carried from the well may be diverted via extensions (not shown) of line **41** or **41'**, to tankage, etc., where paraffin, crude oil, etc., may be recovered.

Foam is formed by mixing together a hot surfactant solution and a gas. The foam must be relatively stable and capable of holding liquid paraffin. Thus, a suitable hot foam source, a foam generator, **70**, a gas source such as an air compressor (not shown) and a gas feed line **71** as well as a heating means **78**, for example a gas burner assembly for raising the temperature of the foamable solution, a foamable solution source (not shown) and solution delivery line **76**, are located on the surface. A suitable conduit, piping **49**, extends from the generator and is connected to both the tubing string **24** and the well annulus **23**. The conduit is connected to the tubing string **24** through flexible conduit **48**, hammer connection **54**, conduit **50** and elbow joint **46**. Valve **52** is used to control flow to the tubing string. The conduit **49** is connected to the well annulus **23** by means of conduit **51** and connection **55** via wellhead **28**. Valve **53** controls flow to the well annulus. Thus foam may be circulated in a normal manner, i.e., down the tubing and up the annulus, or circulation may be reversed, i.e., down the annulus and up the tubing. Operating conditions occasionally may dictate that the foam be reciprocated up and down past the liner to obtain best results. This is accomplished by reversing foam injection sequentially from tubing to liner.

The foam is formed by bringing a hot mixture of a surfactant solution and a gas together in a suitable mixing means, for example, a foam generator. The hot foamable solution is prepared by introducing via line **76** a 0.5–1 weight percent aqueous solution of a sulfated alcohol ethoxylate of the formula $RO(CH_2CH_2O)_{3\text{-}5}SO_3NH_4$ (R is a C_{12}–C_{13} alkyl group) into heating unit **74** where it is heated to 170°–190° F. The heated solution and air are delivered simultaneously to foam generator **70** via lines **73** and **71**, respectively. These delivery rates are adjusted to yield a foam having a gas-to-liquid volume ratio of 5–10, i.e., SCF per gallon to 1. Via line **49** the resulting hot foam having a temperature of about 180° F. is delivered to the well circulation assembly. The hot foam is injected down the well through tubing string **24**. Thus, valve **52** on line **50** is opened to admit foam to the tubing and valve **53** on line **51** is closed to prevent foam from entering the well annulus. Valve **43** on blooie line **41** is opened so that foam may be exhausted from the well annulus at the surface. The hot foam is delivered out the end of the tubing string **24** and is circulated up the well in contact with liner **12** and the deposits **13**, thereby heating and removing paraffin and other undesirable materials therefrom. During and/or after the contacting the foam is circulated at a velocity sufficient to carry the freed paraffin etc., up the annulus **23** to the surface where it is vented via the blooie line **41**. Satisfactory foam velocities are usually in the range 5 to 300 feet per minute.

Minor amounts of foam additives may also be incorporated into the foam, including ammonia for improved cleaning ability, paraffin emulsifying agents of the ionic or anionic types including representative materials such as quaternary ammonium compounds, polyhydric alcohol fatty acid esters, polyethylene oxides and the like (see, for example, Worth, A. H., "The Chemistry and Technology of Waxes," pages 524–542) for improved lifting ability, as well as foam stabilizers and modifiers such as n-dodecanol, n-undecanol, n-tridecanol, n-tetradecanol and mixtures thereof; fatty acid alkanolamides, coconut fatty acid mono- and diethanolamides, natural gums, glycerine, starch, vegetable mucilages, glucose, synthetic thickening agents, polyvinylpyrrolidone, triethanolamine and the like. Such additives are conveniently included in the aqueous solution introduced to the system via line **76**.

DESCRIPTION OF THE ALTERNATIVE EMBODIMENTS

Steam generators are frequently employed in oil well stimulation practice. By the introduction to the foam generator of steam along with air and the foamable solution, the heating accomplished by unit **75** noted above can be accomplished during the foam generation stage. Thus, heating unit **74** may be dispensed with or used in conjunction with steam for the generation of foams where a steam generator is available.

While steam in the absence of another gas can be used to generate a hot foam, such use is not particularly satisfactory because steam is a condensable gas in the present context. Thus a minor cooling of the foam results in the collapse of the foam and the destruction of the circulation fluid. The presence of at least a substantial fraction (5–20 volume percent) of an uncondensable gas in the formation of a hot foam is in general necessary for the maintenance of hot foam circulation fluids in their use in treating a well, or the like, particularly where the foam also functions as a carrier means. Preferably, at least about 40 volume percent of the gas present in a hot foam for use as a circulation fluid in a well is an uncondensable gas.

Representative uncondensable gases useful herein includes air, nitrogen, carbon dioxide, natural gas, ethane, propane, and the like and mixtures thereof.

Representative compounds suitable as condensable gases useful herein include water, methanol, pentane, hexane, heptane, acetone, haloalkanes, and the like compounds having boiling points in the range above about 140° F. and below the desired foam temperature.

Briefly, the amount of the surfactant which should be added to water to form a foamable solution should be in the range from about 0.5 to 1.0 part by weight per 100 parts of water. The foamable solution is mixed with air and/or a suitable gas in a gas-to-liquid volume ratio in the range 1 to 50 SCF to 1 gallon. Superior results are obtained when the hot foam has a gas-to-liquid volume ratio less than about 20.

In circulating hot foam in a well for the removal of petroliferous solids, the foam may be delivered in the neighborhood of the solid in a number of ways including downwardly, as depicted in FIG. **1**, or sidewardly, FIG. **2**, through one or more orifices in pipe string **24** or by a combination of these means.

EXAMPLES

In the following examples a laboratory unit analogous to the foam circulation system of FIG. **1** was assembled in which the terminus of the well bore in the production zone was simu-

lated by a single-necked glass flask having an 8-inch diameter. The correlations from comparisons of data obtained by the use of these laboratory units and from actual field runs have been good. The flask was charged with a mixture of paraffin, crude oil, sand and asphaltenes which had been heated above the melting point of the paraffin and thoroughly stirred. The resulting conglomerate, which approximates the petroliferous paraffinic deposits frequently encountered in oil wells, was then cooled yielding a solid adherent mass.

EXAMPLE 1

As a demonstration of the preferred embodiment an aqueous solution containing 0.5–1 weight percent of a C_{12}–C_{13} alkanol ethoxylate sulfate [$R(OCH_2CH_2)_{3\text{-}5}OSO_3M$] was heated to 180°–200° F. and the hot aqueous solution, and an airsteam mixture were separately introduced into a foam generator at rates sufficient to yield a foam having a gas-to-liquid volume ratio, standard cubic feet per gallon, of about 2–10.

The air to steam volume ratio was varied in the range from about 10–100 to 1, respectively. The resulting foam which had a temperature in the range from about 190°–212° F. was circulated in the unit and contacted with the above described petroliferous solid in the flask. The liberated paraffin, crude oil, and sand were effectively carried by the foam out of the flask and vented from the system. Higher foam temperatures, for example 225° F. and higher, were readily achieved by increasing the system pressure. When a cold foam, e.g., below about 120°, is circulated and contacted with the paraffinic matrix, no effective removal of the adhering solid from the "well" occurs.

EXAMPLE 2

Example 1 was repeated except that the foamable aqueous solution was at the ambient temperature, c.a. 72° F., as was also the air and no steam was employed. The preformed foam having a gas-to-liquid volume ratio, standard cubic feet per gallon, in the range from about 1 to 20 was then heated by passage through a coil immersed in a hot oil bath, 200°–350° F., and circulated into contact with the paraffinic matrix described above. At the contacting the temperature of the foam was in the range from about 140°–180° F., i.e., varied depending upon volume ratios and bath temperatures. Liberated paraffin, crude oil, and sand were effectively carried by the foam out of the flask and vented from the system.

Runs 1 and 2 above demonstrated that petroliferous adherent solids are effectively removed from an inaccessible surface by contacting them with a stable circulation foam having a temperature above about 140° F.

EXAMPLE 3

In the course of the demonstration of example 2 and while circulating the foam at a low velocity, a water phase and an oil phase containing liquid paraffin developed in the flask. The water phase had a composition corresponding to the foamable aqueous solution. The foam flow was discontinued and air alone was passed into this water phase in an effort to generate foam in situ in the zone. A useful foam, i.e., one which could be circulated, could not be produced in this manner. When the circulation of the preformed hot foam was renewed after the in situ foam generation test, water, oil and sand were effectively carried out of the system by the foam.

EXAMPLE 4

In a further variation of example 3 after an accumulation of an oil and water phase in the flask, the flow of the preformed foam was reversed, that is to correspond in FIG. 1, to flow in a well down the annulus 23 and up the pipe string 24 by opening valves 53 and 43' and closing valves 43 and 52. The aqueous and oil phases were driven by the foam up the pipe string and out the alternate blooie line thus unloading the "well."

EXAMPLE 5

The observation was made in run 4 that some asphaltenelike matter tended to adhere to the conduit surface during the traverse out of the system. The addition of ammonia to the foam resulted in the complete removal of this tarlike matter from the surfaces. Only a minor amount of ammonia, less than 1 weight leaving the surfaces clean and free of depositions.

The above examples demonstrate that aqueous foams having a temperature above about 140° F. are effective circulation fluids for use in oil wells and the like for removal of adhering petroliferous or paraffinic deposits from inaccessible surfaces.

We claim:

1. In the treatment of an oil well containing a pipe string by the circulation of a gas-in-liquid foam down the pipe string or the annulus, and up the annulus or pipe string and exhausting the foam from the well, said foam being produced at the surface by the mixing of an aqueous foamable solution and gas, the improvement comprising removing an adherent petroliferous solid from an inaccessible surface in the well by introducing into said well a foam having a temperature in the range from about 140° to 445° F., said foam being under a pressure at least sufficient to maintain the aqueous phase, wherein said foam is prepared from a foamable solution, steam and an amount of an uncondensable gas sufficient to prevent collapse of the foam during the circulation in the well, said amount being at least about 5 to 20 volume percent of the mixture; and wherein said uncondensable gas is selected from the group consisting of air, nitrogen, natural gas, ethane, propane, and mixtures of said gases.

2. The improvement as in claim 1 wherein the gas is a mixture of steam and air and the solid comprises saturated hydrocarbons, aromatic hydrocarbons, asphaltenes and inorganic solids.

3. The improvement as in claim 2 wherein the carbon-containing solid contains an amount of saturated hydrocarbons in parts by weight in the range from about 55 to 90 parts, an amount of aromatic hydrocarbons in the range from about 5 to 15 parts, and an amount of asphaltenes in the range from about 0 to 30 parts.

4. The improvement as in claim 1 wherein the foam has a temperature in the range from about 140° to about 212° F.

5. The improvement as in claim 1 wherein the foam contains an additive selected from the group consisting of ammonia, ionic or anionic paraffin emulsifying agents, foam stabilizers, natural gums and synthetic thickening agents.

6. The improvement as in claim 5 wherein said additive is ammonia.

7. The improvement as in claim 1 wherein the foam has a gas-to-liquid volume ratio in the range from about 1–20 to 1, standard cubic feet per gallon, respectively.

8. The improvement as in claim 1 wherein said foamable aqueous solution has a temperature above about 140° F. and wherein said condensable gas is steam.

9. Apparatus for preforming hot foam for use in a well comprising a foam generator means, a gas source means connecting said gas source with said foam generator means, a steam source means connecting said steam source with said foam generator means, a foamable solution source means connecting said foamable solution source with said foam generator means, a burner heating means for increasing or maintaining the temperature of the foamable solution, a foam outlet from said foam generator means and conduit means connecting said foam outlet with a well for injecting foam down said well.

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