REMOVAL OF WAXY SLUDGES FROM PIPELINES AND OIL WELLS

Clayton A. Carpenter, La Habra, and Paul W. Fischer, Whittier, Calif., assignors to Union Oil Company of California, Los Angeles, Calif., a corporation of California

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This invention relates to the removal of paraffin and waxy sludges from oil wells and from petroleum-carrying pipelines, and in particular concerns new and improved compositions of matter and methods for accomplishing this result.

In many of the oil fields in the United States, particularly in those which produce relatively heavy waxy crude, production is limited as a result of paraffin and waxy sludges depositing from the crude and plugging up the well tubing and pump as well as the oil-producing formation itself. In many instances the flow of oil from a well has been completely arrested as a result of such deposition. A similar deposition of wax and sludge occurs in pipelines which form crude oil gathering and transportation systems, and results in increased pumping costs and/or frequent disassembly and cleanout of the pipeline system.

For the most part, the many attempts to obviate these difficulties have taken the form of heating the crude oil to melt the waxes and sludge and promote their solution in the crude, or employing a solvent to dissolve these materials, or both. The technique of "hot-on-lining" a well, whereby a relatively light petroleum fraction is heated and forced into the well under pressure to dissolve waxy sludges deposited therein, has long been known but the relative ineffectiveness of this technique has equally long been recognized and has led to numerous proposals to employ a solvent other than petroleum distillates. Insofar as is known, however, none of such solvents has proved commercially satisfactory.

It is accordingly an object of the present invention to provide an improved method for removing paraffin, waxy sludges and the like from oil wells and petroleum pipelines.

Another object is to provide a method whereby paraffin, waxy sludges and like deposits are removed from oil wells and petroleum pipelines by means of a solvent.

A further object is to provide new and improved solvents for the paraffin, paraffin sludges and the like which are deposited from crude oils.

Other and related objects will be apparent from the following detailed description of the invention, and various advantages not specifically referred to herein will be apparent to those skilled in the art upon employment of the invention in practice.

We have now found that the above objects and attendant advantages may be realized through the use of a particular type of solvent mixture which has high solvent power for paraffin, waxy sludges and the like and sufficiently high boiling that it can be used at relatively high temperatures. More particularly, we have found that paraffin, waxy sludges and the like which are deposited from even very heavy crude can readily be removed from oil wells, petroleum pipelines and the like by contacting the materials to be removed with a mixed solvent comprising an aromatic hydrocarbon, an ether-alcohol, and a dialkyl ether, all of said components being liquids having boiling points substantially above that of water. By reason of their high-boiling points, such solvent mixtures are admirably adapted to being used in combination with heat, particularly in treating wells as is hereinafter more fully explained.

The aromatic hydrocarbon component of the present solvent mixtures may be any normally liquid aromatic hydrocarbon which has a boiling point above about 100° C., e.g., toluene, xylene, ethylbenzene, cumene, mesitylene, propylbenzene, etc. Mixed aromatic hydrocarbons may also be employed, e.g., petroleum hydrocarbon reformate fractions, kerosene extracts, and mixed aromatics derived from coal tar. Toluene is usually preferred.

The ether-alcohol component may be any normally liquid aliphatic ether of an aliphatic polybasic alcohol, which contains at least one free hydroxyl group and has a boiling point above about 100° C. Suitable ether-alcohols of this type include the mono-methyl-, -ethyl-, -propyl-, and -butyl ethers of ethylene glycol and diethylene glycol, the mono- and di-methyl-, -ethyl-, -propyl-, -butyl ethers of glycerol, the mono-methyl and -ethyl ethers of butanediol, etc. Ether-alcohols of this type containing less than about 12 carbon atoms are preferred.

The other component may be any normally liquid dialkyl ether having a boiling point above about 100° C., e.g., di-n-butyl ether, di-n-amyl ether, di-isamyl ether, di-octyl ether, propyl-amyl ether, ethyl-hexyl ether, methyl-lauryl ether, butyl-octyl ether, etc. Ethers of this type containing less than about 12 carbon atoms are preferred.

The proportions in which the foregoing components are combined to prepare the new solvents are approximately as follows:

<table>
<thead>
<tr>
<th>Component</th>
<th>Percent by volume</th>
</tr>
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<tbody>
<tr>
<td>Aromatic hydrocarbon</td>
<td>50—85</td>
</tr>
<tr>
<td>Aliphatic ether-alcohol</td>
<td>10—40</td>
</tr>
<tr>
<td>Dialkyl ether</td>
<td>5—30</td>
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</table>

A particularly preferred solvent of the present class comprises about 60 and about 75 per cent by volume of toluene, between about 15 and about 30 per cent by volume of the monobutyl ether of ethylene glycol ("Butyl Cellosolve"), and about 5 and about 15 per cent by volume of di-n-butyl ether.

The use of the above-described solvent mixtures for the removal of paraffin, waxy sludges and the like may take a variety of forms. Usually these solvents are most effective when applied in conjunction with heating, but in some instances they may be used cold. In treating pipelines and the like the solvent is merely pumped through the line, preferably under moderate pressure and in a heated condition. Particularly effective results are secured when the direction of flow is reversed periodically, whereby there is achieved a mechanical washing effect which supplements the solvent action. The same general modes of operation may be employed in cleaning out tanks, pumps, refinery equipment and the like in which waxy sludges accumulate.

In treating wells to increase the production thereof, various techniques may be employed ranging from simple application of the cold solvent to the tubing, pump and other pieces of well equipment to more complicated procedures directed to treating the oil-producing formation with the solvent at points considerably removed from the well bore. The following examples will illustrate several ways in which the principle of the invention has been applied to treating wells but are not to be construed as limiting the same.

Example 1

A certain well in the Cut Bank, Montana, field was producing 38.4° API gravity crude at an average rate of
about 6.0 bbls./day. This well was taken out of production on 159 gallons of a 60:30:10 parts by volume mixture of toluene, “Butyl Cellosolve” and di-butyl ether was introduced into the well annulus. Natural gas was then forced into the well until a back-pressure of about 360 p. s. i. was attained. The natural formation pressure was about 260–280 p. s. i., so that the solvent was forced into the formation under a differential pressure of about 80–100 p. s. i. The well was maintained under back-pressure for about 24 hours, after which the pressure was released and the well was placed in production. No appreciable increase in the average daily production from the well which could be attributed to the solvent treatment was immediately observed. After about two months’ operation, however, the production increased by about 18 per cent. This increase was not observed in adjacent wells which had not been treated by the solvent.

Example II

An electrically heated well in the Cut Bank field was producing at an average rate of about 6 bbls./day. Approximately 159 gallons of the solvent employed in Example I were introduced into the well annulus, and heating was continued for about 4 hours with the well shut in. The well was then pressured to about 350 p. s. i. with natural gas, and heating was continued for about 16 hours while maintaining such pressure on the well. The pressure was then released and the well was placed in production. The average daily rate of production immediately rose by about 50 per cent. At the end of a three-month test period the well was still producing at the increased rate.

A particularly preferred embodiment of the invention involves the use of the present class of solvents in conjunction with a “hot-oiling” treatment. As conventionally employed, such treatment in general comprises introducing a heated petroleum hydrocarbon, e. g., kerosene, diesel fuel, gas oil, light crude, etc., into the well and applying pressure to force the hot hydrocarbon deep into the pores and interstices of the oil-producing formation. Since the object of such treatment is to penetrate the formation as deeply as possible with hydrocarbon as hot as possible, it is essential that the hot hydrocarbon be forced into the formation as rapidly as possible. In many wells, however, the formation is so heavily clogged with waxy deposits, and consequently the rate at which the hot hydrocarbon can be forced into the formation is so slow, that the hydrocarbon becomes cold before it penetrates into the formation to any appreciable extent. We have found, however, that if the well is treated with the solvent mixtures provided by the present invention prior to “hot-oiling,” the rate at which the hot hydrocarbon can be forced into the formation can in a great many instances be greatly increased. Consequently, the hydrocarbon penetrates deeply into the formation without undue cooling, and greatly improved results are obtained from the “hot-oiling” treatment. The following example illustrates one way in which the principle of the present invention has been applied to improve greatly the results obtained from “hot-oiling.”

Example III

A certain well in the Cut Bank field was brought in in 1936 at an average production of 58 bbls./day. Over the following 15 years production declined gradually until, in 1951, it was down to 4 bbls./day. In 1951 an electrical heater was installed in the well, whereupon production rose to about 12 bbls./day. Over the next two years production under the influence of heat gradually declined to about 6 bbls./day. The heater was then removed, whereupon production dropped to 5.6 bbls./day over a 1-month period. At this time, a tubing packer was inserted in the well just above the formation, and 159 gallons of a cold 60:30:10 mixture of toluene, “Butyl Cellosolve” and dibutyl ether was introduced into the tubing. The well was pressured up to about 330 p. s. i. and allowed to stand for 3 days, after which time 200 bbls. of hot (300°F.) diesel fuel was introduced into the well. The tubing was pulled and the packer removed and a pump installed, and the well was placed in production one day after the injection of the diesel fuel. During the first week thereafter, the average production was about 34 bbls./day. Within 10 days, production fell to 20 bbls./day. The average production for the next 3 months was 17 bbls./day, and the well continued to produce at about this rate except for temporary declines during extremely cold weather. The overall production secured by the treatment was over 880 bbls. of oil for the 3 months immediately following the treatment. The excellent results secured by the treatment are believed to be due to the fact that the solvent mixture dissolved and/or dispersed heavy waxy deposits in the formation in the immediate vicinity of the bore hole, thereby permitting the hot diesel fuel to penetrate deep into the formation within a relatively short period of time so that a minimum amount of heat was lost from the oil before it had penetrated to the formation. The theory of operation is substantiated by the fact that no difficulty was experienced in injecting the hot oil into the formation at a relatively high rate. However, it should be understood that the invention is not limited by any theory of operation expressed herein.

As will be apparent to those skilled in the art, the principle of the invention may be applied in various ways and in combination with various techniques to effect the removal of paraffin, waxy sludges and the like deposits from crude oil or petroleum distillates and residua in a wide variety of inaccessible places. In its broadest aspects, the invention consists in the herein defined solvent mixtures comprising aromatic hydrocarbons, aliphatic ether-alcohols, and dialkyl ethers, and the method of removing paraffin, waxy sludges and similar deposits from pipelines, oil wells and the like which comprises contacting such deposits with said solvent mixtures to effect their solution and/or dispersion therein.

Other modes of applying the principle of our invention may be employed instead of those explained, change being made as regards the materials or methods disclosed herein, provided the steps or compositions set forth in any of the following claims, or the equivalent of such steps or compositions, be employed or obtained. We, therefore, particularly point out and distinctly claim as our invention:

1. A solvent for paraffin, waxy sludges and the like of petroleum origin comprising between about 50 and about 85 per cent by volume of a normally liquid aromatic hydrocarbon, between about 10 and about 40 per cent by volume of a normally liquid aliphatic ether-alcohol containing at least one free hydroxyl group, and between about 5 and about 30 per cent by volume of a normally liquid dialkyl ether, each of said components having a normal boiling point above about 100° C.

2. A composition according to claim 1 wherein the said aliphatic ether-alcohol and the said dialkyl ether components each contains less than about 12 carbon atoms.

3. A composition according to claim 1 wherein the said aromatic hydrocarbon is toluene, the said aliphatic ether-alcohol is the mono-butyl ether of ethylene glycol, and the said dialkyl ether is di-butyl ether.

4. A solvent for paraffin, waxy sludges and the like of petroleum origin comprising:

| Toluene | 60–75 |
| Mono-butyl ether of ethylene glycol | 15–30 |
| Di-butyl ether | 5–15 |

5. The method of removing paraffin, waxy sludges and the like of petroleum origin from petroleum pipelines.
5 and the like equipment which comprises washing said equipment with a solvent defined by claim 1.

6. The method of removing paraffin, waxy sludges and the like of petroleum origin from petroleum pipelines and like equipment which comprises washing said equipment with a solvent defined by claim 1 in the heated state.

7. The method of cleaning wells which have become clogged with paraffin, waxy sludges and the like of petroleum origin which comprises circulating a solvent defined by claim 1 through the well.

8. The method of treating an oil-bearing formation which comprises introducing into a well penetrating said formation a solvent defined by claim 1, and thereafter applying gas pressure to said solvent to force it into the interstices of said formation.

9. The method of treating an oil-bearing formation which comprises introducing into a well penetrating said formation a solvent defined by claim 1, heating said solvent within the well, and thereafter applying gas pressure on said solvent to force heated solvent into the interstices of said formation.

10. The method of treating an oil-bearing formation which comprises introducing into a well penetrating said formation a solvent defined by claim 1, heating said solvent within the well, and thereafter applying gas pressure on said solvent to force heated solvent into the interstices of said formation.

11. The method of treating an oil-bearing formation which comprises introducing into a well penetrating said formation a solvent defined by claim 1, applying gas pressure to said solvent to force it into the interstices of said formation, and thereafter introducing a heated petroleum hydrocarbon into the well under pressure.

12. The process of claim 11 wherein the solvent employed is a solvent defined by claim 3.

13. The process of claim 11 wherein the solvent employed is a solvent defined by claim 4.

14. The method of treating an oil-bearing formation which comprises introducing into a well penetrating said formation a solvent mixture as defined by claim 4, applying gas pressure to said solvent mixture to force it into the interstices of said formation, introducing a heated petroleum hydrocarbon of the Diesel fuel range into the well, applying gas pressure to said petroleum hydrocarbon to force it into the interstices of said formation, and allowing the well to stand under pressure for several days before withdrawing well fluids therefrom.

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