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USE OF QUATERNARY AMMONIUM SALTS FOR PARAFFIN REMOVAL

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10 Claims. (Cl. 166—41)

This invention relates to the use of quaternary ammonium salts for paraffin removal from metal surfaces in contact with paraffin-rich hydrocarbons. In another aspect it relates to the continuous removal of paraffin from the tubing in a producing well by carrying it to the surface in the moving hydrocarbon fluid. In still another aspect it relates to removing accumulated paraffins in solid chunks from gas and oil well tubing and casing strings by periodic treatment with the composition of this invention.

In oil production, because of the high paraffin content of some crude oils, certain types of producing wells soon become plagued with impeded flow rates, even though the natural fluid energy of the gas or oil in formation may still be substantial. This results from the deposition of paraffins on the metal surfaces of the well tubing, steadily narrowing the flow path for the oil, which will eventually be closed off entirely.

This has necessitated the removal of paraffin deposits by cumbersome mechanical devices or by the inhibition of wax buildup with chemical solvents. In the latter method, the concentration of the solvent in the purging fluid must be sufficiently high so as to achieve its paraffin dissolving function. This necessitates the use of comparatively large volumes of solvent to clean out several hundred, or perhaps thousand, feet of piping—a rather expensive operation, and one in which the results also have not been entirely satisfactory.

I have discovered that in a periodic lubrication treatment, by employing a modest quantity of a commercially available quaternary ammonium salt in a suitable solvent, the paraffin deposition on well tubing, which has built up enough over a period of time to completely plug the tubing, can be overcome in a treatment ranging from about 24 to 240 hours. Alternatively, if it is preferred to avoid the periodic shutdowns due to plugging followed by the batch treatment described above, continuous injection of the additive dispersed in a mineral oil may be practiced. In this latter method, the paraffin would be removed as it is formed, permitting uninterrupted production from the producing well, as long as this is desired or possible under proration allowances. The methods of this invention are appreciably more economical than the present practice of continuous injection of necessarily large quantities of chemical solvents to inhibit the deposition of wax on the walls of the well tubing.

It is an object of this invention to provide a composition, and method of using the same, which inhibits wax deposition from paraffin-rich crude oil.

Another object is to provide a method for substantially preventing the deposition of paraffins from crude oils rich in paraffin on metal surfaces in producing wells.

A further object is to provide a composition and method for removing already formed waxy depositions as solid chunks which are carried to the surface by the hydrocarbon fluid moving in well conduits.

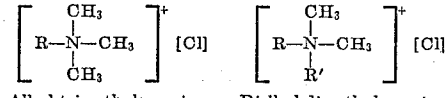
A still further object is to provide a more economical

method for removing paraffin depositions from metal surfaces which are in contact with hydrocarbon fluids during the production and transportation of such fluids.

Various other objects, and advantages and features of the invention will become apparent from the following description and appended claims.

In accordance with the present invention, oil-soluble solutions of quaternary ammonium salts in a suitable organic solvent are prepared for the well treatment.

Specific examples of alkyl quaternary ammonium salts useful in said invention are "Arquads" made by Armour Industrial Chemical Company, which are alkyl and dialkyl quaternary ammonium halide salts. These "Arquads" having the general formulas, for the chloride salt, as follows:



Alkyl trimethylamoniun chloride

Dialkyl dimethylamonium chloride

Of these alkyl quaternary ammonium chloride salts, those having from 5 to 20 carbon atoms in the alkyl group, or in each alkyl group, as the case may be, are especially effective in this invention. The term "alkyl quaternary ammonium halide salt" as used in this specification covers both alkyl and dialkyl salts and mixtures of the same, as many "Arquads" are mixtures. The alkyl radical may be paraffinic, olefinic, diolefinic, acetylinic, or otherwise unsaturated.

For example, octyl trimethylammonium chloride, dioctyl dimethylammonium chloride, decyl trimethylammonium chloride, didecyl dimethylammonium chloride, dodecyl trimethylammonium chloride, didodecyl dimethylammonium chloride, tetradecyl trimethylammonium chloride, ditetradecyl dimethylammonium chloride, hexadecyl trimethylammonium chloride, dihexadecyl dimethylammonium chloride, octadecyl trimethylammonium chloride, dioctadecyl dimethylammonium chloride, octadecenyl trimethylammonium chloride, dioctadecenyl dimethylammonium chloride, octadecadienyl trimethylammonium chloride, dioctadecadienyl dimethylammonium chloride, and mixtures of the same, are all useful in this invention.

Other alcohol-soluble salts of these alkyl quaternary ammonium radicals having 5–20 carbon atoms in each alkyl group, such as the other halides, acetates, salts of other lower carboxylic acids having from 1 to 6 carbon atoms, sulphates, nitrates and phosphates are effective in place of the chlorides, but the chlorides are preferred because they are salts of a stronger acid and a strong base, which makes them ionize better.

Examples of these salts which are all useful in the practice of this invention are octyl trimethylammonium bromide, dioctyl dimethylammonium iodide, decyl trimethylammonium acetate, didecyl dimethylammonium propionate, dodecyl trimethylammonium butyrate, didodecyl dimethylammonium bromide, tetradecyl trimethylammonium iodide, ditetradecyl dimethylammonium acetate, hexadecyl trimethyl ammonium butyrate, dihexadecyl dimethylammonium phosphate, octadecyl trimethylammonium sulfate, dioctyldecyl dimethylammonium nitrate, and octadecenyl trimethylammonium phosphate. Table I provides a tabulation of a number of "Arquads" marketed by the Armour Company and indicates the varied mixtures of alkyl and dialkyl groups useful in this invention.

TABLE I

"R" Groups	Alkyl Quaternary Ammonium Chlorides						Dialkyl Quaternary Ammonium Chlorides		Mixed Monoalkyl and Dialkyl Quaternary Ammonium Chlorides	
	Carbon Chain Length	Arquad 12-33	Arquad 12-50	Arquad C	Arquad S	Arquad T	Arquad 2C-50	Arquad 2C-75	Arquad T-2C	Arquad S-2C
Octyl	8			8			8	8	4	4
Decyl	10			9			9	9	5	5
Dodecyl	12	90	90	47			47	47	23	23
Tetradecyl	14	9	9	18		3	18	18	10	9
Hexadecyl	16			8	10	27	8	8	17	9
Octadecyl	18			5	10	16	10	10	13	10
Octadecenyl	18	1	1	5	35	48			24	18
Octadecadienyl	18				45	6			4	22
Active Ingredient		33	50	50	50	50	50	75	50	50
NaCl (Approx.)		16	1	1	1	1	0.5	0.5	0.5	0.5
Isopropanol (Approx.)		10	34	36	36	36	42	17	36	36
Water (Approx.)		41	15.5	13.5	13.5	13.5	7.5	7.5	13.5	13.5
Form at Room Temp		Liquid	Liquid	Liquid	Liquid	Liquid	Semi-Liquid	Semi-Liquid	Liquid	Liquid

NOTE.—Arquads T-2C and S-2C are mixtures. All the others are either alkyl or dialkyl quaternary ammonium chlorides.

A mixture of 1 part "Arquad T-2C" to 1 part hydrocarbon solvent comprising about 72 percent isopropanol and about 28 percent water is called "Arquad T-2C-50" and was used in the examples described later in this application.

Isopropanol is the preferred alcoholic solvent with the alkyl or dialkyl quaternary ammonium salts, but other aliphatic alcohols having from 1 to 8 carbon atoms are useful in this invention. Methanol, ethanol, 1-butanol, 2-methyl-1-propanol, 2-butanol, and 2-methyl-2-propanol are all useful in this invention, methanol being the next preferred after isopropanol, because they are more polar than the other alcohols, and the alkyl and dialkyl quaternary ammonium halides, acetates, sulfates, nitrates, phosphates, and salts of lower carboxylic acids having from 1 to 6 carbon atoms, that are useful in the invention are more soluble therein.

The lubricating treatment of this invention can be done by means of continuous injection, or on a periodic basis. However, the existence of a packer in the annulus precludes the use of the continuous injection method. Assuming the absence of a packer, and if the well is producing through the tubing, continuous injection of the prepared solution will be through the annulus. Alternatively, if the well is producing through the annulus, the salt solution may be injected through the tubing. In continuous injection, by the use of a chemical pump, solution may be injected into the tubing or through the annulus, as the case may be, at a rate ranging from 1 pint up to 1 gallon per day. To achieve the lower flow rates with the same pump, the prepared solution may be further diluted with water or alcohol.

In the case of a well, the production of which is being prorated, a batch treatment may be preferred. This treatment may be carried on during the period when the well is not producing, and a significantly less amount of the prepared solution should be required than if the treatment is performed only after plugging of the well tubing. An example of the application of the method of this invention follows:

Example I

The intermitter on a gas well was set to blow for 2½ hours, 4 times a day, but little or no liquid was being lifted through the tubing. The flow rate (Q) was 79,000 cubic feet per day (M c.f.d.) of gas while the $P_c^2-P_t^2=28.27$ when a "spot" was taken, with the tubing vented to the atmosphere.

A steel line measurement was run down the tubing. The line tool hit paraffin deposition at 244 feet, at 477 feet, and at 543 feet. The tool dropped very slowly to 721 feet, but could not be lowered below this point.

At 2:40 p.m., ten gallons of Arquad T-2C-50 was lubricated into the tubing. This was immediately followed with eight gallons of water. This load was followed with produced gas introduced at pipeline pressure for a period of about eight minutes, while the annulus was opened to the pit. At 2:50 p.m., the well was shut in, i.e., all valves were closed, until the well pressure exceeded the pipeline pressure. Beginning at 2:55 p.m., the annulus was opened to the pipeline overnight, in order to agitate the fluids.

At 10:40 a.m., the next morning, a spot reading was taken. The flow rate (Q) was now 92,000 cubic feet per day and the $P_c^2-P_t^2=27.12$. At 10:48 a.m., the well was shut in and the tubing was opened to the pit. By 11:00 a.m., the tubing began unloading a few chunks of heavy wax. At 11:08 a.m., the tubing was apparently dead, while the shut-in pressure of the annulus was 181.7 p.s.i.g. At 11:10 a.m., the tubing began unloading more heavy wax in chunks, the wax being well saturated with foam. At 11:18 a.m., the tubing was still breathing, and about ½ gallon of sponge-like wax had accumulated on the ground. At 11:31 a.m., it was still unloading more heavy slubs of wax. At 11:53 a.m., tubing began unloading more wax now mixed with some water. At 12:07 p.m., tubing was again apparently dead, and about 7 gallons of wax on ground had been collected up to this point. At 12:10 p.m., slugging from the tubing of a dry brown wax mixed with foam began. At 12:17 p.m., the tubing began blowing dry gas mixed with occasional chunks of wax. At 12:19 p.m., the annulus pressure was up four pounds to 185.4 p.s.i.g.

At 1:30 p.m., the tubing was blowing gas while still unloading some water and a few more slugs of wax. By 1:35 p.m., the annulus pressure had risen to 189.4 p.s.i.g.

At 1:40 p.m. the well was shut-in to run a steel line measurement. The S.L.M. weight started hitting paraffin at 1520 feet, at 1648 feet, at 1674 feet, at 1682 feet, at 1693 feet, and at 1694 feet. The tool could not be gotten below this latter point. At 2:29 p.m., the tubing was opened straight up to the atmosphere. In five minutes, it began unloading mist and "gunk," with a good amount of water. By 2:50 p.m., the annulus pressure had risen to 190.9 p.s.i.g., while the tubing was unloading a tan colored foamy water. By 2:55 p.m., a total of 8 gallons of heavy wax had been unloaded. A liquid measurement was run for about 5 minutes on the tubing yielding about 2.3 quarts, or a daily rate of 4 barrels. Gas flow from the tubing was 100 thousand cubic feet per day, by pitot tube reading. Several days later another steel line measurement was run. The tool now reached the bottom of the tubing without further treatment.

From previous steel line measurements in other wells of this field, it has been found that the worst paraffin deposits form from about 800 feet to about 2,000 feet. As can be seen from the run described above, several hundred feet of paraffin was removed from the tubing.

Example II

The tubing in a gas well was opened to the pit (vented to the atmosphere), but no gas was producing. The well usually produced through the annulus, but the periodic production of oil and salt water through the tubing had permitted enough paraffin deposition therein, which had completely blocked off the tubing. The column of liquid trapped in the well created a hydrostatic head at the bottom of the well which interfered with the production of gas through the annulus. A "spot" measurement was taken and a flow rate (Q) of 53,000 cubic feet per day (M c.f.d.) was recorded. The $P_c^2-P_t^2$ equals 49.42.

On the first day, five gallons of Arquad T–2C–50, mixed with five gallons of methanol, was lubricated into the one-inch tubing. This was immediately followed with 10 gallons of water. The tubing was next pressured with pipeline gas for a period of several minutes. The tubing was then shut-in and the well was allowed to produce through the annulus.

On the third day, another spot was taken. Q=35 M c.f.d., and $P_c^2-P_t^2=49.78$. At 12:40 p.m., the tubing was repressured with pipeline gas up to 213 p.s.i.g. At 1:00 p.m., the tubing was vented to the atmosphere. Though the annulus pressure was 221 p.s.i.g., the tubing gas flow was too small to measure. At 1:45 p.m., the tubing was shut-in and repressured with pipeline gas. At 2:00 p.m., the tubing was again opened to the atmosphere. At 2:45 p.m., the annulus pressure was up to 225 p.s.i.g. At 3:00 p.m., nothing was coming through the tubing. The tubing was shut-in and the gas flow from the annulus was turned into the pipeline.

On the fourth day, a steel line measurement was run down the tubing to a total depth of 3,188 feet. Paraffin slowed the tool at 1380 feet, at 1700 feet, and again at 1900 to 2200 feet. The annulus was opened to the pit (vented to the atmosphere). The annulus "kicked off" in 7 minutes, producing a milky looking water and paraffin. It was shut-in after an hour and 45 minutes. The annulus was again suddenly opened to the atmosphere. It was repressured with pipeline gas and then the tubing was left open to the pin overnight. On the next day, the tubing would not "kick off." Gas producing through the annulus was then turned into the pipeline while the tubing remained open.

Four days later, a "spot" was taken giving a Q up to 62 M c.f.d. and the $P_c^2-P_t^2$ was down to 29.13. The tubing gas flow rate was still too small to measure. The tubing was shut-in and the slightly increased gas flow through the annulus was directed to the pipeline.

A week later, a second treatment was begun, at which time a "spot" gave a Q=55 M c.f.d. and a $P_c^2-P_t^2=42.93$. Again 5 gallons of Arquad T–2C–50, mixed with 5 gallons of methanol, followed with 10 gallons of water were introduced into the tubing. This load was again followed with produced gas introduced at pipeline pressure for a period of several minutes. The tubing was shut-in over the weekend. On the third day following the second treatment, at 11:11 a.m., the annulus was opened to the pit. At 11:16 a.m., it "kicked off" and made foam and salt water to the pit. At 11:40 a.m., it was shut-in and repressured with pipeline gas at 210 p.s.i.g. At 11:45 a.m., the annulus was again opened to the pit. At 11:51 a.m., it "kicked off" and made a milky-looking water to the pit. At 1:00 p.m., the annulus was again pressured with pipeline gas up to 210 pounds, then the pipeline gas pressure was alternated back and forth between the tubing and the annulus. At 1:30 p.m., the tubing kicked off. By 1:45 p.m., the shut-in pressure on the annulus was up to 280 p.s.i.g. The tubing started producing liquid.

Four days later, the well head pressure was 220 pounds. Tubing was "making" liquid to the pit. The flow rate was measured at 222 M c.f.d. The next day, another "spot" was taken with a Q=35 M c.f.d. and a $P_c^2-P_t^2=49.78$. Tubing was still "making" liquid to the pit with a flow rate of 212 M c.f.d. The well was shut-in overnight. The following day, the shut-in pressure on the annulus was 302.5 p.s.i.g. When the tubing was turned into the pipeline, it died immediately. Upon opening the tubing to the pit, it kicked off. Regular production of gas was started through the annulus, and a pinched tubing gate permitted production of crude oil and salt water therethrough.

P_c, as used in the above examples, means the shut-in pressure of the annulus or tubing, whichever is the higher. P_t stands for the flowing pressure in the annulus. The expression $P_c^2-P_t^2$ is accepted in the art as a measure of the operating efficiency of the well. For any given flow rate, the lower the value of the $P_c^2-P_t^2$, the more efficient the operation of the well.

While some beneficial results are obtained with smaller amounts and in shorter times of treatment, markedly superior results are obtained in the practice of this invention when the treating solution of quaternary ammonium salts in alcoholic solvent is injected in amounts of 1 to 20 gallons, the best results being with 5 to 15 gallons, per well, of from a 2 percent solution to a saturated solution of said salts, said alcoholic solvent containing less than 50 percent water, the best results being obtained with over 5 percent solutions of said salts, later injecting from zero to 20 volumes of water per volume of said injected treating solution, better results being obtained with 0.5 to 2 volumes of water per volume of said treating solution, later injecting natural gas into said tubing at a pressure from a little below pipeline pressure to any pressure available while venting well annulus for a period of preferably 1 to 60 minutes, more preferably from 5 to 15 minutes, and shutting in said well preferably from 1 hour to 7 days, more preferably from 10 to 30 hours, before venting said tubing to the atmosphere.

By natural gas it is intended to cover all conate gas produced from underground strata in which the major component is methane, but containing from zero to small amounts of N_2, CO_2, CO, H_2S, and C_2 to C_{10}, or even higher, carbon chain hydrocarbons in a vapor state in said methane (depending on the pressure and retrograde vaporization of said higher hydrocarbons in said gaseous mixture).

Various modifications of this invention will become apparent to those skilled in the art without departing from the scope and spirit of the invention, and it should be understood that the latter is not necessarily limited to the aforementioned discussion and specification.

We claim:

1. A method of removing deposits of normally solid paraffins from metal surfaces in contact with a hydrocarbon fluid which comprises the steps of injecting between 1 and 20 gallons of a solution of quaternary ammonium salts selected from the group consisting of monoalkyl quaternary ammonium salts, dialkyl quaternary ammonium salts, and mixed monoalkyl and dialkyl quaternary ammonium salts, having from 5 to 20 carbon atoms in each alkyl group in an alcoholic solvent into a well tubing plugged by paraffin deposits, injecting a volume of water into said tubing, following the load in said tubing with a stream of natural gas from at least about pipeline pressure for a period of 1 to 60 minutes while the annulus is vented to the atmosphere, shutting the well in until the well pressure exceeds the pipeline pressure, flowing gas from said well for a period of from 1 hour to 7 days to agitate the injected fluids, and venting said tubing to the atmosphere, thereby permitting sporadic discharge of chunks of paraffin from said tubing by the fluid energy of said hydrocarbon fluid which continues until unimpeded flow of said hydrocarbon fluid is restored.

2. A method of removing deposits of normally solid paraffins from metal surfaces in contact with a hydrocarbon fluid which comprises the steps of injecting between 1 and 20 gallons of a solution of quaternary ammonium salts selected from the group consisting of

monoalkyl quaternary ammonium salts, dialkyl quaternary ammonium salts, and mixed monoalkyl and dialkyl quaternary ammonium salts, having from 5 to 20 carbon atoms in each alkyl group in an alcoholic solvent into a well tubing plugged by paraffin deposits, injecting a volume of water into said tubing, following the load in said tubing with a stream of natural gas at at least about pipeline pressure for a period of 1 to 60 minutes while the annulus is vented to the atmosphere, shutting the well in until the well pressure exceeds the pipeline pressure, flowing gas from said well for a period of from 1 hour to 7 days to agitate the injected fluids, and venting said tubing to the atmosphere, thereby permitting sporadic discharge of chunks of paraffin from said tubing by the fluid energy of said hydrocarbon fluid which continues until unimpeded flow of said hydrocarbon fluid is restored, and repeating said method of treatment until said unimpeded flow is restored.

3. In the transportation of a hydrocarbon fluid through a conduit wherein said fluid contains paraffin constituents which tend to deposit and build up on the surfaces of said conduits in contact with said fluid, the improvement which comprises injecting into said fluid a solution of an alcohol soluble quaternary ammonium salt selected from the group consisting of monoalkyl quaternary ammonium salts, dialkyl quaternary ammonium salts, and mixed monoalkyl and dialkyl quaternary ammonium salts, having from 5 to 20 carbon atoms in each alkyl group in an alcoholic solvent in an amount sufficient to substantially prevent a build up of paraffin deposits on the surfaces of said conduit.

4. A method of removing deposits of normally solid paraffins from metal surfaces in contact with a hydrocarbon fluid which comprises the steps of injecting between 1 and 20 gallons of a solution of quaternary ammonium salts selected from the group consisting of monoalkyl quaternary ammonium salts, dialkyl quaternary ammonium salts, and mixed monoalkyl and dialkyl quaternary ammonium salts, having from 5 to 50 carbon atoms in each alkyl group in an alcoholic solvent into a well tubing plugged by paraffin deposits, following the load in said tubing with a stream of natural gas from at least about pipeline pressure for a period of 1 to 60 minutes while the annulus is vented to the atmosphere, shutting the well in until the well pressure exceeds the pipeline pressure, flowing gas from said well for a period of from 1 hour to 7 days to agitate the injected fluids, and venting said tubing to the atmosphere, thereby permitting sporadic discharge of chunks of paraffin from said tubing by the fluid energy of said hydrocarbon fluid which continues until unimpeded flow of said hydrocarbon fluid is restored.

5. A method of removing deposits of normally solid paraffins from metal surfaces in contact with a hydrocarbon fluid which comprises the steps of injecting between 1 and 20 gallons of a solution of quaternary ammonium salts selected from the group consisting of monoalkyl quaternary ammonium salts, dialkyl quaternary ammonium salts, and mixed monoalkyl and dialkyl quaternary ammonium salts, having from 5 to 20 carbon atoms in each alkyl group in an alcoholic solvent into a well tubing plugged by paraffin deposits, following the load in said tubing with a stream of natural gas at at least about pipeline pressure for a period of 1 to 60 minutes while the annulus is vented to the atmosphere, shutting the well in until the well pressure exceeds the pipeline pressure, flowing gas from said well for a period of from 1 hour to 7 days to agitate the injected fluids, and venting said tubing to the atmosphere, thereby permitting sporadic discharge of chunks of paraffin from said tubing by the fluid energy of said hydrocarbon fluid which continues until unimpeded flow of said hydrocarbon fluid is restored, and repeating said method of treatment until said unimpeded flow is restored.

6. In the transportation of a hydrocarbon fluid through a conduit wherein said fluid contains paraffin constituents which tend to deposit and build up on the surfaces of said conduit in contact with said fluid, the improvement which comprises injecting into said fluid a solution of an alcohol soluble quaternary ammonium salts selected from the group consisting of monoalkyl quaternary ammonium salts, dialkyl quaternary ammonium salts, and mixed monoalkyl and dialkyl quaternary ammonium salts, having from 5 to 20 carbon atoms in each alkyl group in an alcoholic solvent in an amount sufficient to substantially prevent a buildup of paraffin deposits on the surfaces of said conduit, said solution further comprising 33–75 parts by weight of quaternary ammonium salts, between 0.5 and 1.6 parts by weight of sodium chloride, between 10 and 42 parts by weight of hydrocarbon solvent, and between 6.5 and 41 parts by weight of water.

7. In the transportation of a hydrocarbon fluid through a conduit wherein said fluid contains paraffin constituents which tend to deposit and build up on the surfaces of said conduit in contact with said fluid, the improvement which comprises injecting into said fluid a solution of an alcohol soluble quaternary ammonium salts selected from the group consisting of monoalkyl quaternary ammonium salts, dialkyl quaternary ammonium salts, and mixed monoalkyl and dialkyl quaternary ammonium salts, having from 5 to 20 carbon atoms in each alkyl group in an alcoholic solvent in an amount ranging between one pint and one gallon per day sufficient to substantially prevent a build up of paraffin deposits on the surfaces of said conduit, said solution further comprising 33–75 parts by weight of quaternary ammonium salts, between 0.5 and 1.6 parts by weight of sodium chloride, between 10 and 42 parts by weight of hydrocarbon solvent, and between 6.5 and 41 parts by weight of water.

8. A method of removing deposits of normally solid paraffins from metal surfaces in contact with a hydrocarbon fluid which comprises charging a solution of quaternary ammonium salts selected from the group consisting of monoalkyl quaternary ammonium salts, dialkyl quaternary ammonium salts, and mixed monoalkyl and dialkyl quaternary ammonium salts, having from 5 to 20 carbon atoms in each alkyl group in an alcoholic solvent into a well tubing in an amount sufficient to remove said paraffins from the walls of said tubing in large chunks which are carried to the ground surface by the fluid energy of said hydrocarbon fluid moving in said well tubing, said solution further comprising 33–75 parts by weight of quaternary ammonium salts, between 0.5 and 1.6 parts by weight of sodium chloride, between 10 and 42 parts by weight of hydrocarbon solvent, and between 6.5 and 41 parts by weight of water, thereby permitting restoration of unimpeded flow of said hydrocarbon fluid in said well tubing.

9. The method according to claim 8 in which said hydrocarbon solvent is selected from the group consisting of methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol and 2-methyl-2-propanol.

10. A method of removing deposits of normally solid paraffins from metal surfaces in contact with a hydrocarbon fluid which comprises charging a solution of quaternary ammonium salts selected from the group consisting of monoalkyl quaternary ammonium salts, dialkyl quaternary ammonium salts, and mixed monoalkyl and dialkyl quaternary ammonium salts, having from 5 to 20 carbon atoms in each alkyl group in an alcoholic solvent into a well tubing in an amount ranging between one pint and one gallon per day sufficient to remove said paraffins from the walls of said tubing in large chunks which are carried to the ground surface by the fluid energy of said hydrocarbon fluid moving in said well tubing, said solution further comprising 33–75 parts by weight of quaternary ammonium salts, between 0.5 and 1.6 parts by weight of sodium chloride, between 10 and 42 parts by weight of hydrocarbon solvent, and between 6.5 and 41

parts by weight of water, thereby permitting restoration of unimpeded flow of said hydrocarbon fluid in said well tubing.

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CERTIFICATE OF CORRECTION

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

Column 7, line 39, for "50" read -- 20 --.

Signed and sealed this 1st day of October 1963.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents

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