

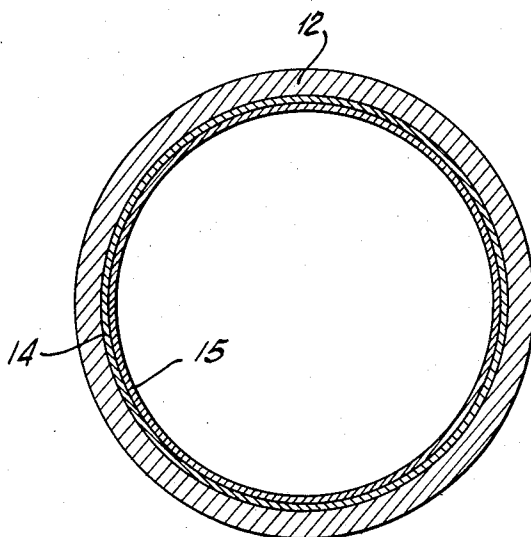
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PREVENTION OF PARAFFIN DEPOSITION

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## PREVENTION OF PARAFFIN DEPOSITION

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13 Claims. (Cl. 137—1)

The present invention relates to the transportation of petroleum through pipes and, more specifically, to the prevention of wax clogging in production or transportation lines from oil wells delivering a waxy product.

The present invention is therefore particularly concerned specifically with the class of producing petroleum wells which tend to lay down objectionable waxy or paraffinic deposits upon the interior surface of the production or gathering pipe system. In wells of this character, the composition of the crude oil is such that the decrease in temperature and/or pressure which the oil undergoes upon being elevated through the production tubing, results in the separation from solution and formation of adherent waxy solids or semi-solids. The fact that cooling occurs through the wall of the tubing, and that wax has a tendency to stick to metal such as iron, result in the deposition of these solids on the tubing surface. In the usual case, a waxy deposit proceeds to build up, progressively constricting the flow passage and seriously impairing the flow of petroleum therethrough. Removal of such waxy deposits is obviously difficult and costly.

It is to such wells, in which the production and gathering system tends to become substantially obstructed by waxy deposits, that the present invention is directed.

In accordance with the present invention, wax separation from solution in the oil is not prevented, but wax deposition on the pipe surface is inhibited and the wax is continuously removed with the oil. This is accomplished by providing upon the interior surface of the production string or pipe carrying the waxy oil an adherent, hydrous film, or coating of a water-wet or hydrous material having a high adhesion tension against water and a low adhesion tension against wax and capable of continuously immobilizing water at its surface and preventing the adhesion of wax thereto. The typical production well to which the present invention is particularly applicable produces, in addition to liquid and gaseous petroleum, connate or formation water. Therefore, the hydrous or hydrophilic coating retains a continuous film of this water strongly adsorbed thereon, and is accordingly repellent to oil and wax so that adherence of waxy material is positively prevented. Where water is not being produced with the oil, water is advantageously injected as described below, since wax is less likely to adhere to these coatings when they are continuously filmed with water.

I have discovered that a coating which comprises a polar material exposing highly hydrophilic chemical groups on its surface, has the required high adhesion tension against water and results in a film of water being attracted to and held against the surface of the coating material to the exclusion of oil and wax. The coating may comprise either an organic or an inorganic material provided that its surface is preferentially wetted by water in the presence of oil. In either case the result is a hydrous surface which inherently inhibits attachment of petroleum solids and particularly waxy deposits, which is in direct contrast to

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the untreated ferruginous surfaces of the usual flow string for which wax has a high affinity.

In accordance with the present invention, therefore, there is provided a coating which (a) displays strong adhesion to the metal pipe; and (b) is more readily wet by water than by oil in the presence of both; and (c) which may advantageously be kept water wet such as by water injection so that the stream of oil within the pipe is continuously in contact with what is, in effect, an aqueous film instead of a metal surface.

Examples of suitable coating materials having a substantially higher adhesion tension for water than for oil and which adhere well to iron are, for instance, the water insoluble compounds of polyhydroxy acids, e. g., the water insoluble iron-containing compounds thereof, such as gallic acid, the sugar acids, ortho-, meta- and pyrophosphoric acids, tannic acid, and the water insoluble ferri- and ferro-cyanides. These compounds can be deposited as a thin adherent film upon iron surfaces by direct reaction of the respective salts or acids with the clean surface of the iron tubing. As a general rule, the above materials, particularly the hydroxy substituted organic acids, tend to form in this manner with the iron surface products which are substantially adherent and which, at the same time, by exposing hydroxyl groups, exhibit a high adhesion tension against water and a relatively low adhesion tension against oil, and therefore are selectively and preferentially wet by water.

As indicated hereinabove, it is within the scope of this invention to provide the surface of the production tubing with a hydrous gel coating, which would include the above-indicated materials, wherein water is held not only on the surface of the material, but also wherein water is held within the micropore structure of the hydrous gel coating itself. Particularly advantageous coating materials are therefore the hydrated gels which form a water insoluble gelatinous compound or precipitate with iron.

Either organic or inorganic water insoluble hydrous gelatinous materials or gels, are suitable. Such, for example, are the above mentioned iron tannates and the aluminum, iron, chromium and tin gel forming oxides, and the like, which can be readily applied to form a thin but continuous coating having a high and preferential affinity for water which is strongly retained as a component of the gel structure.

The invention contemplates resorting to certain techniques for promoting adherence of those coatings in accordance with this invention which are not necessarily highly adherent to a ferruginous surface per se, by the use of a priming coat or undercoat, for instance, treatment of the iron surface with gallic acid to form an adherent iron gallate undercoat in order to promote the adherence of a subsequent layer of an organic or inorganic water insoluble gelatinous material or gel such as silicic acid which has a hydrous gel character. The other above-mentioned water insoluble compounds of polyhydroxy acids, e. g. the water insoluble iron-containing compounds thereof, such as the sugar acids, tannic acid, ortho-, meta-, and pyro-phosphoric acids and the water insoluble ferri- and ferro-cyanides also form a suitable undercoat. The adherence of a subsequent layer of other inorganic oxide gels such as the chromium, tin, iron and aluminum oxide gels, can also be improved by employing the above-indicated materials as an undercoat.

The term "hydrous gel," as used herein, is intended to mean a hydrophilic gel inherently holding substantial free water in its pore structure, and, therefore, as above, presenting to the flowing stream of produced oil, an aqueous surface against which the wax cannot adhere.

The primary advantage of the present invention resides in overcoming the interruption of production and the prior

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costly swabbing of the tubes necessary to permit flow of produced oil.

Referring now to the accompanying drawing which schematically illustrates in cross section an article of manufacture, such as a steel pipe, prepared in accordance with the practice of this invention, the steel pipe 12 is shown provided with an undercoat 14 of an adherent material such as a water-insoluble salt of gallic acid. The material indicated at 14 is desirably employed as an undercoat for a hydrous gel material 15 such as an inorganic, hydrous gelatinous oxide selected from the group consisting of silicon, aluminum, iron, chromium and tin oxide.

It is to be noted that it has been hitherto proposed to coat production tubing with sodium silicate to protect against the corrosive effect of subsurface liquids. Such a proposal is disclosed in U. S. Patent 2,560,331. This patent, however, is not concerned with the type of production experiencing an objectionable deposit of petroleum waxes which form a corrosion protective coating, *per se*. Such corrosion-preventing coatings will not specifically prevent the adhesion of wax, since a continuous, preferentially water-wetted hydrous film is not necessarily maintained. Thus, the present invention is, in direct contrast, concerned with the specific problem of preventing the adherence of wax by maintaining at all times a continuous preferentially water-wetted coating.

As above indicated, the hydrophilic coatings may be formed directly on the surface of the tubing and where water insoluble iron compounds are involved may be laid down by contacting the iron surface with suitable soluble salts of the coating material. Alternatively, the final hydrophilic coating may be applied by suitable means directly to the surface of the tube.

Inorganic gelatinous oxides when employed as a coating are preferably formed *in situ* and are preferably never permitted to dry. For example, in preparing an adherent silica coating, the interior of the tubing is first cleaned of grease by washing with a suitable solvent followed by a dip in dilute hydrochloric acid. The clean metallic surface is then immersed in a solution of gallic acid for a sufficient time to form a substantial blue coating of iron gallate. The resulting water-wetted surface is then dipped into a 20% solution of sodium silicate several times until a uniform and substantial coating of sodium silicate results. This treatment may be followed by dipping in a dilute acid solution such as hydrochloric acid to promote the formation of gelatinous silica. The gel is left in a water wet condition as a result of this treatment.

When this surface was placed in contact with a solution of paraffinaceous heptane or crude oil under conditions favorable for the deposition of paraffin, solid wax separation occurred but no adhesion of the separated wax to the pipe was found as long as the surface remained wet with water.

By way of illustrating the foregoing, a one-quarter inch untreated stainless steel tube was immersed to the extent of 50 square centimeters of its surface area in a waxy petroleum liquid having a cloud point of 45° C. The temperature of the liquid was maintained at about 4° C. The temperature of the stainless steel tube was maintained somewhat below the temperature of the petroleum bath by circulating water at a predetermined temperature there-through. This resulted in deposition upon the stainless steel surface of approximately 200 milligrams of wax in a period only slightly longer than one hour.

By way of comparison, when the stainless steel was treated as previously described, to form a hydrous silica coating, it received no weighable deposit of wax when subjected to the same test while the hydrous silica coating was maintained in a water-wet condition. The silica gel surface was continuously maintained in a water-wet or hydrous condition by the presence of small amounts of water injected in the waxy-oil solution circulating in contact with the tube.

From the foregoing, it is apparent that wax deposition

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is effectively combatted in this manner. Essentially identical results may be realized by coating the tube with any of the other aforementioned inorganic hydrous gelatinous oxides, as for example, the alumina, tin oxide, and chromium oxide gels, and maintaining the gelatinous oxide water wet.

Of course the hydrophilic, water-wetted, iron gallate layer without additional silica gel deposited thereon likewise exhibits substantial resistance to wax deposition because of its exposed hydroxyl groups.

Application of the aforementioned wax repellent coatings to the production string may be practiced prior to its introduction into the well. On the other hand, essentially the same treatment may be applied to the tubing *in situ* in the well by circulating washing fluids to clean the production tubing and thereafter, following the aforementioned steps, leading to the deposition of the desired coating. However, in most instances, continuous injection of a small aqueous stream of suitable hydrophilic coating material into the well casing and thence to the lower end of the flow string, will generally result in a buildup of the desired hydrophilic layer on the interior surfaces of the tubing and at the same time, provide the water to maintain a continuous water film on the resulting deposited coating. For example, a water solution of gallic acid may be continuously injected into the bottom of the well by passing it down through the annular space between the tubing and the well casing, and permitting it to mix with and flow upwardly with the produced oil in contact with the interior surface of the production string. Likewise aqueous solutions of soluble salts, reactive toward iron to produce a water-wet coating such for example, as sodium or potassium salts of the ferri- or ferrocyanides, the sugar acids, phosphoric acids or tannic acids, are continuously injectable in this manner.

This application is a continuation-in-part of my co-pending patent application Serial No. 260,333, filed December 6, 1951, now abandoned.

Obviously, therefore, many modifications and variations of the invention as herein set forth may be made without departing from the spirit and scope thereof, and only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. In the transportation of petroleum through a conduit wherein the petroleum contains waxy materials which tend to build up objectionable deposits of said waxy materials on the interior surface of the conduit, the improvement which comprises providing said conduit with an interior coating comprising a material having a higher adhesion tension against water than against oil and selected from the group consisting of water-insoluble salts of gallic acid, the sugar acids, tannic acid, ortho-, meta-, and pyrophosphoric acids and the water-insoluble ferri- and ferrocyanides and maintaining said coating water-wet so that an adsorbed hydrous film is maintained between the interior surface of the conduit and said petroleum stream, thereby inhibiting adhesion of said material to said conduit.

2. The method according to claim 1 wherein said coating is maintained continuously water-wet by the injection of water into the petroleum stream within the conduit.

3. The method according to claim 1 wherein said coating additionally comprises a hydrous gel deposited on said coating.

4. The method according to claim 1 wherein said coating additionally comprises an inorganic hydrous gelatinous oxide deposited on said coating.

5. The method according to claim 4 wherein said inorganic hydrous gelatinous oxide is selected from the group consisting of silicon, aluminum, iron, chromium and tin oxides.

6. In the transportation of petroleum through a ferrous pipe wherein the petroleum contains waxy material which tends to build up objectionable deposits of

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said waxy material upon the interior surface of the pipe, the improvement which comprises providing said pipe with an interior coating comprising a material having a higher adhesion tension against water than against oil and selected from the group consisting of water-insoluble iron-containing compounds of gallic acid, the sugar acids, tannic acid, ortho-, meta-, and pyro-phosphoric acids and the water-insoluble ferri- and ferro-cyanides, and maintaining said coating water-wet so that an adsorbed hydrous film is maintained between the interior surface of said pipe and said petroleum stream thereby inhibiting adhesion of said waxy material to said pipe.

7. A method according to claim 6 wherein said coating additionally comprises a hydrous gel deposited on said coating.

8. In the transportation of petroleum through a ferruginous conduit wherein the petroleum contains waxy material which tends to build up objectionable deposits of said waxy material upon the interior surface of said conduit, the improvement which comprises depositing upon the interior surface of said pipe a coating of iron gallate, depositing a layer of silicic acid on the resulting iron gallate coating and maintaining the resulting silicic acid coating water-wet so that an adsorbed hydrous film is maintained between the interior surface of the pipe and said petroleum stream thereby inhibiting adhesion of said waxy material to said pipe.

9. An article of manufacture useful for the transportation of petroleum containing waxy material comprising a conduit, the interior surface of which is provided with a coating of a material selected from the group consisting of water-insoluble salts of gallic acid, the sugar acids, tannic acid, ortho-, meta-, and pyro-phosphoric acids and the water-insoluble ferri- and ferro-cyanides.

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10. An article of manufacture in accordance with claim 9 wherein said coating is provided with an adherent film of water.

11. An article of manufacture useful for the transportation of petroleum containing waxy material comprising a ferruginous conduit, the interior surface of which is provided with a coating of a material selected from the group consisting of water-insoluble salts of gallic acid, the sugar acids, tannic acid, ortho-, meta-, and pyro-phosphoric acids and the water-insoluble ferri- and ferro-cyanides and a second coating of an inorganic hydrous gelatinous oxide selected from the group consisting of silicon, aluminum, iron, chromium and tin oxides deposited on the first-mentioned coating.

12. An article of manufacture in accordance with claim 11 wherein said second coating contains water which is held not only on the surface of said second coating but also within the micropore structure of the gelatinous oxide.

13. An article of manufacture useful for the transportation of petroleum containing waxy materials comprising a ferruginous conduit, the interior surface of which is provided with a coating of iron gallate upon which is deposited a hydrous layer of silicic acid.

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