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METHOD OF REMOVING WAX DEPOSITS FROM OIL-WELL TUBING

Abraham Shapiro, Monrovia, Calif., assignor to Socony-Vacuum Oil Company, Incorporated, New York, N. Y., a corporation of New York

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In producing petroleum from some of the deeper wells in California and other localities in which the oil in the formation is at a relatively high temperature, difficulty is often experienced by reason of accumulation of wax deposits in the production tubing. The material of these deposits is generally similar to the rod wax of the Pennsylvania oil fields but differs in containing a considerable proportion of bituminous matter and in being of a tougher consistency. Such deposits may occur throughout the entire length of the tubing string but more often are localized and often occur at considerable depth while the tubing above them is substantially clear. Apparently the location of the deposits is governed by temperature changes in the oil column. Wax deposits of this character have caused serious impediment to flow and in some cases complete stoppage, even in wells flowing at high tubing velocity.

These wax-bitumen deposits are substantially completely soluble in certain organic solvents of high specific gravity, such as chloroform, carbon disulfid and carbon tetrachloride, and it has been the practice to keep the tubing clean by periodic injections of one of these solvents, usually carbon tetrachloride. This practice is effective but is unduly expensive by reason of the large quantity of solvent required to remove any deposits distant from the surface. As the tubing is full of petroleum and as the solvent power for the wax-bitumen deposits decreases rather rapidly with progressive dilution, deposits at depth can be removed only by flooding the tubing and thus displacing substantially the entire oil content, an operation consuming a large quantity of costly solvent.

I have discovered that such deposits may be dissolved and removed from the tubing with the consumption of a relatively very small quantity of solvent by the use of an emulsion adapted to break and release the solvent within a definite and rather narrow temperature range and which may therefore be placed at the particular depth at which it is needed. Such emulsions, described below, are immiscible with petroleum and, by reason of their greater specific gravity, sink through the oil column without change until they reach the temperature level at which they are adapted to break. As the temperature of the oil column increases progressively from the surface downward and as the temperature gradient of any given well is known or may readily be determined in well known ways, it suffices to adjust the breaking point of the emulsion to the temperature obtaining at the level or levels at which the deposits occur. On reaching this temperature level the emulsion separates, releasing the solvent in undiluted condition and the wax is thereby dissolved and caused to pass out of the tubing.

The emulsions which I have prepared and used for this purpose consist essentially of carbon tetrachloride or an equivalent wax-bitumen solvent (which must be heavier than and insoluble in water); a petroleum distillate such as the well-known rubber solvent, and a small quantity of water. These liquids are brought into the condition of an emulsion in which the aqueous is the continuous phase by the use of emulsifying agents such as the oil-soluble petroleum sulfonates and agar-agar or a similar gelatinous substance. The control of the breaking temperature, within limits of 25° Fahr. or less, is effected by varying the proportions of sulfonates and gelatinous substance in the composition.

By way of example, a composition resolving spontaneously over the temperature range from 100° to 125° Fahr. may have the following composition, in per cents by weight:

	Per cent
Carbon tetrachloride	35.00
Carbon disulfid	40.00
Petroleum distillate 60° A. P. I. gravity	14.68
Water	10.00
Oil-soluble sulfonates	0.30
Agar-agar	0.02
	100.00

This composition is prepared by first dissolving the agar-agar in the water and the sulfonates in the mixture of solvents and then bringing the two phases together with agitation. Preferably the solvent is added very slowly to the aqueous phase with constant stirring over a period of say twenty to thirty minutes. Too rapid an addition of the solvent mixture may cause reversal of the emulsion, which must be of the water-continuous type.

In the same manner an emulsion resolving over the temperature range 175° to 200° Fahr. may be prepared in accordance with the following formula:

	Per cent
Carbon tetrachloride	35.00
Carbon disulfid	40.00
Petroleum distillate	13.92
Water	10.00
Oil-soluble sulfonates	1.00
Agar-agar	0.08
	100.00

Emulsions breaking within temperature ranges intermediate the above may be produced by varying the total dosage of the emulsifying agents. Generally speaking, an increase in the sulfonate dosage of about 0.25% and of the dose of agar-

agar of about 0.02% will raise the breaking temperature about 25° Fahr.

Carbon tetrachloride and carbon disulfid are mentioned above as examples of solvents for a mixture of wax and bitumen. These substances may be used singly or in admixture, and may be wholly or in part substituted by other wax solvents such as chlorinated hydrocarbons. These solvents, when liberated from the emulsion, are the functional element of the mixture and their selection and proportioning will be governed by the nature of the deposit to be removed and its relative solubility in the various solvents available. In all cases, however, these solvents must be completely water-insoluble and must be at least as heavy as water.

The purpose of the rubber solvent or similar petroleum distillate is to control the specific gravity of the emulsion and cause it to subside through the oil column in the tubing at a desired rate. Resolution due to temperature change is not instantaneous and if the emulsion subsides too rapidly it might pass in part unbroken through the desired temperature level and thus be wasted. The relation between the solvent and the petroleum distillate is thus variable over a considerable range, remembering that the dilution of the solvent by the distillate somewhat reduces its solvent power for the wax to be removed. The proportion above specified causes the emulsion to subside through tubing filled with oil of 40° A. P. I. gravity at a velocity of about 20 feet per minute.

The oil soluble sulfonates referred to herein are the well known "mahogany" sulfonates resulting from the action of strong sulfuric acid on petroleum distillates. Alternatively I may use various oil-soluble sulfonated esters or fatty acids, as for example sulfonated castor oil or sulfonated oleic acid.

In place of agar-agar I may utilize other gelatinous substances such as glue, gelatine, starch, or the water-soluble gums (e. g., gum arabic).

In the use of these emulsions in a flowing well, the well is shut in and the desired quantity of the emulsion forced into the upper end of the tubing. This quantity should be sufficient to displace the oil from that part of the tubing in which the deposit is known to exist. After this introduction the well is allowed to stand idle for a sufficient period to permit the emulsion to reach the predetermined level, to break and to dissolve the wax-bitumen deposit, ordinarily from one to eight hours. The flow valve is then opened and the solution discharged along with the production normally made by the well.

If the deposits occur along a considerable length of the tubing, or at widely separated intervals, and therefore over a relatively wide temperature range, it may be requisite to use two or more doses of emulsion of different breaking temperatures.

I claim as my invention:

1. The method of removing wax deposits from oil-well tubing which comprises: feeding into the upper end of said tubing an emulsion of a solvent for said deposit in a continuous aqueous phase, said solvent being heavier than and insoluble in water and said emulsion being stabilized to break at substantially the temperature at which said wax deposits exist in said tubing by the use in said emulsion of an oil-soluble sulfonated organic body and a water-soluble gelatinous substance.

2. The method of removing wax deposits from oil-well tubing which comprises: feeding into the upper end of said tubing an emulsion of a solvent for said deposit in a continuous aqueous phase, said solvent being heavier than and insoluble in water and said emulsion being stabilized to break at substantially the temperature at which said wax deposits exist in said tubing by the use in said emulsion of oil-soluble petroleum sulfonates and agar-agar.

3. The method of removing wax deposits from oil-well tubing which comprises: feeding into the upper end of said tubing an emulsion of a solvent for said deposit in a continuous aqueous phase, said solvent being heavier than and insoluble in water and said emulsion being stabilized to break at substantially the temperature at which said wax deposits exist in said tubing by the use in said emulsion of an oil-soluble sulfonated organic body selected from the group consisting of petroleum sulfonates, sulfonated castor oil, and sulfonated, soap-forming fatty acids, and a water-soluble gelatinous substance selected from the group consisting of agar-agar, starch, glue, gelatine and gum arabic.

4. An agent for removing wax deposits from oil-well tubing comprising an emulsion of a water-insoluble, heavier-than-water solvent for said deposits admixed with a minute proportion of an oil-soluble sulfonated organic body, in a continuous aqueous phase containing a minute proportion of a water-soluble gelatinous substance, said aqueous phase constituting about one-tenth of the volume of said emulsion and being the continuous phase thereof.

ABRAHAM SHAPIRO.