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PROCESS FOR CONTROLLING WAX DEPOSITION

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This invention relates to the production and transportation of crude petroleum containing waxy constituent. More particularly, it is directed to controlling the deposition of wax in conduits, such as well tubing or flow lines, through which the crude petroleum passes during the course of its production and transportation.

In the production of crude petroleum a problem not uncommonly encountered is the deposition and accumulation of wax in the well tubing. Crude oils having relatively low wax content do not present such problem, but those in which the content of waxy constituents exceeds a certain amount generally do tend to deposit wax during the course of their production. As the crude oil flows from the producing formation to the surface, a decrease in temperature occurs whereby waxy constituents may be caused to precipitate from the oil and to accumulate on the surface of the tubing and also on the sucker rods in pumping wells. When this occurs, accumulation of wax in the tubing progressively decreases the rate of oil production and thus requires that the tubing be cleaned periodically. The frequency with which the cleaning has to be done varies considerably depending upon the character of the crude oil and the prevailing well conditions. Usual times of pumping or flowing such wells before cleaning becomes necessary range from a few days to several months.

There are certain types of wells where the conditions are such that wax deposition does not occur while the crude petroleum is in the well tubing, although it does occur later. These are generally high pressure gas distillate wells. Upon removal from the well, the hydrocarbons are allowed to expand by reducing the pressure in order to cause cooling which will aid in effecting hydrocarbon condensation. The expanded hydrocarbons are then introduced to a separator to separate the liquid and gas phases from each other. In cases of this kind, it is not unusual for wax deposition to occur in the separator and flow lines so that cleaning of such equipment is eventually required.

The cleaning of wax deposits from wells, flow lines, separators and the like entails considerable expense which raises the overall cost of operating the wells to maintain the desired rate of production. Known methods of cleaning include the use of mechanical scrapers, the employment of solvents adapted to dissolve the wax and/or the use of heat. The most usual practice with pumping wells involves pulling the sucker rods from the well and scraping them each time that removal of the accumulated wax is required, which procedure necessitates the expenditure of considerable labor. In cases where the well is one which is incapable, even before substantial accumulation of wax has occurred, of producing at a rate in excess of its monthly allowable production rate, the decreased production resulting from the progressive deposition of wax and from the necessity of shutting down to clean out the deposits may represent a considerable loss to the producer.

The present invention provides a method for con-

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trolling the deposition of wax in well tubing, as well as in flow lines and other equipment, whereby its accumulation is prevented or the rate of accumulation is substantially retarded. According to the invention, control of the wax depositions is effected by introducing into the crude oil within the system a small inhibiting proportion of an inhibitor the essential active ingredient of which is a certain type of derivative of a hexitan. More specifically, the material used as inhibitor against wax deposition according to the invention is a polyoxyethylene ether of a hexitan partial ester of a high molecular weight organic carboxylic acid. It has now been found that compounds of this class, when introduced periodically or continuously into the flow system, are particularly effective in inhibiting deposition of the wax and preventing or retarding its accumulation upon the surfaces of the well tubing, flow lines, separators and the like.

Compounds of the foregoing class are available commercially and have had wide use for various other purposes in industry. They are prepared by converting a hexitol, such as sorbitol or mannitol, into its cyclic ether form by removal of water from the molecule and partially esterifying the ether with a high molecular weight organic carboxylic acid, and thereafter reacting the product with ethylene oxide to produce the polyoxyethylene derivative. The ether formed from the hexitol is predominantly the mono-ether (hexitan) although it generally contains a minor proportion of the di-ether (hexide); hence the esterified product includes derivatives of each of these ether forms. Sorbitol and mannitol are preferred starting materials for preparing the wax inhibitor compounds of the invention, but any of the other hexitols, including dulcitol, iditol, talitol and allodulcitol, may be used if desired.

The organic carboxylic acid used for esterifying the hexitan should contain 12–22 carbon atoms per molecule and can be a fatty acid, naphthenic acid, resin acid or mixtures thereof. The carboxylic acid may be used in an amount such as to produce either a mono-ester, a di-ester or a tri-ester, since the polyoxyethylene derivatives of all of these types of ester compounds are useful in practicing the invention. Specific examples of organic acids which can be employed are lauric, myristic, palmitoleic, palmitic, stearic, oleic, ricinoleic, linoleic, linolenic, arachidic, erucic, resin acids, hydrogenated resin acids, dehydrogenated resin acids, petroleum naphthenic acids and the like.

The amount of ethylene oxide reacted with the partial esters to produce compounds for use in accordance with the invention should be such that the number of oxyethylene groups is in the range of 4–30 per acid radical. Thus, the total number of oxyethylene groups is from 4 to 30 for the mono-esters, from 8 to 60 for the di-esters and from 12 to 90 for the tri-esters. More preferably, the total number of oxyethylene groups per molecule for each of the three types of esters should be from 15 to 25.

The following are specific examples of compounds for use in practicing the invention: 15 polyoxyethylene sorbitan monolaurate, 20 polyoxyethylene sorbitan monopalmitate, 20 polyoxyethylene sorbitan monostearate, 30 polyoxyethylene sorbitan monooleate, 25 polyoxyethylene sorbitan monoabietate, 20 polyoxyethylene sorbitan mononaphthenate, di-esters and tri-esters corresponding to the foregoing compounds, 20 polyoxyethylene sorbitan tri-tall oil esters, mannitol derivatives corresponding to the foregoing, etc. In the names of the compounds set forth above, the numeral designates the average number of ethylene oxide groups per molecule of ester. The compounds above named, as well as any other such compounds of the class as specified herein, are effective to prevent or retard the deposition of wax from crude oils

upon the surfaces of well tubing, flow lines or other equipment through which the oil is transported.

Compounds of the class defined above tend to be too viscous for convenient use in the field, and some of them are solid materials. It is usually desirable to admix them with a suitable diluent such as kerosene, alcohol, toluene or the like to facilitate handling. Suitable mixtures for use at the well site can be made by mixing approximately equal parts of the active inhibitor compound and the organic diluent.

In practicing the invention the wax inhibitor compound may be introduced either periodically or continuously in small amount into the crude petroleum at the base of the well. As a matter of convenience, this may be done simply by dumping a suitable amount of the material once a day into the annulus between the casing and tubing. The material so introduced will migrate to the bottom of the well and find its way into the well tubing along with crude oil from the formation. When treatment of a well is first begun, it is desirable to introduce from one to five gallons of the specified active compound, admixed with an equal volume of diluent, into the annulus and circulate the fluids through the tubing and back to the annulus for several hours, e. g. 4-12 hours, before the well is allowed to produce. This procedure may be repeated for two or three days. Thereafter, the inhibitor compound may be added once a day to the annulus in relatively small amount. The most economic dosage will vary somewhat from well to well but generally will be in the neighborhood of one pint of the active ingredient (excluding diluent) for each 15-50 bbls. of oil. The effectiveness in retarding deposition of wax tends to improve as the amount of the inhibitor added to the well is increased. Selection of the proper dosage for any particular well can be made by comparison of the costs of operating with and without the inhibitor being added.

It is presently uncertain why the use of compounds in accordance with the invention effectively inhibits the deposition of wax upon the surfaces of the well tubing, flow lines or other equipment in the flow system. However, it is thought that the inhibitor compound forms a thin film on the surface of the tubing and thereby reduces the tendency of the wax to adhere to the metal. In some cases practice of the invention prevents any substantial accumulation of wax in the tubing throughout a long period of operation. In other cases the deposition is not entirely prevented although it is substantially retarded. Furthermore, when deposition does occur while employing an inhibitor compound as above specified, the deposited wax tends to be relatively soft as compared to ordinary rod wax and is considerably easier to scrape from the tubing and sucker rods; hence the time and labor required for the scraping job are substantially reduced.

An illustration of the invention as applied in actual field practice involves a pumping well which was producing crude oil having an A. P. I. gravity of 40, a gasoline content (410° F. end point) of 36% by volume and a wax content of 4% by weight. The maximum oil production rate that could be obtained for this well was 35 bbls. per day, and the well produced only traces of water along with the oil. Prior to application of the invention to this well, its sucker rods had to be pulled and scraped at 45 day intervals in order to maintain production. This cleaning operation usually yielded about 135 gallons of hard rod wax each time the sucker rods were scraped.

The foregoing well was then subjected to treatment according to the invention by introducing daily into the annulus about one quart of a mixture containing 40-50% of inhibitor compound in admixture with diluent. The inhibitor compound employed was 20 polyoxyethylene sorbitan tri-tall oil ester and it was used in admixture with kerosene during a portion of the trial period and with isopropanol during another portion. After a trial period of about 166 days, the sucker rods were pulled and

scraped. In this case only about 25 gallons of wax were obtained; with the wax being relatively soft in contrast to the hard product theretofore deposited on the rods.

During another trial period lasting for about 125 days, this same well was treated with 20 polyoxyethylene sorbitan trioleate in admixture with kerosene in equal volumes. For the first two days, about 2 gallons/day of this mixture was introduced into the annulus and circulated through the tubing for a while. Thereafter one quart/day of the mixture was dumped into the annulus through a lubricator, and treatment in this fashion throughout the test period was continued except for a time of 15 days during which no treatment was done. At the end of the 125 day period, the sucker rods were pulled from the well and scraped. This again yielded only about 25 gallons of relatively soft wax.

Another pumping well located in the same field as the foregoing well had a normal production rate, prior to deposition of wax within the tubing, of 76 bbls./day of oil and 14 bbls./day of water, and it was necessary to clean the well at 30 day intervals in order to maintain the desired production. Normally about 225 gallons of hard rod wax was obtained during each cleaning. Treatment of this well was then begun, utilizing a 50:50 mixture of kerosene and 20 polyoxyethylene sorbitan tri-tall oil ester. During the first three days 2 gallons/day of the mixture was introduced into the annulus and circulated through the tubing for a time; and thereafter the inhibitor mixture was dumped into the annulus in amount of 3 quarts/day. After 43 days of operation, the rods were pulled for inspection and about 25 gallons of wax were removed by scraping. The well was then placed back in operation and the 3 quarts/day treatment was continued. After a period of 47 days more, the rods were again inspected and were found to have accumulated only about 15 gallons of wax. In each of the foregoing inspections, the wax recovered was soft and could readily be scraped from the sucker rods.

The examples described above illustrate the invention as applied to the inhibition of wax deposition within the well tubing. In cases where the wax does not deposit in the well tubing due to the prevailing well conditions but does subsequently deposit in flow lines, separators or other equipment, the inhibitor does not need to be added to the well itself as described above, but instead may be introduced into the crude oil at a suitable point beyond the well head. In any event it should be noted that the inhibitor material should be applied, whether it be within the well or in flow lines or other equipment, prior to any substantial accumulation of wax therein. In other words the polyoxyethylene hexitan partial esters employed according to the present invention do not function as solvents for wax already accumulated on surfaces and are ineffective in removing wax previously deposited. Hence the treatment carried out with these materials should be preceded by a cleaning of the system to remove any wax already accumulated. This permits the inhibitor to come in contact with the metal surfaces and evidently form thereon a film which prevents hard wax from clinging to the metal.

We claim:

1. Process for inhibiting the accumulation of wax from crude petroleum upon surfaces of a system through which the crude petroleum is transported which comprises introducing into the system, in the presence of the crude petroleum and prior to the accumulation of substantial amounts of wax therein, an inhibiting amount of an inhibitor the essential active ingredient of which is a polyoxyethylene ether of a hexitan partial ester of an organic carboxylic acid having 12-22 carbon atoms and selected from the group consisting of fatty, naphthenic and resin acids, said ether containing 4-30 oxyethylene groups per acid radical.

2. Process according to claim 1 wherein said poly-

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oxyethylene ether contains 15-25 oxyethylene groups per molecule.

3. Process according to claim 2 wherein said polyoxyethylene ether is an ether of a sorbitan tri-ester.

4. Process according to claim 1 wherein said polyoxyethylene ether is an ether of sorbitan tri-tall oil ester and contains 15-25 oxyethylene groups per molecule.

5. Process according to claim 1 wherein said polyoxyethylene ether is an ether of sorbitan tri-fatty acid ester and contains 15-25 oxyethylene groups per molecule.

6. Process for inhibiting the accumulation of wax from crude petroleum in the tubing of a producing well which comprises introducing into the well periodically at least once a day an inhibiting amount of a polyoxyethylene ether of a hexitan partial ester of an organic carboxylic acid having 12-22 carbon atoms and selected from the group consisting of fatty, naphthenic and resin acids, said ether containing 4-30 oxyethylene groups per acid radical.

7. Process according to claim 6 wherein the amount of the polyoxyethylene ether introduced is about one pint for each 15-50 bbls. of oil produced from the well.

8. Process according to claim 7 wherein said polyoxyethylene ether is an ether of a sorbitan ester containing 15-25 oxyethylene groups per molecule.

9. Process according to claim 8 wherein said sorbitan ester is a tri-ester.

10. Process for inhibiting the accumulation of wax from crude petroleum in the tubing of a producing well which comprises continuously introducing into the well an inhibiting amount of a polyoxyethylene ether of a hexitan partial ester of an organic carboxylic acid having 12-22 carbon atoms and selected from the group consisting of fatty, naphthenic and resin acids, said ether containing 4-30 oxyethylene groups per acid radical.

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11. Process according to claim 10 wherein the amount of the polyoxyethylene ether introduced is about one pint for each 15-50 bbls. of oil produced from the well.

12. Process according to claim 11 wherein said polyoxyethylene ether is an ether of a sorbitan ester containing 15-25 oxyethylene groups per molecule.

13. Process according to claim 12 wherein said sorbitan ester is a tri-ester.

14. In the transportation of crude petroleum from a well through a flow system wherein wax in the petroleum normally tends to accumulate upon the surfaces of equipment, the method of retarding such accumulation which comprises introducing into the petroleum, prior to substantial accumulation of wax upon such surfaces, an inhibiting amount of a polyoxyethylene ether of a hexitan partial ester of an organic carboxylic acid having 12-22 carbon atoms and selected from the group consisting of fatty, naphthenic and resin acids, said ether containing 4-30 oxyethylene groups per acid radical.

15. Method according to claim 14 wherein said polyoxyethylene ether is an ether of a sorbitan tri-ester containing 15-25 oxyethylene groups per molecule.

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