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CONTROL OF WAX DEPOSITION

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This invention relates to a method of preventing or controlling the deposition of wax in the flow tubings of producing wells and in pipe lines and the like, through which a crude petroleum oil having a tendency to deposit wax is flowing.

In the producing and transporting of oil in many fields the accumulation of wax deposits in the flow tubings of the wells and in lead lines and pipe lines represents a major problem. The problem has been attacked in various ways as, for example, with the use of mechanical scrapers, heating devices and wax solvents. Although these methods serve to keep the wax accumulation under control, they are expensive to employ since they often require shutting off the flow of oil, and they can be practiced only with the expenditure of considerable labor. It has been proposed to inject wax solvents into oil flowing in well tubings or lines prior to the accumulation of wax, but so far as known, this proposal has not been practiced to any extent, apparently because solvents do not exert a favorable effect unless so great a quantity is used as to make the operation uneconomical.

It is, therefore, a principal object of the invention to provide a method of preventing or substantially reducing the accumulation of wax in flow tubing, lead lines, pipe lines and the like, in which a petroleum oil having a tendency to deposit wax is flowing.

Other objects of the invention in part will be obvious and in part will appear hereinafter.

In accordance with the invention the deposition of wax is controlled by injecting a small amount of a wax crystal modifier into the crude oil, this injection preferably taking place before any wax is deposited in the conduit in which it is desired to prevent or reduce wax deposition. Thus, to control the deposition of wax in the flow tubing of a producing well, a wax crystal modifier may be injected continuously into the oil flowing in the tubing below the point where wax has a tendency to separate from the oil. The introduction of the modifier may be made at the bottom of the well. By introducing a modifier into the bottom of the well (i. e. into the oil pool reservoir) wax deposition in pay sands, which occurs in some wells, may be controlled or prevented. The point where wax has a tendency to separate from the oil is different in each well or at least in each field. For example, in a survey of a number of fields this point varied from 300 feet to 1200 feet from the surface.

By introducing a wax crystal modifier into a flowing petroleum oil of the type specified, it ap-

pears deposition of wax is prevented or reduced because precipitation of the wax in the usual physical state is avoided. It appears that the physical state in which the wax is precipitated has an important bearing on whether the wax will form objectionable deposits on the walls of conduits or will remain in the flowing oil. Wax crystal modifiers are effective to inhibit or prevent the formation of large, voluminous, interlaced crystals which adhere to the walls of conduits and form clogging deposits, and to induce the formation of smaller crystals.

Wax crystal modifiers, or pour point depressants as they may be termed depending upon the use to which they are put, comprise a well-known class of compounds which have been employed in the treatment of lubricating oils to remove wax therefrom or to change the characteristics of the wax contained therein. Although they may be of variable chemical constitution, wax crystal modifiers as a class are high molecular weight compounds and compositions. Thus a typical wax crystal modifier is a viscous liquid or semi-solid at ordinary temperatures.

In carrying out the present method the wax crystal modifier is preferably continuously injected into the oil flowing in the conduit, such as the flow tubing of the well, in very small quantities in relation to the amount of oil treated. The modifiers are usually heavy materials and it is preferred to employ them in the form of a solution. The solvent used is preferably also a solvent for the wax. In the usual case the modifier will be introduced in solution in a light petroleum distillate such as a naphtha or kerosene fraction of petroleum, although other wax solvents may be used. As brought out in the following description, certain of the wax crystal modifiers are obtained in solution in light distillates, and these may be used with or without further addition of distillate.

As examples of wax crystal modifiers which may be employed in accordance with the present invention the following are mentioned. One class of wax crystal modifiers is composed of relatively high molecular weight hydrocarbon materials which are sometimes considered as waste materials. These materials, however, contain a sufficient amount of constituents with modifying characteristics to adapt them for use in the present method. Thus, this class includes cracked petroleum tar, sometimes referred to as "pressure-tar" resulting from the liquid or vapor phase cracking of mineral oil for the production of motor fuels; extract materials separated from

petroleum fractions, particularly lubricating oil fractions, during the refining of such fractions with solvents such as furfural, liquid sulfur dioxide and the like; and the polymerized material removed from cracked naphtha by treating the naphtha with a catalytic adsorbent clay. As a specific example of such materials, there may be mentioned the Edeleanu extract from lubricating oil fractions. Polymerized products obtained as a result of treating cracked naphtha in the vapor phase with a catalytic adsorbent clay, such as an acid treated bentonite or fuller's earth, are of special interest. The treatment resulting in the formation of these materials may be carried out at a temperature of around 400° F. and at a pressure slightly above atmospheric. The liquid material formed in this treatment, which will contain polymers of diolefins and other olefinic compounds in the naphtha, is separated from the naphtha vapors and constitutes a material which may be employed in accordance with the present invention. In one case a product of this class had the following tests:

Color-----	Very dark brown
Gravity, °A. P. I.-----	44.2
Distillation, °F.:	
I. B. P.-----	171
5%-----	234
10%-----	263
20%-----	291
30%-----	309
40%-----	321
50%-----	333
60%-----	343
70%-----	353
80%-----	365
90%-----	386
95%-----	440
E. P.-----	566
Recovery %-----	98.0

This material contains a substantial proportion of relatively low boiling hydrocarbons as well as heavier polymerized compounds and may be regarded as a combination of a wax solvent and a wax crystal modifier. This material may be used as such or may be diluted with a petroleum fraction such as a naphtha or kerosene fraction.

The so-called waste materials described above and similar materials may be subjected to pyrogenic reactions to increase their content of constituents having wax crystal modifying characteristics. The pyrogenic treatment may take the form of heating at a temperature and under conditions such as to effect additional condensation or polymerization, but to avoid cracking. However, to obtain especially important modifiers for use in the present process the waste materials may be subjected to destructive heating or cracking as described in United States Patent 2,040,057 to produce a pitch containing constituents which possess wax crystal modifying properties. As disclosed in that patent, the waste material may be subjected to cracking at a temperature of about 850° to around 1000° F. and under pressures which may range from substantially above atmospheric to 400 pounds per square inch or higher. The residue remaining after this treatment, which is in the nature of a pitch, will contain the modifying constituents. In using this pitch, it is preferably extracted with a hydrocarbon solvent such as naphtha or kerosene to dissolve out the soluble constituents, and the

resulting solution is employed for injection into a flowing crude oil.

Other examples of suitable wax crystal modifiers are various condensation products produced by condensing chlorinated heavy hydrocarbons such as chlorinated wax or petrolatum with an aromatic compound such as naphthalene or anthracene. Condensation products of this type are disclosed in United States Patent 1,815,022. Other examples are resins resulting from the desasphalting of residual oil stocks at elevated temperatures with liquefied normally gaseous petroleum hydrocarbons such as propane; lanolin; and esters of higher fatty acids such as butyl stearate. The hydrocarbon materials disclosed above are characterized in that they comprise high molecular weight compounds which contain aromatic nuclei and/or polymerization products. The pyrogenic derivatives are considered to comprise more highly condensed and/or polymerized compounds of the same class.

These materials, as well as other wax crystal modifiers disclosed above, are not wax solvents; that is, wax of the type precipitated in wells and ground lines is substantially insoluble in these materials at ordinary temperatures. As illustrating the fact that these materials are not wax solvents and do not function as such in their normal industrial use, it is pointed out that an accepted theory with respect to the action of these materials in treating lubricating oils is that they are present in such oils as colloids, although they may be added in solution in a solvent, and that it is because of their colloidal nature that they function to vary the characteristics of waxes precipitated from lubricating oils. Whether these materials function in this way in the present process is not established but since they are not wax solvents it is clear this action does not play a part.

In the use of the foregoing materials and similar materials in accordance with the invention, it will be understood that the amount to be employed will vary depending upon the quantity of modifying constituents present in the complex material customarily employed, the wax deposition characteristics of the crude oil, and other factors. It may be stated, however, that the desired results may be obtained with the use of an amount of active constituent corresponding to the order of one part by weight of constituent to several thousand parts by weight of the crude oil.

When practicing the invention in controlling wax deposition in conduits disposed above ground, the injection of the wax crystal modifier is preferably accomplished before the deposition of wax has begun (i. e. when the oil is flowing through clean pipes) and should be continued so long as likelihood of wax deposition exists. In this connection it is pointed out that the deposition of wax in lead lines and pipe lines above ground often varies with atmospheric conditions. Thus, in some cases the injection of a modifier may be necessary only during cold weather.

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

I claim:

1. The method of controlling the deposition of wax in a conduit in which a crude petroleum oil having a tendency to deposit wax is flowing,

which comprises continuously injecting a small amount of a wax crystal modifier into the oil, said wax crystal modifier being a high molecular weight composition in which wax deposited from said crude petroleum oil is substantially insoluble.

2. The method of controlling the deposition of wax in a conduit which is substantially free from deposited wax and in which a crude petroleum oil having a tendency to deposit wax is flowing, which comprises continuously introducing a small amount of a wax crystal modifier into said crude petroleum oil, said wax crystal modifier being a viscous high molecular weight composition in which wax deposited from said crude petroleum oil is substantially insoluble.

3. The method in accordance with claim 2 in which the wax crystal modifier is introduced into the crude petroleum oil in solution in a wax solvent.

4. The method in accordance with claim 2 in which the wax crystal modifier is introduced into the crude petroleum oil in solution in a wax solvent, said wax solvent being a petroleum distillate.

5. The method of controlling the deposition of wax in a conduit in which a crude petroleum oil having a tendency to deposit wax is flowing, which comprises continuously introducing into said flowing oil a small amount of a solution of a wax crystal modifier in a petroleum distillate, said wax crystal modifier being a viscous high molecular weight hydrocarbon composition comprising compounds selected from the group consisting of hydrocarbon polymers and condensation products of high molecular weight aliphatic compounds with aromatic compounds, the wax deposited from said crude petroleum oil being substantially insoluble in said wax crystal modifier.

6. The method of controlling the deposition of wax in the flow tubing of a producing well in

which a crude petroleum oil is flowing, which crude petroleum oil has a tendency to deposit wax during its flow through the tubing to the surface, which comprises continuously introducing a small amount of a wax crystal modifier into the crude petroleum oil at a point in the flow tubing below that at which deposition of wax normally occurs, said wax crystal modifier being a viscous high molecular weight hydrocarbon composition in which wax deposited from said crude petroleum oil is substantially insoluble.

7. The method of controlling the deposition of wax in the flow tubing of a producing well in which a crude petroleum oil is flowing, which crude petroleum oil has a tendency to deposit wax during its flow through the tubing to the surface, which comprises continuously introducing a small amount of a wax crystal modifier in solution in a wax solvent into the crude petroleum oil at a point in the flow tubing below that at which deposition of wax normally occurs, said wax crystal modifier being a viscous high molecular weight hydrocarbon composition comprising compounds selected from the group consisting of hydrocarbon polymers and condensation products of high molecular weight aliphatic compounds with aromatic compounds, the wax deposited from said crude petroleum oil being substantially insoluble in said wax crystal modifier.

8. The method of controlling the deposition of wax in a well producing a crude petroleum oil having a tendency to deposit wax, which comprises continuously introducing into the crude petroleum oil at the bottom of the well a small amount of a wax crystal modifier, said wax crystal modifier being a viscous high molecular weight composition in which the wax deposited from said crude petroleum oil is substantially insoluble.

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