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METHOD OF WAX REMOVAL

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This invention relates to a method of treating solid waxy or paraffinaceous hydrocarbons. More particularly, this invention relates to a method of treating solid waxy materials to alter their physical properties and/or appearance. Still more particularly, this invention relates to a method for removing surface-deposited solid waxy materials.

In accordance with one embodiment the practice of this invention is particularly suitable for the removal of tenacious, solid waxy materials and the like from subsurface well equipment, such as pump rods, well casing and tubing and the like. The practice of this invention is also applicable for the removal of surface-deposited solid waxy materials from pipe lines, lead lines, tanks and the like employed in or associated with oil wells and/or pipe line gathering and transmission systems.

In many oil wells and crude oil producing and gathering lines wax or paraffin accumulation is a serious problem. In those wells wherein paraffin deposition is a problem well equipment is regularly treated to remove waxy deposits therefrom. These treatments sometimes involve the circulation of hot paraffin solvents in contact with the well equipment fouled by the waxy paraffins in order to dissolve and/or melt away the waxy materials in contact therewith, or involve the use of mechanical equipment, such as scrapers or plugs which abrade or wear away the interfering, troublesome paraffin or waxy deposits.

It is an object of this invention to provide an improved method for the removal of waxy deposits from oil well equipment and the like.

Still another object of this invention is to provide a method for reconstituting or otherwise altering the physical properties of waxy materials, such as are deposited on oil well equipment and petroleum pipe lines and the like during the transportation of waxy hydrocarbon fluids therethrough or in contact therewith.

Still another object of this invention is to provide a method for changing solid, tenacious, somewhat sticky, waxy hydrocarbons into finely-crystallized, less tenacious or less sticky waxy hydrocarbons.

How these and other objects of this invention are achieved will become apparent in the light of the accompanying disclosure.

In accordance with this invention solid waxy material is subjected to contact with a gasiform material, such as a gaseous wax solvent or hydrocarbon, which permeates, dissolves or otherwise admixes with said waxy material at an elevated pressure, for example, at a pressure of at least about 1000 p.s.i.g., such as an elevated pressure in the range 1500–5000 p.s.i.g. After a period of time sufficient for the gasiform material to permeate or otherwise enter into or dissolve in the solid waxy material, the pressure exerted by the gasiform material or gaseous hydrocarbon is rapidly reduced. As a result of the above-indicated foregoing treatment the solid waxy material is substantially altered, particularly in physical appearance. For example, when a normally gaseous ali-

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phatic hydrocarbon, e.g., methane, ethane, propane and the like, is subjected to an elevated pressure and maintained in the gaseous form in the presence of solid waxy materials, the gaseous hydrocarbon, which under an elevated pressure acts as a wax solvent, permeates or dissolves into the solid waxy material. When the pressure exerted by the gaseous hydrocarbon on the solid waxy material is suddenly released or otherwise rapidly reduced the solubility of the waxy materials in the pressurized gaseous hydrocarbon, which has permeated or dissolved into the solid waxy materials, in effect, dissolving the solid waxy materials, is suddenly reduced thereby, in effect, causing a sudden reprecipitation of the waxy materials. Due to the sudden reprecipitation the solid waxy materials are formed into finely divided crystals. These fine crystals tend to be carried away or be flushed out of the waxy materials by the gaseous hydrocarbon when the ambient pressure is suddenly reduced. The resulting fine crystalline wax makes up a substantial portion of the residual wax which is granular and amorphous in appearance. Further, it has been observed that wax so treated is no longer sticky or tenacious when applied to a ferruginous surface and the like.

Any gaseous wax solvent or gaseous hydrocarbon may be employed in the practice of this invention. Generally it is desirable to employ a normally gaseous hydrocarbon, such as methane, ethane, propane and the like, or even ethylene, propylene or acetylene, or mixtures thereof or mixtures containing these normally gaseous hydrocarbons. In the practice of this invention it is desirable that the pressurized gaseous hydrocarbon and/or wax solvent be maintained at a temperature above its critical temperature. Accordingly, it is possible to employ in the practice of this invention normally liquid aliphatic hydrocarbons, such as pentanes, hexanes and the like, provided the pressurizing operation is carried out at an elevated temperature above the critical temperature of the thus-pressurized hydrocarbon. As previously indicated, the pressurized gasiform wax solvent or gaseous hydrocarbon employed in the practice of this invention may comprise an admixture of normally gaseous hydrocarbons, such as natural gas, methane-propane admixture, methane-butane admixture, methane-isobutane admixture, or an admixture of a normally gaseous aliphatic hydrocarbon and a normally liquid aliphatic or aromatic hydrocarbon or normally liquid halogenated hydrocarbons (e.g., halogenated aliphatic hydrocarbons) such as methane-benzene admixture, methane-toluene admixture, methane-xylene admixture, methane-carbon tetrachloride admixture and the like. Desirably an admixture comprising a major amount of methane or ethane and a minor amount of a material, such as propane, benzene, carbon tetrachloride and the like, are employed in the practice of this invention.

In accordance with one feature of this invention due to the very high pressure required in the practice thereof, retrograde vaporization of the normally solid waxy materials into the high pressure phase takes place. This retrograde vaporization of the normally solid waxy hydrocarbons into the pressurizing gas phase tends to help in the removal of the waxy solids.

As indicated hereinabove, in the practice of this invention wherein a solid waxy hydrocarbon is in contact with a high pressure gaseous hydrocarbon or wax solvent, such as methane or natural gas or a mixture of methane and propane or carbon tetrachloride, and the pressure suddenly released, evolution of the gaseous hydrocarbon or gasiform materials from the solid waxy material which it has penetrated takes place. This evolution of the gaseous hydrocarbon causes reprecipitation of any solid

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waxy material which was solubilized by the gasiform material which penetrated the solid waxy material. Also, the evolution of the gaseous material from the solid waxy material which it had penetrated tends to flush out or otherwise mechanically remove or displace the resulting recrystallized waxy hydrocarbons. Further, it has been observed that a mechanical disruption of the waxy materials also takes place when the ambient pressure is suddenly released to cause rapid evolution of the gaseous material from the wax, thereby in effect causing the wax to explode.

The practice of this invention is more fully set forth in the accompanying examples wherein experiments were carried out employing a glass-windowed, high pressure test cell. The wax samples were placed in glass test tubes and the tubes, containing the wax samples placed inside the pressure cell opposite a glass window. This arrangement permitted visual observation of the waxy solid materials during the test. Each of the tests were carried out at a temperature of about 75° F.

Example I

A sample of Texwax, a refined, substantially oil-free petroleum wax manufactured and sold by The Texas Company, was placed in a test cell and subjected to contact with natural gas at a pressure of about 5000 p.s.i.g. After a period of time the pressure within the test cell was rapidly released. It was observed that the wax sample being tested disintegrated upon sudden pressure reduction and changed from a glossy, crystalline-appearing waxy material to a granular, amorphous waxy mass.

Example II

A sample of Texwax, see Example I, was subjected to contact with a gaseous admixture comprising 86% vol. methane and 14% vol. propane, at a pressure of 5000 p.s.i.g. After a period of time the pressure exerted by the gaseous hydrocarbon mixture on the wax sample was reduced as rapidly as possible. When the pressure was reduced on the wax sample, the sample disintegrated to an even higher degree than that observed in the test described in Example I.

Example III

Three different waxes were employed in the following tests, viz., rod and tubing waxes and a refined wax fraction from a Dayton crude, the refined wax fraction being a high melting, extremely hard wax. In these tests, propane vapor under its own vapor pressure (approximately 130 p.s.i.g.) at room temperature was introduced into the test cell containing the wax sample. The test cell was connected to an auxiliary test cell which was also filled with propane vapor. With the two test cells thus connected, mercury was introduced into the auxiliary cell. As mercury was introduced into the auxiliary cell, gaseous propane condensed in each cell. The resulting condensed propane had a solubilizing effect upon each of the wax samples tested. Natural gas was then introduced into the test cell and the pressure raised to about 5000 p.s.i.g. As the pressure increased the waxy solids appeared to dissolve in the pressurized gas. The gas pressure within the test cell was then rapidly reduced and gas was observed to be evolved violently from the waxy admixture in the test cell. When each of the test wax samples was removed from the cell it was found that the wax samples had completely disintegrated.

Example IV

Samples of waxy solids, the same as employed in Example III, were contacted with an admixture of natural gas (primarily methane) and carbon tetrachloride. The gaseous admixture comprising 95% vol. natural gas and 5% vol. carbon tetrachloride was compressed to about 5000 p.s.i.g. in an auxiliary test cell. The resulting pres-

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surized gaseous admixture existed as a single gaseous phase. The single gaseous phase was then bled into the glass windowed test cell containing the waxy solids to be tested. Pressure drop during transfer of the gaseous admixture to the test cell caused condensation inside the cell and an accumulation of liquid carbon tetrachloride in the test cell. The test cell pressure was then increased by displacing additional gaseous admixture from the auxiliary cell to the glass windowed test cell. At about 3000 p.s.i.g. the liquid in the test tube in the test cell started to vaporize (retrograde vaporization) and at 4000 p.s.i.g. apparently all of the liquid in the test tube had evaporated. The pressure in the test cell was then increased to 5000 p.s.i.g. and thereafter released as rapidly as possible.

Retrograde condensation of carbon tetrachloride occurred during each of the tests. When the test wax samples were removed from the test cell, the rod and tubing waxes were substantially completely dissolved in the carbon tetrachloride. Any remaining solid wax was not sticky but appeared mobile with the mixture. The refined wax from the Dayton crude was about 50% disintegrated.

It was observed prior to the test that the tubing wax had been found to be very slowly soluble in carbon tetrachloride and that during stirring to effect dissolution within carbon tetrachloride the wax tended to stick to the surface of the beaker and stirring rod. It would appear, therefore, in view of the foregoing tests that when carbon tetrachloride is employed in a high pressure gaseous phase to effect dissolution of the waxy materials tested, the gaseous carbon tetrachloride phase permeates the waxy solids more readily than liquid carbon tetrachloride.

The foregoing experiments indicated the suitability of the practice of this invention for cleaning oil well flow strings, pump rods and other oil well and pipe line equipment with gaseous high pressure solvents or a combination of solvents in admixture with high pressure natural gas and the like. One obvious advantage of the practice of this invention would be the elimination of the necessity for pulling rods and/or tubing for periodic mechanical cleaning to remove the wax therefrom.

As will be apparent to those skilled in the art, many modifications, changes and alterations are possible without departing from the spirit or scope of this invention.

We claim:

1. A method which comprises subjecting solid waxy hydrocarbons to contact with a normally gaseous hydrocarbon at a temperature above the critical temperature of said normally gaseous hydrocarbon so that said normally gaseous hydrocarbon remains in the gaseous state, and at an elevated pressure of at least about 1000 p.s.i.g., maintaining said waxy hydrocarbons in contact with the thus-pressurized normally gaseous hydrocarbon for a period of time sufficient to permit said normally gaseous hydrocarbon to permeate said waxy hydrocarbons a substantial extent and to permit at least a portion of said waxy materials to undergo retrograde vaporization into the thus-pressurized normally gaseous hydrocarbon and subsequently rapidly reducing the pressure exerted by said normally gaseous hydrocarbon upon said waxy hydrocarbons.

2. A method in accordance with claim 1 wherein said gaseous hydrocarbon is methane.

3. A method in accordance with claim 1 wherein said gaseous hydrocarbon is ethane.

4. A method in accordance with claim 1 wherein said gaseous hydrocarbon is propane.

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