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RECOVERY OF HYDROCARBONS FROM SUBSURFACE RESERVOIRS

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The present invention relates to the recovery of oil from a porous subsurface oil bearing formation by cycling an injected high pressure gas through the formation toward a production well to institute and effect production of the formation oil at the production well bore.

The present invention is, therefore, particularly applicable to the recovery of oil from underground reservoirs after primary production methods have been exhausted, when the formation oil is usually in a discontinuous phase and can no longer be caused to flow by water flooding, ordinary gas pressuring, and the like. Its application is especially contemplated in the case of relatively high pressure gas cycling at pressures upwardly of 3,000 p. s. i. This process typically results in materially increasing the volume of subsurface oil by gas solution effect to create a continuous and therefore flowable oil phase. It also results in enrichment of the injected gas phase by formation oil yielding at the production well bore a readily flowable mixture containing formation oil. Irrespective of the exact mechanism involved, it is found that at the high pressures involved the components of the formation oil are delivered to the production well in the resulting readily flowable fluid.

The present invention contemplates the recovery of oil, as above, by means of high pressure gas in the form of a retrograde-enriched mixture comprising a normally gaseous hydrocarbon containing in single-phase admixture therewith a substantial proportion of normally liquid solvent for the heavy constituents of the oil, such as bitumens, asphaltenes and the like, and subject to retrograde condensation upon isothermal pressure decrease. The high pressure gas enters the formation from an injection well extending into the formation at a region spaced from the production well. Typical effective solvents for the asphaltene-bitumen fraction precipitate are, for example, carbon tetrachloride, aromatic hydrocarbons such as benzene, toluene and cumene, pyridine, carbon disulfide and many others.

The injection is continued to force the injected phase through the formation in contact with the oil contained therein and as a result substantial flow of hydrocarbon fluid, including subsurface oil from the oil bearing interstices of the formation, takes place and is instituted toward the producing well.

This procedure is of particular advantage from the standpoint of avoiding clogging or restricting of the minute interstices of the porous subsurface formation by waxy, bitumen or asphalt-like constituents of the oil which otherwise tend to be precipitated by high pressure, light hydrocarbons and particularly the normally gaseous hydrocarbons. Manifestly, the relatively immobile, solid or semi-solid precipitates tend to obstruct the tiny passageways of the internal pore space and therefore decrease permeability of the formation so that fluid flow is decreased and may cease entirely.

The plastic material precipitable by light paraffin hydrocarbons at high pressure is referred to herein as "heavy hydrocarbons" or "heavy constituents" of the for-

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mation oil, and are therefore limited, by definition, to the wax-like, asphaltic or bituminous appearing constituents referred to above irrespective of their exact chemical constitution.

Most crude oils contain these precipitable materials in a quantity sufficient to adversely affect the producing formation. Therefore, in the presence of light gaseous hydrocarbons the recovery of subsurface oil may be materially impaired by deposition of the plastic precipitate in the reservoir structure.

In accordance with the present invention, however, formation of the objectionable precipitate is inhibited by conveying the liquid solvent for the heavy precipitable constituents into contact with the subsurface oil phase as a retrograde-enriched mixture with the injected gas.

The fluid mixture injected into the formation is, in effect, a gas enriched with solvent vapor substantially in excess of the amount of such vapor which the normally saturated gas could carry. In this mixture the highly compressed gas actually dissolves a substantial amount of the solvent liquid while still retaining the desirable characteristics of the gas and is, therefore, for the purpose of the present specification and claims referred to as retrograde-enriched-gas.

Due to its gas-like properties, it accordingly flows readily under injection pressure through the interstices of the oil bearing formation. However, due to the high solvent capacity of the retrograde-enriched-gas and also the high affinity of the gasform mixture for the heavy precipitable constituents of the formation oil, there is a substantial solvent adsorption by the oil which prevents the undesired precipitation. Actually, contact of the retrograde-enriched-gas phase with the oil containing the heavy precipitable constituents alters the phase behavior of the system resulting in what is, in effect, selective absorption by the heavy hydrocarbons of the solvent from the retrograde-enriched-gas. To facilitate utilization of the effect it may be considered as analogous to "salting out" or condensation of solvent from the essentially gasform mixture wherever it comes into contact with the heavy hydrocarbons which might otherwise clog the formation. Obviously from the foregoing, constituents otherwise capable of clogging the formation are accordingly maintained in fluid solution which in a continuous phase may be caused to flush out of the formation or be absorbed by retrograde vaporization in the flow of injected gas.

From the foregoing, it will be seen that the injected retrograde-enriched-gas phase readily permeates the minutest interstices of the formation due to its relatively low viscosity as compared with a liquid solvent which manifestly could be caused to flow therethrough only with considerable difficulty and would tend to channel through the more open passages. Therefore, relatively large amounts of liquid solvent carried in solution in the retrograde-enriched-gas are brought into the formation with the ease of gas flow as contrasted with liquid flow and reach the most restricted regions to maintain the precipitable materials in liquid condition. In short, the extent of permeation of the formation by a gas is materially greater than by a liquid, other conditions being the same.

Moreover, the presence of some liquid phase solvent with the retrograde vapor is not necessarily disadvantageous since the liquid tends to enter the larger pores and thus channel the gasform phase into the more minute interstices.

An additional advantage follows from the fact that as the treating phase approaches the producing well bore, the pressure drops and tends to result in isothermal retrograde condensation of residual solvent in the retrograde-enriched-gas facilitating the maintenance of a continuous phase and effecting an additional washing, cleansing

action about the well bore where high permeability is important. In other words, any excess solvent tends to condense and desirably flush the formation at this point. As above intimated, the normally gaseous constituent of the retrograde enriched gas is preferably a hydrocarbon having a critical temperature lower than reservoir temperature, that is, a gas which under the subsurface conditions encountered will not liquefy, per se. For subsurface temperatures above 100° F., therefore, methane, ethane, and ethylene are typical examples. Of the related hydrocarbons, propane may be used when the subsurface temperatures are above 206° F.

Broadly, however, the normally gaseous constituent may include any normal gas having a critical point below formation temperature and capable of forming a retrograde solvent enriched phase while retaining the essential characteristics of a gas.

The solvent component of the retrograde-enriched mixture, as described above, comprises any normally liquid solvent for the heavy constituents of the oil which otherwise tend to precipitate in the formation, and which will vaporize in the normally gaseous constituent or carrier gas at the formation temperature and pressure in accordance with the phenomenon of retrograde vaporization.

The relative proportions of the normally gaseous and solvent-liquid constituents are those which form a retrograde-enriched-gas phase of substantial liquid solvent concentration at the pressure and temperature of the formation, preferably a solvent content approaching the maximum obtainable under such conditions.

For example, at a formation pressure of 3,730 p. s. i. a. and a formation temperature of 200° F., methane and carbon tetrachloride form a retrograde-enriched gas phase containing 27 mol per cent of carbon tetrachloride. This contrasts with a concentration of only about 1 mol per cent which would be anticipated in the absence of retrograde behavior. At a pressure of 3,610 p. s. i. a. and at a temperature of 180° F., a retrograde gas phase will form having a concentration of 13 mol per cent CCl₄. These represent the approximate optimum ratios of injection of the respective formations. It is apparent, however, that in each case the preferred ratio of gas-solvent injection depends upon the characteristic phase diagram of the gas and solvent employed. This relationship is always fixed, and known or readily determinable, and does not, per se, form any part of the present invention. It, moreover, varies with the gas and solvent selected. However, the phase diagram indicates directly the approximate relative quantity of gas and solvent corresponding to the retrograde-enriched gas desired under the conditions of temperature and pressure prevailing in the formation to be treated.

It is ordinarily contemplated selecting a gas-solvent mixture which under such conditions forms a retrograde gas phase containing at least 10 and preferably above 25 mol per cent of the solvent. However, in the case of a formation oil containing only small fractions of precipitable compounds, smaller concentrations of solvent are adequate to keep the formation open.

The normally gaseous hydrocarbon may comprise a mixture of such gases. In fact, as a general rule, a retrograde-enriched gas phase containing mixtures of normally gaseous hydrocarbons may hold substantially richer quantities of solvent than a retrograde-enriched gas phase based on pure methane alone. It is presumably for the same reason, that the presence of some C₂-C₄ gases in the mixture result in the yield of considerably more of the formation oil at the producing well. This follows from the fact that the heavier fractions of the oil more readily vaporize in the injected gas phase than where methane alone forms the injected carrier gas, and it accounts for the essentially exhaustive oil recovery experienced when proceeding by this method.

Likewise, mixtures of solvents may be employed and

are preferred for the reason that thereby a higher solvent concentration in the retrograde enriched gas likewise follows.

In general the presence of any additional hydrocarbon, intermediate, as regards molecular weight, between the lightest normally gaseous hydrocarbon and the heaviest solvent of the retrograde enriched gas phase, tends to lower the retrograde enriched phase dew point pressure and therefore increase the quantity of solvent which may be carried in the retrograde gas phase. For example, the presence of butane in a methane-decane mixture drastically reduces retrograde dew point pressure. The treatment phase may therefore comprise a mixture of methane, propane, pentane and benzene, or a mixture of methane, butane, hexane and CCl₄, for instance.

In accordance with one specific example illustrating the practice of the present invention, an injection well bore extends into a subsurface formation at a point spaced from a production well bore which enters the same formation. The subsurface formation in the present example comprises a formation depleted as to primary recovery and thereafter exhaustively produced by secondary water drive recovery means. After secondary recovery, however, the formation still contains approximately 50% of original oil.

The oil containing formation in question is located about 8,000 feet below the surface of the ground, is about 10 feet thick and has a temperature of about 230° F. The porosity of the formation, as determined by core samples is about 20%.

Production is effected in the bore hole by injecting into the injection well at a pressure of about 4,000 p. s. i. a. a natural gas composed largely of methane and containing appreciable proportions of C₂-C₆ hydrocarbons. In a typical instance, an injected gas composition is approximately as follows:

Component:	Mol percent
C ₁ -----	72.5
C ₂ -----	16.3
C ₃ -----	8.0
C ₄ -----	2.2
C ₅ -----	0.6
C ₆ -----	0.1
C ₇ + -----	0.3

Flow of hydrocarbon fluid comprising formation oil thereafter commences at the production well bore, but, after a substantial period of production, the permeability of the formation begins to materially decrease as a result of precipitation of asphalt-like material from the oil and resulting restriction of the interstices of the formation.

In order to overcome this difficulty in accordance with the present invention, carbon tetrachloride is continuously forced into the injection well with the natural gas. More specifically, the rate of solvent injection is equal to about 400 barrels of carbon tetrachloride per million cubic feet of natural gas. As injection proceeds, the well head pressure rises to about 3,000 p. s. i. a. at a gas temperature of 90° F. Thereafter injection proceeds continuously under these conditions to cycle the mixed fluid through the formation and institute substantial production at the production well bore. After long periods of time, there is no decrease in permeability and no apparent precipitation of immobile deposits in the formation interstices.

Manifestly, this follows from the fact that under the formation pressure and temperature, the injection mixture necessarily exists as a retrograde enriched gas capable of cycling freely through the formation under the characteristic low viscosity of the gas but containing somewhat over 25% CCl₄ in solution in the gas. Therefore, at the high subsurface pressures involved there is obviously a relatively large concentration of solvent in contact with the oil which tends to condense thereon and

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maintain the precipitable constituents continuously in fluent condition.

In place of the CCl_4 in the above example, approximately the same proportion of benzene or toluene may be employed.

It is particularly important to note that the solvent bearing gas cycled through the formation is readily recoverable upon completion of the oil recovery operation. Thus by the means disclosed above, as much as 90% of the total original oil is recoverable from the formation. When, however, no further oil is produced by this operation the gas remaining in the reservoir and containing the solvent and lighter hydrocarbons is readily displaceable by cycling the formation with dry natural gas and extracting the effluent by conventional natural gas absorption methods. Since the major part of the formation hydrocarbons have been previously produced, no important clogging of the formation can occur at this time and, in any event, cannot seriously impair the migration of the dry gas.

As indicated above, the present invention is particularly applicable to the secondary recovery of oil after primary methods have been exhausted or to the recovery of the final oil after secondary recovery methods as for example water flooding and gas pressure have been applied. It may also be employed to extend and facilitate primary recovery. The significant importance of the process resides in the fact that tremendous quantities amounting frequently to as much as 50% of the original oil in place may remain in the formation after the completion of ordinary recovery. This can be effectively recovered in its substantial entirety by the present methods.

The invention also contemplates raising the formation pressure in cases where the pressure has previously been released to a point below the retrograde region. Thus, where formation pressure is insufficient to support the retrograde enriched phase the necessary pressure may be obtained by injecting sufficient gas to build up the formation pressure to the desired value where the contemplated enriched gas phase can exist.

Obviously many modifications and variations of the invention as above 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. In the recovery of oil from subsurfaces oil bearing formations by forcing gas through the formation from an injection well toward a producing well under a high pressure effective to cause enhanced yields at the producing well of fluid containing said oil, the improvement wherein said high pressure gas injected into said formation from the injection well bore is a retrograde-enriched gas comprising a normally gaseous hydrocarbon containing in single phase admixture therewith a substantial proportion of a normally liquid solvent having a high solvent capacity for heavy asphaltene-bitumen constituents of the formation oil which tend to be precipitated by normally gaseous hydrocarbons dissolved by the

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formation oil and subject to retrograde condensation upon isothermal pressure decrease, thereby inhibiting the precipitation of heavy hydrocarbons in said subsurface formation, and withdrawing the resulting flow of hydrocarbons from said production well.

2. In the recovery of oil from subsurface oil bearing formations by forcing a gas through the formation from an injection well toward a producing well at a high pressure in the retrograde region effective to form with the oil a continuous phase of more readily displaceable fluid containing said oil which flows to the well bore, the improvement wherein said gas injected into said formation from the injection well is a retrograde-enriched gas comprising a normally gaseous hydrocarbon containing in single phase admixture therein a substantial proportion of a normally liquid solvent having a high solvent capacity for heavy asphaltene-bitumen constituents of the formation oil which tend to be precipitated by normally gaseous hydrocarbons and subject to retrograde condensation upon isothermal pressure decrease to substantially inhibit the precipitation of said heavy constituents in said subsurface formation, and withdrawing the resulting flow of hydrocarbons from said production well.

3. The method according to claim 2 in which the retrograde-enriched gas phase contains at least about 10 mol per cent of solvent.

4. The method according to claim 2 in which the retrograde-enriched gas phase contains at least about 25 mol per cent of solvent.

5. The method according to claim 2 wherein the retrograde-enriched gas phase contains a mixture of normally gaseous hydrocarbons.

6. The method according to claim 2 in which the retrograde-enriched gas phase contains a substantial proportion of a hydrocarbon intermediate, as regards molecular weight, between the normally gaseous hydrocarbon and said solvent.

7. The method according to claim 2 wherein the retrograde-enriched gas contains a plurality of solvents.

8. The method according to claim 2 wherein the retrograde-enriched gas passes into the formation at a pressure greater than about 3,000 p. s. i. a.

9. The method according to claim 2 as applied to the recovery of subsurface oil after substantial exhaustion of primary recovery means.

10. The method according to claim 2 wherein said normally liquid solvent comprises a solvent of the class consisting of carbon tetrachloride, benzene, toluene, cumene, pyridine and carbon disulfide.

11. The method according to claim 2 wherein said normally liquid solvent is carbon tetrachloride.

References Cited in the file of this patent

UNITED STATES PATENTS

2,135,319	Bays	Nov. 1, 1938
2,265,923	Normand	Dec. 9, 1941
2,297,832	Hudson	Oct. 6, 1942
2,361,012	Cole et al.	Oct. 24, 1944