

1

2,871,941

IN SITU COMBUSTION WITHIN A SUBSURFACE FORMATION CONTAINING PETROLEUM HYDROCARBONS

Joseph C. Allen, Bellaire, and Robert E. Kunetka, Houston, Tex., assignors to The Texas Company, New York, N. Y., a corporation of Delaware

No Drawing. Application November 29, 1956
Serial No. 624,998

4 Claims. (Cl. 166—38)

This invention relates to production of petroleum from underground petroleum producing formations. More particularly, this invention relates to carrying out an in situ combustion operation within an underground petroleum producing formation.

Various techniques have been proposed for the recovery of petroleum from underground formations and for the treatment of petroleum producing formations. For the recovery of petroleum from petroleum producing formations secondary recovery operations which involve water flooding or thermal recovery methods, in situ combustion, employing at least one injection well and at least one production well have been proposed. In situ combustion has also been proposed as a well remedial treatment to improve the permeability and/or porosity of a petroleum producing formation.

In an in situ combustion operation a high temperature zone is established in the petroleum producing formation in the vicinity of the well bore by suitable heating means. Suitable heating means may comprise an electrical heating device or a gas fired bottom hole igniter or heater. A suitable device for initiating in situ combustion within a bore hole is described in U. S. 2,722,278. Another technique or method, involving spontaneous combustion, for initiating in situ combustion is described in U. S. 2,747,672.

Upon introducing a combustion supporting or an oxygen-containing gas, such as air, into the thus-heated petroleum producing formation via the well bore a high temperature zone, temperature in the range 700°–2500° F., usually in the range 800°–1750° F., created by the reaction between the oxygen and combustible residues within the formation, such as combustible residues resulting from the distillation and/or thermal cracking of the crude oil originally in place or introduced thereinto, will commence to move into the formation outwardly from the well bore in the direction of flow of the hot gaseous combustion products.

Leaving this high temperature zone is a relatively high temperature gas stream at substantially the same temperature which, as it moves outwardly into the formation, loses heat to the formation. By this method the high temperature reaction zone is moved radially outwardly from the well bore without further direct application of heat to the area immediately surrounding the well bore. The distance the high temperature reaction zone moves outwardly, and accordingly the volume of the petroleum producing formation swept by or comprised within the high temperature in situ combustion zone, is determined by the relative magnitudes of the rate of heat generation (combustion of combustible residues) and the rate of heat loss to the surrounding formation.

It has been postulated that the following mechanisms are important in an underground in situ combustion operation for the movement of the high temperature zone radially outwardly from the well bore into the petroleum producing formation. Although the exact mechanism of in situ combustion is not definitely completely known,

2

the following sequence of events in an underground in situ combustion operation is postulated and is presented herein for the purpose of enabling one skilled in the art to better understand the practice of this invention and is not to be construed as limiting this invention in any way.

As the high temperature reaction zone approaches a given volume of the petroleum hydrocarbon-containing formation the temperature of this volume of formation rises. This results in a reduction in the viscosity of the formation fluids therein due to their temperature increase. These fluids may then be moved more readily under the influence of the hot gas stream continuously emanating from the high temperature reaction or combustion zone. As the temperature of this volume of formation continues to rise distillations of the liquids therein begin. The products of these distillations condense in cooler regions of the formation removed from the high temperature combustion zone in the direction of gas flow. These distillations continue as the temperature rises until the heavier components remaining from the petroleum hydrocarbons originally in place within the formation or introduced therein prior to effecting in situ combustion begin to crack or otherwise thermally decompose yielding hydrocarbon gases, coke and similar solid carbonaceous residues. As the temperature continues to rise and the oxygen content of the incoming gas to the given volume of formation increases due to depletion of combustible residues in preceding regions or volumes of the formation, a point will be reached at which the coke or other combustible residues will begin to chemically combine with the oxygen with the resulting release of heat to the formation and the gas stream emanating therefrom. This heat is carried away by the onmoving gas stream and also to a limited extent by conduction to the adjacent regions of the formation. When the coke or combustible residues have been burned away there remains a volume of substantially liquid-free formation which, unless otherwise treated, is then gradually cooled by the relatively cool combustion supporting gas or air entering the thus-treated given portion of the formation via the well bore.

From the above-indicated considerations it is obvious that the rate of heat energy released within the formation should be some function of the quantity of fuel or combustible residues present therein, which is dependent upon type and quantity of the petroleum originally in place and/or combustible material or fuel caused to be deposited within the formation in the zone of in situ combustion. The rate of heat released is also dependent upon the rate at which oxygen is supplied to the combustion zone or, in other words, the rate at which the exothermic combustion process within the formation undergoing treatment is effected. The rate at which heat can be transferred ahead of the high temperature reaction or combustion zone should be dependent on the rate at which the gaseous products of combustion leave the high temperature combustion or reaction zone and should be to some extent dependent upon conduction through the formation itself. Accordingly, some control of the in situ combustion process can be exercised by controlling the oxidation or combustion process occurring with the in situ combustion operation, such as by controlling the amount of oxygen or other oxidizing agent introduced into or present within the high temperature combustion zone in contact with the combustible residues therein.

Accordingly, it is an object of this invention to provide an improved method for the treatment of petroleum-containing or producing formations to enhance or otherwise improve the recovery of petroleum therefrom by an operation involving in situ combustion.

It is another object of this invention to provide an improved method for carrying out an in situ combustion operation.

3

Still another object of this invention is to provide a method for effecting control of an in situ combustion operation.

Yet another object of this invention is to provide a method for initiating and/or maintaining an underground in situ combustion operation.

How these and other objects of this invention are accomplished will become apparent with reference to the accompanying disclosure. In at least one embodiment of the practice of this invention at least one of the foregoing objects will be achieved.

In accordance with the practice of this invention in an in situ combustion operation wherein a subsurface petroleum-containing formation is subjected to a relatively elevated temperature in situ combustion is initiated and/or maintained therein by introducing into said formation prior to subjecting the same to said elevated temperature an oxidizing agent which reacts with petroleum hydrocarbons in said formation at said relatively high temperature to oxidize the same. The oxidizing agent introduced into the formation to contact the petroleum hydrocarbons therein, as indicated hereinabove, may per se oxidize or otherwise react with the petroleum hydrocarbons in the formation at the relatively high temperature and/or may thermally decompose, for example, when subjected to said elevated temperature, or otherwise react with the formation fluids or formation solids present in the formation undergoing treatment to yield an oxidizing agent or free elemental oxygen which in turn reacts with the petroleum hydrocarbons present in the formation to oxidize the same.

The various materials which may be employed in the practice of this invention in an in situ combustion operation to initiate and/or to help maintain the same by supplying in part or in full the oxygen (or heat) requirement for the in situ combustion process includes such materials as class A, those materials or compounds which react with the formation fluids, particularly water, to yield elemental oxygen or a thermally unstable compound which decomposes at the temperature at which in situ combustion is carried out, or at a lower temperature, to yield elemental oxygen; class B, those materials or compounds which directly react with the petroleum hydrocarbons to oxidize the same under conditions of in situ combustion with the concomitant release of a substantial amount of heat to increase the formation temperature to an elevated temperature sufficient for maintaining or initiating in situ combustion; class C, those materials or compounds which react with other materials already present or previously or subsequently introduced into the formation undergoing treatment to yield elemental oxygen or an oxidizing agent capable of oxidizing in situ or otherwise reacting in situ with the petroleum hydrocarbons contained within the formation; class D, those materials or compounds which react with the formation fluids, particularly water, to yield a thermally unstable oxidizing agent which directly reacts with or oxidizes petroleum hydrocarbons present within the formation at said elevated temperature. In some instances the materials employed in the practice of this invention may possess the characteristics of one or more of the above classes. For example, Caro's acid (permonosulphuric acid) reacts with water to form hydrogen peroxide which decomposes at an elevated temperature to yield elemental oxygen. Caro's acid itself reacts directly with hydrocarbons to oxidize the same. Accordingly, Caro's acid comes within class A and class B. Caro's acid might also be considered to come within classes C and D. A chlorate, such as an alkali metal or an alkaline earth metal chlorate, e. g., sodium chlorate or calcium chlorate, is a material which comes within class C, per se, or within class D when acidified with sulphuric acid to yield chloric acid.

Materials suitable for use in the practice of this invention for injection into a subsurface petroleum-con-

4

taining formation to help initiate, promote or maintain in situ combustion therein include such materials as hydrogen peroxide, chromium trioxide, the various alkaline earth metal and alkali metal peroxides, such as barium peroxide and sodium peroxide, Caro's acid, perdisulphuric acid, chlorine dioxide, the sulfur oxides, chloric acid, chlorous acid, iodic acid, perchloric acid, periodic acid, the various alkali metal and alkaline earth metal chlorates and perchlorates such as sodium chlorate and sodium perchlorate, the various alkali metal and alkaline earth metal manganates and permanganates such as sodium manganate and potassium permanganate, the various alkali metal and alkaline earth metal chromates and the per- or poly-chromates such as sodium chromate and sodium dichromates and their corresponding acids, the various alkali metal and alkaline earth metal nitrates such as sodium nitrate, the various nitrogen oxides such as nitrogen dioxide, nitrogen tetroxide, ozone, the various peracids, organic and inorganic, such as peracetic acid, pernitric or pernitrous acid, fuming nitric acid, fuming sulfuric acid, mercuric oxide, the phosphorus oxides, lead dioxide. Various other materials which oxidize petroleum hydrocarbons under temperature conditions of in situ combustion or which react with formation fluids to form elemental oxygen or hydrogen peroxide or which react with other added materials such as strong sulphuric acid or hydrogen peroxide to yield oxidizing agents such as elemental oxygen or hydrogen peroxide are known and may be employed in the practice of this invention.

The subject invention may be practiced in a single well or a multi-well in situ combustion operation. In a single well in situ combustion operation as set forth in copending, coassigned patent application Serial No. 576,486, filed April 5, 1956, in the name of Gerhard Herzog, there is described a single well in situ combustion operation as a remedial treatment to increase the productivity and/or permeability of an underground petroleum producing or petroleum-containing formation. The practice of this invention is particularly applicable to a well remedial treatment since by following the practice of this invention the introduction of oxygen, save perhaps that amount necessary to initiate in situ combustion or in order to reach the desired initial high temperature required to set off in situ combustion, especially when an electrical heater or well igniter is employed, via a separate gas stream introduced through the well bore can be substantially eliminated. The oxidation reaction or the oxygen required to initiate and maintain the in situ combustion operation in the formation surrounding the well bore is maintained, provided or otherwise generated in situ by introducing into the formation a material or compound in accordance with the practice of this invention. The disclosures and teachings of the above-identified patent application, accordingly, are hereby expressly incorporated in and made a part of this disclosure.

The practice of this invention is particularly applicable to an in situ combustion operation employing a plurality of wells, that is, at least one injection well and at least one production well. As in a single well system the total oxygen or heat requirement of the in situ combustion operation may be supplied by introducing into the formation undergoing treatment a material or compound in accordance with the practice of this invention. Desirably an in situ combustion operation carried out in accordance with the practice of this invention utilizes extraneously introduced via the well bore elemental oxygen, either substantially pure oxygen, air, or air enriched with respect to oxygen or having a slightly reduced oxygen content such as an oxygen content in the range 5-15% by volume.

Exemplary of the practice of this invention a hot, concentrated solution of an inorganic oxidizing agent or salt, such as sodium nitrate, sodium chlorate, hydrogen peroxide, sodium chromate or sodium dichromate, Caro's

acid and the like, is introduced into the petroleum producing formation in the zone to be subjected to in situ combustion. As the combustion zone approaches the thus-treated portion of the formation containing the oxidizing agent the vaporable liquids, such as water, distills therefrom leaving behind a residue of solid and/or concentrated oxidizing agent. This residual oxidizing agent is subjected to ever increasing temperatures until it decomposes with the liberation of a substantial amount of heat and/or oxidizing agent or elemental oxygen which becomes immediately available for use in the in situ combustion operation to oxidize the residual petroleum hydrocarbons. Also, the residual oxidizing agent or the oxidizing agent resulting from the high temperature decomposition may react directly with the petroleum hydrocarbons in the formation. In this manner once a high temperature zone has been initiated within a subsurface petroleum-containing formation to which had been added a substantial amount of oxidizing agent, e. g., sodium nitrate, not only is the in situ combustion operation more readily initiated but also in situ combustion is more readily maintained therein, even in some instances without the need for extraneously introduced elemental oxygen.

In the event there is employed in the practice of this invention certain materials such as the alkali metal peroxides and the alkaline earth metal peroxides which react with water or acids to yield the corresponding alkali metal or alkaline earth metal hydroxide or salt and hydrogen peroxide, these materials are introduced or otherwise deposited within the formation to be treated by dispersing or otherwise carrying the peroxide in a substantially inert fluid carrier, such as a petroleum fraction. For example, finely divided barium peroxide and sodium peroxide is suspended in a liquid oil carrier and injected into the formation to be treated by in situ combustion. Upon introduction into the formation the presence of the formation fluids, that is, the presence of water therein, or the presence therein of previously or subsequently injected acid, e. g., concentrated sulfuric acid, leads to the reaction with the thus-introduced peroxide to yield hydrogen peroxide which reacts directly with the petroleum hydrocarbons in the formation undergoing treatment or which decomposes to yield elemental oxygen which is employed or otherwise consumed in the subsequent in situ combustion operation.

Exemplary of the practice of this invention, a hot concentrated aqueous solution of a metal nitrate, such as sodium or potassium nitrate, or a hot aqueous concentrated solution of a metal nitrate and a metal chlorate, such as sodium nitrate and sodium chlorate, is introduced into a subsurface petroleum-containing formation in a volume sufficient to displace the formation water or brine therein for a substantial radial distance surrounding the well bore, e. g., an amount of solution sufficient to displace the formation water or brine for a distance of 3-25 radial feet from the well bore. Thereafter a bottom hole igniter is introduced into the well bore and located adjacent the thus-treated petroleum-containing formation. That section of the formation immediately surrounding the well bore is heated to a temperature of at least about 750° F., preferably in the range 800-1300° F. At the same time while the formation surrounding the well bore is being heated a gaseous stream containing elemental oxygen, such as air, is introduced into the formation via the well bore. After a period of time the water in the aqueous solution introduced into the formation surrounding the well bore is evaporated, leaving behind a solid residue of nitrate and/or nitrate and chlorate salts. As the temperature increases these salts decompose with the evolution of elemental oxygen. The elemental oxygen thus released serves to provide in whole or in part all of the oxygen requirement necessary to effect in situ combustion of the petroleum in that section of the forma-

tion surrounding the well bore undergoing treatment. In fact, it is postulated that once in situ combustion has been established within the treated portion of the formation the introduction of extraneous oxygen via the well bore may be substantially reduced or terminated, there being sufficient oxygen generated by the thermal decomposition of the nitrate and/or nitrate and chlorate salts with the formation to effect continued in situ combustion. For example, once in situ combustion has been adequately established the injection of air via the well bore into the formation undergoing treatment may be discontinued and in the place of air there may be substituted a relatively inert gas or even a gas containing combustible components therein, such as normally gaseous or vaporized hydrocarbons, e. g., methane, propane, butane and the like, to provide a driving force and/or part of the heat energy necessary to maintain in situ combustion by thermal decomposition of the nitrates or chlorates and/or to direct the in situ combustion zone outwardly from the well bore into the formation.

In accordance with yet another embodiment of the practice of this invention there is disposed in the subsurface petroleum-containing formation to undergo in situ combustion an oxidation catalyst such as an alkali metal hydroxide, e. g., potassium hydroxide, or an alkali metal carbonate, such as potassium carbonate, or their corresponding lithium, barium or calcium compounds, which exhibit a catalytic effect or otherwise function as oxidation catalysts thereby permitting the in situ combustion to be more readily initiated and maintained within the formation undergoing treatment. This use of an oxidation catalyst to aid or promote an in situ combustion operation is more completely described and claimed in copending coassigned patent application Serial No. 624,995, filed November 29, 1956, in the name of Allen D. Garrison and Robert E. Kunetka.

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

We claim:

1. A method of initiating or maintaining in situ combustion in a subsurface formation containing in place hydrocarbons which comprises introducing into said formation a compound which undergoes thermal decomposition to yield an oxidizing agent, subjecting that portion of the formation into which said compound is introduced to a temperature sufficiently high to effect thermal decomposition of said compound therein to yield said oxidizing agent and to cause said oxidizing agent to oxidize the in place hydrocarbons within said formation to effect in situ combustion therein.

2. A method of initiating or maintaining in situ combustion within a subsurface formation containing petroleum hydrocarbons therein which comprises introducing into said formation an aqueous solution of an oxygen-containing compound which thermally decomposes to yield elemental oxygen, subjecting that portion of the formation containing the thus-introduced aqueous solution of said oxygen-containing compound to a temperature sufficient to effect thermal decomposition of said compound therein to yield elemental oxygen and to cause the thus-produced oxygen to effect in situ combustion of said petroleum hydrocarbons thereby maintaining an in situ combustion operation within said formation.

3. A method of maintaining in situ combustion within a subsurface formation containing petroleum hydrocarbons therein which comprises introducing into said formation an aqueous solution of a nitrate which undergoes thermal decomposition to yield an oxidizing agent, subjecting said formation containing the thus-introduced aqueous nitrate solution to an elevated temperature and simultaneously introducing into the thus-treated portion

7

of the formation a gaseous stream containing elemental oxygen, said elevated temperature to which said formation is subjected being sufficient to effect thermal decomposition of the nitrate thus introduced into said formation to yield said oxidizing agent and to cause the oxidizing agent released from said nitrate by thermal decomposition to maintain in situ combustion of the petroleum hydrocarbons within said formation.

4. A method in accordance with claim 3 wherein said

5

8

aqueous solution of a nitrate is an aqueous sodium nitrate solution.

References Cited in the file of this patent

UNITED STATES PATENTS

1,806,499	Ranney et al. -----	May 19, 1931
1,870,320	Adams et al. -----	Aug. 9, 1932
2,722,277	Crawford -----	Nov. 1, 1955
2,747,672	Simm -----	May 29, 1956