United States Patent Office

3,180,412
Patented Apr. 27, 1965

3,180,412

INITIATION OF IN SITU COMBUSTION IN A SECONDARY RECOVERY OPERATION FOR PETROLEUM PRODUCTION

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No Drawing. Filed Aug. 7, 1962, Ser. No. 215,459
12 Claims. (Cl. 166—11)

This invention relates generally to the treatment of underground formations which produce petroleum. More particularly, this invention relates to the carrying out of an in situ combustion operation within a permeable underground formation. In accordance with one embodiment, the practice of this invention is directed to a method of initiating in situ combustion within a permeable underground formation, e.g. by initiating spontaneous in situ combustion within a petroleum producing or petroleum bearing underground formation.

Various techniques are practiced 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, such as in situ combustion, employing at least one injection well and at least one production well, have been proposed.

In a conventional in situ combustion operation after a petroleum bearing formation has been heated to a sufficiently high temperature, a combustion-supporting or oxygen-containing gas, such as air or oxygen-enriched air, is introduced into the formation via a well bore. A high temperature zone with a temperature therein in the range 700°–2500° F., created by the reaction between the thus-introduced oxygen and the combustible petroleum residues within the formation, such as combustible residues resulting from the distillation and/or thermal cracking of the petroleum originally in place or introduced thereinto, moves outwardly from the well bore into the formation in the direction of flow of hot gaseous combustion products.

Leaving this high temperature zone is a relatively high temperature gas stream at substantially the same temperature. This high temperature gas stream, as it moves outwardly into the formation, loses heat to the formation. By this method, the high temperature reaction zone moves radially outward 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 the high temperature reaction zone, is dependent upon the relative magnitudes of the rate of heat generation (the combustion of combustible residues) and the rate of heat loss to the surrounding formation.

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

As the high temperature reaction zone approaches a given volume of the petroleum-containing formation in an in situ combustion operation for the recovery of petroleum therefrom or for the treatment of said formation, the temperature of this volume of formation increases. This results in a reduction in the viscosity of the formation liquids (petroleum and brine) therein due to their temperature rise. 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 those cooler regions of the formations outward from the high temperature combustion zone in the direction of gas flow. These distillations continue as the temperature rises until the heavier components remaining within the petroleum originally in place within the formation or introduced thereinto prior to effecting in situ combustion begin to crack or otherwise thermally decompose, yielding hydrocarbon gases, coke and 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 the depletion of combustible residues in preceding volumes of the formation, a point is reached at which the hot coke or hot combustible residues will begin to combine chemically with the oxygen with the resutling 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 is transferred to the adjacent regions of the formation. When the coke and combustible residues have been burned away, there remains a volume of substantially liquid-free formation which, unless otherwise treated, is cooled then gradually by the oncoming relatively cool combustion-supporting gas or air entering the thus-treated given volume of the formation via the well bore.

One difficulty in carrying out an in situ combustion operation involves the operation of initiating in situ combustion. Various methods have been proposed heretofore for initiating in situ combustion. For example, suitable heating means such as electrical heating devices or gas fired bottom hole igniters or heaters suitable for lowering within the bore hole opposite the formation wherein in situ combustion is to be initiated have been employed or suggested. Another method suggested for initiating in situ combustion involves the introduction of phosphorus or similar readily combustible material into the petroleum producing formation to be subjected to in situ combustion.

It is an object of this invention to provide an improved method for initiating in situ combustion within a permeable underground formation.

Another object of this invention is to provide an improved method of initiating spontaneous in situ combustion within a permeable underground formation such as a permeable petroleum producing or petroleum bearing formation.

Still another object of this invention is to provide an improved method for carrying out an in situ combustion operation within a permeable petroleum formation.

Yet another object of this invention is to provide a method of treating or consolidating a permeable underground formation.

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, it has been discovered that a permeable underground formation is improved and/or a spontaneous in situ combustion operation is initiated therein by introducing into such a permeable formation an organic unsaturated compound, such as an unsaturated aliphatic organic compound comprising only carbon, hydrogen and oxygen atoms and containing at least 16 carbon atoms per molecule, and then introducing into the formation containing such an organic compound and into contact with such an organic compound, a gas comprising free oxygen to effect spontaneous in situ combustion of the thus-introduced aliphatic organic compound within the permeable formation. More particularly, it has been found that an oxygenated aliphatic organic compound, such as an unsaturated long chain fatty acid or an unsaturated long chain fatty alcohol or fat or oil, and the glycerides of unsaturated long chain fatty acids, are suitably employed within a permeable underground formation to effect initiation of in situ combustion therein.

Unsaturated aliphatic compounds comprising only carbon, hydrogen and oxygen atoms and containing at least 16 carbon atoms per molecule, which are suitably employed in the practice of this invention, include the various aliphatic, long chain olefinic acids and the corresponding alcohols and esters, such as the triglycerides thereof. Exemplary unsaturated organic compounds which are suitably employed in the practice of this invention include linoleyl alcohol, linolenyl alcohol, linoleyl acid, linoleic acid, linolenic acid, eleostearic acid, eleostearyl alcohol, ricinoleic alcohol, clupadonyl alcohol and clupadonic acid.

Particularly useful in the practice of this invention are the unsaturated non-hydrocarbon oils, particularly those oils, so-called drying oils or so-called semi-drying oils, having an iodine number greater than 100, especially greater than 130. By definition, an iodine number is the number of grams of iodine absorbed by 100 grams of fat or oil. Those oils having an iodine number below 100 are considered substantially non-drying oils, those oils having an iodine number in the range 100–130 are considered semi-drying oils, and those oils having an iodine number greater than 130 are considered drying oils. Suitable non-hydrocarbon oils, vegetable and animal (mammal or fish), or mixtures thereof, which may be employed in the practice of this invention include corn oil, cottonseed oil, sesame seed oil, sunflower seed oil, soy oil, poppyseed oil, perilla oil, tung oil, oiticica oil, linseed oil and the fish oils, such as herring oil, sardine oil, menhaden oil, whale oil, seal oil, porpoise body oil, dolphin oil and the like. In general, any unsaturated non-hydrocarbon oil, animal or vegetable, having an iodine value in excess of 130, is suitable in the practice of this invention. For the most part, these oils, such as linseed oil and the like, comprise triglycerides of unsaturated long chain fatty monocarboxylic acids.

Desirably and in accordance with one embodiment of the practice of this invention, there is admixed with the non-hydrocarbon oil introduced into the permeable formation undergoing treatment a suitable oxidation promoter. The organic nitrogen bases, such as pyridine, pyrrole, piperidine, aniline and dimethylaniline, are particularly useful as oxidation promoters to pormote a spontaneous in situ combustion in accordance with this invention. Desirably also, the unsaturated non-hydrocarbon oil or unsaturated aliphatic compound introduced into an underground formation also contains admixed therewith an oxidation catalyst or dryer, such as cobalt naphthenate, cobalt tallate, cobalt octoate, and similar iron or lead driers. However, even with the use of a suitable oxidation promoter and a suitable oxidation catalyst, it has been found that some oils having a very high iodine number are not suitable choices due to the presence of strong acetylenic bonds making such oils not easily oxidizable for the purpose of initiating in situ combustion, e.g. isano oil and compounds thereof. Further, certain oils may contain natural oxidation inhibitors such as tocopherols, which are normally present in vegetable oils and which are removed with the color bodies in producing refined grades.

In some instances, in accordance with the practice of this invention, particularly when the unsaturated aliphatic organic compound is a normally solid material or possesses a viscosity too high for easy injection into a permeable underground formation, the unsaturated oxidizable material is thinned with or dissolved in or admixed with a suitable solvent or diluent. Particularly suitable as a carrier is a light hydrocarbon naphtha, VMP naphtha, Stoddard's solvent, and aromatic naphthas such as the xylenes, turpentine and the like.

In accordance with one embodiment or feature of this invention, there is incorporated in admixture with the material introduced into the permeable formation to initiate and to undergo spontaneous combustion therein a suitable minor amount, in the range 0.25–10% by weight, of finely divided, powdered magnesium or magnesium dust. The powdered magnesium, once spontaneous in situ combustion has been initiated, greatly increases the amount of heat released and the temperature generated during in situ combustion within the formation undergoing treatment.

In accordance with yet another embodiment of the practice of this invention an amount, such as minor amount, of crude petroleum, particularly crude petroleum or a fraction thereof derived from the formation undergoing treatment, may be admixed with the unsaturated organic compound or unsaturated non-hydrocarbon oil employed.

Any suitable oxygen-containing fluid such as air, air enriched with oxygen, or substantially pure oxygen may be employed in the practice of this invention. Air, preheated to a temperature above 100° F., preferably about 200° F. or higher, is particularly suitable for initiating a spontaneous in situ combustion in accordance with this invention.

The practice of this invention is particularly useful when it is desired to carry out an in situ combustion operation for the recovery of petroleum from an underground petroleum producing formation. It is a usual practice when an underground in situ combustion operation is contemplated to establish a zone of permeability through the petroleum producing formation, extending from an injection well to a producing well. When this zone of permeability has been established, the actual in situ combustion operation can be started. By employing the practice of this invention, i.e., by introducing an unsaturated organic compound or drying oil of the type described herein into the petroleum producing formation immediately adjacent the wall bore and then by passing air therethrough to establish this zone of permeability, an operator may establish the zone of permeability by flowing air therethrough and may also thereby simultaneously initiate the actual in situ combustion operation so that when the zone of permeability has been established, the in situ combustion operation has also been initiated or is about to be initiated.

However, it is not necessary that complete permeability be established between an injection well and a producing well, insofar as the formation adjacent the well bore be found receptive to gas injection. In this manner, the volume of the producing formation adjacent the well bore can become saturated with injected spontaneously ignitible mixture especially if there should be a permeability barrier between the injection and production wells.

From a safety point of view, it is desirable to start combustion within the formation. Without having detailed knowledge of the transition mechanism, it is known that the chemical mixture used for the spontaneous ignition does not remain in liquid state during the time combustion of the petroleum takes place. Laboratory experiments in ignition have shown the presence of a paint-like polymer and no trace of a liquid chemical mixture in the experimental sand masses. Low temperature oxidation of spontaneous ignitible mixtures such as disclosed above, converts the mixtures from liquid form into a plastic-like solid. Following this solidification, the reaction continues with the final products being carbon monoxide, carbon dioxide and water. By carefully controlling the rate of such an exothermic reaction, the in situ petroleum is distilled.

The oxidation of the spontaneous ignitible mixture, being exothermic, raises its own temperature, that of the surrounding formation, and the petroleum contained therein. It will also raise the temperature of the injected combustion-supporting gases, e.g., air which are provided the formation. The injected gases thus heated come in contact with the petroleum present in the formation and begin its oxidation. By the time the formation has reached some temperature believed to be 400° F. or more, the injected chemical mixture has been used up but the oxygen saturated fractions of petroleum now begin to oxidize themselves exothermally, raise the temperature further, and sustain combustion as long as enough oxygen is supplied. It is this last reaction which initiates the in situ combustion. The injected gases heated by the combustion carry the combustion zone forward, and the hot dry formation left behind preheats other injected gases provided the combustion zone.

It is considered essential that the initiation of in situ combustion be a minimum of a two-stage process. The initial rate for combustion supporting gas injection must be low in order not to cool the injected chemical mixture and the formation during an induction period when oxygen is absorbed and higher oxides are formed. Further, to react with sufficient rapidity so that a rapid temperature rise takes place, the chemical mixture must have a large surface area exposed to the oxidizing fluid. Such a large surface area can be only within the formation and not within the well bore. Therefore, in practice, it is desirable to inject the chemical mixture for at least six inches or more into the formation adjacent the well bore. This amounts to about 11 lbs. of linseed fatty acids per square foot of well bore area, in addition to the amount needed to fill the well bore to the top of the formation under treatment. The initial injection rate of the combustion-supporting gases after ignition and the burn has started is preferably at 2.3 cu. ft. per minute per square foot of area and will vary depending on the distance the combustion front moves away from the well bore. At the first stage of injection, the rate is not more than ¼ or ⅓ of the rate after the burn has started.

In support of the two-stage process described above, the following is an illustrative example: With well head pressure of 30 p.s.i., a spontaneously ignitible chemical mixture was displaced into the well bore with nitrogen ahead and behind the mixture. Injection of air was started at the rate of approximately 200 M c.f.d. Maximum injection pressure was 310 p.s.i. after fifteen minutes, which pressure decreased to 140 p.s.i. in approximately thirty minutes. The injection of air was continued with monitoring of adjacent observation wells for temperature data and gas analysis. On the following day, the low volume compressor was taken off stream and replaced by a high volume compressor at a full capacity of 1.4 MM c.f.d. The temperature began to rise in an adjacent observation well within 45 minutes, with a maximum temperature observed of 2172° F. Because of this extreme temperature and several mechanical failures, the air injection was discontinued till the well was under control again and the compressor rate was reduced to 850 M c.f.d., with increased gas production in adjacent pattern wells noticed thereafter.

As another illustration of the practice of the invention, air under pressure was provided the well bore to displace fluid therefrom and to establish air permeability and/or receptivity in the formation. As indicated by a flow meter that adequate air permeability had been established, the well was bled down from approximately 600 p.s.i.g. to atmospheric pressure. Immediately thereafter, approximately 800 pounds of linseed fatty acids were introduced into the well bore. These chemicals were displaced from the tubing inserted into the well bore by 60 cu. ft. of nitrogen injected immediately behind the chemicals thereby providing a cushion of inert atmosphere.

On the following day, during the initial period and several hours thereafter, an attempt was made to hold the flow rate of air injection at about 5400 cu. ft. per hour, the rate being established on the basis of laboratory experiments. Two days later on, the well was bled down for indications of in situ combustion, the effects of which were indicated by thermocouple readings above 200° F. and gas analysis with a CO_2 concentration of 3%. Also, the strange odor of cracked and partially oxidized hydrocarbons characteristic of in situ combustion was noted in the effluent gases. All these phenomenon were determined to be sufficient evidence that spontaneous combustion had taken place. Injection of air was resumed immediately, with the combustion raising the temperature up to about 1150° F.

Injection of air at increasing rates, up to 19,500 cu. ft. per hour, was continued for the three following days, the injection being interrupted periodically and the well allowed to cool when temperatures in excess of 300° F. were noted.

On the following day, with a flowing pressure of ¼ p.s.i.g., the well was shut in, and the pressure stabilized at ½ p.s.i.g. Gas sample Burrell analysis showed 28.4% as CO_2 and 1% as O_2, with production to be resumed at a later date.

Also, the following examples further illustrate the practice of this invention.

EXAMPLE NO. 1

An in situ combustion test cell, provided with thermocouple leads therein and having wall heaters which were controlled to approximate adiabatic operation, was packed to within 4–5 inches of the top with 38.4 lbs. of an admixture made up of 40 lbs. of Galveston sand and 2.4 lbs. of 20° A.P.I. West Columbia crude. Thereafter 500 ml. of linseed fatty acids (predominantly a mixture of oleic, linoleic, and linolenic acids) and 5 ml. of 6% cobalt naphthenate, as an oxidation catalyst, and 5 ml. of dimethylaniline, as a combustion promoter, was poured in the top. The head of the test cell was then bolted and while still in the vertical position, air pressure was applied to the test cell sufficient to force the resulting catalyzed admixture of linseed fatty acids into the sand-oil mixture. The test cell was then placed in a horizontal position.

Compressed air at 100 p.s.i.g. was allowed to enter the test cell and a valve at the exit gas line of the cell was used to regulate the rate of air flow therethrough. A flow meter and a wet test meter in series were used to measure the rate of flow of exit gas from the cell. Initially, during the test, the air flow rate was set at 0.035 cubic feet per minute (c.f.m.). Within 15 minutes, that portion of the cell (Section 1) nearest the entry of air began to register a rising temperature on the temperature recorder. Heat was then applied to the outside of Section 1 of the test cell with an electric heating element, which also contained a thermocouple, to maintain the outside and inside temperatures the same. Any unbalance in temperature was registered as an unbalance on a microammeter. By this means the temperature difference between the outside and inside wall of the test cell probably did not exceed 7° F. The same procedure was used with the remainder of the test cell sections (total of fourteen sections), but no heat was applied until the inside of test cell section was hotter than the outside.

After 30 minutes, the air flow rate was increased to 0.055 c.f.m. About three hours later, the air flow rate was increased to 0.070 c.f.m. This last air flow rate increase showed an increase in the rate of temperature rise within the test cell and by this time temperatures in excess of 400° F. were indicated within Section 2 of the test cell. The air flow rate was then increased to 0.103 c.f.m. and subsequently to 0.200 c.f.m. and maintained at this rate for the remainder of the test (total of about 14 hrs.). Sections 1 and 2 of the test cell indicated temperatures therein in excess of 1000° F. The rest of the test sections indicated temperatures between 780° F. and 910° F. During this experiment, the normal yield of recovered oil was also obtained.

EXAMPLE NO. 2

Other investigations relative the initiation of in situ spontaneous combustion employing linseed fatty acids together with dimethylaniline and cobalt naphthenate in the presence of crude oil and turpentine indicated that relatively high temperatures indicative of in situ spontaneous combustion could be obtained within a relatively short time. The following admixtures exhibited a marked increase in temperature, above 200° F., within a relatively short period of time, less than about 7 hours: (1) an admixture comprising 95% by volume linseed fatty acids plus 5% by volume crude oil (20° A.P.I. West Columbia); (2) an admixture comprising 90% linseed fatty acids and 10% crude oil; (3) an admixture comprising 80% linseed fatty acids and 20% crude oil; (4) an admixture comprising 17.6% crude oil, 70.6% linseed fatty acids and 18.8% gum turpentine; (5) an admixture comprising 11.8% gum turpentine and 88.2% crude oil.

EXAMPLE NO. 3

In the test the same experimental procedure set forth with rspect to Example 1 was employed, save that 500 ml. of raw linseed oil to which had been added 5 ml. of 6% cobalt naphthenate and 5 ml. of dimethylaniline were employed. In this test after ignition, the in situ combustion proceeded in a normal manner and within a relatively short time (8 hours) Section 4 of the test cell exhibited a temperature of 940° F. At this time the test was concluded since it was indicated that spontaneous in situ combustion had occurred and that the in situ combustion process was well underway.

An examination of the test data observed with respect to the tests set forth in Examples 1, 2 and 3 indicated that at the beginning of the spontaneous in situ combustion operation, an excessive amount of air flow might remove heat from the sand mass undergoing test more rapidly than the heat could be generated therein by spontaneous combustion. As the temperature increased, however, e.g., above about 400° F., preferably at about 600° F., the rate of air flow into the test cell could be substantially increased, such as about twofold that used at 500° F., about threefold that used at about 400° F. and about fourfold that used at about 200° F.

EXAMPLE NO. 4

Further spontaneous in situ combustion tests employing commercially available high iodine number (in excess of 130) fatty oils, acids and alcohols were carried out. From these tests it was observed that the linseed fatty acids, primarily an admixture comprising oleic, linoleic and linolenic acids, were the most reactive of these materials tested. Temperatures in the test cell in the range 240°–260° F. were reached easily with air at normal pressures and within a relatively short time, about 10 hours. Of the unsaturated fatty alcohols, best results with respect to the initiation of spontaneous in situ combustion were obtained with those alcohols which have as an impurity its corresponding acid. The fish oils tested also exhibited in situ spontaneous combustion. The following materials were tested: linseed fatty acids (Iod. No. 180 min.), chinawood fatty acids (Iod. No. 158–165), putty oil (Iod. No. 150–180), LCP fish oil (Iod. No. 170–195), C_{18} unsaturated alcohols (Iod. No. 173), C_{20-22} unsaturated alcohols (Iod. No. 181).

EXAMPLE NO. 5

In another test a Dewar flask was packed with absorbent cotton soaked with catalyzed raw linseed oil. During the test the temperature within the flask after a period of about 60 hours of air flow therethrough rose to a value much above 400° F. and cotton within the flask was badly charred.

EXAMPLE NO. 6

Additional tests employing substantially pure oxygen instead of air and various sand pack compositions were carried out in a manner similar to that set forth in connection with Example 5. The sand pack compositions tested for the initiation of spontaneous in situ combustion are set forth in accompanying Table I.

Table I

Charge	Test No.					
	1	2	3	4	5	6
Galveston sand, grams	700	700	700	700	700	700
Boiled linseed oil, ml	65	------	------	------	60	------
Raw linseed oil, ml	------	65	------	60	------	------
6% Co naphthenate, ml	------	1	------	0.8	------	------
Dimethylaniline (DMA), ml	------	1	------	0.8	------	------
Gum turpentine, ml	10	10	------	------	------	------
20° API crude+.01% vanadium naphthenate, ml	------	------	75	------	------	------
20° API crude+2% ammonium vanadate, ml	------	------	------	------	------	75

Tests 3 and 6 did not give evidence of spontaneous in situ combustion. Two of the sand packs (catalyzed raw linseed with turpentine and boiled linseed oil with gum turpentine) gave in situ combustion temperatures well above 200° F. When the more volatile components thereof had vaporized and formed an explosive mixture within the test cell, in both cases the vacuum flasks containing the sand packs were shattered upon explosion.

Further experimentation has revealed taht the following mixtures will ignite readily for in situ combustion when injected into formations containing crude oil.

(1) Raw linseed oil	98% by wt.
Typical properties:	
Saponification value	189–195
Iodine value	170–190
Acid value	4 max.
N,N-dimethylaniline	1% by wt. (commercial).
6% Cobalt naphthenate	1% by wt. (drier grade).

(2) Same as above except that aniline is substituted for N,N-dimethylaniline.

(3) Water white distilled linseed fatty acids	98% by wt.
Typical properties:	
Saponification value	197–204
Iodine value	180-min.
Acid value	197–204
N,N-dimethylaniline	1% by wt.
6% Cobalt naphthenate	1% by wt.

(4) Same as above except that aniline is substituted for N,N,-dimethylaniline.

On the other hand, there has been no indication of in situ combustion when the following mixtures were used, leading to the presumption of lack of ignition thereof.

	Percent
(1) Isano oil	[1] 100
(2) Isano oil	98
N,N-dimethylaniline	1
Cobalt naphthenate	1

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[1] A high iodine value oil containing an acetylenic triple bond.

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. In accordance with one practice of this invention adapted to an in situ combustion operation employing a plurality of wells, an air injection well and an oil production well, a fracture is created between these wells, preferably by means of hydraulic fracturing, thereby creating a zone of high permeability between these wells. This high permeability zone is then partially filled with a spontaneous in situ combustion agent in accordance with this invention and spontaneous in situ combustion initiated therein.

The subject invention may be practiced also in connection with a single well for well remedial treatment since by following the practice of this invention, sandy or incompetent formations are consolidated. Moreover, the practice of this invention is particularly applicable to a single well in situ combustion treatment operation as disclosed in coassigned Patent No. 2,906,340, issued to Gerhard Herzog on September 29, 1959, the disclosure of which patent is incorporated herein by this reference. In this patent, 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, wherein is disclosed the introduction of a hydrocarbon oil into an injection well prior to the introduction of an oxidizable liquid mixture.

Although considerable emphasis has been placed in this disclosure on the use of unsaturated fatty acid compounds (linseed oil, linseed oil acids and the like) and unsaturated aliphatic compounds containing at least 16 carbon atoms, there may be employed in the practice of this invention other materials which suitably undergo spontaneous combustion, such as unsaturated aliphatic compounds and hydrocarbons containing as low as 5 carbon atoms per molecule and which may contain in addition to carbon and hydrogen atoms other atoms such as nitrogen and/or sulfur and/or phosphorus and/or oxygen.

In a recapitulation of the preceding disclosure, reference is made to the copending, coassigned application for patent, Serial No. 863,044, filed December 30, 1959, by Charles D. Woodward and Billy H. Towell, now U.S. Patent No. 3,126,960, and to the coassigned Patent No. 3,019,838, issued February 6, 1961 to Don L. Harlan, Joel A. Battle, Jr. and Joseph C. Allen, the disclosures of which are incorporated herein. In summary, the disclosures of the above-identified application and the patent are directed to a method for the completion of a well bore involving the setting of casing and production tubing housed in the casing and with a packer between the tubing and casing, the end of the tubing being adjacent the bottom of the bore hole, displacing oil in the well bore with water so that the oil-water interface is above the final packer seat location, pulling the tubing and packer up the bore hole and setting the packer below the oil-water interface (e.g. approximately 50 ft. above the petroleum bearing formation) with the open end of the tubing being located adjacent the bottom of the petroleum bearing formation, after which the casing-tubing annulus is filled with water under pressure to help hold the packer seated. To initiate ignition, air receptivity and/or permeability are established, after which the well bore is purged with nitrogen and then ignition chemicals are displaced to the formation with nitrogen followed by air injection at reduced rates, increased later after ignition has been accomplished to continue in situ combustion.

In a representative operation, a minimum air injection rate of 1,000 M s.c.f.d. to establish receptivity and/or permeability in the formation will be maintained until the injection pressure has been stabilized for at least one half hour, stabilization being considered to have been reached when the pressure decrease is not more than 20 p.s.i.g. per hour.

Thereafter, two volumes of nitrogen will be injected into the well bore, the volume of the nitrogen being determined by the capacity of the production tubing string and the capacity of the well bore annular spacing below the packer.

Then a volume of ignition chemicals are displaced into the well bore with nitrogen, the volume of chemicals being used at an average rate of one 55 gallon drum for each 3 to 4 feet of pay thickness, while the volume of nitrogen used to displaced the chemicals into the well bore and to purge the chemicals into the well bore will depend upon the pressure required for each well. A sufficient volume of nitrogen will be injected to establish receptivity of the nitrogen to the formation at a decreaseing pressure gradient.

Then, to initiate ignition and in situ combustion air injection will be at the rate of 200 M c.f.d. for 8 hours, 300 M c.f.d. for 8 hours and then, as required, an increase to about 1.5 million cubic feet per day at an injection pressure of 200 p.s.i.

It should be noted that in a 2-directional line drive projection, there may be a departure from linearity, and altering the injection rates in the several injection wells can overcome or mitigate such possible undesirable behavior, and a better sweep efficiency would be obtained.

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

We claim:

1. In a thermal recovery method of treating a permeable petroleum bearing underground formation penetrated by an injection well and a production well, the steps including establishing a zone of receptivity in said formation adjacent said injection well by flowing air therethrough purging said injection well by an inert gas, introducing into said formation through said injection well a liquid mixture comprising an unsaturated aliphatic organic compound comprising only carbon, hydrogen and oxygen atoms and containing at least 16 carbon atoms per molecule and an organic nitrogen base as an oxidation promoter by displacement by an inert gas, subsequently introducing a fluid into said formation containing the liquid mixture introduced therein comprising free oxygen for spontaneous reaction with said unsaturated aliphatic organic compound therein raising the temperature of said formation adjacent said injection well for ignition thereof with conversion of said mixture introduced into said formation from liquid form, and thereafter flowing air through said zone of receptivity in said formation at a substantially higher rate than that of the subsequently introduced fluid to effect in situ combustion therein.

2. A method in accordance with claim 1 wherein said unsaturated aliphatic organic compound is selected from the group consisting of fatty acids, fatty alcohols and fatty oils.

3. In the method of initiating in situ combustion in a permeable petroleum bearing underground formation traversed by a bore hole, the steps including establishing a zone of receptivity in said formation by flowing air therethrough, providing an inert gas to said formation through said bore hole, introducing into said formation a fluid mixture including an unsaturated non-hydrocarbon oil having an iodine number in excess of 100 and an organic nitrogen base as an oxidation promoter by displacement by an inert gas, subsequently introducing into said formation through said bore hole a stream of an oxygen-containing gas for a period of time sufficient to increase the temperature of said underground formation for ignition with conversion of the introduced mixture from liquid form, and flowing air into said zone of receptivity at a substantially higher rate than that of the subsequently

introduced stream of gas to initiate in situ combustion of petroleum within said formation, said organic nitrogen base being dimethylaniline.

4. In the method of initiating in situ combustion within a permeable petroleum bearing underground formation traversed by a bore hole, the steps comprising establishing a zone of receptivity in said underground formation adjacent said bore hole by flowing air therethrough, providing an inert gas to said bore hole, introducing into said formation through said bore hole a liquid mixture comprising a petroleum solvent, a drying oil having an iodine number in excess of 100, and an organic nitrogen base as an oxidation promoter by displacement by an inert gas, and subsequently introducing air at a lower rate into contact with said drying oil of said mixture introduced into said formation for a period of time sufficient to effect conversion of said mixture introduced into said formation from liquid form and then at a higher rate to effect ignition of the petroleum in said formation and thereby to initiate in situ combustion within said formation.

5. In the method as defined in claim 4, said solvent being turpentine, said drying oil being linseed oil, said organic nitrogen base being dimethylaniline, and said inert gas being nitrogen.

6. The method of initiating in situ combustion within a permeable petroleum bearing underground formation penetrated by at least an injection well comprising forming a zone of receptivity in said underground formation by flowing air therethrough, purging said injection well by an inert gas, introducing into said formation a liquid mixture comprising an unsaturated aliphatic organic compound containing at least 16 carbon atoms per molecule, an organic nitrogen base for the promotion of oxidation, a petroleum solvent, and an oxidation catalyst by displacement by an inert gas, subsequently introducing through said injection well into said formation exposed to said liquid mixture a gaseous stream containing free oxygen for a period of time sufficient to increase the temperature of the treated formation by oxidation of said organic compound therein with conversion from liquid form for ignition of the petroleum in said formation, and flowing air through said zone of receptivity in said formation at a substantially higher rate than that of the subsequently introduced gaseous stream for in situ combustion therein.

7. In the method as defined in claim 6, said unsaturated aliphatic organic compound being selected from the group consisting of fatty acids, fatty alcohols and fatty oils, said petroleum solvent being turpentine, said oxidation catalyst being cobalt naphthenate, and said inert gas comprising nitrogen.

8. In the method of initiating in situ combustion in a permeable petroleum bearing underground formation penetrated by an injection well and a production well, wherein prior to the initiation of the in situ combustion there is introduced into said formation through said injection well a liquid mixture of an unsaturated aliphatic non-hydrocarbon compound containing only carbon, hydrogen and oxygen and having at least 16 carbon atoms per molecule together with an oxygenation catalyst, said liquid mixture being capable of spontaneous oxidative reaction with air at the temperature and pressure of said underground formation with the liberation of heat, and wherein this is followed by the introduction of air through said injection well into said formation into contact with said liquid mixture for effecting in situ combustion of petroleum within said formation, the improvement which comprises, following the introduction of said liquid mixture, introducing a gaseous fluid selected from the group consisting of air and air diluted with an inert gas at a lower rate effective to produce a controlled reaction with said liquid mixture to effect the conversion of said unsaturated compound to mainly gaseous reaction products without explosive violence while liberating insufficient heat to initiate in situ combustion of said petroleum but at the same time liberating sufficient heat to raise the temperature of petroleum and the immediately surrounding formation adjacent the inlet end of said formation to a degree at which further temperature rise of said petroleum and the immediately surrounding formation occurs upon continued passage of said gaseous fluid therethrough, and then continuing the passage of a gaseous fluid selected from said group at a higher rate to sweep said gaseous reaction products resulting from the reaction of substantially all of said introduced unsaturated compound from said inlet end of the said formation before the temperature of petroleum therein reaches in situ combustion temperature, then continuing the flow of said gaseous fluid at a rate to initiate in situ combustion of said petroleum in the formation.

9. In the method in accordance with claim 8, the step of introducing a quantity of a hydrocarbon oil through said injection well into said formation prior to the introduction of said liquid mixture.

10. In the method in accordance with claim 8, the steps of purging said injection well by an inert gas prior to and following the introduction of said liquid mixture.

11. In the method in accordance with claim 8, the flow of said gaseous fluid initiating in situ combustion being at a rate providing 2.3 cubic feet per minute per square foot of area adjacent said inlet end exposed to the heat of reaction of said introduced unsaturated compound, said lower rate being in the range of ¼ to ⅕ thereof.

12. In the method in accordance with claim 8, said lower rate being in the range of 200,000 to 300,000 cubic feet per day, the rate of flow of said gaseous fluid initiating in situ combustion being in the range of four to five times as much.

References Cited by the Examiner

UNITED STATES PATENTS

2,793,697	5/57	Simm et al.	166—39
2,818,118	12/57	Dixon	166—11
2,863,510	12/58	Tadema et al.	166—38
3,019,838	2/62	Harlan	166—39
3,026,937	3/62	Simm	166—11 X

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