

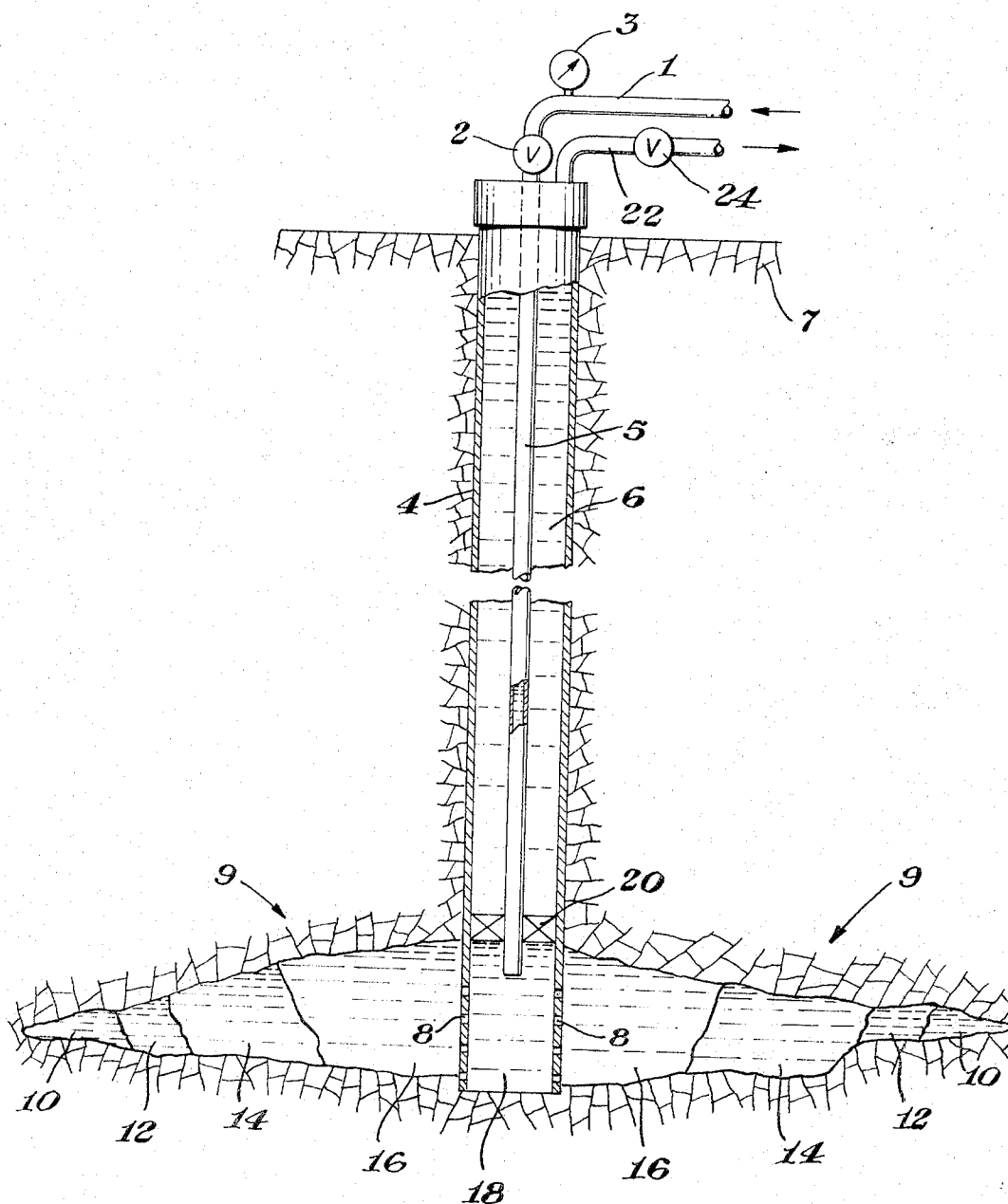
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WELL STIMULATION METHOD EMPLOYING HYPERGOLIC MIXTURES

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WELL STIMULATION METHOD EMPLOYING
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ABSTRACT OF THE DISCLOSURE

The method of stimulating production from a well penetrating a fluid-bearing stratum in a subterranean formation having passageways therein, employing a fuel and an oxidizing agent which consists essentially of (1) providing in the well a liquid selected from the class consisting of non-combustible liquids and relatively unreactive fuels; (2) injecting an oxidizing agent into the wellbore, said agent being preceded by a spacer selected from the class consisting of solid resilient spacer plugs, non-combustible liquids, and such plugs and non-combustible liquids conjointly in combination when a fuel is employed in Step (1); (3) injecting a relatively unreactive liquid fuel into the wellbore; (4) injecting a relatively reactive fuel into the wellbore; and (5) injecting a displacing liquid into the wellbore at sufficient pressure to force liquids from the wellbore into the formation in a state of sufficient turbulence to intermix injected liquids and bring some oxidizer and some relatively reactive fuel into intimate contact to form hypergolic mixtures which spontaneously detonate producing heat, pressure, and added turbulence to effect further intermixing of oxidizing agent and relatively unreactive fuel at the detonating conditions thereof whereby a series of detonations and explosions ensue rubblizing and fracturing the formation.

The invention relates to improving production of a fluid from a subterranean formation penetrated by a well.

Fluids, e.g. water, brine, oil, and gases, are commonly produced from subterranean reservoirs via wells drilled thereinto. Production of a fluid from a subterranean formation requires (1) a higher pressure in the formation than at the wellhead (which may exist naturally but is usually required to be induced as by providing a pump or by introducing a gas or liquid to increase the pressure on the fluid in the formation or by in situ combustion of formation hydrocarbons), (2) assured communication between the formation fluid in place and the wellbore. Such communication is directly related to a property of reservoir rock known as permeability.

Permeability varies greatly from formation to formation and even within the same formation due to a number of conditions, particularly such geologic conditions as intrusions and the like. For the purpose of improving communication in a subterranean formation such treatments as acidizing, hydraulic fracturing, and explosive fracturing are employed.

The invention contemplates an improved explosive fracturing method which provides improved fluid communication in a formation.

The invention is a method of stimulating production of fluid from a fluid-bearing formation penetrated by a wellbore, which contains at least some passageways therein. Therefore, if no natural fissures or fractures or etched channels from a prior treatment exist, passageways must be provided, as by hydraulic fracturing, acidizing, or conventional explosions, prior to the steps of the invention. Such fractures or channels, when not already present, may be provided as a separate step, or following the steps of the invention by forcing liquid employed during treatment

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back into the formation at greater than fracturing pressure.

In brief, the invention is carried out by (1) providing, in a fractured or naturally permeable formation penetrated by a well, a liquid which is either non-combustible (will not burn) or is combustible (will burn, i.e. a fuel) but is relatively unreactive (as subsequently defined); (2) injecting a liquid oxidizing agent into the wellbore of the well (which is preceded by a spacer when a relatively unreactive fuel is employed in Step 1); (3) injecting into the wellbore a relatively unreactive liquid fuel; (4) injecting down the wellbore a relatively reactive fuel which forms a hypergolic mixture when in contact with the oxidizing agent employed, at sufficient pressure (preferably provided by injecting a displacing liquid down the wellbore) to force at least some of each of the liquids so injected back into the passageways of the formation, the accompanying turbulence being sufficient to intermix at least some of the relatively active fuel with at least some of the oxidizing agent to make a hypergolic mixture (i.e. one which spontaneously detonates) and to intermix some of the oxidizing agent with some of the relatively unreactive fuel to provide additional combustible mixture which is ignited by the spontaneously detonated hypergolic mixture to produce a series of detonations and explosions well back in the formation.

The term "non-combustible" as used herein, means not ignitable, detonatable, or otherwise reactive with oxygen even in the presence of an oxidizing agent at advanced temperatures or in the presence of extrinsic igniters or detonators at the conditions of the level being treated. Non-combustible liquids are water, brine, and CCl_4 .

The term "relatively reactive fuel," as used herein, means that the fuel so described forms a self-detonating or self-igniting mixture when admixed with the oxidizer employed, at the level of the formation being treated. The term "relatively unreactive fuel," is the corollary thereof, i.e., it means that a fuel so described does not form a spontaneous or self-igniting or self-detonating mixture when admixed with the oxidizer present at the level being treated, but does detonate or ignite in the presence of an oxidizer upon contact with already detonated or ignited fuel.

The word "hypergolic," as used herein, is that quality or property of a fuel and oxidizer mixture which detonates or ignites spontaneously at the existing ambient conditions at the level of treatment (i.e. ignites or detonates without the aid of an extrinsic detonating or igniting agent or means when intermixed or brought into contact with each other). Accordingly, as used herein, a hypergolic mixture results when the oxidizer and relatively reactive fuel come into intimate contact with each other under conditions of pressure and temperature to result in spontaneous combustion.

The means of injection of the liquids employed in the practice of the invention are those commonly used in subterranean formation treatments, e.g., oil well stimulation treatments, employing high velocity pumps suitably positioned in proper piping arrangements which are provided with proper flow control and pressure indicator means and which lead from supply sources thereof to the wellhead and there are suitably connected for subsequent injection of the treating liquids down the wellbore to the desired level.

In the practice of the invention, the liquid provided in the step identified as (1) may be any liquid which is either non-combustible or relatively unreactive, as defined above. It may be water, brine, or a relatively unreactive fuel or such liquid emulsified or gelled. The water, brine, or relatively unreactive fuel may already be in the formation. If not already so present, it is injected thereinto. When a

non-combustible liquid is employed in Step (1), then the injection of the liquid oxidizer of Step (2) may immediately follow. In some instances, a formation to be treated has present therein a relatively reactive crude oil which means (as explained hereinabove) one which forms a hypergolic mixture when admixed with the oxidizer agent employed. Among such crude oils are those having an unusually high percentage of unsaturated or branched hydrocarbons. When such relatively reactive fuel is present, there must be provided, prior to Step (2), a non-combustible liquid to serve as a spacer liquid, which is injected in sufficiently large amounts to prevent premature intermixing of the relatively reactive fuel already in the well with oxidizer subsequently injected.

The oxidizer employed in Step (2) of the invention is concentrated nitric acid or fuming nitric acid.

Illustrative of the relatively unreactive fuels (as defined above) employed in the invention may be any one or mixture of a number of fuels which do not make a hypergolic mixture when admixed with the oxidizing agent employed, predominant among which are kerosene, diesel oil, gas oils, crude oil, nitroalkanes, and the like, and mixtures thereof.

The relatively reactive fuel to employ (as defined above) includes certain alcohols, particularly furfuryl alcohol, and amines, particularly aniline. It is recommended that, prior to treatment according to the invention, that the formation be fractured. It is also recommended that the well penetrating the formation be provided with a string of tubing.

The preferred method of carrying out the invention on a formation which already contains passageways therein and is penetrated by a well provided with a string of tubing comprise the following steps: (1) Inject a relatively unreactive fuel down the string of tubing, such fuel (as above defined) forming a non-hypergolic mixture when subsequently admixed with the oxidizer employed. (2) Inject either a non-combustible liquid such as water, brine, or carbon tetrachloride, to serve as a spacer liquid, into the string of tubing, or insert a resilient rubber or plastic plug which can be moved along the tubing by the pressures employed but yet will retain its relative position as it passes down the tubing, or employ both a spacer liquid and plug. (3) Inject concentrated nitric acid or fuming nitric acid into the wellbore. (4) Inject a relatively unreactive fuel, e.g. nitropropane, into the wellbore, which may be more of the same fuel used in Step (1) or a different one and, of course as defined, must form a non-hypergolic mixture with the oxidizer, at the level of treatment. (5) Inject a relatively reactive fuel, i.e., one which forms a hypergolic mixture when brought into contact with the oxidizer present, among such fuels being aniline, furfuryl alcohol, the xylenes, benzene, or highly unsaturated and/or highly branched liquid hydrocarbons. The liquids thus injected are maintained in a spaced-apart and, accordingly, unmixed state in the wellbore. (6) Inject a displacing liquid, e.g. water, brine, diesel oil, crude oil, kerosene, or the like down the wellbore in sufficient quantity and at sufficient pressure to force at least some of the oxidizer and at least some of the relatively reactive fuel into the formation to cause intermixture thereof in the formation, the mixtures so formed (being hypergolic) detonating and creating turbulence which, in turn, brings some of the oxidizer into contact with the relatively unreactive fuel, which under the resulting conditions of heat and pressure also detonates, resulting in a series of high velocity explosions which shatters and rubblizes adjacent portions of the formation.

When both separatory resilient plastic or rubber plugs and an inert liquid are employed as a spacer, such resilient separating plugs may be used between all liquid employed in the treatment to insure separation of the liquids during injection until the oxidizer and at least some of the relatively reactive fuel are in the formation.

Reference to the annexed drawing shows a well pene-

trating a formation during a treatment at the stage just prior to applying sufficient pressure on the displacing liquid to force treating liquids into the formation and cause intermixing and detonation therein.

The well there shown is provided with liquid supply line 1 equipped with valve 2 and pressure gauge 3, casing 4, and tubing 5 thereby providing annulus 6 between the tubing and casing. The well penetrates formation 7. Perforations 8 are shown at stratum 9 where treatment is desired. A single fracture (enlarged for purposes of illustration) in stratum 9 shows the presence of the liquids which have been injected according to the invention just after entrance into the formation but prior to applying the final pressure on the displacing liquid to force the components of the hypergolic mixture into the formation with the inherent accompanying turbulence resulting in intermixture thereof. The liquids in the fracture are identified as follows: 10 is a non-combustible liquid or preferably a relatively unreactive fuel; 12 is the oxidizing agent; 14 is a relatively unreactive fuel (which may or may not be the same type as 10 where a fuel is used in Step 1); 16 is a relatively reactive fuel; 18 is a displacing liquid. Packer 20 in annulus 6 provides a means of controlling pressure in the stratum being treated. Discharge line 22, equipped with valve 24, leads from annulus 6 for outflow of liquid, e.g. displacing liquid used in the treatment.

The relative positions of the liquids in the stratum, as shown in the drawing, are somewhat idealized for purposes of illustration. Limited intermingling of adjacent liquids, e.g. oxidizer and relatively unreactive fuel, likely occurs during passage through the perforations. Such intermingling is desirable. Any intermingling of oxidizer and relatively reactive fuel which are non-adjacent liquids during injection, before such liquids are deep in the stratum, is undesirable and is prevented in the practice of the invention by employing an appropriate amount of a non-combustible spacer liquid, preferably a relatively high viscosity liquid, and desirably also provided with separatory resilient plugs on the lower and upper ends thereof while in the wellbore. Accordingly, as proven by examples, illustrating the invention, explosions do not occur until the oxidizer and a portion of the relatively reactive fuel are well back in the stratum.

It is understood that, following injection of the displacing liquids, the relative positions of the liquids as shown in the drawing will no longer exist but, as a result of turbulence there will first be an intermixing of some of the oxidizer with some of the relatively unreactive fuel and some of the relatively unreactive fuel with some of the relatively reactive fuel followed by intermixing of some of the oxidizer and relatively reactive fuel. The last named intermixing produces hypergolic mixtures which spontaneously explode creating heat, pressure, and relatively violent turbulence throughout the liquids which intermixes the relatively unreactive fuels and oxidizer at detonating conditions. Therefore, there ensues a series of explosive reactions involving both types of fuel resulting in effective fracturing and rubblizing of adjacent portions of the formation.

The invention is not to be confused with known methods of well treatment wherein hypergolic mixtures have been employed. Such methods heretofore have required special mixing equipment. Known methods have also usually produced but one detonation. In the present invention, the reactants are maintained spaced-apart until they are back in the formation at the level at which treatment is desired, whereupon they become mixed, producing a series of detonations as the relatively reactive fuel becomes mixed with oxidizer to produce dispersed hypergolic mixtures which in turn ignites or detonates dispersed mixtures of relatively unreactive fuel and oxidizer. The following examples are illustrative of the practice of the invention:

Example 1

A well penetrating a formation provided with a bottom plug at a depth of 3851 feet and equipped with a casing

provided with six jet-hole perforations at a depth of 3839 feet was to be treated. The formation had previously been fractured, employing 640 barrels of crude oil, containing 31,000 pounds of flint sand in suspension, at a rate of injection of 19 barrels per minute. Production just prior to treatment according to the example was ascertained.

Treatment was carried out as follows:

(1) Twenty-one barrels of a mixture of crude oil and kerosene were pumped down the well and portions of the mixture forced into the formation.

(2) This was followed by pumping 2½ barrels of brine, as a spacer liquid, into the wellbore.

(3) One hundred and sixty gallons of red fuming nitric acid were then pumped into the wellbore.

(4) Thirty-five gallons of gelled water as a second spacer liquid were then pumped into the wellbore.

(5) One hundred and fifty gallons of 2:1, by volume, 2-nitropropane:aniline mixture were then pumped into the wellbore.

(6) Water, gelled by admixture therewith of a natural gum, to serve as a displacing liquid, was then pumped into the wellbore at sufficient pressure to force some of the red fuming nitric acid and relatively reactive fuel into the formation.

Entrance of the fuming nitric acid and the furfuryl alcohol-aniline mixture into the formation and subsequent intermixing thereof was immediately detected by an abrupt increase in pressure, measured at the wellhead, of from 500 to 2250 p.s.i.g., followed by a gradual falling off of pressure. This abrupt change was followed by four other abrupt changes showing the following gauge reading changes, in p.s.i.: 900 to 1600; 1250 to 1850; 1500 to 3250; and from 0 to 5000 (the 5000 p.s.i.g. pressure reading was undoubtedly low because the instrument was unable to record a pressure above 5000 p.s.i.g.). Production after treatment was about twice that prior to treatment.

Example 2

A well having a plugged off depth at 3952 feet was provided with a 4½ inch casing containing six jet-hole perforations at a depth of 3917 feet. It has previously been fractured employing 480 barrels of gelled crude oil containing 35,000 pounds of flint sand suspended therein at a rate of 15.8 barrels per minute. Production at the time of treatment was ascertained.

(1) Twenty-two barrels of a mixture of kerosene and crude oil were pumped down the wellbore and some thereof forced into the formation.

(2) One hundred, twenty gallons of red fuming nitric acid were then pumped into the wellbore.

(3) Thirty-five gallons of gelled water containing thirty pounds of guar gum per 1000 gallons was pumped into the wellbore as a spacer liquid.

(4) One hundred and ten gallons of nitro-propane were then pumped into the wellbore.

(5) One hundred and ten gallons of aniline were pumped into the wellbore. Thereafter a flush or displacing liquid consisting of brine was pumped into the wellbore at sufficient pressure to force some of the aforementioned component of the hypergolic mixture (oxidizer and relatively reactive fuel) into the formation. A sudden rise in pressure at the wellbore of from 1750 to 3100 occurred almost immediately after beginning the injection of the displacing fluid.

(6) Thirty-nine barrels of the displacing liquid, in all, were pumped into the wellbore. The well was shut in for 24 hours. Thereafter the tubing and packer were withdrawn from the well. Production following the treatment represented approximately twice the barrels per day, compared to the production prior to the treatment.

Reference to the above examples shows that the well is improved and production increased by treatment in accordance with the invention.

Having described our invention what we claim and desire to protect by Letters Patent is:

1. The method of stimulating production from a well penetrating a fluid-bearing stratum in a subterranean formation having passageways therein, employing a fuel and an oxidizing agent which consists essentially of (1) injecting a liquid down the well at sufficient pressure to fracture the formation; (2) providing in the well a liquid selected from the class consisting of non-combustible liquids and relatively unreactive fuels; (3) injecting an oxidizing agent into the wellbore, said agent being preceded by a spacer selected from the class consisting of solid resilient spacer plugs, non-combustible liquids, and such plugs and non-combustible liquids conjointly in combination when a fuel employed in Step (2); (4) injecting a relatively unreactive liquid fuel into the wellbore; (5) injecting a relatively reactive fuel into the wellbore; and (6) injecting a displacing liquid into the wellbore at sufficient pressure to force liquids from the wellbore into the formation in a state of sufficient turbulence to intermix injected liquids and bring some oxidizer and some relatively reactive fuel into intimate contact to form hypergolic mixtures which spontaneously detonate producing heat, pressure, and added turbulence to effect further intermixing of oxidizing agent and relatively unreactive fuel at the detonating conditions thereof whereby a series of detonations and explosions ensue rubblizing and fracturing the formation.

2. The method according to claim 1 wherein a non-combustible liquid is employed in Step (2).

3. The method according to claim 1 wherein a relatively unreactive fuel is employed in Step (2) and a spacer is positioned in the wellbore following Step (2) and prior to injecting the oxidizing agent in Step (3).

4. The method according to claim 3 wherein the spacer is a liquid having a viscosity of at least 50 centipoises.

5. The method according to claim 3 wherein at least one resilient solid plug is positioned in the wellbore between Steps (2) and (3) to supplement the spacer liquid.

6. The method according to claim 3 wherein the liquid employed in Step (2) is a natural formation liquid already present therein.

7. The method according to claim 1 wherein a spacer, selected from the class consisting of solid resilient plugs and non-combustible liquids, is employed between Step (4) and Step (5).

8. The method according to claim 1 wherein the displacing liquid is a brine.

9. The method according to claim 1 wherein said oxidizer is selected from the class consisting of concentrated nitric acid and fuming nitric acid.

10. The method according to claim 1 wherein the relatively unreactive fuel is selected from the class consisting of kerosene, diesel oil, gas oils, crude oil, nitroalkanes, and mixtures thereof.

11. The method according to claim 1 wherein the relatively reactive fuel is selected from the class consisting of furfuryl alcohol, aniline, xylenes, benzene, highly unsaturated liquid hydrocarbons, and highly branched liquid hydrocarbons.

12. The method according to claim 1 wherein the displacing liquid of Step (6) is injected at a pressure sufficient to fracture the formation.

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