

1

3,104,706

WELL FRACTURING

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The invention pertains to increasing the flow of a fluid from a fluid-bearing subterranean formation penetrated by a well by the use of an explosive mixture.

Fluids, e.g., oil or gas, contained in the subterranean formation, are usually obtained by drilling a well into the formation and providing a pressure differential to force the fluids from the formation to the earth's surface.

Fluid is contained in spaces between the solid portions of the formation, such spaces varying greatly in size and shape and are usually described as pores, cavities, channels, and the like. The ratio by volume of such spaces to the volume of the formation is known as porosity. The extent to which the spaces, e.g., pores, are interconnected and thereby provide passage of fluids to the formation is known as permeability.

The flow of a fluid from a formation by providing a pressure differential is often greatly hampered and sometimes completely stopped because the fluid flow from appreciable, and sometimes extensive, portions of the formation is obstructed by more or less impermeable intervening rock or other compact solids, thus blocking free flow of the fluid to the well.

Various methods of stimulating the flow of fluids from wells penetrating fluid-bearing formations which are at low levels of production include such methods as acidizing, hydraulic fracturing, and detonating or igniting an explosive composition which has been positioned in or injected down the well.

Acidizing consists essentially of injecting an aqueous solution of an acid, usually hydrochloric acid, often containing an inhibitor to metal attack, into a well requiring treatment. The acid reacts with the formation and causes cavities and channels to be created in the formation. Hydraulic fracturing generally refers to injecting a liquid, often a thickened oil or an oil-water emulsion, and preferably containing suspended particulated solids as a propping agent, e.g., sand, into a formation to effect fracturing of the formation. Acidizing and hydraulic fracturing may be combined by employing an acidic fracturing fluid.

Stimulating the flow of a fluid from a formation by the use of an explosive includes what is generally referred to as "shooting" the well with such an explosive as nitroglycerine, which has long been employed for such purposes.

Acidizing is inherently limited to formations composed substantially of a carbonate-containing rock, e.g., limestone or dolomite. Hydraulic fracturing requires elaborate pumps, and blending equipment when sand is employed, to provide the high pumping rates required for effective hydraulic fracturing. Furthermore, hydraulic fracturing is generally difficult to direct into the portions of the formation where improved communication is most desired.

The use of liquid explosives such as nitroglycerine is

2

fraught with the dangers associated with handling them. Solid explosives such as nitrocellulose and dynamite are detonated, in the wellbore itself and, therefore, are definitely less desirable than an explosive composition which could be forced back into the formation prior to detonation.

Fracturing a subterranean formation penetrated by a well by injecting down the well and into the formation a mixture of liquids and subsequently detonating the mixture is described in copending application S.N. 838,051, filed September 4, 1959, now Patent No. 3,075,463. The liquid mixture first injected down the well according to that application consists of an oxidizing agent, e.g., fuming nitric acid, and a reducing agent, e.g., a nitroalkane such as 2-nitro-propane, the reducing agent usually being referred to therein as a fuel. The mixture of oxidizing and reducing agents is subsequently detonated either by a shock or heat type igniter e.g., heat produced by passing an electric current through a conductor in contact with said emulsion or by injecting into the well and into contact with at least a portion of the mixture already injected into the well a liquid igniter which chemically ignites the mixture in the formation. Chemical detonation or ignition of the liquid mixture thus injected into the formation is the preferred way of practicing the invention. The igniter is usually aniline, furfuryl alcohol, or a mixture thereof. However, a number of other effective liquid igniters are described in said application.

Although the method of fracturing described in application S.N. 838,051 represents a definite improvement in the fracturing of wells, the reducing agent and oxidizing agent selected therein are limited to those which do not immediately separate into phases upon admixture together. For example, the use of such fuels (reducing agents) as gas oils, diesel fuel, and kerosene are not fully satisfactory when employed with the preferred oxidizing agent named therein, viz., fuming red nitric acid or fuming white nitric acid, due to their immiscibility with the acid.

A need, therefore, exists for an improved well fracturing method employing a liquid mixture which is safe for necessary handling, which readily penetrates a subterranean formation, which employs a readily available fuel with a highly effective and a readily available oxidizing agent, which is a substantially stable one-phase liquid for a sufficient time to inject it into a well and back in the formation, and which is detonatable upon being subjected to shock or heat or to contact with a liquid chemical igniter.

The invention consists of injecting down a well penetrating a subterranean formation an emulsion consisting of an oxidizing agent, a reducing agent which hereinafter will usually be referred to as a fuel, and an emulsifying agent and subsequently detonating or igniting the emulsion thus injected by subjecting the emulsion to shock or heat, or by injecting down the well and into contact with at least a portion of the emulsion a liquid chemical which produces a hypergolic composition when thus brought in contact with the emulsion. An explosion is thus produced which propagates through the remaining emulsion, which has permeated the formation, producing fractures in the formation.

A preferred embodiment of the invention includes the step of incorporating into the emulsified oxidizing and

3

reducing agent mixture an activator selected from the class consisting of aliphatic esters or mixtures of such esters containing between 4 and 14 carbon atoms per molecule or nitric acid solutions of inorganic oxygen-containing salts that readily yield reactive oxygen when present in the hypergolic composition.

If, desired, the treatment of the well in accordance with the invention may be either preceded by or followed by conventional fracturing or, if the well is already fractured, it may be treated according to the invention and then, if desired, again fractured by hydraulic fracturing. It has been found that combining conventional fracturing with the improved fracturing method of the invention has resulted in particularly improved production from wells so treated.

The reducing agent employed in the practice of the invention may be any fuel which does not spontaneously react with the oxidizing agent and is emulsifiable therewith, but which can be ignited or detonated by heat, shock, or chemical means. Illustrative of a reducing agent or fuel to employ are nitroalkanes, nitroaranes, aliphatic alcohols and ethers, suspensions of particulate hydrocarbon solids in a hydrocarbon liquid, alkyl dihalides, and liquid hydrocarbons. The preferred reducing agent, i.e., fuel, is a liquid hydrocarbon such as a petroleum fraction, e.g., diesel oil, gas oil, distillate, naphtha, kerosene, or mixtures thereof.

Oxidizing agents useful in the practice of the invention may be any oxidizing agent that does not spontaneously react with the fuel at conditions found prior to injection into the well. Among such oxidizing agents are liquid halogens, hydrogen peroxide, perchloric acid, nitric acid, and fuming nitric acid. Nitric acid or fuming nitric acid may have admixed therewith concentrated sulfuric acid, or preferably fuming sulfuric acid. Fuming sulfuric acid thus employed usually contains between 15 and 20 percent SO_3 dissolved in concentrated H_2SO_4 . The preferred oxidizing agent to employ is fuming nitric acid, particularly red fuming nitric acid. Red fuming nitric acid consists of an aqueous solution of HNO_3 having dissolved therein NO_2 . Red fuming nitric acid may be prepared by passing NO_2 into nitric acid, preferably concentrated nitric acid, or by reacting an alkali metal nitrate, e.g., KNO_3 with fuming H_2SO_4 . A discussion of fuming nitric acids and their preparation may be found in Mellor's *A Comprehensive Treatise of Inorganic and Theoretical Chemistry*, vol. VIII, page 563 et seq. Concentrated nitric acid usually is considered to be about 68 percent HNO_3 dissolved in water and at that percentage has a stable boiling point. Nitric acid having a concentration of HNO_3 which is appreciably greater than 68 percent is known as white fuming nitric acid. Such white fuming nitric acid usually contains between 85 and 98 percent HNO_3 , the balance consisting of water and up to about 0.5 NO_2 .

The ratio of the oxidizing agent to the fuel is not highly critical but it is recommended that more than enough of the oxidizing agent be present to convert all the hydrocarbons in the fuel to CO , CO_2 , and H_2O .

The emulsifying agent employed in the practice of the invention may be any emulsifier which is capable of forming a stable emulsion between the oxidizer and the fuel. By stable emulsion is meant one that will not stratify appreciably within the time required to inject the emulsion thus made into the well and subsequently detonate the emulsion thus injected. In some well treating operations 10 to 15 minutes might be an adequate time but it is recommended that an emulsifier be employed that will make an emulsion which is substantially stable for at least 30 minutes and preferably for 60 minutes or longer. Preferred emulsifiers to employ in the practice of the invention are gilsonite, asphalt, and tarry residues from coal tar distillations, e.g., quinoline residues. Asphaltum, more commonly referred to as asphalt, is a bituminous semi-solid hydrocarbon mixture thought to have been formed by the evaporation of the more volatile con-

4

stituents therefrom. It is either black or brown in color with a pitchy luster. It is found naturally, often in exposed beds, e.g., those of western United States and Trinidad. Gilsonite or uintaite is a variety of asphalt originally obtained largely in Uinta County, Utah, having superior emulsifying properties for oil-acid mixtures. The amount of emulsifier to employ in the practice of the invention is between 40 and 400 pounds per 1000 gallons of emulsion. The preferred range of emulsifier to employ is between 80 and 250 pounds per 1000 gallons of emulsion.

When an activator, e.g., an aliphatic ester or nitric acid solution of an oxygen-yielding compound, is employed to facilitate the detonation or ignition of the oxidizing and reducing agent mixture it is usually employed in an amount of between about 5 and 20 percent by weight of the emulsion. Among such esters are lower alkyl acetates, butyrates, and laurates. Among such oxygen-yielding compounds are potassium and sodium chlorate, perchlorate, permanganate, and dichromate.

Illustrative of the chemical igniter to employ in the practice of the invention are especially powerful oxidizing or reducing agents. The latter are more commonly employed among which are aniline, alkyl substituted aniline, furfuryl alcohol, dichlorpropene, monochloropropane, ethylenediamine, diethylenetriamine, and alkyl mercaptans. A particularly effective igniter liquid is a mixture of furfuryl alcohol and aniline.

The invention is preferably carried out by admixing an asphalt-type emulsifier with a fuel such as kerosene, in an amount stated above, and then admixing the oxidizing agent, preferably red fuming nitric acid, with the fuel containing the emulsifier, agitating the mixture thus made to form an emulsion, and injecting the emulsion down the well and thence into the formation. If an ester is employed to aid the subsequent ignition, it may be admixed either with the oxidizing agent or the reducing agent or in the mixture of the two and thereby form a part of the emulsion thus injected into the well.

The mixture so injected is then detonated. If a high velocity detonator is employed, e.g., a blasting cap or Primacord (pentaerythritoltetranitrate), such may be placed in the well either before or after the injection of the emulsified oxidizing and reducing agent mixture. If the emulsion is to be ignited by a chemical means, which is the preferred mode of practicing the invention, such chemical igniter is injected down the well and into contact with the emulsion.

The following procedure is one mode of practicing the invention: A predetermined quantity of the emulsion prepared as above is injected down the well by a pumping means, e.g., one similar to that used in acidizing, and a rubber plug is positioned in the wellbore, conveniently near the top thereof. A buffering liquid usually consisting of the fuel employed in the preparation of the emulsion, is then pumped down the well on top of the plug, the plug thereby forced downward until the buffering liquid is all in the wellbore. A second plug is placed in the wellbore in a manner similar to the placement of the first plug. The chemical igniter liquid then is pumped down the well on top of the second plug thereby forcing the plug downward until the igniter liquid is in the wellbore, a third plug is then placed in the wellbore in a manner similar to the placement of the two previous plugs. Thereafter a flush liquid, usually more of the fuel previously employed, is pumped into the well on top of the third plug with sufficient force and in sufficient quantity to force the plugs and the liquids therebelow and therebetween out of position and down into the well whereby the igniter liquid is brought into contact with the explosive emulsion in the bottom of the well and in the adjacent formation, thereby rendering it hypergolic. The ensuing explosion shatters and fractures the formation thereby providing passageways therethrough for fluid from the formation and improving their production therefrom. The technique followed for injecting the mixture of oxidizing and re-

5

ducing agents into the well and subsequently injecting the igniter liquid is largely a matter of the practice preferred. The above mode is set out only as one which has been found to be particularly convenient and effective.

Examples were run to illustrate the practice of the invention employing asphalt type emulsifiers with kerosene and red fuming nitric acid which consisted of 98 to 99.5 percent HNO₃ (balance water) having dissolved therein about 14 percent by weight NO₂. The procedure was as follows: 0.12 gram of the emulsifier set out in Table I was admixed with 1 milliliter of kerosene and the mixture thus made admixed with 4 milliliters of the red fuming nitric acid and emulsified by forcing the mixture thus made through a small aperture in accordance with known emulsifying techniques. The stability of the emulsions thus made was then observed by placing each of the thus made emulsions in a glass, vertically disposed, graduated vessel and observing the length of time required for about 1/2 the emulsion to break and the time required for substantially all the emulsion to break. The time required for breaking of the emulsion is set out in Table I.

TABLE I

Emulsification of Kerosene and Red Fuming Nitric Acid

Volume kerosene—1 ml.
Volume red fuming nitric acid—3 ml.
Weight emulsifier—0.12 g.

Example No.	Emulsifier used	Emulsion breakout in minutes	
		Half	Complete
Blank	None	<0.1	0.1
1	Standard Gilsonite ¹	60.0	120.0
2	Select Gilsonite ²	60.0	120.0
3	Blown Asphalt ³	30.0	60.0
4	Quinoline Residues	5.0	10.0

¹ Standard Gilsonite; American Gilsonite Co.; softening point, 373° F.
² Select Gilsonite; American Gilsonite Co.; softening point, 280° F.
³ Asphalt that has been treated by blowing oxygen gas therethrough. Berry's blown asphalt No. 566; Berry Asphalt Co.; melting point, 270° F.

An examination of the results of Table I shows that a stable emulsion was prepared by adding the emulsifier to the kerosene and thereafter adding thereto the fuming nitric acid and emulsifying. The results further show that gilsonite is superior to blown asphalt or quinoline residues as an emulsifier for use in the practice of the invention.

Emulsions were again prepared following the procedure employed for those set out in Table I except that the emulsifier was added to the fuming nitric acid instead of to the kerosene and the acid-emulsifier mixture thereafter admixed with the kerosene. Emulsions were thus formed which were satisfactory but less stable than those prepared in Table I wherein the emulsifier was added to the kerosene instead of to the fuming nitric acid prior to emulsifying the acid and kerosene.

Emulsions were again prepared following the procedure employed in Table I, placed in a ventilated hood behind a suitable protective wall but which provided observation of the emulsions, and 0.1 milliliter of furfuryl alcohol added to each emulsion by means of a dropper. In all cases very rapid burning of the emulsions occurred thereby showing the hypergolic character of the mixture consisting of the emulsion and the chemical detonator or igniter, viz., furfuryl alcohol.

To show the effect of adding a suitable activator to the emulsion of oxidizing and reducing agents employed according to the invention, prior to detonation, examples were run according to the following procedure: To 0.85 milliliter of kerosene was added, 0.1 gram of the standard gilsonite employed in the examples of Table I and 2.5 milliliters red fuming nitric acid. The mixture was emulsified by passing it through an aperture as in the preparation of the emulsion of the examples of Table I. Thereafter, 0.5 milliliter of one of the esters set out in Table

6

II was added to each of three examples. One of the examples was run as a blank and therefore no ester was added thereto. The emulsion thus prepared containing the ester was placed in a ventilated hood behind suitable protection where it could be observed and a measured quantity of furfuryl alcohol added thereto, dropwise, until ignition occurred. The ester employed, the amount of igniter used, and the length of time of burning are set out in Table II.

TABLE II

Effects of Activators on Burning Rates

Fuel—0.85 ml. kerosene
Oxidizer—2.5 ml. red fuming nitric acid
Emulsifier—0.1 g. standard gilsonite
Igniter—furfuryl alcohol (added dropwise)

Example No.	Activator added	Igniter used in ml.	Burning time in min.
5	None	0.4	2.0
6	0.5 ml. Ethyl acetate	0.3	1.5
7	0.5 ml. Amyl acetate	0.2	1.3
8	0.5 ml. Ethyl laurate	0.2	1.3

Reference to Table II shows that the presence of the aliphatic esters definitely reduced the requirement for the amount of igniter and the time required for the emulsion to burn completely.

The examples of Table II were repeated employing nitric acid solutions containing about 0.5 gram of potassium chlorate, potassium permanganate, or potassium dichromate. The amount of igniter required and rate of burning were similarly affected as when the ester was employed.

Since the burning rate of a combustible mixture is accelerated by increased pressure and the force of an explosion of an explosive mixture is also accelerated by increased pressure, the following examples were run. The procedure employed was as follows: 100 milliliters of 20 to 40 mesh sand (U.S. Standard Sieve Series) were placed in a bomb made of a bull plug provided with a pressure gauge. The bomb was 4 inches in diameter and had a volume of 2000 milliliters. The sand contained 40 milliliters of pore space, i.e., it had a porosity of 40 percent.

The bomb was provided at the top with a means for introducing nitrogen gas and for venting the bomb and with an assembly for introducing liquids consisting of three 1/4 inch diameter pipe lines, two of which merged into an aluminum nozzle prior to entering the bomb, thereby providing for the entrance of only two separate lines into the bomb. Each line had a flow control means therein. Each of the three lines led from a separate supply vessel, each of which was provided with nitrogen gas pressure. Into one supply vessel connected to one of the two merging lines was placed a solution consisting of 12 milliliters of kerosene, 0.6 gram of standard gilsonite, and 0.6 milliliter of amyl acetate and into the supply vessel connected to the other of the two merging lines were placed 30 milliliters of fuming red nitric acid. Into the supply vessel connected to the third line, which entered the bomb directly, were placed 2 milliliters of furfuryl alcohol.

Nitrogen gas pressure was applied to the two supply vessels, one of which contained the organic solution of kerosene, ester and emulsifier and the other of which contained the fuming nitric acid, and the flow control means in the lines were opened simultaneously. The contents of the two vessels were thus simultaneously forced through the nozzle thereby forming an emulsion of the thus merged acid and organic solution as they entered the bomb. Flow through the lines thus employed was then closed, the flow control means in the third line opened, and the furfuryl alcohol forced by nitrogen pressure into the bomb and into contact with the emulsified fuming

nitric acid-kerosene-ester mixture thereby effecting ignition of the mixture. Initial pressure on the system was controlled by regulating the nitrogen gas pressure applied to the furfuryl alcohol vessel. The pressure applied in the examples thus run is set out in Table III together with the effect of such variations in pressure on the ensuing ignition.

TABLE III

Effect of Pressure on Explosive Emulsion

Example No.	Pressure on system in atmospheres	Increase in pressure on ignition in p.s.i.	Resulting reaction
9-----	1	0	Igniter burned partially.
10-----	2	25	Igniter burned completely.
11-----	34	750	Explosion occurred.

The effect of increasing the pressure on the explosive emulsion in accordance with the invention as shown in Table II, is to intensify the explosion which ensues upon detonation. Such intensified explosion emphasizes the enhancing effect of increased pressure on the ensuing reaction. A pressure of 34 atmospheres, it is to be observed, is definitely less than the pressure usually encountered in oil and gas producing formations. Therefore, at the greater pressures usually existing in producing zones, a much more pronounced explosion would result.

A number of advantages can be realized in the practice of the invention, among which are all the advantages of U.S. application S.N. 838,051 are to be realized but in addition thereto: lower grade and more readily available fuel may be employed; emulsifying agents useful in the practice of the invention are procurable at relatively low cost; the use of an activator of the type illustrated by the aliphatic esters reduces the quantity of igniter liquid required and shortens the burning period which is evidence of a more violent reaction and consequently a more shattering and effective fracturing operation on a formation being treated.

Having described the invention, what is claimed and desired to be protected by Letters Patent is:

1. A method of fracturing a subterranean formation penetrated by a well comprising injecting down the well and into the formation a potentially explosive emulsion consisting essentially of a liquid reducing agent selected from the class consisting of nitroalkanes, nitroaranes, alkyl alcohols, alkyl ethers, suspensions of particulate hydrocarbon solids dispersed in a liquid hydrocarbon, alkyl dihalides, and liquid hydrocarbons, (2) an oil-water emulsifying agent, and (3) an oxygen-containing compound which releases oxygen for reaction with the reducing agent at and above the ignition temperature of the reducing agent and subsequently detonating said emulsion in the formation.

2. The method of claim 1 wherein an excess of the oxidizing agent over the stoichiometric amount required to react fully with the reducing agent is employed.

3. The method of claim 1 wherein detonation is effected by means of a high velocity shock-type detonator.

4. The method of claim 1 wherein detonation is effected by passing electrical current through a conductor in contact with said emulsion.

5. The method of claim 1 wherein detonation is effected by injecting down a well and into contact with a portion of said emulsion a liquid chemical which renders said emulsion hypergolic.

6. The method of fracturing a subterranean formation penetrated by a well comprising injecting down the well and into the formation a potentially explosive emulsion consisting of (1) a reducing agent selected from the class consisting of nitroalkanes, nitroaranes, alkyl alcohols, alkyl ethers, and suspensions of particulate hydrocarbon solids dispersed in a liquid hydrocarbon, and alkyl dihalides, and liquid hydrocarbons, (2) an emulsifying agent selected from the class consisting of gilsonite and asphalt, and (3) an oxidizing agent selected from the class consisting of nitric acid red fuming nitric acid, white fuming nitric acid, mixtures of concentrated sulfuric acid and fuming nitric acid, mixtures of fuming sulfuric acid and fuming nitric acid, liquid halogens, hydrogen peroxide, and perchloric acid, and detonating the emulsion thus injected into the well.

7. The method of claim 6 wherein the reducing agent is a liquid hydrocarbon.

8. The method of claim 6 wherein detonation is effected by means of a pentaerythritoltetranitrate cord.

9. The method of claim 6 whereby detonation is effected by injecting down the well and into contact with at least a portion of said emulsion a liquid chemical igniter selected from the class consisting of aniline, alkyl substituted aniline, furfuryl alcohol, ethylene diamine, butyl amine, diethylene amine, dichloropropene, monochloropropane, and mixtures thereof.

10. The method of claim 9 wherein the liquid detonator is a mixture of furfuryl alcohol and aniline.

11. The method of claim 6 wherein the emulsion contains between 5 and 20 percent of an activator selected from the class consisting of aliphatic esters containing between 4 and 14 carbon atoms per molecule and mixtures thereof.

12. The method of claim 11 wherein detonation is effected by a liquid chemical igniter.

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