United States Patent [19]

Roberts

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[54] **METHOD OF FRACTURING A FORMATION USING A LIQUID EXPLOSIVE**

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[21] Appl. No.: **200,860**

Related U.S. Application Data

[62] Division of Ser. No. 860,883, Oct. 27, 1969, abandoned.

[52] **U.S. Cl.** **166/299,** 102/23

[51] **Int. Cl.** **E21b 43/26**

[58] **Field of Search** 166/299, 271, 259, 166/308; 102/23

[56] **References Cited**

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[57] **ABSTRACT**

A liquid explosive is described which has a small critical diameter, is safe to handle, is capable of use in cold climates and yet is compatible with the higher temperatures commonly present in subterranean formations, which includes a nitroparaffin compound having dissolved therein a nitramine explosive, a ballistic modifier and a detonation aid in such proportions that the critical diameter of the explosive is on the order of 1/32 inch. Other constituents may also be added for controlling the consistency and ballistic properties as well as the manufacturing and handling properties of the explosive. A thickening or gelling agent is also preferably added to retain the ballistic modifier as well as any other suspended solids in a uniform dispersion. A method of fracturing well formations for enhancing their productivity, using such liquid explosives, is described.

5 Claims, No Drawings

METHOD OF FRACTURING A FORMATION USING A LIQUID EXPLOSIVE

This is a division of application Ser. No. 860,883, filed Oct. 27, 1969, now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a liquid explosive which is particularly suitable for fracturing a geological formation adjacent a well bore, for bringing in the well or for increasing the productivity of a well which has substantially ceased to produce oil, water or gas, and to a method of using the explosive for that purpose. The liquid explosive, particularly certain embodiments described herein, is suitable for other applications, such as quarrying, expecially where an explosive composition is required which will conform to the formation in which it is placed, which is not adversely affected by oil, water or other geological fluids normally present, and which has a high explosive power. The liquid explosive disclosed herein is especially suited to well fracturing, however, because of its ability to propagate an explosion through a network of narrow fissures in a geopligical formation. The term "narrow fissures" or "fine fissures" as used herein means those fissures which may be created in geopligcal strata adjacent well bores, commonly by hydraulic fracturing, and having widths from approximately ¼ inch down to fractions of a millimeter.

To bring in a well, after it has been drilled it is usally necessary to increase the permeability of the producing formation to stimulate flow in the well. This has commonly been done by "shooting" the well with a nitroglycerin charge, acidizing (in certain types of formations) or hydraulic fracturing. Similarly, when a formerly productive well has ceased to produce, the pay zone may be fractured to reactivate the well. The purpose of fracturing is to increase the permeability of the productive formation, or pay zone, permitting flow from the producing formation into and up the well bore.

Explosive fracturing was originally carried out by placing a nitroglycerin charge in the well bore and detonating it. Such charge may be desensitized nitroglycerin in liquid or gel form or a mixture of pure nitroglycerin and ethylene glycol dinitrate (EGDN). The disadvantages of nitroglycerin, used for many years for this purpose, are many. For example, it is extremely shock sensitive and difficult to handle in transport; all nitroglycerins are too sensitive, for example, to be pumped or poured into a well and must be carefully placed there, either in gel form or as desnesitized liquid. Liquid and slurry explosives other than nitroglycerin have been tried but in general have not been successful, for reasons including instability, segregation of constituents, detonation problems and vulnerability to leaching and dilution by fluids in well bores. Solid high explosives have also been used, but cannot be made to conform to the well bore, let alone the productive formation, and consequently are of limited effectiveness. "Bore shots", as fracturing operations are called when the explosive is placed wholly within the well bore, tend to destroy the bore, and while they do result in exposing more of the surface of the formation to the bore, they do not materially increase the permeability of the formation itself. It has been found tht the fracturing of a large volume of the formation, for optimum increase

in permeability, requires an explosive having a small critical diameter which can be loaded back into the formation itself, permitting it to propagate an explosion through the narrow fissures and crevices of the formation. Nitroglycerine, for example, has been shown to propagate an explosion in fissures as narrow as 1/32 inch, according to Eakin and Miller, "Explosives Research to Improve Flow Through Low Permeability Rock", Paper No SPE 1715 (Third SPE of AIME Drilling and Rock Mechanics Conference, 1967). Other methods limit effective propogation of the explosion to a relatively small radius around the well bore bottom.

2. History of the Prior Art

To overcome these drawbacks, expermients have been conducted for several decades with liquid explosives other than nitroglycerin and with slurry explosives, which are dispersions of solid explosives or of one or more explosive constituents suspended in water or some other medium. Liquid (including slurry) explosives have the advantage of being able to conform to and thus more readily fill the well bore, resulting in greater explosive power. It is important that explosives of this kind be capable of being pressured back into the geological formation adjacent the well bore in order to obtain complete, even and adequate fracturing of the formation and to minimize damage to the well bore and to any casing installed in the well.

A serious problem in liquid and slurry explosives developed to date has been their inability to undergo pressurization into a well formation, and still be capable of consistent and reliable detonation without the necessity of using complex and expensive detonating systems. In certain instances indispensible constituents of the explosive are filtered out in passing through the narrow fissures and pores of the formation. In other cases, exposure to fluids in the well bore or formation causes dilution of the explosive, rendering it incapable of detonation, or leaches out certain of its essential constituents.

Other explosive compositions are highly diameter sensitive, meaning that they are incapable of being detonated in cross sections of less than a certain diameter. Diameter sensitivity is a measure of the capability of an explosive compound to propagate an explosion in narrow passages such as geological fissures. Diameter sensitivity as used herein has reference to the ability of a composition to propagate an explosion along a tube filled with the composition, containing a restricted orifice of a given diameter, so that the explosion propagates past the orifice and is not extinguished by the reduced diameter of the composition. Thus, an explosive with a diameter sensitivity (or critical diameter) of 1 inch, placed in a tube of greater diameter will propagate an explosion past a 1 inch diameter orifice but is incapable of propagating an explosion past an orifice of lesser diameter. This indicates that the same explosive will propagate an explosion in a 1 inch diameter geological fissure.

Reference to this problem is made in U.S. Pat. No. 3,301,724, issued as recently as Jan. 31, 1967, in which it is stated:

> "A remarkable property of my inventive compositions is that they are able to propagate even in a small diameter drill hole, such as, for example, three inches in diameter. Many commercially used blasting compositions, such as may be produced from ammonium nitrates and diesel oil mixtures

perform well in the mass and will propagate in a large diameter drill hole, such as six inches or larger, but fail to propagate at three inches or four inches diameter."

Clearly, however, even propagation in a 3 inch diameter hole is totally inadequate to permit effective use of such explosives for fracturing well formations. Although explosives exist which are not materially diameter sensitive, compositions using such explosives have encountered one or more of the drawbacks mentioned above rendering them unsuitable for well fracturing applications. Certain of such explosives are so highly unstable as to be dangerous, while others are so insensitive to detonation in well formations that resort must be made to complex arrangements of multiple shaped charges for detonation.

Temperature and related conditons encountered both in handling and transporting liquid explosive and in detonating them underground also adversely affect known explosives. For example, TNT dissolved in suitable liquid explosive solvents crystallizes out of liquid explosives at the low temperatures prevalent in many oil producing areas, making handling difficult and rendering the remaining constituents, in some cases, highly unstable. Temperatures in underground formations, on the other hand, are often high enough to cause auto-ignition of some explosives. Most previously known explosives have not been usable over temperature ranges wide enough for well fracturing applications.

A further serious problem in fracuring geological formations with liquid explosives has been auto-ignition due to overheating of the explosive as it is forced through fissures under pressure. Merely limiting the flow rate of the explosive has not adequately eliminated this problem, for a minimum pumping rate must be maintained in order to avoid having to overcome the excessive static pressure head each time the flow rate falls too low.

SUMMARY OF THE INVENTION

This invention is based on the discovery that nitroparaffin compounds, which are themselves explosives but which are very diameter sensitive (having critical diameters on the order of ¼ inch), may be rendered sufficiently diameter insensitive to be highly effective for well fracturing by dissolving therein certain high explosive nitramine compounds, in particular RDX, HMX and mixtures thereof. It has further been discovered that such compositions which include a detonation aid and a suitable ballistic modifier (all defined herein) in certain proportions form a liquid explosive having an extremely small critical diameter and which is not subject to the abovementioned deficiencies; in particular, it is highly suitable for well fracturing over a wide range of temperature conditions without its detonation characteristics being adversely affected by such conditions, such as by the crystallization out of solution of TNT or other constituents.

By using nitromethane as the nitroparaffin constituent of the liquid explosive, it has been discovered that a particularly small critical diameter, on the order of 1/64 inch, can be achieved which is especially suitable for well fracturing applications.

In addition, auto-ignition of the explosive is prevented by selecting the constituents of the liquid explosive in accordance with the invention to minimize the formation and buildup of nitric oxides at elevated temperatures, and by regulating the pumping rate of the explosive so that it is high enough to assure continuous flow, yet low enough to preclude undue frictional heating.

Detonation aids are constituents which enhance the detonability and energy of the explosive, such as nitroglycerin and PETN (pentaerythritol tetranitrate). A ballistic modifier is a constituent which affects the ballistic properties of the explosive, such as brisance, as well as its explosive energy. A nitramine explosive is one containing a nitramine group. Other constituents may be added to provide desired manufacuring and/or handling characteristics.

An embodiment of the invention particularly suitable for well fracturing applications is a solution of nitromethane saturated with one of the nitramine high explosives mentioned above. Nitroglycerin or another detonation aid is present in about seven to 20 percent by weight. Finely divided metallic powder may be added as a ballistic modifier, to enhance the brisance of the explosive, along with a gelling agent.

As previously explained, fine fissures created through hydraulic or equivalent fracturing in geological formations range generally from ¼ inch down to submillimeter levels. The diameter sensitivity required in an explosive compound for any given application depends upon the width of the fissures in which it must propagate an explosion. The width distribution of fissures in a given formation varies depending on the type of initial fracturing used to create the fissures and on the nature of the geological formation, and the diameter sensitivity of the explosive to be used should be chosen accordingly. It has been found that the explosive compound need not be capable of propagating an explosion back through all of the finest fissures in the formation, for highly effective fracturng, but should be capable of propagating an explosion throughout a substantial part of the formation. It will thus be seen that, in general, the smaller the critical diameter of the explosive utilized (i.e., the smaller the diameter through which it will propagate an explosion) the better the explosive will be for a given well fracturing application.

DESCRIPTION OF PREFERRED EMBODIMENTS

The major constituent of the liquid explosive described herein is a nitroparaffin compound, and may be any one of nitromethane, nitroethane, nitropropane and tetranitromethane, singly or in combination. The explosive contains between 5 and 80 percent nitroparaffin by weight. Unless otherwise noted, all proportions herein are by weight. Such nitroparaffin compounds are not readily soluble in or desensitized by water, oil or other fluids commonly found in underground formations. Of the above nitroparaffins, nitromethane is preferred because it has been found to have the greatest explosive power and it is capable of dissolving greater amounts of nitroamines and other organic solids than the C_2 and C_3 nitroparaffins.

Importantly, embodiments of the invention in which the nitroparaffin is nitromethane have been found to exhibit a critical diameter materially smaller than with other nitroparaffins, and consequently to be particularly useful where propagation in small diameters is desired. The sensitivity to detonation of such compositions is higher than for those with the heavier nitroparaffins, however, and compromises must be made in some cases between small critical diameter and insensi-

tivity, depending on the particular end use for the explosive.

According to the invention, a detonation aid, a nitramine explosive and a ballistic modifier are dissolved or suspended in the nitroparaffin. It will be recognized by those skilled in the art that certain of the constituents are present in the form of suspended solids and to that extent the explosive is actually a slurry; however, the term liquid explosive as used herein is intended to encompass slurries as well as liquids.

A nitramine explosive is defined herein to mean any of cyclotrimethylene trinitramine (RDX), cyclotetramethylene tetranitramine (HMX), or other high explosives containing nitramine groups which are soluble to the required extent in nitroparaffins and are compatible with the other constituents of the explosive. The precise mechanism whereby such nitramine explosives reduce the critical diameter of nitroparaffins is not fully understood. However, it is suspected that such nitramine explosives dissociate in solution to form ionic nitramine compounds, which compounds may aid in sensitizing the nitroparaffin in the desired manner. One or more of such nitramine explosives preferably constitutes between about five and 10 percent of the composition.

A detonation aid as used herein means nitroglycerin, pentaerythritol tetranitrate (PETN) and other explosive nitroglycols or glycol esters such as TMETN (Trimethyloltrinitrate) and TEGDN (Triethyleneglycoldinitrate), singly or in combination. As used herein, nitroglycerin refers to the commercially available forms of that compound, which ordinarily comprise mixtures of about 30 percent pure nitroglycerin with about 70 percent EGDN. These forms vary from about 50/50 to 30/70, and this ratio is not critical for purposes of the present invention. The explosive preferably comprises between about seven and 20 percent of a detonation aid, which percentage may vary according to the explosive power of the particular detonation aid used.

A ballistic modifier as used herein refers to a finely divided metallic powder commonly used in the explosives field, preferably aluminum, magnesium, zirconium, beryllium or titanium or alloys thereof. The ballistic modifier advantageously has a maximum particle size less than about 15 microns, and is preferably between about 8 and 12 microns in diameter, to minimize settling out or straining out of the particles and to enhance its reactivity. A larger particle size can be tolerated, but will reduce the reactivity of the metal and render it more susceptible to settling or filtering out. It constitutes between about five and 20 percent of the explosive.

In addition to the above constituents, a thickening or gelling agent is preferably added in order to retain the solid constituents of the explosive in an even dispersion and to provide the desired handling qualities, which agent preferably constitutes between about one and five percent of the explosive. Such gelling agent may be nitrocellulose, cellulose acetate, methyl cellulose or cellulose acetate butyrate. Other gelling or thickening agents common to the explosive art may alternatively be used, the agent chosen being dependent upon the particular constituents of the explosive and the desired handling characteristics for particular applications.

Additionally, the explosive may include up to about four percent of one or more processing aids, for example, wetting agents (i.e., monoleates, stearates, palmitates, etc.), a thixotropic agent (i.e., pyrolytic silica such as Cab-O-Sil a trademark of Cabot Corporation). Chalk, resorcinol, ethyl centralite, NDPA (nitrosodiphenylamine) or other suitable stablizers (including acid scavengers) such as will be familiar to those skilled in this art may also be added, constituting up to about 3 percent of the explosive.

A preferred embodiment of the invention comprises about 65-75 percent nitromethane, about 8-12 percent nitroglycerin or other nitrated glycols, about 6-10 percent RDX and about 10 percent aluminum powder, to which are added about one percent nitrocellulose, about two percent Cab-O-Sil and about one percent chalk or other stabilizers. The critical diameter of typical formulations of this embodiment is on the order of 1/32 inch, and may be better than 1/64 inch. The "critical diameter" of an explosive is commonly determined in a reducing diameter test fixture, which is a fixture having a passage with successively small diameters, to be filled with the explosive and detonated at the large end. The point at which an explosion ceases to propagate thus determines the critical diameter of the explosive.

Generally, as the amounts of nitramine explosive, detonation aid or ballistic modifier are reduced, the critical diameter of the explosive increases. As the amounts of these constituents are increased, on the other hand, with corresponding decreases in the proportion of nitroparaffin, the impact sensitivity of the explosive increases. The particular amounts used of these constituents will therefore vary with specific performance requirements of the explosive. Formulations of the abovementioned preferred embodiment of the invention can generally be detonated with a number eight blasting cap and may have an impact sensitivity on the order of 100 centimeters for a two kilogram weight as measured on a Picatinney Arsenal impact sensitivity test apparatus. The formulations are insensitive to detonation by electrical discharge, and will not detonate when subject to about a 20,000 volts at 1,000 amps discharge between electrodes immersed in the explosive.

Explosives according to the present invention may be formulated by mixing the constituents in accordance with procedures commonly employed in the explosives art. For example, the above-mentioned preferred embodiments may be formulated by adding the detonation aid and RDX to the nitromethane, along with the Cab-O-Sil and chalk, while stirring. The nitrocellulose may then be added, after which the aluminum powder is mixed in to form an even dispersion. The manner of formulation of the explosive is thus not critical, and any of the following specific embodiments of the invention may be prepared in accordance with the above described method or using any ohter procedure common to explosive manufacture.

EXAMPLE I

CONSTITUENT	PARTS
Nitromethane	66
Nitroglycerine	10
RDX	9
Aluminum Powder	12
Nitrocellulose	1
Cab-O-Sil	1
Chalk	1

EXAMPLE II

CONSTITUENT	PARTS
Nitromethane	69
PETN	10
Cellulose Acetate	1
Magnesium	11
RDX	7
Cab-O-Sil	1
Resorcinol	1

EXAMPLE III

CONSTITUENT	PARTS
Nitromethane	68
TEGDN	9.5
Nitrocellulose	1
HMX	7
Aluminum	11
Cab-O-Sil	2
Resorcinol	1.5

EXAMPLE IV

CONSTITUENT	PARTS
Nitromethane	70
Nitroglycerin	9
Nitrocellulose	1
RDX	7
Aluminum	10
Cab-O-Sil	2
Chalk	1

EXAMPLE V

CONSTITUENT	PARTS
Nitroethane	71
Nitroglycerine	9.2
HMX	5
Magnesium	12.3
Cab-O-Sil	1
Chalk	0.75

It is stated above that auto-ignition may be prevented by selection of the constituents and control of the pumping rate as described herein. It is theorized that auto-ignition is caused by a temperature rise in the explosive resulting from friction as the liquid is pressured through underground fissures, causing nitro compounds in the explosive, particularly nitrocellulose and nitroglycerin, to dissociate and form nitrogen oxides. The nitrogen oxides sensitize and catalyze the decomposing constituents, rendering the explosive unstable and lowering its deflagration point. Auto-ignition and detonation follow, rendering nitro-containing explosives dangerous to use in well fracturing except in accordance with the methods described herein.

According to the invention, for well fracturing applications in particular, the constituents of the explosive are chosen to minimize the formation of nitrogen oxides which lead to instability. In particular, constituents, capable of forming nitro-compounds (i.e., those with NO_2 groups) are selected which have high decomposition temperatures, i.e., decomposition temperatures higher than the temperature of the explosive at whatever pumping rate is to be used. Further, adequate amounts of acid scavenger, preferably of the kind which do not themselves include nitro-compounds, are included to neutralize the nitrous and nitric acids formed by the evolving nitrogen oxides, preventing the explosive from becoming unstable. Chalk or resorcinol are suitable for this purpose. In addition, the pumping rate is controlled as described in the following paragraphs to prevent the formation and buildup of nitrogen oxides.

As previously mentioned, the explosive described herein is particularly suitable for fracturing the productive formations surrounding oil or gas wells to increase the productivity of the well. In order to prevent undue mixing of the explosive with well fluids during loading, the explosive is preferably injected into the well directly at the level where fracturing is desired, i.e., the producing stratum, through a pipe or injectin tube extending from the surface to the desired level. Such pipe or tubing may be provided with a one-way valve at its lower end to prevent entry of fluids from the well. For most wells, between about 30,000 and 75,000 pounds of explosive are loaded through an injection tube into the well bore and forced back into the formation to be fractured, leaving only enough explosive in the bore to permit initiation of the charge. After the injection tube is removed, a standard high explosive initiator (i.e., a timed nitroglycerine detonator) may be lowered into the explosive remaining in the bore and upon detonation, the desired fracturing is obtained over a large volume of the formation, as opposed to the relatively local fracturing in the bore hole which has resulted when using explosives incapable of detonation within the fine crevices and fissures of the formation.

In order to prevent auto-ignition, the pumping rate of the explosive is preferably controlled to achieve a flow rate low enough to prevent undue overheating of the explosive, yet high enough so that it is not necessary to continually overcome static friction in keeping the explosive flowing. The maximum pumping will vary in accordance with the specific constituents and constituent amounts employed and the permeability temperature and other properties of the formation being fractured. In general, it is believed that in an explosive composition including on the order of 2 percent and preferably between about 1.5 percent and 2.5 percent by weight, of an acid scavenger such as chalk, the pumping rate should be between about 4 and 13 gallons per minute. As used herein, "undue heating" means heating to a temperature at which, given the decomposition temperatures of the nitro compounds and the proportion of acid scavenger in the particular explosive, nitrogen oxides tend to build up sufficiently to cause auto-ignition.

It will be apparent to those skilled in the art that various modifications of the above embodiments may be made without departing from the scope and spirit of the invention, which is defined by the following claims.

I claim:

1. A method of fracturing the productive formation of a water, oil or gas well containing a network of geological fissures to increase the permeability of said formation and thereby enhance the productivity of the well, utilizing a viscous, pourable liquid explosive consisting essentially of between about 50 and 80 percent by weight of a nitroparaffin explosive having dissolved therein between about five and 10 percent by weight of a nitramine explosive, between about seven and 20 percent by weight of a detonation aid, between about five and 20 percent by weight of a ballistic modifier, sufficient thickening agent to maintain an even dispersion of any particulate solids in said explosive and an acid scavenger, comprising: injecting said liquid explosive through an injection tube into the well bore; forcing said liquid explosive back into the productive formation to be fractured at a rate low enough to prevent undue heating of the explosive and yet high enough to maintain the flow without continually having to overcome static friction, and leaving a sufficient amount of said explosive in the well bore to initiate the explosive in the formation; and detonating the explosive in the

well bore to fracture the formation, the amount of acid scavenger being sufficient, at said rate, to prevent auto-ignition through buildup of nirogen oxide.

2. A method of fracturing the productive formation of a water, oil or gas well containing a network of geological fissures to increase the permeability of said formation and thereby enhance the productivity of the well, utilizing a viscous, pourable liquid explosive consisting essentially of between about 65 and 75 percent by weight of a nitroparaffin explosive having dissolved therein between about six and 10 percent by weight of a nitramine explosive, between about eight and 12 percent by weight of a detonation aid, between about five and 20 percent of a ballistic modifier, between about one and five percent by weight of a thickening agent for maintaining an even dispersion of any particulate solids in said explosive and an acid scavenger, comprising: injecting said liquid explosive through an injection tube into the well bore at the level of the productive formation to be fractured; forcing said liquid explosive back into the productive formation to be fractured at a rate low enough to prevent undue heating of the explosive and yet high enough to maintain the flow without continually having to overcome static friction, and leaving a sufficient amount of said explosive in the well bore to initiate the explosive in the formation; and detonating the explosive in the well bore to fracture the formation, the amount of acid scavenger being sufficient, at said rate, to prevent auto-ignition through buildup of nitrogen oxide.

3. A method as defined in claim 2 wherein said nitramine explosive and said thickening agent are selected to have decomposition temperatures above the temperature of the explosive at said rate.

4. A method as defined in claim 3 wherein the amount of acid scavenger is between about 1.5 and 2.5 percent by weight.

5. A method as defined in claim 3 wherein said rate at which the explosive is forced back into the productive formation is between about four and 13 gallons per minute.

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UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,747,679

DATED : July 24, 1973

INVENTOR(S) : Leonard N. Roberts

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

1st Page - 1st Column. The following was omitted. Please add:

-- [73] Assignee: Talley-Frac Corporation, Pryor, Okla. --

Under "Related U. S. Application Data" change:

"[62] Division of Ser. No. 860,883, Oct. 27, 1969, abandoned."

to

-- [62] Division of Ser. No. 869,883 filed Oct. 27, 1969, now patent number 3,663,324. --

Signed and Sealed this

ninth Day of *September 1975*

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks