

**Enhanced Real-time Propellant Activation during Downhole-mixed
Fracture Stimulation Process for Low-permeability Stripper Wells**

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Enhanced Real-time Propellant Activation during Downhole-mixed Fracture Stimulation Process for Low-permeability Stripper Wells

ABSTRACT

Enhanced fracture stimulation processes are generally used in the petroleum industry to increase the recovery of hydrocarbon reserves. In the in the United States in particular, more efficient and cost-effective reservoir fracturing treatments are needed to enhance the recovery of oil and natural gas in those stripper wells that are characterized by low-permeability reservoirs. Proposed is a well test project comprising the development and field-testing of a novel fracture stimulation that utilizes a chemically-induced in situ fracturing process that is combined with hydraulic fracturing stimulation to maximize reservoir fracture propagation.

Proposed is the research and development of a down-hole blending mixture of propellants and various oxidizers that are pumped separately (and safely) down the wellbore for reaction and generation of secondary fracturing energy in the hydraulically induced reservoir fracture. With the proposed process, various propellants may be pumped down the casing for admixture with oxidizers to generate secondary fractures to augment the fractures created by hydraulic fracturing, which theoretically should result in greater fracture length extension and significantly enhanced hydrocarbon flow to the wellbore. Proposed are the admixture of propellants and oxidizers, including encapsulated or time-delay propellants and activators, concurrent with NETL-RealtimeZone's patented downhole-mixed stimulation process, whereby one stimulation component is pumped down the casing while the second stimulation fluid (energizing gases and/or proppants may be included in either fluid) is pumped down the tubing and thereby blended down-hole to form, in real-time, a composite fracturing fluid prior to entry into the reservoir fracture. Encapsulated or otherwise time-delayed chemical reactions may be used to facilitate placement of the propellants further into the reservoir formation, prior to reaction. This simple well completion system is safely and easily utilized at the well site and enables dramatic improvements in reserve recovery efficiency, safety, and cost savings.

This proposed project would be field tested initially in a stripper well with a low permeability reservoir in the Permian Basin, however, success of this proposed novel fracturing technique would prove up numerous applications in other lower permeability oil and natural gas stripper reservoirs in geographic basins throughout the United States, and ultimately worldwide. The cost savings and value of enhanced reserve recoveries that could be provided by widespread industry application of this technology are potentially substantial. Deliverable work product would include a patent application related to this project, which if commercialized would be widely licensed to all interested stimulation service providers.

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Exhibit One

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**Post-stimulation Tracer Survey for Downhole-mixed Nitrogen & Borate gel
stimulation treatment in stripper well**

INTRODUCTION

Realtimzone, Inc. has recently conducted research and development of patented systems for downhole-mixed stimulation processes and a real-time tracer diagnostic and fracturing procedure that are partially funded by the Department of Energy's National Energy Technology Laboratory and by contributions of effort and services from several energy service providers in the Permian Basin of New Mexico. As discussed via paper presentation at the Society of Petroleum Engineering (SPE)'s Annual Technical Conference and Exhibition in October, 2002, (SPE 77676; *Real-Time Downhole-Mixed Stimulation Fracturing Process*, by Scott, Covatch & Carrasco) multiple stimulation field-tests to date have successfully proved the concept of downhole-mixing of composite fracturing fluids. This field proven real-time stimulation system results in lower treating pressures and the ability to modify stimulation treatments on the fly, however, further research and experimental stripper well test work is hereby proposed for the development of a propellant-enhanced test procedure that is comprised by in situ ignition of propellant concurrent with a hydraulic fracturing process. The proposed stripper test well is located in Eddy County, New Mexico.

It is anticipated that if successful, this experimental well test work will safely demonstrate the logistic simplicity of the proposed propellant-downhole-mix fracturing process, which should result in increased reservoir fracture extension and greater reserve recoveries in stripper wells characterized by low-permeability reservoirs. Safety considerations are paramount with any explosive propellant system, and this proposed experimental process provides prudently cautious methods for safely achieving improved reservoir hydraulic-chemical fracture propagation.

EXECUTIVE SUMMARY-

The research, development and field-testing of an experimental reservoir stimulation process for stripper wells was proposed in a stripper well located in the Permian Basin. Proprietary experimental processes were evaluated for the proposed well test pumping of a patent-pending, chemically-induced in situ fracturing process concurrent with RealtimeZone's patented, downhole-mixed hydraulic fracture stimulation process.

The proposed down-hole blending of a chemical mixture of propellant and oxidizer was designed to be pumped separately, and safely, to generate secondary fracturing energy within the hydraulically induced reservoir fractures. The propellants would be pumped down the casing for admixture with oxidizers that are pumped down tubing to generate an energy release in the hydraulically-induced formation fractures, which theoretically should create secondary fracture extensions. A primary goal is safely achieving greater overall fracture extension in situ by downhole-mixed chemical reaction, which will enhance hydrocarbon flow to the wellbore further than is typically accomplished by hydraulic fracturing processes alone.

The proposed admixture of propellants and oxidizers, including encapsulated or time-delay propellants and activators, would occur concurrent with hydraulic fracturing, whereby one stimulation component is pumped down the casing while the second stimulation fluid (gases, energized fluids and/or proppants may be included in either fluid) is pumped down the tubing and thereby blended down-hole. It is anticipated that this chemical-hydraulic fracturing process will be safely and easily pumped at the experimental well site, and as such would enable dramatic improvements in reserve recovery efficiency, safety, cost savings, and overall reservoir fracturing success due to greater fracture propagation compared to existing hydraulic fracture processes.

A provisional patent application was filed and further research conducted pertaining to propellants, oxidizers, and the use of said materials in the downhole environment. An extensive patent search found only one relevant U.S. patent that was slightly related to the proposed propellant-activation process. Thus it was anticipated that after the field-test, deliverable work product would include a continuation of the existing patent-pending application. However, field-testing was not accomplished due to the unexpected reluctance to participate by the major oilfield stimulation service companies. This sudden reluctance was unanticipated and was reportedly (from verbal communications with various service company personnel) due to a U.S. well site accident that occurred either in late 2003 or 2004 that resulted in the serious injury and death of well site personnel due to the accidental surface-discharge of propellants.

At this juncture, we remain disappointed that there are no stimulation service providers interested in conducting a well test, at virtually any cost, due to their paranoia

conducted from May 2003 through May 2004 to evaluate and delineate the best methods of implementation of the proposed system. After an extensive search of literature and issued patents, a pertinent United States patent by Colgate, et al (SEE APPENDIX i) was used to help the project investigator better develop an improved propellant-induced fracturing process that relied on downhole-mixing to provide numerous safety features. Colgate's patent provided for use of solid or semisolid propellant grains that were packed together in the wellbore so as to create voids within the propellant volume, with said grains of near-uniform size such as could be easily pumped along with proppant-sized material. With said grains bonding together under sufficient strength due to hydraulic pressure, Colgate theorized that this packing of propellant would substantially delay the fluidization of the propellant that might naturally occur by the onset of Taylor unstable burning.

Avoidance of Taylor unstable burning is desirable to prevent the undesirable launching (i.e. like a rocket) of the drill pipe during the stimulation process. Colgate's patent claims included having spherical propellant grains are bonded together with a glue that would also function as a propellant or propellant component. The propellant types included ammonia-based chemicals, nitrocellulose, black powder, various fuels, polymerized Rubber and Aluminum, and a monobase or double base propellant comprised from the group consisting of nitrocellulose in combination with nitroglycerine. Said glue types include epoxies, polycarbonates and ureas, however, besides glue.

Colgate's patent also claimed the use of a viscous fluid, such as viscous petroleum oil, for suspension of the propellant grains for the purpose of avoiding fluidization and too-rapid burning of the propellant, which would theoretically result in the onset of Taylor unstable burning and potentially the dangerous and undesirable launching of the well's tubing or casing string. The uncontrolled growth of a Taylor instability due to rapidly burning propellant surface leads to an uncontrolled increase of burning area and hence the uncontrolled increase of pressure. Taylor instability may initiate detonation and the explosive energy release of detonation. Hence, uncontrolled Taylor instability growth is to be avoided for these purposes. According to Colgate, Taylor instability may be prevented by use of solid propellants that have pores filled with viscous and slow-burning materials.

The reasoning for having the wellbore-packed propellant burn relatively slow is to generate fracturing gas pressure in a time that is a small multiple (e.g. 2 to 10 times) of the dynamic time of the system. In this regard, it is not desired to shock the formation because this compacts the rock and wastes energy that would otherwise be used to deform and initiate and propagate fractures. Fracturing with detonating explosives typically results in a shock wave that generally compacts the reservoir rock, as opposed to opening new fractures. While a slower gas release is thus desired, too slow a release results in the gas or fluid bleeding off into the formation.

By downhole-mixing of propellant and oxidizers, as planned in the proposed well test, the undesirable incidence of Taylor unstable burning is avoided by control of the propellant burn rate, which controls resultant pressure generation. Realltimezone's work to date includes a U.S. Patent; *Real-time reservoir fracturing process* (Scott & Covatch) that is incorporated by reference (SEE APPENDIX ii). A similar downhole-mixed process would substantially improve the processes and safety of downhole propellant activation. Furthermore, this work has resulted in the proposed process of downhole-mixing of propellant with a foaming agent such as Nitrogen or Carbon Dioxide, which lessens propellant grain-to-grain contact geometries and at small concentrations could be used in real-time to control propellant burn rate (and thus totally avoid Taylor unstable burning). The particular advantage of downhole-mixing is that the oxidizer and propellant are physically separated until admixture in the reservoir fractures. This approach is much safer to handle and transport and is practically immune to unexpected surface detonation.

Colgate's patent mentions in a less preferred embodiment that pumping of the propellant slurry could be accomplished via a down hole nozzle during burning and at a velocity sufficiently great so that the burn front does not climb up the injection string (thereby either launching the tubing string or reaching the surface as an explosion). However, certain difficulties occur with this approach. First, the viscosity of the oil must be low for rapid pumping, yet high in order to minimize the burning rate of the propellant. In other words, a lower viscosity will give too high a burn rate and higher viscosity oils are essentially hard to rapidly pump, due to viscous pipe losses. Also, if a slurry of pre-mixed fuel and oxidizer is pumped at a high pressure, there is the potential danger of ignition by friction in the pump valves or pipe, which could lead to an

explosion. Avoidance of these potential dangers further supports mixing the propellant down hole for safe, in situ combustion within hydraulically-induced fractures.

RESULTS AND DISCUSSION

Proprietary experimental processes were evaluated for the proposed well test to facilitate the pumping of a patent-pending, chemically-induced in situ fracturing process concurrent with RealtimeZone's patented, downhole-mixed hydraulic fracture stimulation process. The proposed down-hole blending of a chemical mixture of propellant and oxidizer was designed to be pumped separately, and safely, to generate secondary fracturing energy within the hydraulically induced reservoir fractures. The propellants would be pumped down the casing for admixture with oxidizers that are pumped down tubing to generate an energy release in the hydraulically-induced formation fractures, which theoretically would create secondary fracturing and pressure generation to extend the hydraulically-induced fractures.

A comprehensive review of patents issued through 2004 was conducted along with interviews of numerous oilfield personnel that indicated experience with propellant stimulation treatments, mostly related to the downhole-ignition of jet fuel, however, this study included a review of explosive canisters used in wells since 1985 in New Mexico by various companies. After detailed analysis it was decided to proceed with a well test using jet fuel that would be pumped behind a methanol foam frac job into the hydraulically-induced fractures and then ignited by downhole mixing with oxidizers.

The proposed admixture of propellant and oxidizer in the well test would occur concurrent with hydraulic fracturing, whereby one stimulation component is pumped down the casing while the second stimulation fluid is pumped down the tubing and thereby blended down-hole. It was anticipated that this chemical-hydraulic fracturing process would safely and easily be pumped at the experimental well site, and as such would enable dramatic improvements in reserve recovery efficiency, safety, cost savings, and overall reservoir fracturing success.

A chemist was retained by Realtimezone to assist in the project work and a provisional patent application was filed concurrent with further chemical research of

propellants, oxidizers, and the use of said materials in the downhole environment. It was generally anticipated that after the field-test, deliverable work product would include a continuation of the existing patent-pending application. However, field testing was not accomplished due to the unexpected reluctance to participate by the major oilfield stimulation service companies. From earlier positive indications, this sudden reluctance was unanticipated and was reportedly (from verbal communications with various service company personnel) due to a U.S. well site accident that occurred either in late 2003 or 2004 that resulted in the serious injury and death of well site personnel due to the accidental surface-discharge of propellants.

At this juncture, we remain disappointed that there are no stimulation service providers interested in conducting a well test, at virtually any cost, due to their paranoia regarding safety issues. The proposed chemical-hydraulic fracturing process would be safer than any other known process for ignition of propellant to generate reservoir fractures, however, Realtimezone remains unsuccessful in convincing service companies to participate in an experimental well test as earlier proposed. Ongoing research and the patent-pending application has been shelved as a result. If any stimulation companies express future interest in propellant-activated stimulation, this technology will be made freely available and as such, the work done to date was instrumental in determining that a safer and more efficient process exists for downhole-ignition of propellants for the purpose of enhanced reservoir stimulation.

REFERENCES

**Real-Time Downhole-Mixed Stimulation Fracturing Process*, SPE 77676, by George Scott III, Realtimezone, Gary Covatch, NETL, and Art Carrasco, Halliburton
Copyright 2002; Society of Petroleum Engineers Inc.

*This paper was prepared for presentation at the SPE Annual Technical Conference and Exhibition held in San Antonio, Texas, 29 September–2 October 2002.

Fast-burning nitrocellulose compositions, U.S. Patent No.6,645,325, November 11, 2003
by Russell Nickel

Modified nitrocellulose based propellant composition, U.S. Patent No. 5,218,166, June 8, 1993, by Schumacher; John B

BIBLIOGRAPHY

George L. Scott III

EDUCATION

1981: B.S. Geology with academic emphasis in Petroleum Engineering-New Mexico Tech @ Socorro, New Mexico.

1983: Graduate study in geophysics & petroleum engineering-U.T. @ Austin, Texas. Also numerous courses related to petroleum recovery, E.O.R., reservoir evaluation and well stimulation procedures. Law school courses related to patenting processes and intellectual property law.

EMPLOYMENT

1981-1982: Drilling rig roughneck

1983-1988: Well log analyst- Permian Basin of Texas and New Mexico. Work included well site evaluation, petroleum reservoir mapping

1988-1990: Exploitation manager for Permian Hunter Corp.

1990-1992: Manager of exploration and reservoir stimulations for Strata Production Company in the Permian Basin, New Mexico & Texas.

1992-1996: Well consultant in the Permian Basin, New Mexico and Texas.

1997-1998: CO₂ field development geology for Ridgeway Arizona in Arizona

1998-1999: Research & development of oilfield technologies, RealtimeZone

1999-Present: Development of patented stimulation procedures and real-time diagnostic system working with Department of Energy (NETL) and licensed to Halliburton Energy Services.

PROFESSIONAL ACCOMPLISHMENTS

Pioneered research and development of innovative solutions related to real-time reservoir completion processes. Expertise gained through hundreds of well completions in Colorado, Texas, Arizona and New Mexico. Reservoir delineation of significant reserves in numerous oil and gas fields in the Permian Basin. Geologic discovery of proven reserves of 3.0+ TCF in U.S.'s third largest CO₂ & Helium gas field in Arizona. Solved various well completion problems common to industry and authored or co-authored numerous U.S. Patents related to oilfield technology, including (a) commercially utilized pipelift machine to eliminate chronic oilfield injuries, (b) real-time downhole-mixed fracturing system, and (c) real-time tracer diagnostic system. Associated with RealtimeZone, a company specializing in reservoir evaluation, real-time reservoir fracturing and reservoir spectral analysis. Membership in S.P.E., AAPG, and Roswell Geological Society.

LIST OF ACRONYMS AND ABBREVIATIONS

RTZ: RealtimeZone, Inc.

P.I.: Principal Investigator (George Scott)

NETL: National Energy Technology Laboratory

HES: Halliburton Energy Services

CO₂: Carbon Dioxide

N₂: Nitrogen

APPENDICES

i

United States Patent

4,681,643

Colgate, et al.

July 21, 1987

Fast burning propellants

Abstract

A solid or semisolid propellant comprising grains of propellant or propellant components bonded together so as to create voids within the propellant volume, said grains bonded together with sufficient strength to substantially delay the fluidization of the propellant by the onset of Taylor unstable burning, said propellant having a rapid burn rate below that associated with Taylor unstable burn. In another embodiment, the grains are held within and the voids are filled with viscous fluid binder such as a petroleum oil, said binder functioning to hinder Taylor unstable burning and yet permit very rapid burning within the propellant volume.

Inventors:

Colgate; Stirling A. (4616 Ridgeway, Los Alamos, NM 87544); Roos; George E.
(P.O. 284, Burns Flat, OK 73624)

Appl. No.:

538578

Filed:

October 3, 1983

Current U.S. Class:

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149/65; 149/72; 149/73; 149/76; 149/77;

149/79; 149/94; 149/95; 149/96; 149/97; 149/110;
149/111; 149/112; 149/113; 149/114; 149/115

Intern'l Class:

C06B 045/02

Field of Search:

149/2,21,110-
115,43,44,46,61,63,65,72,73,76,77,79,94,95,96,97

References Cited [Referenced By]

U.S. Patent Documents

3673286	Jun., 1972	Remaly et al.	149/110.
3725154	Apr., 1973	McCulloch et al.	149/110.
3986909	Oct., 1976	Macri	149/5.
3995559	Dec., 1976	Bice et al.	149/15.
4038112	Jul., 1977	Asaoka	149/110.

Primary Examiner: Lechert, Jr.; Stephen J.

Attorney, Agent or Firm: Brumbaugh, Graves, Donohue & Raymond

Parent Case Text

This application is a continuation-in-part of application Ser. No. 06/220975, filed 12/29/80, now abandoned.

Claims

We claim:

1. A solid or semisolid propellant comprising grains of propellant or propellant components bonded together so as to create voids within the propellant volume, said grains being of near-uniform size such that they have less than about a 20% size variation between the largest and smallest grains, said voids comprising from about 10% to about 50% of the propellant volume, said grains bonded together with sufficient strength to substantially delay the fluidization of the propellant by the onset of Taylor unstable burning, said propellant thereby having a rapid burn rate of from about 10 cm sec.sup.-1 to about 10.sup.4 cm sec.sup.-1.
2. A propellant according to claim 1 wherein said grains have less than about a 10% size variation between the largest and smallest grains.

3. A propellant according to claim 2 wherein said voids comprise from about 10% to about 20% of the propellant volume.
4. A propellant according to claim 3 wherein said grains are bonded together with a glue.
5. A propellant according to claim 4 wherein said glue also functions as a propellant or propellant component.
6. A propellant according to claim 5 wherein said glue is nitrocellulose.
7. A propellant according to claim 4 wherein said grains are black powder.
8. A propellant according to claim 4 wherein said grains comprise separate grains of oxidizer and grains of fuel.
9. A propellant according to claim 8 wherein said grains of oxidizer are selected from the group consisting of NH₄NO₃, NH₄ClO₄, NH₄ClO₃, NaNO₃, NaClO₃, NaClO₄, KNO₃, KClO₃ and KClO₄ and said grains of fuel are selected from the group consisting of hydrocarbon and aluminum.
10. A propellant according to claim 3 wherein said grains are substantially spherical in shape.
11. A propellant according to claim 1 wherein said propellant grains are a monobase or double base propellant selected from the group consisting of nitrocellulose and nitrocellulose in combination with nitroglycerine.
12. A propellant according to claim 11 wherein said propellant grains are bonded together by bridges of said propellant, said bridges having been formed by the use of a solvent for the propellant that has first been permitted to partially dissolve the surface of the grains such that when the solvent is removed said grains are bonded together by bridges of said propellant.
13. A propellant according to claim 11 wherein said grains are bonded together by a glue, said glue comprising nitrocellulose which has been dissolved in a solvent, and wherein said solvent has been removed by drying after the grains are glued together.
14. A propellant according to claim 11 wherein the grains are bonded together with a glue that yields a high volume of inert gas when burned.
15. A propellant according to claim 14 wherein the glue is selected from the group consisting of polycarbonates and ureas.
16. A propellant according to claim 1 wherein said propellant is heterogeneous and comprises grains of NH₄NO₃, polymerized Rubber and Aluminum.

17. A propellant according to claim 16 wherein said grains are bonded together with a glue, said glue selected from the group consisting of epoxy in combination with KClO.sub.4 and urethane in combination with KClO.sub.4.
18. A propellant according to claim 1 wherein said propellant has a burn rate of from about 10 cm sec to about 10.sup.3 cm sec.sup.-1.
19. A propellant according to claim 1 wherein said grains have a diameter of from about 0.5 cm to about 0.05 cm.
20. A propellant comprising grains of propellant or propellant components held within a fluid binder, said binder being sufficiently viscous so as to hinder the fluidization of the propellant volume by the onset of Taylor unstable burning and yet sufficiently fluid so as to permit the binder to flow during burning due to unequal stresses in the propellant volume and thereby to permit the surface shape of the propellant to continuously change during burning, said surface shape change during burning being sufficient to produce a burn rate of from about 10 m sec.sup.-1 to 100 m sec.sup.-1.
21. A propellant according to claim 20 wherein the binder is a petroleum oil.
22. A propellant according to claim 21 wherein the binder is selected from the group consisting of tar and bunker fuel oil.
23. A propellant according to claim 21 wherein the binder has a viscosity in the range between that of road tar and bunker C fuel oil.
24. A propellant according to claim 20 wherein the binder has a viscosity of at least 3000 poise.
25. A propellant according to claim 21 wherein at least some of the grains of propellant components are oxidizers.
26. A propellant according to claim 22 wherein at least some of the grains of propellant components are oxidizers.
27. A propellant according to claim 23 wherein at least some of the grains of propellant components are oxidizers.
28. A propellant according to claim 24 wherein at least some of the grains of propellant components are oxidizers.
29. A propellant according to claim 25 wherein at least some of the grains of propellant components are oxidizers selected from the group consisting of NH.sub.4 NO.sub.3, NH.sub.4 ClO.sub.3, NH.sub.4 ClO.sub.4, NaNO.sub.3, NaClO.sub.3, NaClO.sub.4, KNO.sub.3, KClO.sub.3 and KClO.sub.4.

30. A propellant according to claim 26 wherein at least some of the grains of propellant components are oxidizers selected from the group consisting of NH₄NO₃, NH₄ClO₃, NH₄ClO₄, NaNO₃, NaClO₃, NaClO₄, KNO₃, KClO₃ and KClO₄.

31. A propellant according to claim 27 wherein at least some of the grains of propellant components are oxidizers selected from the group consisting of NH₄NO₃, NH₄ClO₃, NH₄ClO₄, NaNO₃, NaClO₃, NaClO₄, KNO₃, KClO₃ and KClO₄.

32. A propellant according to claim 28 wherein at least some of the grains of propellant components are oxidizers selected from the group consisting of NH₄NO₃, NH₄ClO₃, NH₄ClO₄, NaNO₃, NaClO₃, NaClO₄, KNO₃, KClO₃ and KClO₄.

33. A propellant according to claim 20 wherein said grains of propellant or propellant components are from about one micron to about one mm. in size.

Description

BACKGROUND OF THE INVENTION

The acceleration of rockets by the use of propellants is a well known technology. When propellants are used to accelerate vehicles into space, the rocket acceleration must be large compared to gravity (5 to 10 times g) so that impulse (force times time) is not wasted against gravitational force. When a rocket is in orbit or otherwise substantially uninfluenced by gravity the acceleration may be much smaller because gravity is no longer a limitation. Military rockets, on the other hand, must accelerate extremely rapidly, yet often the structure of the vehicle or the propellant composition limits the practical acceleration to a range of from 100 to 1000 g.

Rockets also find use in the rocket accelerated rod apparatus (RAR) such as is described in U.S. Pat. No. 3,509,821 for rapid penetration into dense media such as rock or metal. In RAR applications, an acceleration of several times 10⁴ g is required if the rod is to be used for commercial applications of boring holes in rock or ground. The high acceleration is required so that the stand-off distance required for the rocket-rod to attain the required penetration velocity can be reasonably small, e.g. 10 meters. A typical velocity required for substantial penetration is approximately 2000 meters per second with the result that the acceleration (within a distance of about 10 meters) is approximately 20,000 g. Conversely, the time of acceleration of burning time of the propellant is very short, e.g. $t = 2d/v$ perspective to 10⁻² seconds. Therefore there is a need for very fast burning propellants for rapid acceleration of projectiles for commercial uses.

In U.S. Pat. No. 3,616,855, which relates to the bulking and caving of underground ore bodies, a solid propellant is used to heave the ground after prestressing the formation by injecting an appropriate settable propping material. In such applications of earth fracturing (which is a form of bulking) there also exists a need for particular propellant burn properties. As discussed in U.S. Pat. No. 3,616,855, the propellant should burn (i.e. form the bulking or fracturing gas) in a time that is a small multiple (e.g. 2 to 10 times) of the dynamic time of the system. In this regard, it is not desired to shock the formation because this compacts the rock and wastes energy that would otherwise be used to lift it and form fractures. Fracturing with detonating explosives have shown that the shock wave in general compacts the ground or rock and does not in general open new fractures. While a slower gas release is thus desired, too slow a release results in the gas or fluid being lost into the formation. Hence the gas should be released within a period of approximately 2 to 10 times the dynamic time of the system.

A typical case is a well 3500 feet (1 km) deep. The time for a compression wave to reach the surface and return, i.e. the dynamic time, is roughly 2 seconds for a formation having a sound speed of 1 km sec.sup.-1. Hence the gas release time from a preferred fracturing or bulking propellant should be 5 to 10 seconds.

The placement of the propellant will be within the bore hole, for example a bore hole 8 inches in diameter and 1200 feet or 300 meters in length. The propellant must burn a length of 300 meters in 20 seconds, or a burn velocity of 15 meter sec.sup.-1. This also is in the range of burn velocity that is the objective of the present invention, but not available in conventional propellants.

There are thus two circumstances where a fast burning propellant is needed for useful purposes: fast rocket acceleration and underground well fracturing. In both cases the burn rate and hence the minimum pressure of the burning gases is roughly the same, namely several hundred MPA or 10 to 20 thousand PSI. This higher pressure is the result of the mass flow times gas velocity, or the time rate of change of momentum of the combustion gases. It is the useful pressure for either accelerating the rocket, or forcing the combustion gases into the rock for fracturing. Hence the high pressure of combustion is a necessary and useful result of a fast burning propellant. The magnitude of the pressure is determined by the geometry or confinement of the burn. It is this geometry or confinement that leads to two different mechanisms of fast burning propellants of this disclosure.

SUMMARY OF THE INVENTION

The propellants according to the present invention are solid propellants, since liquid propellants require pumps and plumbing. At high burn rates, pumps and plumbing become too massive.

The classical method for obtaining a fast burning solid propellant is to cast the solid propellant in a shape called a "grain" that has a large surface to volume ratio. A solid

propellant burns at a rate dependent upon the pressure. This rate is proportional to:

$(\text{pressure})^{\gamma}$

where

$\gamma < 1$ for stable burn, and typically at a surface, $\gamma \text{ about } 1/2$.

Hence one might think that merely going to very high pressure by the constriction of a nozzle would allow all desired burn rates. This is not true for two reasons:

(1) the required high pressure (e.g. 1000 atmospheres or 14,000 PSI) to obtain a typical burn rate of about 20 cm sec.⁻¹ with a conventional propellant would require a casing strength (and hence weight) far too great--e.g. equal to the propellant weight--for a useful rocket. Of course, even greater casing weights would be required if burn rates substantially in excess of 20 cm sec.⁻¹ and contemplated by the present invention (i.e. up to about 10⁴ cm sec.⁻¹) were to be obtained.

(2) Monopropellants do not have a constant factor γ in the above equation and if pressure is high enough the desired burn or deflagration turns into a detonation of such high velocity that the rocket would be destroyed.

Thus both practical weight and burn instabilities prohibit normal stable fast propellant burn with conventional propellants. Therefore, as a practical matter, the fast burn rates achievable according to the present invention must be achievable with pressures not exceeding about 1000 atmospheres, and usually not exceeding a tenth of that.

Hence in current practice if one desires all the propellant to burn in a short time, one makes a large surface area with thin webs of propellant. Burning then proceeds from both sides of the thin web.

For example if the burn time is to be 10⁻² seconds for a propellant that burns at 5 cm s.⁻¹, then the web thickness must be 1 mm. This is a thin web for a large rocket. This geometry, where the propellant is fluted in cross section, is also chosen such that the burning area remains roughly constant during the course of burning, so that the rate of production of combustion gases remains roughly constant.

If all the grain area is ignited at once, the burning will penetrate the webs rapidly and hence consume the propellant rapidly. The rocket casing and nozzle must confine the burn pressure. The nozzle converts the pressure to exhaust velocity and hence impulse.

The principal limitation of the thin webs of the standard grain geometry is the mechanical strength of the webs. If they are too thin, they cannot support the stress of the velocity of the high pressure combustion gases. The webs break and chunks of burning propellant are blown out the nozzle. This may choke the nozzle, lead to too rapid

burn, and blow up the rocket. Hence there is a major requirement to produce a geometry for fast stable propellant burn.

The object of this invention is to disclose two geometries to achieve this objective: the first is end-burning of controlled size "chunks" of glued propellant, and the second is the controlled Taylor unstable burning of a viscous semi-solid semi-liquid propellant.

These two mechanisms relate to one another. Taylor instability comes about because of a differential pressure across a density discontinuity, i.e. the acceleration of a heavy fluid by a light one. In the case of propellant burn the combustion gases are the low density fluid and the propellant is the heavy fluid. The uncontrolled growth of a Taylor instability at a burning propellant surface leads to an uncontrolled increase of burning area and hence uncontrolled increase of pressure. This explodes the rocket casing. It may initiate detonation, i.e. converts propellant burn, a deflagration, to the explosive energy release of detonation. Hence uncontrolled Taylor instability growth is to be avoided for these purposes.

Taylor instability is damped by viscosity and prevented entirely by strength or rigidity of materials. The reason for solid propellants is to prevent the growth of Taylor instability at the burning surface. This disclosure is concerned with both the rigid case as well as the controlled growth of viscosity.

A rigid propellant is usually formed in a grain and the limit of burn rate is set by the thickness of the webs. Here we describe another method of obtaining a high burn rate using a rigid propellant. According to the invention, a propellant is provided which is comprised of near-uniform size particles--i.e. particles having less than about 20% size variation, and preferably less than about 10% size variation. By thus controlling the size variation of the respective particles, the size of the voids created when the particles are glued together (e.g. as by gluing them over approximately 20% of their surface area) are likewise controlled and of near-uniform size. Depending upon the shape and size of propellant particles chosen, the void size can be easily controlled and a void volume of from 10% to 50% of the total propellant volume can be maintained.

In one typical case the particles in a useful example are 0.2 cm (2 mm) diameter spheres glued over 20% of their surface area. The resulting glued structure results in a very strong rigid matrix. The matrix is so strong that the high pressure of burning does not crush the matrix. Instead it stably supports a high pressure--pressures of several hundred MPA, 10,000 to 20,100 PSI. Hence once the glued structure is ignited, the burn front progresses through the structure without breaking or crushing the propellant. The ignition of the structure starts at a surface and the controlled, near-constant size of the interconnected voids between particles allows the burning gas to propagate the ignition flame into the matrix. This flame progression is controlled by both the tortuosity of the surface area and by the voids between particles or spheres of propellant. By properly controlling the ignition properties, the void size, and the grain size, the flame front speed in the matrix can be controlled and hence the ignition

rate of the matrix. The grain must be consumed in the time the flame front passes by. Hence the grain size must be controlled as well as the void size.

A given grain must be consumed in the time for the flame front to propagate the flame front's own width. Hence the size of the grain is determined by the propellant's burn properties, void spaces and flame propagation. Typically the burn velocity is 100 to 1000 cm sec.sup.-1. The solid propellant burn rate might be 5 cm sec.sup.-1 at the burn pressure determined by the nozzle area.

The flame front width is determined by the void spaces and ignition properties and typically might be about 5 cm. Thus the burn time per grain might be 0.05 to 0.005 seconds. Therefore the grain radius would be 0.25 to 0.025 cm (0.5 to 0.05 cm diameter). The 0.2 cm diameter spheres referred to above fall within this range. The result is a fast burning propellant where the burn front is a finite thickness or penetration into the structure.

It is important to note in this regard that the present invention differs from previously known sponge or foam compositions. Such sponge or foam compositions normally contain voids of non-uniform size which comprise from 95% to 98% of the propellant volume, and as such are known to burn at an uncontrolled rate substantially faster than that contemplated by the present invention. While such compositions perform satisfactorily as ignitors for other higher density propellants, they lack the density (and hence the ability to provide sufficient impulse) and controlled burning characteristics (due to the lack of strength of the foam and the wide disparity in particle size and void size) required of a true propellant.

The second method of making a fast burning propellant is to control the viscosity of the solid propellant. Viscosity determines the rate of Taylor unstable growth and hence determines the rate of new area of the burning front. Viscosity stabilizes small wave lengths and prevents them from growing. For a given viscosity, surface acceleration, and density ratio only wave lengths larger than a given size will grow. If the lateral extent of the burning front were infinite, then larger wave lengths could grow and the area of burning could increase without limit. On the other hand if the propellant is confined in a tube of diameter D , then the largest wave length that can grow is limited to D .

Hence if the largest wave length that can grow is the diameter, and the growth of smaller wave lengths is limited by viscosity, a combination can be chosen such that the rate of production of new area by Taylor instability is limited.

As noted above, the phenomena known as Taylor unstable burning occurs when a heavy fluid is accelerated by a light fluid and an instability takes place at the interface whereby the light fluid interpenetrates the heavy fluid with "fingers" of penetration (e.g. as will occur if one attempts to support water with air). If the density difference is large, the depth of penetration is a fraction of (e.g. 1/3) the distance the whole mass moves during acceleration. In the usual rocket the hot (light) exhaust gases push

on the high density propellant. The only reason these two systems do not mix by Taylor instability is that the heavy material, the propellant, is semirigid and does not "flow" like a fluid.

However, it has been found that there is a more rapid burning of solid propellant when no binder is used in a conventional solid propellant mixture so that the mixture of, for example, $KClO_4$ and Aluminum is "fluidized" by the reacting gases and fingers of flame penetrate into the propellant. This has the result of causing a much faster overall burn of the fuel. The problem with this mode of propellant burn is that it is too fast and approximates an uncontrolled deflagration. It has been found that the Taylor unstable mixing progresses into the propellant at a fraction ($\approx 1/10$) of the sound speed of the propellant combustion gases. (These experiments were performed with powdered propellants.) Since the sound speed is large $C_s \approx 1.5 \times 10^3 \text{ m sec}^{-1}$, the resultant burn velocity $1 \text{ to } 2 \times 10^2 \text{ m sec}^{-1}$ is too great for practical use. This rapid burn generates too high a pressure (about 10^4 atmospheres, 140,000 PSI) for the feasible structural strength of any rocket casing.

We demonstrate our understanding of the phenomena by calculating the above experimental result. One can calculate the expected burn rate in Taylor unstable burning by assuming that the Taylor instability occurs only when the in situ burning has proceeded far enough to fluidize the propellant by generating enough high temperature gas

to fill the interstices to a pressure equal to or greater than the free surface pressure of the burn front. This fluidized propellant then allows Taylor unstable mixing to occur at a mean velocity that is a fraction, e.g. $1/2$ to $1/3$, of the combined (propellant solids and fluidizing gas) sound speed of the mixture. If the mass fraction of the burn necessary to reach this pressure is f_{mass} , then the combination sound speed of the mixture becomes

$$C_{\text{mix}} = C_s f_{\text{mass}}^{1/2}$$

The sound speed of the mixture is increased proportionally to the square root of the increase in the effective density of the mixture. If f_{mass} equals $1/10$, then the burn rate, R , becomes

$$R \approx \frac{1}{3} C_{\text{mix}}$$

On the other hand the burn rate R leads to a pressure P_{burn} for a free surface burn, i.e. without a nozzle, of

$$P_{\text{burn}} = R \rho v_{\text{exhaust}}$$

where v_{exhaust} is congruent the specific impulse times g which is the velocity corresponding to the conversion of the internal energy to kinetic energy. $\rho = \text{density}$

of propellant. Therefore $\frac{P_{burn}}{P_{max}} = \frac{f_{void}}{f_{mass}}$ On the other hand the fraction of propellant that must be burned to reach a given pressure in the interstices (i.e. void volume) of a heterogeneous propellant of fractional void volume f_{void} (assumed small) becomes $\frac{P_{burn}}{P_{max}} = \frac{f_{void}}{f_{mass}}$ Here, if the void volume were 1%, then the mass fraction, f_{mass} , that would have to be burned to reach a pressure P_{burn} equal to the maximum confined pressure $\frac{\rho C_s^2}{\gamma}$, would be also 1%. Thus $\frac{P_{burn}}{P_{max}} = \frac{f_{void}}{f_{mass}}$ For typical values of a propellant of $KClO_4$ and powdered aluminum, $C_s \approx 10^3 \text{ m sec}^{-1}$, $\gamma \approx 1.4$ so that $\frac{P_{burn}}{P_{max}} = \frac{f_{void}}{f_{mass}} = 20\%$ so that $R \approx 2 \times 10^2 \text{ m sec}^{-1}$. This is just in the range observed. This results in too large a pressure for practical application, ≈ 7500 atmospheres, or 110,000 PSI.

The fastest solid propellants burn at about 0.1 m sec^{-1} while Taylor unstable burning burns at a rate approximately 10^3 times faster. It is thus the object of this invention to provide a means to control the burn rate of a solid or semisolid propellant to values intermediate between these extremes i.e. from 10 to about 10^4 cm sec^{-1} and preferably from about 10^2 to about 10^3 cm sec^{-1} . This is accomplished according to either of two preferred embodiments, one of which prevents the onset of Taylor unstable burning by forming a rigid strong matrix of glued, near-constant size particles or chunks, the other of which imposes a velocity limitation in the nonlinear phase of Taylor instability growth.

Looking to the first embodiment, a conventional powder propellant when packed together yields a structure of mass which contains voids, typically comprising from 10% to 50% of the volume of the structure or mass. As pointed out above, it is the flow of gas through the interstices of the inter-grain void spaces that allows the "fluidization" of the propellant and the very rapid Taylor unstable burn. In this regard, it is important to note that with respect to conventional solid propellants, voids are purposely carefully eliminated for this very reason, i.e. voids will normally permit the onset of Taylor instability.

According to the present invention, however, the voids are retained (preferably comprising from 10% to 20% of the propellant volume), but one grain is glued rigidly to the next so that the fluidization process cannot take place. Thus the Taylor unstable burning mode also cannot take place. Gas will flow to a limited extent between the grains, but the large increase in the area of unstable burning will not take place--unless and until the glue strength disappears due to melting or burning of the glue. The thicker the glue bond, grain to grain, and the more refractive the glue, then the longer it will take for the grain to become free and enter the fluidized fraction of the propellant. In other words the stronger the glue the slower the burn. The slowing down of the burn rate below that associated with free particle Taylor unstable burn is desired.

As pointed out above, foamed propellants such as are used for fast ignition will not work as a fast propellant, one because the density is so low that only a very small

mass of propellant is possible inside a casing, and secondly the strength of the foam is too small or weak to support high pressure, high stress rapid burn, and third the velocity of burn is uncontrollably high due to the wide dispersion in particle size.

The second embodiment differs from the first in that the "glue" is a viscous fluid, such as a heavy oil, which fills the voids between the grains. This viscous fluid serves not to delay the actual onset of Taylor instability (such as is imposed by the time it takes the glue to lose strength by melting or burning), but instead permits the continuous surface changes during burning normally associated with Taylor instability but at a substantially slower rate (i.e. as mentioned above a velocity limitation is imposed upon the nonlinear phase of Taylor instability growth rate due to the viscosity and shear stress of the fluid). With respect to this second embodiment, a burn rate of from about 10 to about 10 m sec.sup.-1 is preferred.

Unlike the first embodiment of the invention, wherein substantially uniform particle size is important, the second embodiment permits the particle size to vary substantially. Typical particle diameters resulting from conventional manufacturing methods and usable in the present invention range from about one micron to about one mm.

This second embodiment is particularly useful in well fracturing because the large quantity of propellant that must be used calls for a relatively low cost propellant. In addition, because the propellant is placed at great depth, considerable pressure compacting of the propellant may occur due to the length of the column as well as fluid pressures. Hence it may be impractical to use void-containing propellants that are glued particle to particle such as are contemplated by the first embodiment.

DESCRIPTION OF EXEMPLARY EMBODIMENTS

EXAMPLE 1

Cracked black powder grains were screened to 1/16 to 3/32 inch size such that the grain size distribution was relatively narrow--i.e., a size distribution to within 50%. The grains were then coated with a glue that also functions as a propellant. The glue was made by dissolving a high nitrogen nitrocellulose, i.e., 12 to 12.5% nitrogen, in a solvent such as acetone, ether, or ether alcohol. In initial trials, the mass fraction of combustible glue was roughly 5 to 10% although other percentages will give different burn rates. The coated grains were then packed in an open end tube--a rocket casing 10 cm long--and allowed to dry (i.e. the solvent of the glue was allowed to evaporate). When the dried and cured propellant was ignited, it burned stably in about a tenth of a second. This gives a burn rate of 100 cm sec.sup.-1. A smaller mass fraction of glue--say 1%--increases this burn rate by another factor of 10. If a heterogeneous propellant like NH₄ClO₄ or KClO₄ plus Aluminum is used, the glue can take the form of a combustible hydrocarbon such as epoxy or urethane. The ratio of glue to aluminum to oxidizer should be such as to create a

stoichiometric balance for highest performance although a slower burn rate may require a compromise of performance. It will also be appreciated by one skilled in the art that other common oxidizers may be used according to the invention such as the compounds having Na, K, and NH₄ as the cation and NO₃, ClO₃ and ClO₄ as the anion.

EXAMPLE 2

In another embodiment the monobase or double base powders (Nitrocellulose or nitrocellulose plus nitroglycerine) may be pre-formed into balls all accurately the same size, or more complicated shapes, grains, as is well known in military cannon technology. The simplest shape, called ball powder, is ideally suited to the present concept of a controlled fast-burning propellant. A ball powder can be made of a predetermined cut of different size balls so that different packing fractions are achieved, i.e. different ratios of void space to propellant space. In addition the maximum ball size determines the burn rate as an additional delay time to the glue melting time. In this case the glueing of such a matrix is relatively simple. In one case the prepacked powder can be wetted with a solvent like ether or acetone or other well known solvent for nitrocellulose and the solvent allowed to partially dissolve the grains, e.g. balls, for a predetermined length of time. The solvent is then allowed to drain out and the dissolved surfaces of the grains then act as their own glue.

The subsequent evaporation of the solvent from within the volume of the propellant is facilitated by the fact that the void space interconnects the whole volume and hence air transport of the solvent can readily take place.

Alternately, for slower burning of the same propellant at a high chamber pressure, for example greater than 1000 PSI, it may be desirable to use a thicker glue layer filling 1/2 the void space. Then the balls should be precoated with glue before packing. The glue in this case preferably is a propellant also so that it adds to the reactive mass. Again nitrocellulose dissolved in solvent is an advantageous choice. However there may be circumstances where high specific impulse may not be the only consideration, but instead a high volume of gas may be desired. Then a glue that gives a high volume of inert gas when heated such as polycarbonates or ureas could be advantageously used.

EXAMPLE 3

The particular advantage of heterogeneous propellants where oxidizer and fuel are physically separated in the matrix--such as NH₄NO₃, Thiokol rubber, and aluminum--is that they are much safer to handle and transport and are considered practically immune to detonation. Accidental ignition is however possible and, while not necessarily as catastrophic as a detonation, is nonetheless serious. Hence, there is a need to make safer very fast burning heterogeneous propellants. Again the heterogeneous propellant can be preformed into grains and then the grains glued to one another in a fashion entirely analagous to the homogeneous propellants. The

standard heterogeneous propellant that uses a polymerized rubber, for example Thiokol, is not as easily dissolved in place as nitrocellulose, and so the preferred embodiment in this case requires that a glue be added to the grains before casting. Again the pre-polymerized rubber combined with fuel (aluminum) is one choice but many self-polymerizing glues with oxidizers added like epoxy and KClO₄ or urethane and KClO₄ are feasible.

EXAMPLE 4

In this example the propellant is considered to be a heterogeneous mixture that is fluidized with a viscosity η . The scale of the heterogeneity is the grain size δ of oxidizer or oxidizer-fuel grains. The instability growth is already initiated at large amplitude by the different properties of density and temperature of the burning grain boundaries and the viscous fluid. If the burn pressure is P , then the differential acceleration, Δa , will be of the order $\frac{P}{\rho \delta}$ where ρ is the average density and $\Delta \rho$ the density difference between grains and fluid. The differential acceleration will be balanced by a shear stress from the velocity gradient, $(\Delta v / \delta)$ in the viscous fluid of viscosity η .

The viscosity shear stress is approximately $2\eta(\Delta v / \delta)$ so that balancing of forces yields

$$(\Delta a) \rho = 2\eta(\Delta v / \delta)$$

or $\Delta v = \frac{\delta \Delta a}{2\eta}$ Choosing typical values, the typical grain size of the cheapest commercial oxidizer, NaNO₃, is $\delta \approx 0.1$ mm. The density contrast between the cheapest viscous fluid fuel, i.e. petroleum oils and tars, and NaNO₃ is $\frac{\Delta \rho}{\rho} \approx \frac{1}{3}$. The typical pressure required for fracturing a well 1 km deep would be 300 atmospheres. Then the intergrain or instability flow velocity would be

$$\Delta v \approx \frac{0.5 \times 10^4}{2 \times 10^3} \text{ meters sec}^{-1}$$

This formula of course does not hold unless η is quite large such that Δv is much less than sound speed, e.g. $\Delta v \ll 2 \times 10^3$ meter sec⁻¹. Otherwise the assumption of neglecting inertial forces in favor of viscous forces would not apply. However, because a relatively slow speed (compared to sound speed) of $\Delta v \approx 10$ to 20 meter sec⁻¹ is desired, a viscous fluid binder or fuel of $\eta \approx 3000$ poise will be necessary. Since SAE 50 automotive oil has a viscosity at 100 degree F. of roughly 1/10 this value (260 poise) it can be seen that the viscous fluid should have a viscosity between a typical road tar and bunker C fuel oil. This is fortunate because for the proposed use these residual oils are the least expensive.

Therefore a typical embodiment of a viscous solid propellant for oil well fracturing or underground bulking could combine the cheapest oxidizer NaNO₃ blended with

a residual oil such as to form the products $\text{NaO} + \text{N}_2 + \text{H}_2\text{O} + \text{CO}_2$. In addition, in order to ensure burning of the relatively refractory oxidizer NaNO_3 , one can increase the flame temperature by the addition of powdered Aluminum or a similar high energy fuel. In this case, depending upon the stoichiometric fraction, some of the heavy oil will be just vaporized rather than burned. The effectiveness of this vaporized oil as a fracturing gas is comparable to the combustion product gases. This then becomes a preferred mixture.

If the heavy oil has a low value of H to C of .congruent.1, then an excess of fuel may yield less oxygen and the products CO , CO_2 and H_2 . This is slightly preferred in fracturing because the steam (H_2O) will give up its heat to fractures and liquefy to water, thereby reducing the useful gas volume for fracturing.

EXAMPLE 5

The limiting viscosity of a viscous binder is a solid. Coal will not re-form with heat, but as a pulverized solid it can give a fast burning rate as a powder depending on particle size. The natural bitumen "Gilsonite" has the peculiar properties that it can be ground as a solid, but then partially reformed as a plastic and so a variable degree of binding can be achieved between oxidizer and fuel particles. This also can lead to medium to fast burning rate propellant just as the glued grain example.

EXAMPLE 6

A typical embodiment of well fracturing with a fast burning propellant starts with the completion of a well, for example 8" in diameter although larger or smaller diameters are entirely feasible. The volume of propellant to be burned is determined by the desired fracture system. Typically volumes of very large fracture or stimulation operations are of the order of 10,000 barrels or 2000 cubic meters. A gasified solid propellant expands to a volume of roughly 100 times the propellant volume to a typical formation pressure of 200 atmospheres (3000 PSI).

The energy content of the propellant is roughly 5×10^{10} ergs/gm giving rise to a pressure of .perspectiveto. 10^{11} dynes cm^{-2} . The adiabatic expansion of the propellant gases from 10^{11} dynes to 200 atmospheres, or 2×10^8 dynes cm^{-2} , results in a volume change of $(10^{11} / (2 \times 10^8))^{\frac{1}{\gamma}}$. .perspectiveto.85 fold. Since the density of the propellant is somewhat greater than unity, the volume of gases should be roughly 100 times the volume of propellant. The expansion of the gases may not be entirely adiabatic depending upon the back pressure in the burning region. However, if the expansion is at constant enthalpy, the volume of gas will be greater up to the ratio $V_1 / V_2 = P_1 / P_2$.perspectiveto.500. Hence the adiabatic approximation is the lower limit of available fracture volume.

In the above circumstances, the initial propellant charge of 10 m³ should be the equivalent of 1000 m³ or 5000 barrels of pumped fracture fluid.

Next a string is set with an igniter at the base (preferably Thermite or other high temperature burning igniter) and with the maximum diameter that will go down the hole--e.g. 8" in the present example. The strength of the string must be great enough to contain the propellant in place. In this example $L = \text{Vol}/\text{area}$. perspective to 300 meters assuming a pipe string wall thickness of 1/4", enough to hold the added fracture pressure during the transient burn period and assuming a competent formation as backup of the well liner. The top of the string can be closed off with a packer or stemmed with a weak cement or sand if later drill back is expected. The advantage of the weak cement or sand stem is that in the event of a blow-out from unforeseen reasons the propellant and cement particles could vent to the surface with lessened danger to personnel in the immediate vicinity.

The propellant is mixed down hole with preheated viscous oil and oxidizer. In this regard, NaNO_2 is preferred as it is the cheapest oxidizer. By mixing down hole, one avoids the danger of preignition and possible danger to personnel.

EXAMPLE 7

In a less preferred embodiment, one might consider pumping the propellant slurry through a nozzle down hole during burning at a velocity sufficiently great so that the burn front does not climb up the injection string. In this way one could avoid the difficulty of setting a casing string, and instead use cheaper, smaller diameter tubing.

However, certain difficulties can be foreseen with this approach. First, by the previous analysis the viscosity of the oil must be low for rapid pumping, yet high in order to control the burning rate of the propellant. The high viscosity of 3000 poise essentially precludes rapid pumping because of viscous pipe losses. A lower viscosity will give too high a burn rate. Finally if a slurry of pre-mixed fuel and oxidizer is pumped at a high pressure, there is always the danger of ignition by friction in the pump valves and piping. This could lead to an explosion. Hence the propellant is preferably mixed in the relative safety of down hole and burned in situ.

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United States Patent

6,439,310

Scott, III , et al.

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Real-time reservoir fracturing process

Abstract

Methods are disclosed for hydraulic fracturing of subterranean reservoir formations using various combinations of gelled fluid, nitrogen, and carbon dioxide base components, in association with proppant and other additives. Selected base components are pumped down a wellbore tubing while other selected base components are simultaneously pumped down the wellbore tubing-casing annulus for downhole mixing into a composite fracturing fluid in the downhole region of the wellbore proximal to the reservoir objective. Thereby, changes may be timely effected in the composite fluid composition and fluid properties, substantially immediately prior to the composite fluid entering the formation. Such real-time modifications may be effected to readily preempt screenout occurrences and may facilitate composite fluid compositions which otherwise are frequently undesirable to pump from the surface. Such composite fluid combinations include components phases of each of carbon dioxide, nitrogen and a base fluid. Proppant concentrations within the composite fluid entering the formation may be effected in real time without the wellbore-volume lag-time inherent in prior art methods.

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Parent Case Text

This application claims priority from U.S. provisional application 60/232,717 filed Sep. 15, 2000.

The invention described herein in part was made in the performance of work supported by the U.S. Department of Energy. Thereby, the U.S. Government has certain rights in the invention.

Claims

What is claimed:

1. A method of hydraulically fracturing a subterranean formation penetrated by a wellbore, at least a portion of the wellbore including a tubing string having a tubing bore and a casing string, the casing string and tubing string forming a casing annulus, a portion of the well bore not including the tubing string therein forming a casing bore, the method comprising:

injecting carbon dioxide into the wellbore via one of the tubing bore and the casing annulus at a first injection flow rate;

simultaneously injecting nitrogen into the wellbore via the other of the tubing string and casing annulus at a second injection flow rate;

simultaneously injecting an aqueous fracturing fluid into the wellbore with at least one of the carbon dioxide and nitrogen, at a third injection flow rate;

combining the carbon dioxide, the nitrogen and the aqueous fracturing fluid in the casing bore to form a downhole mixed composite fracturing fluid having a mixed fluid composition;

injecting the downhole mixed composite fracturing fluid from the casing bore into the subterranean formation at a hydraulic pressure sufficient to hydraulically fracture the

formation; and

selectively varying one or more of the first injection flow rate, the second injection flow rate, and the third injection flow rate to modify in real time the mixed fluid composition of the downhole mixed composite fracturing fluid, forming a modified downhole mixed composite fracturing fluid.

2. The method as defined in claim 1, further comprising:

adding a solid material proppant to the aqueous fracturing fluid to form a proppant laden downhole mixed composite fracturing fluid having another mixed fluid composition; and

thereafter injecting the proppant laden downhole mixed composite fracturing fluid from the casing bore into the subterranean formation at hydraulic pressures sufficient to hydraulically fracture the formation.

3. The method as defined in claim 2, further comprising:

selectively varying one or more of the first injection flow rate, the second injection flow rate, and the third injection flow rate to modify in real time the another mixed fluid composition of the proppant laden downhole mixed composite fracturing fluid.

4. The method as defined in claim 2, wherein a quantity of proppant in the proppant laden downhole mixed composite fracturing fluid is selectively adjusted in real time by varying at least one of the first injection flow rate, the second injection flow rate, and the third injection flow rate.

5. The method as defined in claim 2, further comprising:

monitoring in real time within the well bore a location in the formation of at least one radioactive tracer provided in at least a portion of one or more of the downhole mixed composite fracturing fluid and the proppant laden downhole mixed composite fracturing fluid by monitoring radioactive emissions from the at least one radioactive tracer; and

varying at least one of the first injection flow rate, the second injection flow rate, and the third injection flow rate in response to the monitored radioactive emissions.

6. The method as defined in claim 1, further comprising:

while selectively varying one or more of the first injection flow rate, the second injection flow rate and the third injection flow rate, increasing a viscosity of the modified downhole mixed composite fracturing fluid as compared to the downhole mixed composite fracturing fluid and cause viscous inter-fingering of the modified downhole mixed composite fracturing fluid within the downhole mixed composite fracturing fluid within the subterranean formation.

7. The method as defined in claim 1, further comprising:

adding to the aqueous fracturing fluid a selected amount of one or more additives from a group comprising chemical additives, gelling agents, alcohols, salts, fluid loss additives, and encapsulated additives; and

selectively varying the selected amount of the one or more of additives added to the aqueous fracturing fluid in response to selectively varying one or more of the first injection flow rate, the second injection flow rate and the third injection flow rate.

8. The method as defined in claim 1, further comprising:

adding a cross-linkable gelling agent to at least one of the carbon dioxide, the nitrogen and the aqueous fracturing fluid; and

adding a cross-linking agent to another of the carbon dioxide, the nitrogen, and the aqueous fracturing fluid such that the cross-linkable gelling agent and the cross-linking agent mix downhole in the casing bore in the composite fracturing fluid and cross-link at least a portion of the cross-linkable gelling agent.

9. A method of hydraulically fracturing a subterranean formation penetrated by a wellbore, at least a portion of the wellbore including a tubing string having a tubing bore and a casing string, the casing string and tubing string forming a casing annulus, a portion of the well bore not including the tubing string therein forming a casing bore, the method comprising:

injecting an aqueous fracturing fluid down one of the casing annulus and the tubing bore at a first injection flow rate;

simultaneously injecting an energized fluid down the other of the casing annulus and the tubing bore at a second injection flow rate;

combining the energized fluid and the aqueous fracturing fluid in the casing bore to form a first downhole mixed composite fracturing fluid having a first mixed fluid composition;

injecting the first downhole mixed composite fracturing fluid from the casing bore into the subterranean formation at a hydraulic pressure adequate to fracture the formation; and

selectively varying one or more of the first injection flow rate and the second injection flow rate to modify in real time the first mixed fluid composition of the first downhole mixed composite fracturing fluid to form a second downhole mixed composite fracturing fluid.

10. The method as defined in claim 9, further comprising:

adding a solid material proppant to the aqueous fracturing fluid to form a proppant laden

downhole mixed composite fracturing fluid having a second mixed fluid composition;
and

thereafter injecting the proppant laden downhole mixed composite fracturing fluid from the casing bore into the subterranean formation at hydraulic pressures sufficient to hydraulically fracture the formation.

11. The method as defined in claim 10, wherein a quantity of proppant in the composite fracturing fluid is adjusted in real-time by varying at least one of the first injection flow rate and the second injection flow rate.

12. The method as defined in claim 10, further comprising:

selectively varying one or more of the first injection flow rate and the second injection flow rate to modify in real time the second mixed fluid composition.

13. The method as defined in claim 10, further comprising:

monitoring in real time within the well bore a location in the formation of at least one radioactive tracer provided in at least a portion of one or more of the downhole mixed composite fracturing fluid and the proppant laden downhole mixed composite fracturing fluid by monitoring radioactive emissions from the at least one radioactive tracer; and

varying at least one of the first injection flow rate and the second injection flow rate in response to the monitored radioactive emissions.

14. The method as defined in claim 9, wherein the energized fluid further comprises:

at least one of carbon dioxide and nitrogen.

15. The method as defined in claim 9, further comprising:

while selectively varying one or more of the first injection flow rate and the second injection flow rate, increasing a viscosity of the second downhole mixed composite fracturing fluid as compared to the first downhole mixed composite fracturing fluid and cause viscous inter-fingering of the second downhole mixed composite fracturing fluid within the first downhole mixed composite fracturing fluid, within the subterranean formation.

16. The method as defined in claim 9, further comprising:

adding a gelling agent to one of the aqueous fracturing fluid and the energized fluid; and

adding a cross-linking agent to the other of the aqueous fracturing fluid and the energized fluid, such that the gelling agent and the cross-linking agent mix downhole in the casing bore.

17. A method of hydraulically fracturing a subterranean formation penetrated by a wellbore, at least a portion of the wellbore including a tubing string having a tubing bore and a casing string, the casing string and tubing string forming a casing annulus, a portion of the well bore not including the tubing string therein forming a casing bore, the method comprising:

injecting a first aqueous fracturing fluid including a cross-linkable gelling agent down one of the casing annulus and tubing at a first injection rate;

injecting a second aqueous fracturing fluid including a gel cross-linking agent down the other of the casing annulus and the tubing at a second injection rate;

combining the first aqueous fracturing fluid and the second aqueous fracturing fluid in the casing bore to form a downhole mixed composite fracturing fluid having a first mixed fluid composition;

injecting the downhole mixed composite fracturing fluid from the casing bore into the subterranean formation at pressures sufficient to hydraulically fracture the formation; and

selectively varying one or more of the first injection flow rate and the second injection flow rate to modify in real time the first mixed fluid composition of the downhole mixed composite fracturing fluid.

18. The method as defined in claim 17, further comprising:

adding a solid material proppant to one or more of the first aqueous fracturing fluid and the second aqueous fracturing fluid to form a proppant laden downhole mixed composite fracturing fluid having a second mixed fluid composition; and

thereafter injecting the proppant laden downhole mixed composite fracturing fluid from the casing bore into the subterranean formation at pressures sufficient to hydraulically fracture the formation.

19. The method as defined in claim 18, further comprising:

varying at least one of the first injection flow rate and the second injection flow rate to selectively modify in real time at least one of a physical property and a chemical property of at least one of the first mixed fluid composition and the second mixed fluid composition.

20. The method as defined in claim 19, wherein selectively adjusting in real time at least one of a physical property and a chemical property further comprises:

selectively varying a viscosity physical property to cause viscous inter-fingering of fluids in the subterranean formation.

21. The method as defined in claim 18, wherein a quantity of proppant in the proppant laden downhole mixed composite fracturing fluid is selectively adjusted in real time by varying at least one of the first injection flow rate and the second injection flow rate.

22. The method as defined in claim 17, further comprising:

monitoring in real time within the well bore a location in the formation of at least one radioactive tracer provided in at least a portion of one or more of the downhole mixed composite fracturing fluid and the proppant laden downhole mixed composite fracturing fluid by monitoring radioactive emissions from the at least one radioactive tracer; and

varying at least one of the first injection flow rate and the second injection flow rate in response to the monitored radioactive emissions.

23. The method as defined in claim 17, further comprising:

injecting an energizing fluid comprising one or more of carbon dioxide and nitrogen with one or more of the first aqueous fracturing fluid and the second aqueous fracturing fluid.

Description

ORIGIN OF THE INVENTION

1. Field of the invention

This invention relates to hydraulic fracturing in petroleum and natural gas reservoirs, and more particularly to real-time modification thereof by downhole mixing of fracturing components.

2. Background of the Invention

A typical reservoir *stimulation* process involves hydraulic fracturing of the reservoir formation and proppant placement therein. The fracturing fluid and proppant are typically mixed in pressurized containers at the surface of the well site location. This surface-mixed composite fracturing fluid is generally comprised of an aqueous fracturing fluid, proppant, various chemical additives, including gel polymers, and often energizing components such as carbon dioxide (CO₂) and nitrogen (N₂). After adequate surface mixing, the composite fracturing fluid is pumped via high-pressure lines through the wellhead and down the wellbore, whereupon ideally the fluid passes into the reservoir formation and induces fractures. Successful reservoir *stimulation* fracturing procedures typically increase petroleum fluid and gas movement from the fractured reservoir rock into the wellbore, thereby enhancing ultimate recovery.

Reservoir *stimulation* procedures are capital intensive. Implementation difficulties arise with many known *stimulation* methods due to various problems, including limitations associated with surface mixing of the *stimulation* fluid. Typically, a viscous, surface-mixed composite *stimulation* fluid is injected at pressures adequate to create and propagate fractures in the reservoir. The pressures required to pump such *stimulation* treatments are relatively high, particularly during injection of the gelled, thickened fluids that may be used to propel proppant into the fractures. These pumping pressures often will increase during the treatment process to an excessive limit, whereupon the operator promptly and prematurely terminates the treatment. Otherwise, serious problems may result, including rupture of surface equipment or wellbore casing and tubulars.

Excessive treating pressures may also occur abruptly during the *stimulation* fracturing process as a result of premature screenout. Such screenouts are a common problem known in industry that may occur during a fracturing treatment when the rate of *stimulation* fluid leakoff into the reservoir formation exceeds the rate in which fluid is pumped down the wellbore, thus causing the proppant to compact within the fracture, and into the wellbore. This problem of premature screenout is discussed in U.S. Pat. No. 5,595,245, which is hereby incorporated by reference.

When premature screenout is observed during a fracturing treatment, the operator may elect to reduce the proppant quantity, density, or concentration of proppant per volume of fluid, in order to prevent the occurrence of the screenout. However, when the reduction in proppant concentration is made at the surface, a significant amount of time typically passes before the pumped fluid with altered proppant concentration actually reaches the formation.

A potential problem associated with surface-blended composite fluids is that inhibitors are required to prevent viscous gelling of the *stimulation* fluid prior to pumping downhole. Highly viscous gels are typically desirable for effective transport of proppant, however, if viscous gelling occurs too early, such as in the tanks and flowlines, or before the fluid is pumped down the well, the efficiency of the overall *stimulation* job may be compromised due to higher pressures and lower pump rates. To avoid premature gelling, various known chemical inhibitors that include encapsulated or chemically coated inhibitors may be mixed into the composite fluid mixture at the surface to provide a time delayed gelling of the composite fracturing fluid. In addition, other known additives may be incorporated at the surface in an attempt to predictably control the rate of gelling, such as inhibitors to time-delay activation of cross linked polymer gels, which prevents premature gelling of the composite fracturing fluid. A serious shortcoming of this surface-mixed approach, however, is either gelling too early, or too late as evidenced by inadequate gel quality, which frequently results in poor proppant transport and premature screenout.

Typically in many wells the fracturing treatments are terminated prematurely, or reduced in size due to excessive pumping pressures that result from surface mixed and pumped fracturing treatments. In older wells, the premature gelling of the composite fracturing fluid creates a significant potential of exceeding the rated casing or tubing burst pressure.

In a 12,000 feet well, for instance, surface wellhead treating pressures often exceed 10,000 psi. whereas bottomhole treating pressures at the reservoir formation depth are significantly higher due to the combination of hydrostatic weight of the composite fracturing fluid (in wellbore) plus surface pumping pressures and friction pressure. The resultant bottomhole treating pressures, if excessive, may crush or fracture proppants in the fracture, which is undesirable due to the release of fines, fracture closure and overall formation damage.

Higher treating pressures are detrimental in terms of requiring lower pump rates, and thereby often alter the overall fracturing *stimulation* design at the well site. Frequently, the volumetric amount of composite fracturing fluid and proppant that are pumped is lower than desired due to restricted pump rates. Typically higher pumping pressures result in larger horsepower requirements, the usage of more pump engines, and higher cost. Reservoir *stimulation* fracturing is a capital intensive process, and ineffective reservoir *stimulation* treatments result in a significant loss of both expended capital and the potential recovery of hydrocarbon reserves.

A typical industry fracturing procedure may commence with mixing of the composite fracturing fluid in storage tanks located on the surface at the well site. The composite fracturing is typically comprised of aqueous gelled fluid, chemical additives and energizers such as N₂ and CO₂. After mixing, the composite fracturing fluid is pumped via high-pressure lines through the wellhead, down the wellbore and injected into the induced formation fractures. The pumping procedure is typically initiated with the pumping of a pad stage, which is typically fluid without proppant, followed by various stages of fluid containing proppant, and upon termination of the proppant-laden fracturing stage by pumping of the flush stage, which is generally fluid without proppant. This aforementioned sequence occurs when the treatment is pumped as designed, and in the absence of problems including excessive treating pressures and premature screenout.

Another typical industry *stimulation* technique is known in industry as hydraulic notching or "hydrajetting", whereby fluid is injected downhole to cut slots into the production casing or openhole reservoir formation, and thereby induce fractures in the reservoir formation. Conversely this technique may also be used in openhole and horizontal well *stimulation* procedures. This known *stimulation* procedure comprises pumping limited proppant concentration during fracturing through casing or in openhole formation, whereby fluid with proppant is typically pumped via tubing through Tungsten jet nozzles that are located at the distal end of the tubing. In the hydrajetting process, mixing of the tubing and annular flow-streams occurs adjacent to the reservoir formation as generally similar fluids are simultaneously pumped down casing. This procedure is typically limited to *stimulation* applications involving smaller fractures where proppant concentrations are relatively low (usually less than 5 pounds per gallon) in comparison to most typical sand-fracturing techniques, and furthermore the total amounts of proppant that are placed in the fracture are relatively low.

The hydrajetting process may include pumping of different fluids simultaneously down annulus and tubing, in terms of one fluid type consisting of proppant. This process is

flexible in allowing different fluid types including acid to be used, but is also relatively expensive in comparison to typical known fracturing techniques. Annular rates are adjusted to maintain fracturing pressures as fractures are generated by the hydrjet fracturing process. A limitation in the use of this system occurs, however, as jets may become eroded during the fracturing injection process, in addition turbulent flow patterns may disperse proppant in the near-wellbore fractures. The proppant washout may be due to a Bernoulli affect, whereby the annular pressures are lower than the fracture tip pressures.

SUMMARY OF THE INVENTION

In accordance with the present invention, there is provided a real-time hydraulic fracturing process in which substantial quantities of both nitrogen and carbon dioxide may be separately injected, via the tubing string and casing annulus, to form, in the downhole region of the wellbore, a composite fracturing fluid that may include an aqueous-based fluid, a proppant, N₂ and CO₂ energizers and various other chemical components. This inventive process may be used to stimulate reservoirs in vertical and horizontal wells, and in openhole and cased wells. The inventive system may also be used for enhanced reservoir recovery procedures to remediate depleted reservoirs in mature fields, via short phase tertiary CO₂ injection.

Downhole-blending proximal to the reservoir zone is accomplished by dual injection of different fluids through coiled or conventional tubing and casing annulus. A composite fracturing fluid is thus created downhole prior to injection into the reservoir formation fracture. The aqueous based fracturing fluid may be incorporated into either or both of the gases at the surface and may include proppant and other chemical components, which form the composite fracturing fluid upon mixing downhole. This *downhole-mixed* fracturing fluid is blended downhole to avoid excessive friction pressures and then injected at a desirable thickened viscosity and at a pressure sufficient to implement hydraulic fracturing of the selected reservoir interval.

Known additives, including thickening agents, may be incorporated into the base-fluid to increase fluid viscosity, to improve proppant suspension, leak-off and related rheological properties. Carbon dioxide may be provided in liquid phase via the tubing and nitrogen may be provided in gaseous phase via the casing, or conversely the carbon dioxide may be injected down the casing and nitrogen down the tubing. Thorough mixing of the propping agent with the composite *stimulation* fluid preferably occurs immediately above or adjacent to the reservoir interval where the induced reservoir fracture or fractures are propagated. The procedure of downhole-mixing may be accomplished concurrent with tracer monitoring, in real-time, as described in our U.S. Pat. No. 5,635,712 (Scott-Smith), which is hereby incorporated by reference.

In the event of a premature screenout, an operator typically immediately ceases pumping proppant down the casing annulus and the fracturing job is terminated prematurely, or conversely the operator might attempt to abruptly increase the rate of pumping in an often futile endeavor to create new fracture growth, or increase the existing fracture width.

However, these known techniques typically do not always yield satisfactory results, and may even worsen the problem in terms of screening out, fracturing out of the desired reservoir zone, or ruining the wellbore casing due to excessive pressures and resultant pipe rupture.

A variety of problems are avoided in real-time by this method of downhole mixing, which provides the ability to substantially instantaneously modify *stimulation* treatment by rapid changes in pump rate, fluid rheology and proppant concentrations. This inventive system typically minimizes friction pressures and thus provides lower treating pressures and higher pumping and injection rates. Downhole mixing facilitates true real-time modification of the fracture treatment, and provides near instantaneous alteration of fluid viscosity and proppant concentrations at the reservoir, as is described further below.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic cross-sectional representation of a fracturing procedure showing the various stages involved.

FIG. 2 illustrates a typical downhole-blended real-time hydraulic fracturing operation illustrating surface facilities and pump trucks, with simultaneous injection of different components down tubing and casing to form a composite fracturing fluid in the downhole region.

FIGS. 3-5 illustrate variations and/or consecutive progression of *downhole-mixed* well *stimulation* procedures with pumping of various components down tubing and casing annulus.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

FIG. 1 illustrates various stages during a typical fracturing treatment sequence, whereby fracturing fluid is blended downhole and pumped in pre-pad (10), pad (20), proppant (30) and flush (40) stages. As indicated, aqueous fluid, which might also be comprised of gelled hydrocarbons, is pumped down casing (50) while the tubing 60 is a "dead string", which provides the operator measurement of bottomhole treating pressure during the fracturing process. Alternately, the surface-mixed composite fracturing fluid may be pumped down tubing (60), or the same fluid may be pumped simultaneously down both tubing and casing. The composite fracturing fluid is generally comprised of various additives, including gel, proppant, or energizers including CO₂ and Nitrogen, which are mixed at the surface prior to pumping down the well for injection into the formation to induce fracturing.

In the inventive embodiment illustrated in FIG. 2, the novel process of employing carbon dioxide, nitrogen, aqueous fluid and other chemical additives in accordance with downhole mixing may be understood by reference to the hydraulic fracturing operation as indicated. Aqueous gel (65) with Nitrogen (70), and liquid CO₂ (80) are pumped concurrently down casing (50) and tubing (60) respectively, at constant or variable ratios

during successive treatment stages. The liquid CO₂ (80) is pumped from storage tank via high pressure line (110) by pump (120) through the wellhead (130) and down the tubing (60) during simultaneous pumping of gelled fluid (140) with methanol and Nitrogen (70) down the cased wellbore (50). Downhole-mixing forms a composite fracturing fluid (150) above or adjacent to perforations (160), which are located proximal to the desired reservoir (170) objective. A hydraulically induced fracture (180), shown in cross-sectional view, contains the composite fracturing fluid (150). Alternate arrangements of surface equipment, for mixing various components at the surface, are possible. The fluid content of the composite fracturing fluid is typically subject to water leakoff into reservoir formation (170). Different combinations of known fluid components and chemical additives may be mixed downhole to reduce the fluid leakoff.

FIGS. 3-5 show a *downhole-mixed* fracturing procedure sequentially as the treatment progresses through various stages. FIG. 3 shows the initial fracturing fluid (190) pumped via casing into the reservoir zone of the well adjacent to the reservoir formation to be fractured. Fracture initiation is established (as evidenced by formation breakdown pressure) whereupon the formation mechanically fails and one or more fractures (180) are formed during injection of this initial pad stage (190) into the reservoir formation. The initiation of a fracture or fractures in the formation usually is accompanied by a relatively abrupt and substantial decrease in bottomhole treating pressure, which is monitored by operator at the well site surface.

FIG. 4 shows the subsequent mixing downhole of composite fracturing fluid (150), as fluid component (200) is pumped via casing and CO₂ (80) is concurrently pumped down tubing. In this embodiment, the pump rates may be varied for the purpose of achieving desirable fracture growth and proppant placement within the reservoir zone. In addition, fluid rheology may be selectively altered, in real-time, as a result of modification of relative pump rates at surface of tubing versus casing. Both the composite fracturing fluid rheology and proppant concentration may be modified essentially at or near the perforations, in real-time. This system facilitates prompt changes in proppant concentration, which is particularly important under certain circumstances such as when attempting to avoid premature screenout of the fracturing treatment. Avoidance of premature screenout may be achieved by prompt reduction of proppant concentration in the downhole region by increasing the rate of clean (i.e. without proppant) fluid or energizer (CO₂, Nitrogen) relative to the proppant-laden aqueous fluid. Avoidance of screenout in real-time thus may be achieved by increasing the relative rate of clean fluid, or energizer, from tubing, with respect to sand-laden fluid that is pumped via casing. Both tubing and casing flowstreams may separately or together include chemical additives that are specifically applied to further minimize the rate of fluid leakoff into the formation, which contributes toward the occurrence of premature screenout.

FIG. 5 illustrates the pumping of a proppant-laden slurry (210) including energizers (such as N₂) down casing concurrent with the pumping of CO₂ (80) down tubing. Real-time modification of the composite fracturing fluid (150) and to another composite fracturing fluid (160), including varied proppant concentration, may be facilitated by adjusting the injection rates of tubing and casing relative to each other. The net composition of the

composite fracturing fluid (i.e. rheologic properties) and proppant concentrations may be altered as desired by altering the rates that the tubing and casing components are pumped. For example, the composite fracturing fluid may be adjusted, in real-time, from a ratio of 40% CO₂-30% N₂-30% aqueous fluid slurry (with proppant) to a 80% CO₂-15% N₂-15% aqueous fluid slurry by increasing the volumetric rate of CO₂ pumped down tubing. Although the pumping equipment is located at the surface, like a syringe the effectuated increase in tubing pump rate is immediately evidenced at the bottom of the wellbore and results in a real-time change in the composite fracturing fluid entering the formation. As a result, the proppant concentration is changed in real-time by the increased ration of clean fluid or CO₂ relative to the proppant-laden slurry. The rate of change may be further accentuated by simultaneously decreasing the casing annular pump rate while increasing the tubing pump rate, such as might be indicated by premature screenout and the need to radically reduce proppant entry into the formation.

According to the present invention, each of at least two fluids used for fracturing formations penetrated by subterranean wellbores may be pumped down respective tubular conduits, simultaneously, to mix and interact in a downhole portion of the wellbore forming a composite fracturing fluid therein, which is then pumped into the formation/reservoir.

The pump rate of fluid in one or both tubular conduits may be selectively and individually varied to effect changes in composition of the composite fluid, substantially in real time to exert improved control over the fracturing process, including the quality, physical and chemical properties of the composite fluid entering the formation. Proppant transport qualities thereby may also be modified substantially in real time. Other benefits may also be realized, such as reduced friction losses, reduced hydraulic horsepower requirements, and improved pump rate limits over the restrictions that may be imposed by wellbore tubular sizes.

By providing separate conduits for respective separate fluid compositions at the surface, composite downhole fracturing fluid combinations that might otherwise have been impractical if mixed at the surface, may be permissible. For example, a first fracturing fluid phase including carbon dioxide may be pumped down the tubing, while a second fluid phase including nitrogen, gelled aqueous fluid and proppant may be pumped down the casing annulus. The first and second fluid phases may combine and mix downhole in the casing to form a composite fracturing fluid that might otherwise have exhibited too much friction loss to have been pumped from the surface as a composite fracturing fluid. In like fashion, cross-linking may be performed downhole in the casing without relying on "delayed" cross-linking techniques that result from predictable fluid pH changes. For example, a borate gel may be incorporated concurrently with CO₂, which if mixed at the surface the CO₂ would act as an efficient breaker of the borate gel crosslinking action.

Often, a desirable embodiment may of downhole-mixing may be used to create viscous inter-fingering of CO₂ or other gaseous phases within the aqueous pad fluid that is present in the formation fracture. Although mixing along the interfaces of the different density phases may also occur, the vertical separation of discrete phases in the fractures, due to

fluid phase or density variations, may likely result. Under some circumstances this discrete separation of different phase types in the fracture is desirable, such as to avoid placement of proppant in water-productive zones, or to avoid fracturing into gas-oil, gas-water, or water-oil contacts in the reservoir.

The term "aqueous fracturing fluid" as used herein may be defined broadly to encompass any liquid fracturing fluid, including water based fluids, alcohol based fluids, or crude oil based fluids, or any combination thereof. Energizers such as carbon dioxide and/or nitrogen may be pumped down one or both tubular conduits, individually or in combination with one of the aqueous fracturing fluids or some portion thereof. "Carbon dioxide" may include liquid carbon dioxide, and may also include carbon dioxide miscibly dissolved in a liquid, or foamed with another liquid as either the continuous or discontinuous phase. "Nitrogen" may include also include nitrogen or a nitrogen containing compound alone, or mixed with, foamed, or partially dissolved in a liquid, or without a liquid. Carbon dioxide in the liquid phase is highly soluble in water, however, nitrogen is relatively insoluble in water, even at comparatively high pressures commonly encountered at the bottom of a well.

Water based fracturing fluids may include fresh water based fluids, sea water based fluids, or brine solutions, and may further include added salt compounds, such as KCl and NaCl. Alcohol based fracturing fluids may include aliphatic alcohols such as methanol, ethanol, isopropyl alcohol, tertiary butyl alcohol and/or other alcohol based compounds. Oil based fracturing fluids may also be included within the term "aqueous fracturing fluid" as used herein, and may include "live oil," "dead oil," "crude oil," "refined oil," condensate, or other hydrocarbon based fluids. Any combination of gelling, thickening, cross-linking, or other known fracturing fluid additives may be included in any of the above fracturing fluids.

Another embodiment comprises pumping aqueous fluid with proppant and other chemicals additives, including methanol or other alcohols, down casing while concurrently pumping CO₂ down tubing. Or conversely CO₂ may be mixed with Nitrogen, or 100% Nitrogen may be pumped down tubing for admixture with fluid components. As a result of pumping this configured embodiment, the composite fracturing fluid that is comprised of aqueous fluid, methanol, proppant and CO₂, is pumped at substantially reduced pumping pressures relative to the current industry practice of first mixing said components in surface tanks prior to pumping down the wellbore. The advantages of this downhole-blended embodiment include lower treating pressures, lower horsepower pumping requirements, and lower overall costs related to the procedure. In addition, this procedure provides means for adjusting both fluid rheology and proppant concentration in real-time. Said adjustments in rheology include changes in gel strength, viscosity, and gel-breaker quality.

In another inventive embodiment, downhole-mixing may be achieved by the pumping of aqueous gel crosslinking agents down tubing or casing, while concurrently pumping gel crosslinking activators and other chemical additives down casing or tubing, respectively, to result in a more precisely controlled crosslinking of the composite gelled fracturing

fluid. Cross-linking agents may be blended in the downhole region with polymeric thickening agents comprising borate gels or multivalent metal ions such as titanium, zirconium, chromium, antimony, iron, and aluminum. The cross-linking agents and polymer combinations include, but are not limited to mixing guar and its derivatives as a polymer with a cross-linking agent of titanium, zirconium or borate; a polymer composition of cellulose and its derivatives cross-linked with titanium or zirconium; acrylamide methyl propane sulfonic acid copolymer cross-linked with zirconium.

Downhole mixing provides efficient turbulent dispersion of both carbon dioxide and nitrogen in the gelled aqueous fluid. This downhole-blending procedure may also be conducted with either or both Nitrogen and CO₂ added into the *downhole-mixed* composite fracturing fluid, in various stages or the entirety of the fracturing treatment. Or conversely, Nitrogen and CO₂ energizers may not be required in some circumstances, such as when adequate reservoir pressures are present to assure a relatively prompt flowback and cleanup of the composite fracturing fluid. CO₂ may be supplied as a liquid at about -10.degree. F. to 10.degree. F. and at a pressure of about 250 to 350 psig. Nitrogen may be supplied as a gas, normally at ambient temperature of from about 65.degree. F. to 115.degree. F. The composite fracturing fluid may be at a pressure at the wellhead that is typically within the range of from less than 1,000 to more than 12,000 psig.

In addition, various chemical additives may be mixed downhole to modify gel quality. *Downhole-mixed* hydrophilic gels may be employed, which swell when water molecules are encountered. As a result, gels may be primed by downhole-mixing with activators and known chemicals to create freshly reactive hydrophilic gels that drastically increase fluid viscosity whenever water-productive zones are encountered, thus plugging or sealing fractures as a result. Thus, as fracture propagation out of a desired reservoir interval occurs, hydrophilic molecules may be created in the downhole region for binding water molecules and concurrently sealing the fracture to minimize unwanted water production.

Enhanced gels may be created by downhole blending. Chemical mixtures that are created or activated by downhole-mixing may be employed to modify relative fluid or gas flow characteristics of the reservoir rock. Relative reservoir permeability may be modified by application of known chemicals and known activators that are mixed in the downhole region, particularly those that react relatively rapidly, as compared to current practices of pumping surface-admixed gels that often may be compositionally unstable. CO₂ and nitrogen may be included in this process. CO₂, nitrogen and various other known additives including surfactants may be mixed downhole to alter wetting properties and interfacial tension angles between the hydrocarbon and reservoir rock. The gel rheology and ratios of nitrogen and carbon dioxide to the aqueous fracturing fluid may be altered at various stages of operation, in real-time, if a sudden unanticipated change in bottomhole treating pressure occurs, or as early premature screenout is evidenced or suspected.

During the fracturing process, a typical propping agent, such as Ottawa frac sand or ceramic particles, may be employed in concentrations ranging from less than 0.5 to 15

pounds of sand per gallon of fracturing fluid. Viscosifying agents may be employed to increase the viscosity of the aqueous solution and to increase the propping agent concentration, which may be progressively increased, or decreased as desired during the fracturing treatment.

Subsequent to the injection of the propping agent into the fracture, it may be desirable to complete the operation with the injection of a wellbore flushing fluid that is absent propping agent. This flushing fluid functions to displace previously injected propping agent into the fracture and reduces the accumulation of undesirable quantities of propping agent within the well proper. The flush stage may also include various chemical additives including resin activators and inhibitors.

At the conclusion of the displacement of proppant-containing fluid, the fracturing operation normally is concluded by the injection of a flushing fluid to displace the propping agent into the fracture. The well may then be shut in for a period of time to allow the injected fluid to reach or approach a state of equilibrium, with both the carbon dioxide and the nitrogen in the gaseous phase. After the well is placed on production by flowing the well back, via a positive pressure gradient extending from the reservoir to the surface via the wellbore, the co-mingled nitrogen and carbon dioxide function to effectively displace the aqueous fracturing fluid from the formation. This provides a clean-up process at the conclusion of the fracturing operation since both nitrogen and carbon dioxide displace fluids from the formation.

By using the inventive process of downhole mixing, the operator has more options when faced with premature screenout. These options include simultaneously increasing pump rate down the tubing with circulation of the casing fluid into pits, or conversely, the operator may elect to dilute proppant concentration entering the reservoir in real-time by increasing the pump rate of clean fluid relative to the pump rate of proppant-containing slurry, thus decreasing the amount of proppant per volume of composite fracturing fluid entering the formation. This inventive downhole mixing method may also be used to avoid screenout by increasing the effective admixture of additives for the purpose of minimizing fluid loss to the formation, in real-time.

As a practical matter, the addition of polymeric thickening agents, and other additives incorporated therewith, hydration of the aqueous fluid to form the initial gel, and the addition of propping agent may be accomplished under ambient surface temperature and pressure conditions. Injection of these components via tubing and casing is accomplished to induce downhole-mixing adjacent to the reservoir.

A cross-linking agent may be injected separately (down tubing) from the other chemical components (down casing), so that initiation of cross-linking reaction occurs downhole immediately prior to injection of the composite fluid into the reservoir. This facilitates avoidance of a premature increase in viscosity of the fracturing fluid as it travels downhole in the casing or tubing, which often occurs with surface-mixed composite fluids. Premature viscosification of the fracturing fluid creates excessive treating pressures as a result of friction loss. During a fracturing procedure, increased fluid

friction requires increasing hydraulic horsepower, which increases costs and often restricts overall pump injection rates.

The composition of the aqueous phase of the fracturing fluid may include polymer gelling agents, surfactants, clay stabilizers, foaming agents, and potassium salt. Methanol may be added to the fracturing fluid in those cases where the formation contains substantial quantities of clay minerals. It is often times desirable to add from about 10-20 volume percent methanol to the fracturing fluid in such circumstances. Polymeric thickening agents are useful in the formation of a stable fracturing fluid. Examples of known thickening gelling agents may contain one or more of the following functional groups: hydroxyl, carboxyl, sulfate, sulfonate, amino or amide. Polysaccharides and polysaccharide derivatives may be used, including guar gum, derivatized guar, cellulose and its derivatives, xanthan gum and starch. In addition, the gelling agents may also be synthetic polymers, copolymers and terpolymers. Cross-linking agents may be combined with the solution of polymeric thickening agents including multivalent metal ions such as titanium, zirconium, chromium, antimony, iron, and aluminum. The cross-linking agents and polymers may be combined as desired via downhole mixing. These combinations include but are not limited to (1) admixing guar and its derivatives as a polymer with a cross-linking agent of titanium, zirconium or borate; (2) polymer composition of cellulose and its derivatives cross-linked with titanium or zirconium; (3) acrylamide methyl propane sulfonic acid copolymer cross-linked with zirconium. The amount of thickening agent utilized depends upon the desired viscosity of the aqueous phase and the amount of aqueous phase mixed downhole in relation to the energized phase, that is, the liquid carbon dioxide and nitrogen phase. As the amount of liquid carbon dioxide and nitrogen increases, the amount of aqueous phase will commonly be 20% to 50%. Reservoir injection rates and composition of the component fracturing fluid will vary in the downhole region as a function of modification of relative pump rates for tubing and casing. This allows the operator to control proppant concentration and relative gas-fluid ratios as the composite fluid enters the reservoir fracture, all of which may be varied or kept constant, in real-time as desired by the operator.

Additives and water are typically admixed into an aqueous fracturing fluid at the surface throughout the fracturing operation, or the gelled fluid may be formulated before the operation and kept in surface storage tanks until needed. Various additives as described may then be blended into the water in the tanks, or via downhole blending, depending on the operator's objective intent. After additives are thoroughly blended with the water, the water becomes "gelled", whereby the thickened aqueous fluid may be transferred from the storage tanks to a blender. Proppant, when required, may be added via mixing tub attached to the blender at a selected rate to achieve the required concentration, in pounds per gallon of liquid, to obtain the desired downhole concentration. The treating fluid or gel-proppant slurry may be transferred by transfer pumps at a low pressure, usually about 100-300 psi, to high pressure generally greater than 500 psi, by tri-plex pumps. The tri-plex pumps inject the separate fracturing components into the treating lines that are connected directly at the wellhead to tubing and casing, at a desired rate and pressure adequate to hydraulically fracture the formation.

Carbon dioxide may preferably be introduced in the liquid phase down the bore of the tubing string, whereas typically nitrogen is pumped in the gaseous phase down the casing (annular area between the tubing string and the casing). The agitation and turbulent shearing associated with downhole blending provides adequate mixing of the carbon dioxide and nitrogen within the aqueous fluid mixture. Downhole mixing according to this invention also provides uniform blending of carbon dioxide and nitrogen with the aqueous phase and forms a composite fracturing fluid with desirable proppant-carrying properties.

The aqueous base fluid phase may contain various chemical additives routinely used by those skilled in the art, including gelled hydrocarbons, and may be pumped separate for mixing downhole. For example, polymers, cross-linking agents, catalysts, and surfactants, and the aqueous phase may also contain one or more biocides, surface tension reducing non-emulsifying surfactants, clay control agents, salts, fluid loss additives, buffers, gel breakers, iron control agents, paraffin inhibitors and alcohols. Various of these components may be injected separately via tubing and casing for admixture in the downhole region of the well.

Having described specific embodiments of the present invention, it will be understood that other modifications thereof may now be apparent to those skilled in the art. The invention is thus intended to cover all such modifications of downhole blended fracturing, which are within the scope of the appended claims.

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