

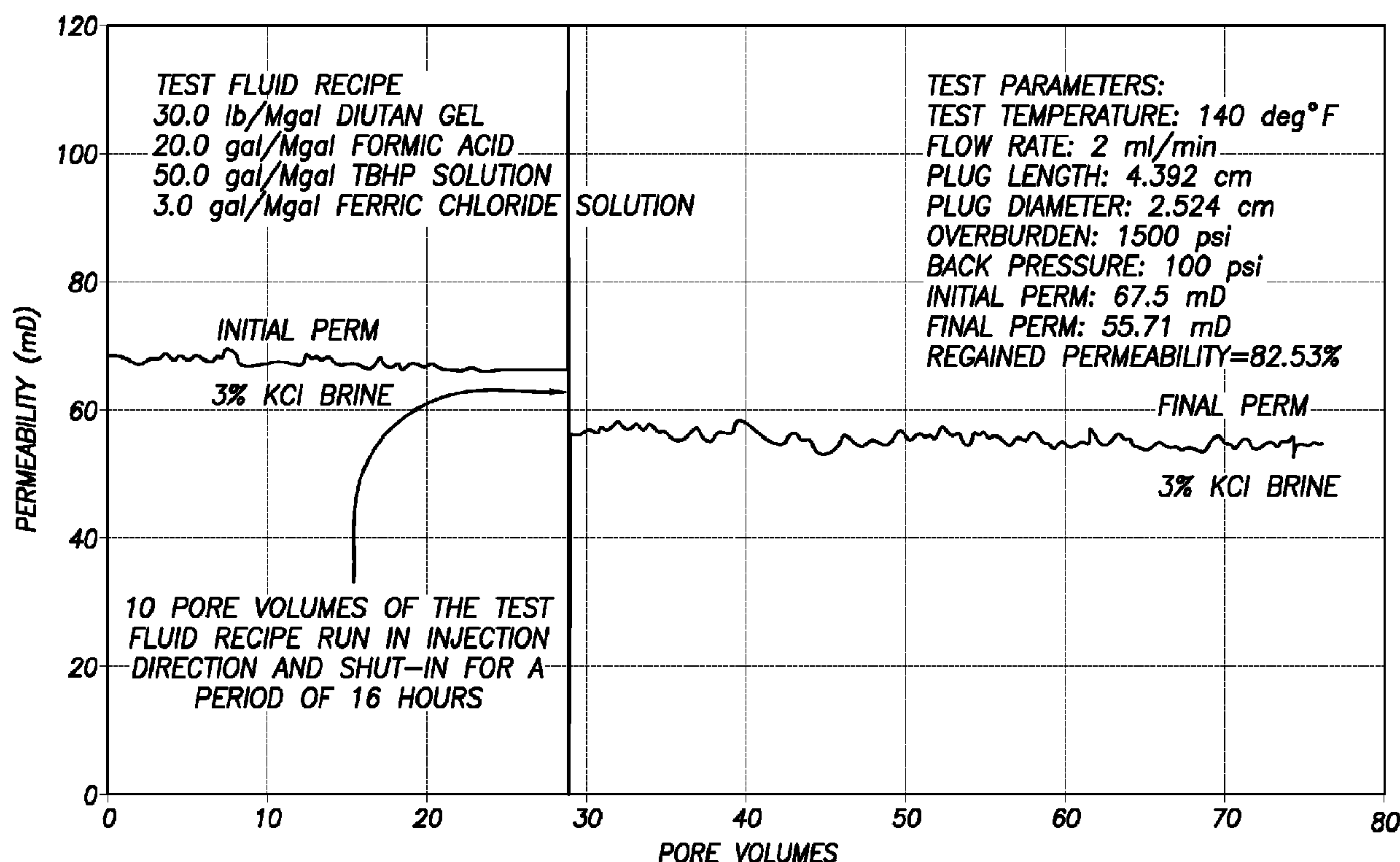


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(72) **Inventeurs/Inventors:**
GEORGE, SHOY C., IN;
SALGAONKAR, LALIT P., IN;
PATIL, PRAJAKTA RATNAKAR, IN
(73) **Propriétaire/Owner:**
HALLIBURTON ENERGY SERVICES, INC., US
(74) **Agent:** NORTON ROSE FULBRIGHT CANADA
LLP/S.E.N.C.R.L., S.R.L.

(54) **Titre : DECOMPOSITION DE DIUTANE EN UTILISANT UN ACTIVATEUR METALLIQUE A 140 °F OU MOINS**
(54) **Title: BREAKING DIUTAN WITH METAL ACTIVATOR DOWN TO 140 °F OR LOWER**

REGAIN PERMEABILITY TEST ON ALOXITE CORE 400 mD (AIR)



(57) **Abrégé/Abstract:**

A method of gravel packing a treatment zone of a well includes the steps of: (A) forming a treatment fluid including a continuous aqueous phase and gravel, wherein the aqueous phase includes: (i) water; (ii) diutan; (iii) oxidizer in the range of 0.1% to 2% by weight of the water; (iv) organic acid in the range of 0.5% to 5% by weight of the water; and (v) transition metal compound in the range of 0.001% to 0.25% by weight of the water; and (B) introducing the treatment fluid into the treatment zone; wherein the

(57) **Abrégé(suite)/Abstract(continued):**

design temperature is less than 180°F; wherein the continuous phase of the treatment fluid has a viscosity in the range of 10 cP to 75 cP at the design temperature; and wherein the concentration of the organic acid is less than would cause the diutan to salt out at the design temperature.

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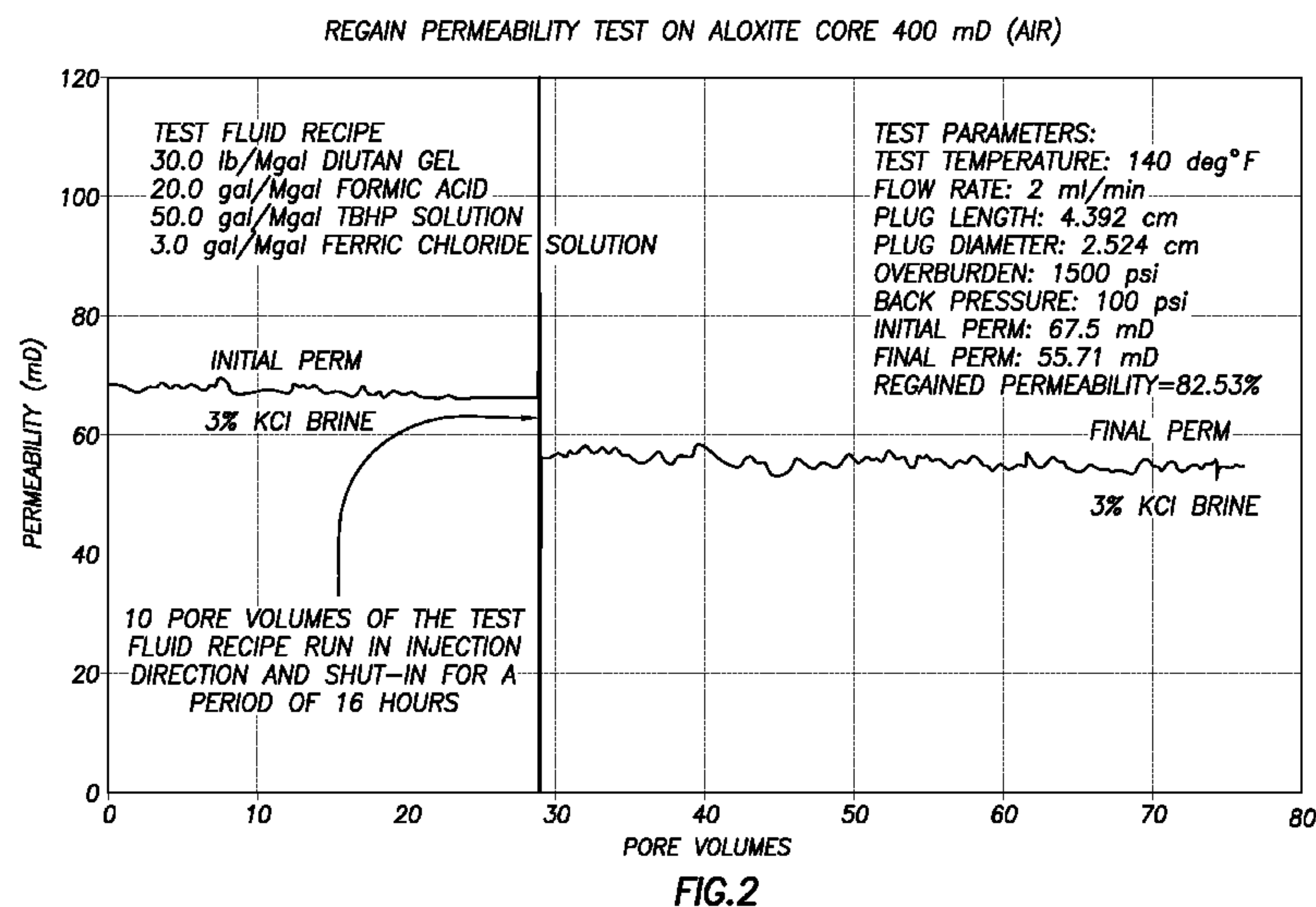
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- (71) Applicant: **HALLIBURTON ENERGY SERVICES, INC.** [US/US]; 10200 Bellaire Boulevard, Houston, TX 77072 (US).
- (72) Inventors: **GEORGE, Shoy, C**; Chittattukara House, Kodakara, 680684 Thrissur (IN). **SALGAONKAR, Lalit, P**; 6/Prasad Apartment, Lane No. 1, Dahanukar Colony, Kothrud, 411038 Pune (IN). **PATIL, Prajakta, Ratnakar**; B1/F6 Tara Residency, Near Gandhi Lawns, Kothrud, 411038 Pune (IN).
- (74) Agent: **ALBANESI, Todd, E**; Booth Albanesi Schroeder LLC, 1601 Elm Street, Suite 1950, Dallas, TX 75201 (US).

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(54) Title: BREAKING DIUTAN WITH METAL ACTIVATOR DOWN TO 140 °F OR LOWER



(57) Abstract: A method of gravel packing a treatment zone of a well includes the steps of: (A) forming a treatment fluid including a continuous aqueous phase and gravel, wherein the aqueous phase includes: (i) water; (ii) diutan; (iii) oxidizer in the range of 0.1% to 2% by weight of the water; (iv) organic acid in the range of 0.5% to 5% by weight of the water; and (v) transition metal compound in the range of 0.001% to 0.25% by weight of the water; and (B) introducing the treatment fluid into the treatment zone; wherein the design temperature is less than 180°F; wherein the continuous phase of the treatment fluid has a viscosity in the range of 10 cP to 75 cP at the design temperature; and wherein the concentration of the organic acid is less than would cause the diutan to salt out at the design temperature.

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BREAKING DIUTAN WITH METAL ACTIVATOR DOWN TO 140 °F OR LOWER**TECHNICAL FIELD**

[0002] The inventions are in the field of producing crude oil or natural gas from subterranean formations. More particularly, the present invention relates to methods of reducing the viscosity of well treatment fluids that include diutan or a diutan derivative. The present invention has particular application to gravel packing.

BACKGROUND**Producing Oil and Gas**

[0003] In the context of production from a well, oil and gas are understood to refer to crude oil and natural gas. Oil and gas are naturally occurring hydrocarbons in certain subterranean formations.

[0004] To produce oil or gas from a reservoir, a well is drilled into a subterranean formation, which may be the reservoir or adjacent to the reservoir. A well includes a wellhead and at least one wellbore from the wellhead penetrating the earth. Typically, a wellbore must be drilled thousands of feet into the earth to reach a hydrocarbon-bearing formation. Generally, the greater the depth of the formation, the higher the static pressure and temperature of the formation.

[0005] Generally, well services include a wide variety of operations that may be performed in wells, such as drilling, cementing, completion, and intervention. Well services

are designed to facilitate or enhance the production of desirable fluids from or through a subterranean formation. A well service usually involves introducing a well fluid into a well.

[0006] Drilling, completion, and intervention operations can include various types of treatments that are commonly performed in a wellbore or subterranean formation. For example, a treatment for fluid-loss control can be used during any of drilling, completion, and intervention operations. During completion or intervention, stimulation is a type of treatment performed to enhance or restore the productivity of oil and gas from a well. Stimulation treatments fall into two main groups: hydraulic fracturing and matrix treatments. Fracturing treatments are performed above the fracture pressure of the subterranean formation to create or extend a highly permeable flow path between the formation and the wellbore. Matrix treatments are performed below the fracture pressure of the formation. Other types of completion or intervention treatments can include, for example, gravel packing, consolidation, and controlling excessive water production. Still other types of completion or intervention treatments include, but are not limited to, damage removal, formation isolation, wellbore cleanout, scale removal, and scale control. Of course, other well treatments and treatment fluids are known in the art.

Acidizing

[0007] Acidizing is a type of stimulation treatment, which is performed below the reservoir fracture pressure in an effort to restore or enhance the natural permeability of the reservoir rock. Well acidizing is achieved by pumping acid into the well to dissolve limestone, dolomite and calcite cement between the sediment grains of the reservoir rocks. There are two types of acid treatment: matrix acidizing and fracture acidizing

[0008] In matrix acid job, acid is pumped into the well and into the pores of the reservoir rocks. In this form of acidization, the acids dissolve the sediments and mud solids that are inhibiting the permeability of the rock, enlarging the natural pores of the reservoir and stimulating flow of hydrocarbons.

[0009] While matrix acidizing is carried out at a pressure less than the fracture pressure of the reservoir rock, fracture acidizing involves pumping highly pressurized acid into the well, physically fracturing the reservoir rock and dissolving the permeability

inhibitive sediments. This type of acid job forms channels through which the hydrocarbons can flow.

Hydraulic Fracturing

[0010] Hydraulic fracturing is a common stimulation treatment. The purpose of a fracturing treatment is to provide an improved flow path for oil or gas to flow from the hydrocarbon-bearing formation to the wellbore. A treatment fluid adapted for this purpose is sometimes referred to as a fracturing fluid. The fracturing fluid is pumped at a sufficiently high flow rate and pressure into the wellbore and into the subterranean formation to create or enhance one or more fractures in the subterranean formation. Creating a fracture means making a new fracture in the formation. Enhancing a fracture means enlarging a pre-existing fracture in the formation.

[0011] The formation or extension of a fracture in hydraulic fracturing may initially occur suddenly. When this happens, the fracturing fluid suddenly has a fluid flow path through the fracture to flow more rapidly away from the wellbore. As soon as the fracture is created or enhanced, the sudden increase in the flow of fluid away from the well reduces the pressure in the well. Thus, the creation or enhancement of a fracture in the formation may be indicated by a sudden drop in fluid pressure, which can be observed at the wellhead. After initially breaking down the formation, the fracture may then propagate more slowly, at the same pressure or with little pressure increase. It can also be detected with seismic techniques.

Proppant for Hydraulic Fracturing

[0012] A newly-created or newly-extended fracture will tend to close together after the pumping of the fracturing fluid is stopped. To prevent the fracture from closing, a material is usually placed in the fracture to keep the fracture propped open and to provide higher fluid conductivity than the matrix of the formation. A material used for this purpose is referred to as a proppant.

[0013] A proppant is in the form of a solid particulate, which can be suspended in the fracturing fluid, carried downhole, and deposited in the fracture to form a proppant pack. The proppant pack props the fracture in an open condition while allowing fluid flow through the permeability of the pack. The proppant pack in the fracture provides a higher-

permeability flow path for the oil or gas to reach the wellbore compared to the permeability of the matrix of the surrounding subterranean formation. This higher-permeability flow path increases oil and gas production from the subterranean formation.

[0014] A particulate for use as a proppant is usually selected based on the characteristics of size range, crush strength, and solid stability in the types of fluids that are encountered or used in wells. Preferably, a proppant should not melt, dissolve, or otherwise degrade from the solid state under the downhole conditions.

[0015] The proppant is selected to be an appropriate size to prop open the fracture and bridge the fracture width expected to be created by the fracturing conditions and the fracturing fluid. If the proppant is too large, it will not easily pass into a fracture and will screenout too early. If the proppant is too small, it will not provide the fluid conductivity to enhance production. In the case of fracturing relatively permeable or even tight-gas reservoirs, a proppant pack should provide higher permeability than the matrix of the formation. In the case of fracturing ultra-low permeable formations, such as shale formations, a proppant pack should provide for higher permeability than the naturally occurring fractures or other micro-fractures of the fracture complexity.

[0016] Appropriate sizes of particulate for use as a proppant are typically in the range from about 8 to about 100 U.S. Standard Mesh. A typical proppant is sand-sized, which geologically is defined as having a largest dimension ranging from about 0.06 millimeters up to about 2 millimeters (mm). (The next smaller particle size class below sand sized is silt, which is defined as having a largest dimension ranging from less than about 0.06 mm down to about 0.004 mm.) As used herein, proppant does not mean or refer to suspended solids, silt, fines, or other types of insoluble solid particulate smaller than about 0.06 mm (about 230 U.S. Standard Mesh). Further, it does not mean or refer to particulates larger than about 3 mm (about 7 U.S. Standard Mesh).

[0017] The proppant is sufficiently strong, that is, has a sufficient compressive or crush resistance, to prop the fracture open without being deformed or crushed by the closure stress of the fracture in the subterranean formation. For example, for a proppant material that crushes under closure stress, a 20/40 mesh proppant preferably has an API crush strength of at least 4,000 psi closure stress based on 10% crush fines according to procedure API RP-56. A 12/20 mesh proppant material preferably has an API crush strength of at least 4,000 psi

closure stress based on 16% crush fines according to procedure API RP-56. This performance is that of a medium crush-strength proppant, whereas a very high crush-strength proppant would have a crush-strength of about 10,000 psi. In comparison, for example, a 100-mesh proppant material for use in an ultra-low permeable formation such as shale preferably has an API crush strength of at least 5,000 psi closure stress based on 6% crush fines. The higher the closing pressure of the formation of the fracturing application, the higher the strength of proppant is needed. The closure stress depends on a number of factors known in the art, including the depth of the formation.

[0018] Further, a suitable proppant should be stable over time and not dissolve in fluids commonly encountered in a well environment. Preferably, a proppant material is selected that will not dissolve in water or crude oil.

[0019] Suitable proppant materials include, but are not limited to, sand (silica), ground nut shells or fruit pits, sintered bauxite, glass, plastics, ceramic materials, processed wood, resin coated sand or ground nut shells or fruit pits or other composites, and any combination of the foregoing. Mixtures of different kinds or sizes of proppant can be used as well. In conventional reservoirs, if sand is used, it commonly has a median size anywhere within the range of about 20 to about 100 U.S. Standard Mesh. For a synthetic proppant, it commonly has a median size anywhere within the range of about 8 to about 100 U.S. Standard Mesh.

[0020] The concentration of proppant in the treatment fluid depends on the nature of the subterranean formation. As the nature of subterranean formations differs widely, the concentration of proppant in the treatment fluid may be in the range of from about 0.03 kilograms to about 12 kilograms of proppant per liter of liquid phase (from about 0.1 lb/gal to about 25 lb/gal).

Sand Control & Gravel Packing

[0021] It is well known in the subterranean drilling and completion art that particulate materials such as sand may be produced during the production of hydrocarbons from a well traversing an unconsolidated or loosely consolidated subterranean formation. Numerous problems may occur as a result of the production of such particulate. For example, the particulate causes abrasive wear to components within the well, such as tubing, pumps

and valves. In addition, the particulate may partially or fully clog the well creating the need for an expensive workover. Also, if the particulate matter is produced to the surface, it must be removed from the hydrocarbon fluids by processing equipment at the surface.

[0022] Gravel packing is commonly used as a sand-control method to prevent production of formation sand or other fines from a poorly consolidated subterranean formation. In this context, “fines” are tiny particles, typically having a diameter of 43 microns or smaller, that have a tendency to flow through the formation with the production of hydrocarbon. The fines have a tendency to plug small pore spaces in the formation and block the flow of oil. As all the hydrocarbon is flowing from a relatively large region around the wellbore toward a relatively small area around the wellbore, the fines have a tendency to become densely packed and screen out or plug the area immediately around the wellbore. Moreover, the fines are highly abrasive and can be damaging to pumping and oilfield other equipment and operations.

[0023] Placing a relatively larger particulate near the wellbore helps filter out the sand or fine particles and prevents them from flowing into the well with the produced fluids. The primary objective is to stabilize the formation while causing minimal impairment to well productivity.

[0024] The particulate used for this purpose is referred to as “gravel.” In the oil and gas field, and as used herein, the term “gravel” is refers to relatively large particles in the sand size classification, that is, particles ranging in diameter from about 0.1 mm up to about 2 mm. Generally, a particulate having the properties, including chemical stability, of a low-strength proppant is used in gravel packing. An example of a commonly used gravel packing material is sand having an appropriate particulate size range. For various purposes, the gravel particulates also may be coated with certain types of materials, including resins, tackifying agents, and the like. For example, a tackifying agent can help with fines and resins can help to enhance conductivity (*e.g.*, fluid flow) through the gravel pack.

[0025] In one common type of gravel packing, a mechanical screen is placed in the wellbore and the surrounding annulus is packed with a particulate of a larger specific size designed to prevent the passage of formation sand or other fines. Typically, the liquid carrier fluid is returned to the surface by flowing through the screen and up a wash pipe. The gravel is deposited around the screen to form a gravel pack, which is a highly permeable allowing

hydrocarbon fluid to flow easily while blocking the flow of the particulate carried in the hydrocarbon fluids. As such, gravel packs can successfully prevent the problems associated with the production of particulate materials from the formation.

[0026] It is also common, for example, to gravel pack after a fracturing procedure, and such a combined procedure is sometimes referred to as a “frac-packing.”

[0027] Like with placing a proppant in a subterranean formation during hydraulic fracturing, in gravel packing a viscosified fluid can be used to help transport and place the gravel in the well.

Carrier Fluid for Particulate

[0028] A well fluid can be adapted to be a carrier fluid for particulates.

[0029] For example, a proppant used in fracturing or a gravel used in gravel packing may have a much different density than the carrier fluid. For example, sand has a specific gravity of about 2.7, whereas water has a specific gravity of 1.0 at Standard Laboratory Conditions of temperature and pressure. A proppant or gravel having a different density than water will tend to separate from water very rapidly.

[0030] As many well fluids are water-based, partly for the purpose of helping to suspend particulate of higher density, and for other reasons known in the art, the density of the fluid used in a well can be increased by including highly water-soluble salts in the water, such as potassium chloride. However, increasing the density of a well fluid will rarely be sufficient to match the density of the particulate.

Increasing Viscosity of Fluid for Suspending Particulate

[0031] Increasing the viscosity of a well fluid can help prevent a particulate having a different specific gravity than an external phase of the fluid from quickly separating out of the external phase.

[0032] A viscosity-increasing agent can be used to increase the ability of a fluid to suspend and carry a particulate material in a well fluid. A viscosity-increasing agent can be used for other purposes, such as matrix diversion, conformance control, or friction reduction.

[0033] A viscosity-increasing agent is sometimes referred to in the art as a viscosifying agent, viscosifier, thickener, gelling agent, or suspending agent. In general, any

of these refers to an agent that includes at least the characteristic of increasing the viscosity of a fluid in which it is dispersed or dissolved. There are several kinds of viscosity-increasing agents and related techniques for increasing the viscosity of a fluid.

[0034] In general, because of the high volume of fracturing fluid typically used in a fracturing operation, it is desirable to efficiently increase the viscosity of fracturing fluids to the desired viscosity using as little viscosity-increasing agent as possible. In addition, relatively inexpensive materials are preferred. Being able to use only a small concentration of the viscosity-increasing agent requires a lesser amount of the viscosity-increasing agent in order to achieve the desired fluid viscosity in a large volume of fracturing fluid.

Polymers for Increasing Viscosity

[0035] Certain kinds of polymers can be used to increase the viscosity of a fluid. In general, the purpose of using a polymer is to increase the ability of the fluid to suspend and carry a particulate material. Polymers for increasing the viscosity of a fluid are preferably soluble in the external phase of a fluid. Polymers for increasing the viscosity of a fluid can be naturally occurring polymers such as polysaccharides, derivatives of naturally occurring polymers, or synthetic polymers.

[0036] Treatment fluids used in high volumes, such as fracturing fluids, are usually water-based. Efficient and inexpensive viscosity-increasing agents for water include certain classes of water-soluble polymers.

[0037] As will be appreciated by a person of skill in the art, the dispersibility or solubility in water of a certain kind of polymeric material may be dependent on the salinity or pH of the water. Accordingly, the salinity or pH of the water can be modified to facilitate the dispersibility or solubility of the water-soluble polymer. In some cases, the water-soluble polymer can be mixed with a surfactant to facilitate its dispersibility or solubility in the water or salt solution utilized.

[0038] The water-soluble polymer can have an average molecular weight in the range of from about 50,000 to 20,000,000, most preferably from about 100,000 to about 4,000,000. For example, guar polymer is believed to have a molecular weight in the range of about 2 to about 4 million.

[0039] Typical water-soluble polymers used in well treatments include water-soluble polysaccharides and water-soluble synthetic polymers (*e.g.*, polyacrylamide). The most common water-soluble polysaccharides employed in well treatments are guar and its derivatives.

[0040] As used herein, a “polysaccharide” can broadly include a modified or derivative polysaccharide. As used herein, “modified” or “derivative” means a compound or substance formed by a chemical process from a parent compound or substance, wherein the chemical skeleton of the parent is retained in the derivative. The chemical process preferably includes at most a few chemical reaction steps, and more preferably only one or two chemical reaction steps. As used herein, a “chemical reaction step” is a chemical reaction between two chemical reactant species to produce at least one chemically different species from the reactants (regardless of the number of transient chemical species that may be formed during the reaction). An example of a chemical step is a substitution reaction. Substitution on a polymeric material may be partial or complete.

Single- or Multi-Chain Polymers

[0041] A polymer can be classified as being single chain or multi chain, based on its solution structure in aqueous liquid media. Examples of single-chain polysaccharides that are commonly used in the oilfield industry include guar, guar derivatives, and cellulose derivatives. Guar polymer, which is derived from the beans of a guar plant, is referred to chemically as a galactomannan gum. Examples of multi-chain polysaccharides include xanthan, diutan, and scleroglucan, and derivatives of any of these. Without being limited by any theory, it is currently believed that the multi-chain polysaccharides have a solution structure similar to a helix or are otherwise intertwined.

Fluid Damage to Proppant Pack or Matrix Permeability

[0042] In well treatments using viscous well fluids, the material for increasing the viscosity of the fluid can damage the permeability of the proppant pack or the matrix of the subterranean formation. For example, a treatment fluid can include a polymeric material that is deposited in the fracture or within the matrix. By way of another example, the treatment

fluid may include surfactants that leave unbroken micelles in the fracture or change the wettability of the formation in the region of the fracture.

[0043] Breakers are utilized in many treatments to mitigate fluid damage in the formation. However, breakers and other treatments are subject to variability of results, they add expense and complication to a fracture treatment, and in can still leave at least some fluid damage in the formation.

Breaker for Viscosity of Fluid with Polysaccharide

[0044] After a treatment fluid is placed where desired in the well and for the desired time, the fluid usually must be removed from the wellbore or the formation. For example, in the case of hydraulic fracturing, the fluid should be removed leaving the proppant in the fracture and without damaging the conductivity of the proppant bed. To accomplish this removal, the viscosity of the treatment fluid must be reduced to a very low viscosity, preferably near the viscosity of water, for optimal removal from the propped fracture. Similarly, when a viscosified fluid is used for gravel packing, the viscosified fluid must be removed from the gravel pack.

[0045] Reducing the viscosity of a viscosified treatment fluid is referred to as “breaking” the fluid. Chemicals used to reduce the viscosity of treatment fluids are called breakers. Other types of viscosified well fluids also need to be broken for removal from the wellbore or subterranean formation.

[0046] No particular mechanism is necessarily implied by the term. For example, a breaker can reduce the molecular weight of a water-soluble polymer by cutting the long polymer chain. As the length of the polymer chain is cut, the viscosity of the fluid is reduced. For instance, reducing the guar polymer molecular weight to shorter chains having a molecular weight of about 10,000 converts the fluid to near water-thin viscosity. This process can occur independently of any crosslinking bonds existing between polymer chains. In the case of a crosslinked viscosity-increasing agent, for example, one way to diminish the viscosity is by breaking the crosslinks.

[0047] Thus, removal of the treatment fluid is facilitated by using one or more breakers to reduce fluid viscosity.

[0048] Breakers must be selected to meet the needs of each situation. First, it is important to understand the general performance criteria of breakers. In reducing the viscosity of the treatment fluid to a near water-thin state, the breaker must maintain a critical balance. Premature reduction of viscosity during the pumping of a treatment fluid can jeopardize the treatment. Inadequate reduction of fluid viscosity after pumping can also reduce production if the required conductivity is not obtained.

[0049] A breaker should be selected based on its performance in the temperature, pH, time, and desired viscosity profile for each specific treatment.

[0050] In fracturing, for example, the ideal viscosity versus time profile would be if a fluid maintained 100% viscosity until the fracture closed on proppant and then immediately broke to a thin fluid. Some breaking inherently occurs during the 0.5 to 4 hours required to pump most fracturing treatments. One guideline for selecting an acceptable breaker design is that at least 50% of the fluid viscosity should be maintained at the end of the pumping time. This guideline may be adjusted according to job time, desired fracture length, and required fluid viscosity at reservoir temperature. A typical gravel pack break criteria is a minimum 4-hour break time.

[0051] Chemical breakers used to reduce viscosity of a fluid viscosified with a viscosifying polymer used in fracturing or other subterranean applications are generally grouped into three classes: oxidizers, enzymes, and acids. The breakers operate by cleaving the backbone of polymer either by hydrolysis of acetyl group, cleavage of glycosidic bonds, oxidative/reductive cleavage, free radical breakage or combination of these processes. A breaker should be selected based on its performance in the temperature, pH, time, and desired viscosity profile for each specific treatment.

Breaking of Multi-Chain Polysaccharides More Difficult

[0052] Fluids viscosified with a multi-chain polysaccharide can be more difficult to break than fluids viscosified with a single-chain polysaccharide. In particular, there are few methods available to break the fluid viscosity of a fluid viscosified with a multi-chain polysaccharide at low temperatures (below 180 °F or 82.2 °C), and they suffer from various problems. In particular, it is desirable to have a breaker system operative for diutan at least in

this temperature range, which would be particularly useful in low-temperature gravel packing applications.

SUMMARY OF THE INVENTIONS

[0053] The inventions are in the field of producing crude oil or natural gas from subterranean formations. More specifically, the inventions generally relate to methods and compositions for treating a subterranean formation. More particularly, the present invention relates to methods of reducing the viscosity of treatment fluids that include diutan or a diutan derivative, which is particularly useful in low-temperature gravel packing applications.

[0054] In an embodiment, a method of gravel packing a treatment zone of a well is provided. The method includes the steps of:

(A) forming a treatment fluid comprising a continuous aqueous phase and gravel, wherein the continuous aqueous phase comprises:

(i) water;

(ii) a viscosity-increasing agent selected from the group consisting of diutan, clarified diutan, a water-soluble derivative of diutan, and any combination thereof;

(iii) a water-soluble oxidizer or source of a water-soluble oxidizer, wherein the concentration of the water-soluble oxidizer is in the range of 0.1% to 2% by weight of the water of the continuous phase;

(iv) a water-soluble organic acid or source of a water-soluble organic acid, wherein the water-soluble organic acid has a pKa(1) in the range of 1 to 5 and the concentration of the water-soluble organic acid is in the range of 0.5% to 5% by weight of the water of the continuous phase; and

(v) a water-soluble transition metal compound or source of a water-soluble transition metal compound, wherein the concentration of the water-soluble transition metal compound is in the range of 0.001% to 0.25% by weight of the water of the continuous phase; and

(B) introducing the treatment fluid into the treatment zone of the well;

wherein the design temperature of the treatment zone of the well is less than 180 °F (82.2 °C);

wherein the continuous phase of the treatment fluid has or develops a viscosity in the range of 10 cP to 75 cP at the design temperature; and

wherein the concentration of the water-soluble organic acid is less than the concentration that would cause the viscosity-increasing agent to salt out from the continuous aqueous phase at the design temperature.

[0054a] In accordance with one aspect of the present invention, there is provided a method of gravel packing a treatment zone of a well, the method comprising the steps of: (A) forming a treatment fluid comprising a continuous aqueous phase and gravel, wherein the continuous aqueous phase comprises: (i) water; (ii) a viscosity-increasing agent selected from the group consisting of diutan, clarified diutan, a water-soluble derivative of diutan, and any combination thereof; (iii) a water-soluble oxidizer or source of a water-soluble oxidizer, wherein the concentration of the water-soluble oxidizer is in the range of 0.1% to 2% by weight of the water of the continuous phase; (iv) a water-soluble organic acid or source of a water-soluble organic acid, wherein the water-soluble organic acid has a pKa(1) in the range of 1 to 5 and the concentration of the water-soluble organic acid is in the range of 0.5% to 5% by weight of the water of the continuous phase; and (v) a water-soluble transition metal compound or source of a water-soluble transition metal compound, wherein the concentration of the water-soluble transition metal compound is in the range of 0.001% to 0.25% by weight of the water of the continuous phase; and (B) introducing the treatment fluid into the treatment zone of the well; wherein the treatment zone of the well has a design temperature that is less than 180 °F (82.2 °C); wherein the continuous phase of the treatment fluid has or develops a viscosity in the range of 10 cP to 75 cP at the design temperature; and wherein the treatment fluid has a cloud point and the step (A) of forming a treatment fluid comprises determining a concentration of the water-soluble organic acid that is less than the concentration that would lower the cloud point below a value that would cause the viscosity-increasing agent to salt out from the continuous aqueous phase at the design temperature.

[0054b] In accordance with another aspect of the present invention, there is provided a method of gravel packing a treatment zone of a well, the method comprising the steps of: (A) forming a treatment fluid including a continuous aqueous phase and gravel, wherein the aqueous phase comprises: (i) water; (ii) diutan; (iii) oxidizer in the range of 0.1% to 2% by weight of the water; (iv) organic acid in the range of 0.5% to 5% by weight of the water; and (v) transition metal compound in the range of 0.001% to 0.25% by weight of the water; and (B) introducing the treatment fluid into the treatment zone; wherein the treatment zone has a design temperature that is less than 180 °F; wherein the continuous phase of the treatment fluid has a viscosity in the range of 10 cP to 75 cP at the design temperature; and wherein the treatment fluid has a cloud point and the step (A) of forming a treatment fluid comprises determining a concentration of the organic acid that is less than the concentration that would lower the cloud point below a value that would cause the diutan to salt out at the design temperature.

[0055] These and other aspects of the invention will be apparent to one skilled in the art upon reading the following detailed description. While the invention is susceptible to various modifications and alternative forms, specific embodiments thereof will be described in detail and shown by way of example. It should be understood, however, that it is not intended to limit the invention to the particular forms disclosed.

BRIEF DESCRIPTION OF THE DRAWING

[0056] The accompanying drawing is incorporated into the specification to help illustrate examples according to the presently most-preferred embodiment of the invention.

[0057] **Figure 1** is a graph of the reduction in viscosities (cP) over time (Hrs) of six different test fluids of 30 lb/Mgal clarified diutan, wherein the breaker system has varied concentrations of t-butyl hydro peroxide (“TBHP”) as oxidizer, formic acid as organic acid, and FeCl_3 as transition metal activator.

[0058] **Figure 2** is a graph of a test fluid according to the invention, showing that the regained permeability value of 82.5% was achieved.

DESCRIPTION OF PREFERRED EMBODIMENTS AND BEST MODE

Definitions and Usages

Interpretation

[0059] The words or terms used herein have their plain, ordinary meaning in the field of this disclosure, except to the extent explicitly and clearly defined in this disclosure.

[0060] If there is any conflict in the usages of a word or term in this disclosure and one or more patent(s) or other documents, the definitions that are consistent with this specification should be adopted.

Patent Terms

[0061] The words “comprising,” “containing,” “including,” “having,” and all grammatical variations thereof are intended to have an open, non-limiting meaning. For example, a composition comprising a component does not exclude it from having additional components, an apparatus comprising a part does not exclude it from having additional parts, and a method having a step does not exclude it having additional steps. When such terms are used, the compositions, apparatuses, and methods that “consist essentially of” or “consist of” the specified components, parts, and steps are specifically included and disclosed.

[0062] The indefinite articles “a” or “an” mean one or more than one of the component, part, or step that the article introduces.

[0063] Whenever a numerical range of degree or measurement with a lower limit and an upper limit is disclosed, any number and any range falling within the range is also intended to be specifically disclosed. For example, every range of values (in the form “from a to b,” or “from about a to about b,” or “from about a to b,” “from approximately a to b,” and any similar expressions, where “a” and “b” represent numerical values of degree or measurement) is to be understood to set forth every number and range encompassed within the broader range of values.

Well Terms

[0064] In the context of production from a well, oil and gas are understood to refer to crude oil and natural gas. Oil and gas are naturally occurring hydrocarbons in certain subterranean formations.

[0065] A “subterranean formation” is a body of rock that has sufficiently distinctive characteristics and is sufficiently continuous for geologists to describe, map, and name it.

[0066] A subterranean formation having a sufficient porosity and permeability to store and transmit fluids is sometimes referred to as a “reservoir.”

[0067] A subterranean formation containing oil or gas may be located under land or under the seabed off shore. Oil and gas reservoirs are typically located in the range of a few hundred feet (shallow reservoirs) to a few tens of thousands of feet (ultra-deep reservoirs) below the surface of the land or seabed.

[0068] A “well” includes a wellhead and at least one wellbore from the wellhead penetrating the earth. The “wellhead” is the surface termination of a wellbore, which surface may be on land or on a seabed. A “well site” is the geographical location of a wellhead of a well. It may include related facilities, such as a tank battery, separators, compressor stations, heating or other equipment, and fluid pits. If offshore, a well site can include a platform.

[0069] The “wellbore” refers to the drilled hole, including any cased or uncased portions of the well. The “borehole” usually refers to the inside wellbore wall, that is, the rock face or wall that bounds the drilled hole. A wellbore can have portions that are vertical, horizontal, or anything in between, and it can have portions that are straight, curved, or branched. As used herein, “uphole,” “downhole,” and similar terms are relative to the direction of the wellhead, regardless of whether a wellbore portion is vertical or horizontal.

[0070] As used herein, introducing “into a well” means introduced at least into and through the wellhead. According to various techniques known in the art, tubulars, equipment, tools, or well fluids can be directed from the wellhead into any desired portion of the wellbore.

[0071] As used herein, a “well fluid” broadly refers to any fluid adapted to be introduced into a well for any purpose. A well fluid can be, for example, a drilling fluid, a cementing composition, a treatment fluid, or a spacer fluid. If a well fluid is to be used in a relatively small volume, for example less than about 200 barrels (about 32 m³), it is sometimes referred to in the art as a wash, dump, slug, or pill.

[0072] As used herein, the word “treatment” refers to any treatment for changing a condition of a portion of a wellbore or an adjacent subterranean formation; however, the word “treatment” does not necessarily imply any particular treatment purpose. A treatment usually involves introducing a well fluid for the treatment, in which case it may be referred to as a treatment fluid, into a well. As used herein, a “treatment fluid” is a fluid used in a treatment. Unless the context otherwise requires, the word “treatment” in the term “treatment fluid” does not necessarily imply any particular treatment or action by the fluid.

[0073] Broadly, a zone refers to an interval of rock along a wellbore that is differentiated from uphole and downhole zones based on hydrocarbon content or other features, such as permeability, composition, perforations or other fluid communication with the wellbore, faults, or fractures. A zone of a wellbore that penetrates a hydrocarbon-bearing zone that is capable of producing hydrocarbon is referred to as a “production zone.” As used herein, a “treatment zone” refers to an interval of rock along a wellbore into which a well fluid is directed to flow from the wellbore. As used herein, “into a treatment zone” means into and through the wellhead and, additionally, through the wellbore and into the treatment zone.

[0074] The term “design temperature” refers to an estimate or measurement of the actual temperature at the downhole environment at the time of a well treatment. That is, design temperature takes into account not only the bottom hole static temperature (“BHST”), but also the effect of the temperature of the well fluid on the BHST during treatment and other factors known in the field. Because treatment fluids may be considerably cooler than BHST, the difference between the two temperatures can be quite large. Ultimately, if left undisturbed, a subterranean formation will return to the BHST.

Variations in Well Fluids

[0075] Unless the specific context otherwise requires, a well fluid or treatment fluid refers to the specific properties and composition of a fluid at the time the fluid is being introduced into a well. In addition, it should be understood that, during the course of a well operation such as drilling, cementing, completion, or intervention, or during a specific treatment, the specific properties and composition of a type of well fluid can be varied or several different types of well fluids can be used. For example, the compositions can be varied to adjust viscosity or elasticity of the well fluids to accommodate changes in the concentrations of particulate to be carried downhole. It can also be desirable to accommodate expected changes in temperatures encountered by the well fluids during the course of the treatment. By way of another example, it can be desirable to accommodate the longer duration that an earlier-introduced treatment fluid may need to maintain viscosity before breaking compared to the shorter duration that a later-introduced treatment fluid may need to maintain viscosity before breaking. Changes in concentration of a particulate, viscosity-

increasing agent, breaker, or other additives in the various treatment fluids of a treatment operation can be made in stepped changes of concentrations or ramped changes of concentrations.

Physical States and Phases

[0076] A substance can be a pure chemical or a mixture of two or more different pure chemicals.

[0077] As used herein, “phase” is used to refer to a substance having a chemical composition and physical state that is distinguishable from an adjacent phase of a substance having a different chemical composition or different physical state.

[0078] As used herein, if not other otherwise specifically stated, the physical state or phase of a substance (or mixture of substances) and other physical properties are determined at a temperature of 77 °F (25 °C) and a pressure of 1 atmosphere (Standard Laboratory Conditions) without applied shear.

Solubility Terms

[0079] A substance is considered to be “soluble” in a liquid if at least 10 grams of the substance can be dissolved in one liter of the liquid when tested at 77 °F and 1 atmosphere pressure for 2 hours and considered to be “insoluble” if less soluble than this.

[0080] As will be appreciated by a person of skill in the art, the hydratability, dispersibility, or solubility of a substance in water can be dependent on the salinity, pH, or other substances in the water. Accordingly, the salinity, pH, and additive selection of the water can be modified to facilitate the hydratability, dispersibility, or solubility of a substance in aqueous solution. To the extent not specified, the hydratability, dispersibility, or solubility of a substance in water is determined in deionized water, at neutral pH, and without any other additives.

[0081] The “source” of a chemical species in a solution or fluid composition, can be a substance that makes the chemical species chemically available immediately or it can be a substance that gradually or later releases the chemical species to become chemically available.

Fluids

[0082] Every fluid inherently has at least a continuous phase. A fluid can have more than one phase. The continuous phase of a well fluid is a liquid under Standard Laboratory Conditions. For example, a well fluid can in the form of be a suspension (solid particles dispersed in a liquid phase), an emulsion (liquid particles dispersed in another liquid phase), or a foam (a gas phase dispersed in liquid phase).

[0083] As used herein, a water-based fluid means that water or an aqueous solution is the dominant material, that is, greater than 50% by weight, of the continuous phase of the substance, excluding the weight of any dissolved salts.

[0084] In contrast, “oil-based” means that oil is the dominant material by weight of the continuous phase of the substance. In this context, the oil of an oil-based fluid can be any oil. In general, an oil is any substance that is liquid Standard Laboratory Conditions, is hydrophobic, and soluble in organic solvents. Oils have a high carbon and hydrogen content and are relatively non-polar substances, for example, having a polarity of 3 or less on the Synder polarity index. This general definition includes classes such as petrochemical oils, vegetable oils, and many organic solvents. All oils can be traced back to organic sources.

Apparent Viscosity of a Fluid

[0085] Viscosity is a measure of the resistance of a fluid to flow. In everyday terms, viscosity is “thickness” or “internal friction.” Thus, pure water is “thin,” having a relatively low viscosity whereas honey is “thick,” having a relatively higher viscosity. Put simply, the less viscous the fluid is, the greater its ease of movement (fluidity). More precisely, viscosity is defined as the ratio of shear stress to shear rate.

[0086] A Newtonian fluid (named after Isaac Newton) is a fluid for which stress versus strain rate curve is linear and passes through the origin. The constant of proportionality is known as the viscosity. Examples of Newtonian fluids include water and most gases. Newton’s law of viscosity is an approximation that holds for some substances but not others.

[0087] Non-Newtonian fluids exhibit a more complicated relationship between shear stress and velocity gradient (i.e., shear rate) than simple linearity. Thus, there exist a number of forms of non-Newtonian fluids. Shear thickening fluids have an apparent viscosity

that increases with increasing the rate of shear. Shear thinning fluids have a viscosity that decreases with increasing rate of shear. Thixotropic fluids become less viscous over time at a constant shear rate. Rheopectic fluids become more viscous over time at a constant shear rate. A Bingham plastic is a material that behaves as a solid at low stresses but flows as a viscous fluid at high stresses.

[0088] Most well fluids are non-Newtonian fluids. Accordingly, the apparent viscosity of a fluid applies only under a particular set of conditions including shear stress versus shear rate, which must be specified or understood from the context. In the oilfield and as used herein, unless the context otherwise requires it is understood that a reference to viscosity is actually a reference to an apparent viscosity. Apparent viscosity is commonly expressed in units of centipoise (“cP”).

[0089] Like other physical properties, the viscosity of a Newtonian fluid or the apparent viscosity of a non-Newtonian fluid may be highly dependent on the physical conditions, primarily temperature and pressure.

Gels and Deformation

[0090] The physical state of a gel is formed by a network of interconnected molecules, such as a crosslinked polymer or a network of micelles. The network gives a gel phase its structure and an apparent yield point. At the molecular level, a gel is a dispersion in which both the network of molecules is continuous and the liquid is continuous. A gel is sometimes considered as a single phase.

[0091] Technically, a “gel” is a semi-solid, jelly-like physical state or phase that can have properties ranging from soft and weak to hard and tough. Shearing stresses below a certain finite value fail to produce permanent deformation. The minimum shear stress that will produce permanent deformation is referred to as the shear strength or gel strength of the gel.

[0092] As used herein, unless otherwise specified or the context otherwise requires, a substance referred to as a “gel” is subsumed by the concept of “fluid” if it is a pumpable fluid.

[0093] In the oil and gas industry, however, the term “gel” may be used to refer to any fluid having a viscosity-increasing agent, regardless of whether it is a viscous fluid or

meets the technical definition for the physical state of a gel. A “base gel” is a term used in the field for a fluid that includes a viscosity-increasing agent, such as guar, but that excludes crosslinking agents. Typically, a base gel is mixed with another fluid containing a crosslinker, wherein the mixture is adapted to form a crosslinked gel. Similarly, a “crosslinked gel” may refer to a substance having a viscosity-increasing agent that is crosslinked, regardless of whether it is a viscous fluid or meets the technical definition for the physical state of a gel.

Viscosity and Gel Measurements

[0094] There are numerous ways of measuring and modeling viscous properties, and new developments continue to be made. The methods depend on the type of fluid for which viscosity is being measured. A typical method for quality assurance or quality control (QA/QC) purposes uses a couette device, such as a Fann Model 35 or 50 viscometer or a ChandlerTM 5550 HPHT viscometer, that measures viscosity as a function of time, temperature, and shear rate. The viscosity-measuring instrument can be calibrated using standard viscosity silicone oils or other standard viscosity fluids.

[0095] Due to the geometry of most common viscosity-measuring devices, however, solid particulate, especially if larger than silt (larger than 74 micron), would interfere with the measurement on some types of measuring devices. Therefore, the viscosity of a fluid containing such solid particulate is usually inferred and estimated by measuring the viscosity of a test fluid that is similar to the fracturing fluid without any proppant or gravel that would otherwise be included. However, as suspended particles (which can be solid, gel, liquid, or gaseous bubbles) usually affect the viscosity of a fluid, the actual viscosity of a suspension is usually somewhat different from that of the continuous phase.

[0096] As used herein, unless otherwise specified or unless the context otherwise requires, the apparent viscosity of a fluid (excluding any suspended solid particulate larger than silt) is measured with a FannTM Model 35 type viscometer with an F1 spring, B1 bob, and R1 rotor at a shear rate of 511 1/s and at 77 °F (25 °C) and a pressure of 1 atmosphere. For reference, the viscosity of pure water is about 1 cP.

[0097] A substance is considered to be a fluid if it has an apparent viscosity less than 5,000 cP (independent of any gel characteristic).

[0098] As used herein, a fluid is considered to be “viscous” if it has an apparent viscosity of 10 cP or higher. The viscosity of a viscous fluid is considered to break or be broken if the viscosity is reduced to 5 cP or lower. In many applications, however, it is desirable to achieve a complete break of less than 3 cP.

General Measurement Terms

[0099] Unless otherwise specified or unless the context otherwise clearly requires, any ratio or percentage means by weight.

[0100] Unless otherwise specified or unless the context otherwise clearly requires, the phrase “by weight of the water” means the weight of the water of the continuous phase of the fluid without the weight of any viscosity-increasing agent, dissolved salt, suspended particulate, or other materials or additives that may be present in the water.

[0101] Any doubt regarding whether units are in U.S. or Imperial units, where there is any difference, U.S. units are intended. For example, “gal/Mgal” means U.S. gallons per thousand U.S. gallons.

[0102] Unless otherwise stated, mesh sizes are in U.S. Standard Mesh.

[0103] The micrometer (μm) may sometimes be referred to herein as a micron.

General Purposes

[0104] Diutan gels are commonly used in gravel packing operations at temperatures from 180 °F to 270 °F. The purpose of this invention is to disclose a breaker system that can successfully reduce the viscosity of a diutan gel at temperatures below 180 °F, and preferably down to a temperature at least as low as 140 °F.

[0105] Diutan provides superior sand settling properties compared to other water-soluble polymers as viscosity-increasing agents, which can allow for reduced polymer loadings with potentially lower frictions to allow for longer completions.

[0106] Diutan is commonly used in a concentration of about 5 lb/Mgal to about 100 lb/Mgal, depending on the desired viscosity and other properties of a fluid at the design temperature. For example, about 25 lb/Mgal of diutan in water may be used for a design temperature of about 140 °F to provide a fluid viscosity of about 25 cP.

[0107] Depending on the application, field requirements often demand breaking of a fluid viscosified with diutan in less than 4 days at temperatures from 140 °F to 180 °F. The breaking must not be too soon, however, which would adversely affect the sand suspension properties of the fluid during the time required for placing a particulate, such as a gravel for gravel packing. For such applications, a new and different breaker system is required. A breaker system for diutan capable of meeting such field requirements would allow for making a valuable treatment fluid, which could be used, for example, for gravel carrying fluid systems. A particularly useful application, for example, would be open hole gravel packing, where the treatment fluid would be increase the current maximum length of open hole gravel packing at such low temperatures. For such an application, the breaking time should not be less than 2 hours.

Oxidizers Offer Insufficient Breaking of Diutan at Low Temperature

[0108] While oxidizing agents may be effective to at least partially break treatment fluids comprising a diutan composition, the use of oxidizing breakers in combination with diutan may interfere with a subterranean formation's ability to regain a desired level of permeability. This may be due in part to residual treatment fluids or reaction products that remain in the formation after the treatment fluid is broken. In particular, it is believed that oxidizing agents may not substantially degrade or otherwise reduce the presence of diutan-producing bacterial bodies in the subterranean formation. These bacterial bodies are thought to be at least partially responsible for creating a physical barrier in the formation which reduces permeability.

[0109] In addition, oxidizing breakers have not been able to provide a complete break of a diutan polymer backbone at temperatures below 200 °F (93 °C). For example, reduced regained-permeability values have been seen when oxidizing breakers were used at lower temperatures. A permeability regain of less than 80% after a treatment with a treatment fluid containing diutan is considered poor or less than acceptable.

Organic Acids Offer Insufficient Breaking of Diutan at Low Temperature

[0110] Organic acids are typically used to break diutan polymer gels.

[0111] For example, US Patent No. 7,584,791 issued September 8, 2009 discloses a method of using organic acids such as formic and acetic acids to break diutan fluids at temperatures within the range of 180 °F to 270 °F. Breaking the diutan polymer has been achieved by adjusting the pH of the gravel-pack fluid with internal organic acid breakers such as formic acid and acetic acid. Regained permeability values were excellent when fluid comprising of diutan polymer was broken by adjusting the fluid pH with these acids to the proper level.

[0112] Acid breakers applicable to diutan from 180 °F to 220 °F typically use formic acid, which causes breaking by reducing the pH of the system to a level sufficient to degrade the polymer backbone. At effective concentrations, formic acid provides a break time of 2 to 3 days in the temperature range of 180 °F to 220 °F. Breaker times shorter than 2 to 3 days at temperatures above 180 °F can be achieved at using higher formic acid loadings.

[0113] To provide a break time of less than 4 days at temperatures below 180 °F would require higher loadings of formic acid. For example, preliminary break tests at 160 °F with 40 lb/Mgal diutan gels have indicated the requirement of nearly 35 to 40 gal/Mgal formic acid to reduce the viscosity below 5 cP at 511 sec⁻¹ in 3 to 4 days. Using diutan gels at 140 °F would require much higher concentrations of formic acid to break the viscosity of the fluid in a reasonable time.

[0114] Unfortunately, using higher concentrations of formic acid or other such organic acid would adversely affect the properties of the well fluid. For example, higher formic acid loadings severely affect the particulate suspension properties of fluids viscosified with diutan. In addition, one of the things that can cause the polymer to salt-out is the low pH of the fluid. Since the breakers for this system are organic acids, using high amount of these acids can cause the salting-out issue. At high loadings of formic acid, the cloud point of the gel system is reduced, which can cause serious lumping when the breaker is added. As used herein, the “cloud” point or “salt out” point is the concentration of the polymer that is insoluble in a specific solution (for example, an aqueous 7% KCl solution with a specific concentration of acid and pH) at a specific temperature (for example, the design temperature), which is indicated by the change of the solution from clear to cloudy. For these reasons, diutan viscosified fluids with higher acid loadings are unsuitable for applications that include suspending particulate, such as gravel packing.

Combination of Oxidizer and Acid Insufficient to Break Diutan at Low Temperature

[0115] In addition, a combination of oxidizing and acid breakers at reasonable concentrations is insufficient to break the viscosity of a fluid viscosified with diutan at low temperatures of less than 180 °F. For example, either or both the concentration of the oxidizer or the acid would be required in high concentrations that would interfere with the function of the treatment fluid. High concentrations of oxidizer provide poor formation permeability regain. High concentrations of acid lower the cloud point of diutan or clarified diutan.

Low-Temperature Breaker System for Diutan

[0116] Due to the above challenges, there is a need to identify an alternate breaker system that can successfully reduce or break the viscosity of diutan fluids at a design temperature below 180 °F, and preferably at least as low as 140 °F.

[0117] According to the invention, a breaker system including an oxidizer, organic acid, and a transition metal activator is useful for diutan at low temperatures of less than 180 °F, and at temperatures down to at least as low as 140 °F. Breaking at even lower temperatures is believed to be feasible with such a breaker system. The breaker system is effective down to at least as low as 140 °F without requiring high loadings of organic acid that is, without requiring the use of concentrations of the acid that would cause the salting out of the diutan in the treatment fluid at the design temperature.

[0118] According to a preferred embodiment, the breaker system includes t-butyl hydro peroxide (“TBHP”), formic acid, and ferric chloride.

Methods for Treating a Treatment Zone of a Well

[0119] The present invention relates to methods of treating a treatment zone of a well with a treatment fluid viscosified with a diutan or derivative and having a breaker system according to the invention.

[0120] Accordingly, a method of treating a treatment zone of a well is provided. The method includes the steps of:

- (A) forming a treatment fluid comprising a continuous aqueous phase and gravel, wherein the continuous aqueous phase comprises:

- (i) water;
 - (ii) a viscosity-increasing agent selected from the group consisting of diutan, clarified diutan, a water-soluble derivative of diutan, and any combination thereof;
 - (iii) a water-soluble oxidizer or source of a water-soluble oxidizer, wherein the concentration of the water-soluble oxidizer is in the range of 0.1% to 2% by weight of the water of the continuous phase;
 - (iv) a water-soluble organic acid or source of a water-soluble organic acid, wherein the water-soluble organic acid has a pKa(1) in the range of 1 to 5 and the concentration of the water-soluble organic acid is in the range of 0.5% to 5% by weight of the water of the continuous phase; and
 - (v) a water-soluble transition metal compound or source of a water-soluble transition metal compound, wherein the concentration of the water-soluble transition metal compound is in the range of 0.001% to 0.25% by weight of the water of the continuous phase; and
- (B) introducing the treatment fluid into the treatment zone of the well;
- wherein the design temperature of the treatment zone of the well is less than 180 °F (82.2 °C);
- wherein the continuous phase of the treatment fluid has or develops a viscosity in the range of 10 cP to 75 cP at the design temperature; and
- wherein the concentration of the water-soluble organic acid is less than the concentration that would cause the viscosity-increasing agent to salt out from the continuous aqueous phase at the design temperature.

[0121] More particularly, the present invention provides a very simple, effective, and relatively safe means of breaking treatment fluids viscosified with a diutan or derivative at design temperatures down to at least as low as 140 °F.

[0122] A treatment fluid according to the invention is preferably adapted to have break times in the range of 1 to 5 days at temperatures in the range of 140 °F to 180 °F. More preferably, the breaker is effective to provide a break time in the range of 2 to 4 days down to a temperature of 140 °F at temperatures in the range of 140 °F to 180 °F.

[0123] A particularly useful application for this invention is gravel packing.

[0124] As used herein, a short break time means less than 5 days, preferably less than 3 days, and more preferably less than 2 days at a temperature within the temperature range of 140 °F to 180 °F. Nevertheless, it is also desirable that the break time not be too short, that is, preferably at least 1 day, more preferably at least 2 days. Accordingly, a break time includes break times in the range of 1 day to 5 days at a temperature within the temperature range of 140 °F to 180 °F.

[0125] While the methods of the present invention may be suitable for use in a variety of subterranean treatments, they may be particularly useful in treatments for subterranean formations or treatment zones having low design temperatures, such as those between 140 °F and 180 °F. One of the many advantages of the present invention is that it may allow for a controlled decrease in the viscosity of a viscosified treatment fluid. In some embodiments, a breaker system of the present invention may be able to break a treatment fluid comprising a diutan or derivative at temperatures down to 140 °F, while providing satisfactory particulate suspension for a desired minimum time, *e.g.* 4 hours.

[0126] The methods of the present invention may be used in any subterranean operation involving the introduction of a treatment fluid into a subterranean formation wherein the viscosity of the treatment fluid is decreased, including, gravel-packing operations, frac-packing operations, well bore cleanout operations, and the like. In certain embodiments of the present invention, the treatment fluid may be introduced into a portion of a subterranean formation so as to create a “plug” capable of diverting the flow of fluids that are introduced to the well bore at some point after the plug has formed (*e.g.*, other treatment fluids) to other portions of the formation. In those embodiments, the breaker then may be allowed to reduce the viscosity of the fluid within the formation's pores, which may at least partially restore the flow of fluids through that portion of the subterranean formation.

Continuous Aqueous Phase

[0127] The continuous aqueous phase of the treatment fluid is a liquid. However, it is contemplated that the treatment fluid can be foamed or an emulsion. The continuous aqueous phase of the treatment fluid is preferably adapted to carry a particulate, such as gravel for gravel packing. In an embodiment, however, the treatment fluid is not foamed or an emulsion. As used herein, a foamed fluid has at least 5% by volume of a gas.

[0128] According to the invention, the treatment fluid is a water-based fluid wherein the continuous aqueous phase of the fluid is greater than 50% by weight water (excluding the weight of dissolved any salts).

[0129] The water preferably is present in the treatment fluids suitable for use in the present invention in an amount at least sufficient to substantially hydrate the viscosity-increasing agent. In some embodiments, the aqueous phase, including the dissolved materials therein, may be present in the treatment fluids in an amount in the range from about 5% to 100% by volume of the treatment fluid.

[0130] Preferably, the water for use in the treatment fluid does not contain anything that would adversely interact with the other components used in accordance with this invention or with the subterranean formation.

[0131] The aqueous phase can include freshwater or non-freshwater. Non-freshwater sources of water can include surface water ranging from brackish water to seawater, brine, returned water (sometimes referred to as flowback water) from the delivery of a well fluid into a well, unused well fluid, and produced water. As used herein, brine refers to water having at least 40,000 mg/L total dissolved solids.

[0132] In some embodiments, the aqueous phase of the treatment fluid may comprise a brine. Examples of suitable brines include calcium bromide brines, zinc bromide brines, calcium chloride brines, sodium chloride brines, sodium bromide brines, potassium bromide brines, potassium chloride brines, sodium nitrate brines, sodium formate brines, potassium formate brines, cesium formate brines, magnesium chloride brines, mixtures thereof, and the like. The brine chosen should be compatible with the formation and should have a sufficient density to provide the appropriate degree of well control. Additional salts may be added to a water source, *e.g.*, to provide a brine, and a resulting treatment fluid, having a desired density. Brines, where used, may be of any weight.

[0133] Salts may optionally be included in the treatment fluids of the present invention for many purposes, including, for reasons related to compatibility of the treatment fluid with the formation and formation fluids. To determine whether a salt may be beneficially used for compatibility purposes, a compatibility test may be performed to identify potential compatibility problems. From such tests, one of ordinary skill in the art with the benefit of this disclosure will be able to determine whether a salt should be included

in a treatment fluid suitable for use in the present invention. Suitable salts include, but are not limited to, calcium chloride, sodium chloride, magnesium chloride, potassium chloride, sodium bromide, potassium bromide, ammonium chloride, sodium formate, potassium formate, cesium formate, mixtures thereof, and the like. The amount of salt that should be added should be the amount necessary for formation compatibility, such as stability of clay minerals, taking into consideration the crystallization temperature of the brine, *e.g.*, the temperature at which the salt precipitates from the brine as the temperature drops.

Viscosity-Increasing Agent Including Water-Soluble Polymer having Diutan Backbone

[0134] A viscosity-increasing agent suitable for use in the methods of the present invention is selected from the group consisting of diutan, one or more clarified diutans, one or more water-soluble derivatives of diutan, and any combination thereof.

[0135] Despite certain suggestions in the field to the contrary, diutan and clarified diutan are well known to be not readily crosslinkable with a transition metal. For example, US Patent No. 7,621,334 issued November 24, 2009 discloses that suitable viscosities could be obtained for acidic treatment fluids that comprise gelling agents that comprise diutant without using crosslinkers.

[0136] Accordingly, transition metals are not expected to be included in treatment fluids viscosified with diutan or a clarified diutan. Unless a derivative of diutan has functional groups that can be crosslinked with a transition metal, diutan derivatives are not expected to be readily crosslinkable with a transition metal. In addition, the viscosity should be sufficient for the purpose of the treatment fluid, but not higher than necessary as this would make the fluid more difficult to break and more difficult to clean up from the treatment zone. Using diutan or clarified diutan in gravel-packing applications, for example, it is not necessary and not desirable to crosslink the viscosity-increasing agent, where, for example, a viscosity in the range of 10 cP of up to about 75 cP is desired. A fluid viscosified with diutan or derivative thereof is considered not crosslinked unless the viscosity is well above 75cP.

Diutan

[0137] Diutan gum (commonly referred to simply as diutan) is a multi-chain polysaccharide that is sometimes used to increase viscosity in well fluids. Diutan's

thickening, suspending, and stabilizing properties in aqueous fluids makes it especially useful as suspension systems in gravel packing.

[0138] In general, diutan is a polysaccharide which may be prepared by fermentation of a strain of sphingomonas, for example Sphingomonas sp. ATCC 53159. Diutan may also be referred to as a polysaccharide designated S-657 or S-8 in some literature. Its structure has been elucidated as having a repeat unit of a hexasaccharide with a tetrasaccharide repeat unit in the backbone that comprises glucose and rhamnose units and a di-rhamnose side chain. Details of the diutan gum structure may be found in an article by Diltz et al., “Location of O-acetyl Groups in S-657 Using the Reductive-Cleavage Method,” Carbohydrate Research, Vol. 331, pp. 265-270 (2001). Details of preparing diutan gum may be found in U.S. Patent No. 5,175,278, filed Sep. 4, 1990 by Jerry A. Peik, Suzanna M. Steenbergen, and George T. Veeder. Diutan is composed principally of carbohydrate, about 12% protein and about 7% (calculated as O-acetyl) acyl groups, the carbohydrate portion containing about 19% glucuronic acid, and the neutral sugars rhamnose and glucose in the approximate molar ratio of 3:2. Other details on diutan can be found in U.S. Pat. No. 6,620,775, filed Nov. 26, 2001 by Philip E. Winston and John M. Swazey. It is believed to have thickening, suspending, and stabilizing properties in aqueous or non-aqueous solutions.

Clarified Diutan

[0139] The term “clarified diutan” as used herein refers to a diutan that has improved turbidity or filtration properties as compared to non-clarified diutan. In some embodiments, suitable clarified diutans may have been treated with enzymes or the like to remove residual cellular structures, such as cell walls. In some embodiments, suitable clarified diutans may be produced from genetically modified or bioengineered strains of bacteria or other strains of bacteria that allow the clarified diutan to have improved functional properties such as filterability, turbidity, etc.

[0140] In some embodiments, the viscosity-increasing agents suitable for use in the methods of the present invention may comprise a clarified diutan, wherein the clarified diutan at a 0.1% concentration in deionized water, in a 1 cm optical cell, has a transmittance at 350 nanometers (“nm”) wavelength of at least about 20%. In some embodiments, the clarified

diutan has a transmittance in the range of about 20% to about 90%. One of ordinary skill in the art with the benefit of this disclosure will recognize that the transmittance of any particular treatment fluid may also vary depending on the addition of certain additives, the composition of the treatment fluid, the degree of hydration of the diutan, the temperature, and the pH of the treatment fluid.

[0141] Additional information regarding clarified diutan may be found in U.S. Patent Publication Nos. 2008/0194427, 2008/0194428, 2008/0194430, each published August 14, 2008, each having for named inventors Thomas D. Welton, Richard W. Pauls, Lulu Song, Jason E. Bryant, Sean R. Beach; and Ian D. Robb, and each entitled “Treatment Fluids Comprising Diutan and Associated Methods”.

Diutan Derivative

[0142] In one embodiment, the diutan or clarified diutan may be modified by genetic engineering or bacteria selection or the result of chemical treatment or derivatization of a diutan. An example of such a modification would be where a portion of the diutan is oxidized or hydrolyzed. Suitable clarified diutan may also be present in a form that will only partially hydrate or will not hydrate at ambient temperature. This form of clarified diutan may be chemically modified, chemically coated, genetically modified, or produced from a new strain of bacteria.

Sources of Diutan

[0143] Examples of suitable sources of a diutan may include those disclosed in U.S. Patent No. 5,175,278 and U.S. Patent Publication Nos. 2006/0121578, 2006/0199201, 2006/0166836, 2006/0166837, and 2006/0178276. Diutan can be obtained from CP Kelco US Inc. (Houston), the commercial name being GeovisTM.

Advantages of Diutan, Clarified Diutan, or Derivatized Diutan

[0144] A fluid viscosified with a diutan or derivatized diutan can enable a substantial amount of design flexibility for a number of applications that would benefit using

a shear-thinning, low-damage fluid system including, for example, gravel packing, fluid loss control, and friction pressure reduction.

[0145] A fluid viscosified with a diutan or derivatized diutan can enable a simple mixing procedure and rapid viscosity development in a number of water-based fluids including for example, fresh water, potassium or sodium chloride brines, and sodium bromide brines. The polymer can be rapidly dispersed in an aqueous phase without going through a complex mixing protocol or an extended hydration period. Its ease of mixing and rapid hydration apply to seawater and mono-valent brines used in completion operations.

[0146] Diutan viscosified fluid can provide excellent particulate suspension under static conditions at temperatures up to 270 °F (132.2 °C). It is a shear thinning fluid that has relatively low viscosity at high shear rates and high viscosity at low shear rates, which is useful in many types of treatment applications.

[0147] Because such fluids have high viscosity under low shear conditions, it can be useful to suspend particulates similar to a fluid viscosified with a cross-linked polymer. In addition, the high viscosities under low shear attained with these polymer loadings can be used to help control fluid losses during workover and completion operations with reduced damage to the formation.

[0148] At lower polymer concentrations, a fluid with diutan or a derivative can produce a “slick water” or “slick brine” consistency to help reduce pumping friction pressures.

Form and Concentration

[0149] The viscosity-increasing agent can be provided in any form that is suitable for the particular treatment fluid or application of the present invention. In certain embodiments, the viscosity-increasing agent may be provided as a liquid, gel, suspension, or solid additive that is admixed or incorporated into a treatment fluid used in conjunction with the present invention.

[0150] The viscosity-increasing agent should be present in a treatment fluid in a form and in an amount at least sufficient to impart the desired viscosity to a treatment fluid. If used in a gravel packing fluid, the treatment fluid contains the viscosity-increasing agent in an amount sufficient to provide suspension of particulates such as sand. Preferably, the

concentration of the viscosity-increasing agent is at least sufficient such that the continuous phase of the treatment fluid is greater than 10 cP at the design temperature. For example, the amount of diutan in the gravel packing fluid can range from about 0.01% to about 2.0% by weight and preferably between 0.1% to about 1.0%. Other diutan concentrations are also contemplated for various subterranean formation applications. For example, in some embodiments, the amount of viscosity-increasing agent used in the treatment fluids suitable for use in the present invention may vary from about 5 pounds per 1,000 gallons of treatment fluid ("lbs/Mgal") to about 100 lbs/Mgal. In gravel packing embodiments, the amount of viscosity-increasing agent included in the treatment fluids suitable for use in the present invention may vary from about 20 lbs/Mgal to about 80 lbs/Mgal. In embodiments in which the amount of diutan approaches 100 lbs/Mgal, the diutan may act to increase the viscosity of the treatment fluid so that the treatment fluid may be used as a diverting fluid or fluid loss pill to seal a formation.

Optional Additional Viscosity-Increasing Agent

[0151] Other, additional viscosity-increasing agents may or may not be included in the treatment fluid, provided they do not adversely interact with the breaker system. In some embodiments, diutan may be used in combination with other viscosity-increasing agents so that the diutan only imparts its viscosity once the treatment fluid has entered the formation to provide viscosity at elevated temperatures where other viscosity-increasing agents may no longer provide adequate viscosity. Suitable additional viscosity-increasing agents may include polysaccharides and galactomannan gums. Depending on the application, one viscosity-increasing agent may be more suitable than another. One of ordinary skill in the art with the benefit of this disclosure will be able to determine if an additional viscosity-increasing agent should be included for a particular application based on, for example, the desired viscosity of the treatment fluid and the design temperature.

[0152] In an embodiment, the continuous aqueous phase of the treatment fluid excludes a viscosity-increasing agent that is not selected from the group consisting of diutan, a clarified diutan, or a water-soluble derivative of diutan. In other words, the aqueous phase excludes a viscosity-increasing agent that does not have a diutan polymer backbone.

Viscosity-Increasing Agents Not Crosslinkable with Transition Metal

[0153] In another embodiment, the continuous aqueous phase of the treatment fluid excludes any viscosity-increasing agent that can be readily crosslinked with a transition metal in the treatment fluid and at the design temperature.

Breaker System Including Metal Activator

[0154] The breakers suitable for use in the present invention generally include: (a) a water-soluble oxidizer, (b) a water-soluble organic acid having a pKa(1) in the range of 1 to 5; and (c) a water-soluble transition metal compound.

[0155] Preferably, the water-soluble oxidizer is in the range of about 0.1 % to about 2% by weight of the water of the continuous phase. More preferably, the water-soluble oxidizer is in the range of about 0.5% to about 1% by weight of the water of the continuous phase.

[0156] Preferably, the water-soluble organic acid is in the range of about 0.5 % to about 5% by weight of the water of the continuous phase. More preferably, the water-soluble oxidizer is in the range of about 1% to about 4% by weight of the water of the continuous phase. These are less the concentrations that would be useful for acidizing treatments.

[0157] Preferably, the transition metal compound or source of a water-soluble transition metal compound is in the range of about 0.001% to about 0.25% by weight of the water of the continuous phase. More preferably, the transition metal compound or source of a water-soluble transition metal compound is in the range of about 0.002% to about 0.1% by weight of the water of the continuous phase. These concentrations are less than the concentrations that would be useful for crosslinking a polymeric viscosity-increasing agent such as diutan.

[0158] Examples of oxidizers include chlorites, hypochlorites, chlorates, perchlorates, and other analogous halogen compounds, perborates, and peroxides. The oxidizer is preferably an peroxide. According to a most preferred embodiment, the oxidizer is t-butyl hydroperoxide ("TBHP", also known as 2-methylpropane-2-peroxol), which is commercially available in aqueous solution.

[0159] Preferably, the organic acid is non-halogenated based on environmental concerns. Examples of suitable organic acids include formic acid (pKa 3.77), and acetic acid

(pKa 4.79). Most preferably, the organic acid is formic acid, which is commercially available as a concentrated liquid.

[0160] The transition metal activator is preferably selected from the group consisting of manganese, vanadium, cobalt, and iron having an oxidation state in the range of at least 2, and preferably in the range of 2 to 4. More preferably, the transition metal activator is selected from the group consisting of manganese +2 or +3; vanadium +3 or +4; cobalt +2; and iron +3. Most preferably, the transition metal compound is a ferric compound. Preferably, the transition metal is not chelated. For example, according to the presently most preferred embodiment, the transition metal compound is a ferric chloride.

pH and pH Adjuster

[0161] The pH of the continuous aqueous phase of the treatment fluid is less than 7.

[0162] In certain embodiments, the treatment fluids of the present invention can comprise a pH-adjuster other than the viscosity-increasing agent, the oxidizer, the organic acid, and the transition metal compound. Preferably, the pH adjuster does not have undesirable properties, as discussed above. In addition, it is preferred that the pH adjuster avoid strong acids such as hydrochloric acid. Strong acids are highly corrosive to metals downhole.

[0163] Preferably, the organic acid and any other pH-adjuster are present in an amount sufficient to maintain or adjust the pH of the fluid to a pH of less than 5 at the time of introducing. More preferably, the organic acid and any other pH-adjuster are present in an amount sufficient to maintain or adjust the pH of the fluid to a pH in the range of about 3 to about 5.

Particulate in Treatment Fluid

[0164] In an embodiment, the treatment fluid can include a particulate. A particulate, such as gravel, can be used in the present invention. Examples include sand, gravel, bauxite, ceramic materials, glass materials, polymer materials, wood, plant and vegetable matter, nut hulls, walnut hulls, cottonseed hulls, cured cement, fly ash, fibrous materials, composite particulates, hollow spheres or porous particulate. It should be understood that the term “particulate,” as used in this disclosure, includes all known shapes of

materials including substantially spherical materials, oblong, ellipsoid, rod-like, polygonal materials (such as cubic materials), mixtures thereof, and the like.

[0165] In some embodiments in which the treatment fluid comprises particulates, the treatment fluid may be capable of suspending at least a portion of the particulates contained therein. Treatment fluids comprising particulates may be used in any method known in the art that requires the placement of particulates in a subterranean formation. For example, treatment fluids of the present invention that comprise particulates may be used, *inter alia*, to form a gravel pack in or adjacent to a portion of the subterranean formation.

Other Well Fluid Additives

[0166] In certain embodiments, the treatment fluids suitable for use in the methods of the present invention also can optionally comprise other commonly used well fluid additives, such as those selected from the group consisting of surfactants, bactericides, fluid loss control additives, stabilizers, chelants, scale inhibitors, corrosion inhibitors, hydrate inhibitors, clay stabilizers, salt substitutes (such as trimethyl ammonium chloride), relative permeability modifiers (such as HPT-1TM commercially available from Halliburton Energy Services, Duncan, Oklahoma), sulfide scavengers, fibers, nanoparticles, and any combinations thereof.

[0167] It should be understood, however, that in an embodiment the treatment fluid does not include hydraulic cement and the treatment fluid is not a hydraulic cement composition.

Forming a Treatment Fluid

[0168] The method includes a step of forming a treatment fluid, wherein the treatment fluid includes: a continuous aqueous phase and gravel. The continuous aqueous phase includes:

- (i) water;
- (ii) a viscosity-increasing agent selected from the group consisting of diutan, clarified diutan, a water-soluble derivative of diutan, and any combination thereof;
- (iii) a water-soluble oxidizer or source of a water-soluble oxidizer, wherein the concentration of the water-soluble oxidizer is in the range of 0.1% to 2% by weight of the water of the continuous phase;

(iv) a water-soluble organic acid or source of a water-soluble organic acid, wherein the water-soluble organic acid has a $pK_a(1)$ in the range of 1 to 5 and the concentration of the water-soluble organic acid is in the range of 0.5% to 5% by weight of the water of the continuous phase; and

(v) a water-soluble transition metal compound or source of a water-soluble transition metal compound, wherein the concentration of the water-soluble transition metal compound is in the range of 0.001% to 0.25% by weight of the water of the continuous phase.

[0169] The treatment fluid may be prepared at the job site, prepared at a plant or facility prior to use, or certain components of the treatment fluid (*e.g.*, the aqueous phase and the viscosity-increasing agent) may be pre-mixed prior to use and then transported to the job site. Certain components of the treatment fluid may be provided as a “dry mix” to be combined with liquid or other components prior to or during introducing the treatment fluid into the subterranean formation.

[0170] In certain embodiments, the preparation of these treatment fluids of the present invention may be done at the job site in a method characterized as being performed “on the fly.” The term “on-the-fly” is used herein to include methods of combining two or more components wherein a flowing stream of one element is continuously introduced into flowing stream of another component so that the streams are combined and mixed while continuing to flow as a single stream as part of the on-going treatment. Such mixing can also be described as “real-time” mixing. In some embodiments of the present invention, the diutan viscosity-increasing agent may be mixed into the base fluid on the fly.

Introducing the Treatment Fluid into the Well

[0171] Often the step of delivering a well fluid into a well is within a relatively short period after forming the well fluid, *e.g.*, less within 30 minutes to one hour. More preferably, the step of delivering the well fluid is immediately after the step of forming the well fluid, which is “on the fly.” It should be understood that the step of delivering the treatment fluid into the wellbore can advantageously include the use of one or more fluid pumps.

[0172] The treatment fluid may be provided and introduced into the subterranean formation in certain embodiments of the present invention by any means known in the art. In certain embodiments, the treatment fluid may be introduced into the subterranean formation by pumping the treatment fluid into a well bore that penetrates a portion of the subterranean formation.

[0173] In an embodiment, the step of introducing comprises introducing under conditions for gravel packing the portion of the wellbore.

[0174] In an embodiment, the step of introducing is below the fracture pressure of the portion of the well.

Flow Back Conditions

[0175] In an embodiment, the method includes the step of flowing back from the treatment zone. Preferably, the step of flowing back is within 5 days of the step of introducing. In another embodiment, the step of flowing back is in the range of 2 to 4 days of the step of introducing.

After Well Treatment, Producing Hydrocarbon from Subterranean Formation

[0176] Preferably, the method further includes, after the step of introducing, and preferably after a step of flowing back from the treatment zone, a step of producing hydrocarbon from the subterranean formation. This is a desirable objective.

Examples

[0177] To facilitate a better understanding of the present invention, the following examples of certain aspects of some embodiments are given. In no way should the following examples be read to limit, or define, the entire scope of the invention.

Break Tests

[0178] The following break tests illustrate the breaking of a diutan using a breaker system according to the invention at temperatures down to 140 °F. Preliminary testing has been conducted to confirm the breaking of diutan to very low viscosities 5 cP (at 511 sec⁻¹ shear on a Fann 35 viscometer) in 3 days at 140 °F.

[0179] A typical treatment fluid can be prepared by taking 980 ml of the appropriate brine in a 1 liter Waring® blender jar. In this example, the brine contained KCl at a concentration of 7% w/v. BE-3S™ and BE-6™ as bactericides were added to the above brine under continuous stirring at a concentration of 0.15 lb/Mgal respectively. 12.0 lb/Mgal of iron chelating agent was then added and allowed to dissolve completely. This was followed by addition of 30 lb/Mgal of diutan powder. Contents were allowed to mix for 10 minutes maintaining about a 1 inch vortex without entrapping any air during the mixing interval. The contents were allowed to remain static for about an hour to allow complete hydration of the gelling agent. Once the gel was hydrated, 20 gal/Mgal of NEA-96M™ as non-emulsifier surfactant was added to complete the gel preparation procedure.

[0180] A typical break test at 140 °F was carried out using 200 ml of the above hydrated diutan gel. The gel was placed under stirring in a 300 ml Waring® blender jar. In the present example, 5.0 gal/Mgal of TBHP solution (68 to 72%) as oxidizer was added to the gel under stirring followed by addition of 20 gal/Mgal of 94 -96% formic acid. This was followed by addition of 0.75 gal/Mgal ferric chloride solution (38-40%). Once all these were properly mixed, the break test gel mixture was taken in a glass bottle and placed in a pre-heated constant-temperature water bath maintained at a test temperature of 140 °F. At the desired time interval, the test bottle was taken out of the water bath and the apparent viscosity of the break test gel mixture was measured on a Fann 35 viscometer at 300 RPM (corresponds to 511 sec^{-1} shear rate). In the present example, after 3 days (72 hours), an apparent viscosity of 2.0 cP was observed. The result of varying the amounts of individual breaker components of the breaker system (TBHP solution, formic acid and ferric chloride solution) at 140 °F on the apparent viscosity of 30 lb/Mgal diutan gel at various time intervals is depicted in **Figure 1**.

[0181] Breaking tests are shown in **Table 1** for a 30 lb/Mgal diutan hydrated in water with 7 % KCl, which provides a fluid having an initial viscosity of about 25 cP.

Table 1

Test Composition	Diutan Loading (lb/Mgal)	Breaker Composition used at 140 °F			Apparent Viscosity (cP) on Fann 35 @ 511 sec ⁻¹		
		TBHP Solution (68–72%)	Formic Acid (94–96%)	Ferric Chloride Solution (38–40%)	Day 1	Day 2	Day 3
1	30	5.0 gpt	20 gpt	0.75 gpt	18	7	2
2	30	5.0 gpt	--	0.75 gpt	26	26	26
3	30	--	20 gpt	0.75 gpt	26	26	26
4	30	5.0 gpt	20 gpt	--	26	26	26
5	30	--	50 gpt	--	25	25	25
6	30	5.0 gpt	--	--	25	25	25

[0182] From **Table 1**, it can be observed that only composition 1 can give reduced viscosity at 140 °F that is in presence of oxidizer (TBHP), organic acid (formic acid) and an activator (Ferric Chloride). Absence of any one of the component from composition 1 will not achieve desire breaking.

[0183] The chart of **Figure 1** shows the effect of varying the amounts of individual breaker components of the breaker system at 140 °F on the apparent viscosity of 30 lb/Mgal diutan loading at various time intervals. All these test fluids included: (a) 1,2,3-propanetricarboxylic acid, 2-hydroxy-, trisodium salt, dihydrate 100%, in solid form, as an iron chelating agent; (b) 2,2-dibromo-3-nitrilopropionamide 97.5%, in solid form, as a bactericide; (c) 2-bromo-2-nitro-1,3-propanediol, 95-100%, in solid form, as bactericide; and (d) a surfactant “NEA-96MTM”, a general surfactant, which is commercially available from Halliburton Energy Services, Inc. in Duncan, Oklahoma. The chart of **Figure 1** shows that desired break times can be achieved by optimizing the concentrations of the components of the breaker system, which included TBHP, formic acid, and ferric chloride solution.

[0184] In addition, the breaker system for such a diutan loading can achieve a very low viscosity of less than 5 cP within a short time of less than 3 days at 140 °F. The added advantage of this breaker system is the use of concentrations of the breaker system (and any one of its components) at less than the concentration that would contribute to salting out of the of the diutan to achieve short break times at temperatures between 140 °F and 180 °F, making it practical for field applications. At temperatures higher than 140 °F, break times shorter than 3 days are likely to be achieved, if desired.

[0185] Both the polymer loading and the breaker component concentrations can affect break time, of course.

Regained Permeability Test

[0186] Regained permeability measurement was carried out using a cylindrical Aloxite™ core (400 mD permeability to air) with dimension of 1 inch in diameter and 2 inch in length. The core with one end considered as the injection end and the other end as the production end was placed inside Hassler sleeve assembly. The entire Hassler sleeve assembly was placed inside an air oven maintained at the test temperature of 140 °F. An overburden pressure of 1,100 psi was applied over the Hassler sleeve assembly to ensure the flow of test fluids through the core and avoid the test fluids from bypassing the core and flowing through the core-sleeve annulus. The initial and final permeability measurement was carried out at the test temperature of 140 °F by flowing API brine in the production direction before and after the treatment stage. The treatment stage was run by flowing the test fluid recipe through the core in the injection direction. The treatment stage comprised of flowing a total of 10 pore volumes of the test fluid through the aloxite core. The test fluid recipe comprised of 30 lb/Mgal diutan gel mixed with a breaker system made up of 5.0 gal/Mgal of TBHP solution (68 to 72%) as oxidizer, 20 gal/Mgal of 94 to 96% Formic acid and 3.0 gal/Mgal Ferric chloride solution (38 to 40%). As depicted in **Figure 2**, a regained permeability value of 82.5% was achieved.

Conclusion

[0187] Therefore, the present invention is well adapted to attain the ends and advantages mentioned as well as those that are inherent therein.

[0188] The particular embodiments disclosed are illustrative only, as the present invention may be modified and practiced in different manners apparent to those skilled in the art having the benefit of the teachings herein. The various steps according to the disclosed elements or steps can be combined advantageously or practiced together in various combinations to increase the efficiency and benefits that can be obtained from the invention.

CLAIMS:

1. A method of gravel packing a treatment zone of a well, the method comprising the steps of:

(A) forming a treatment fluid comprising a continuous aqueous phase and gravel, wherein the continuous aqueous phase comprises:

- (i) water;
- (ii) a viscosity-increasing agent selected from the group consisting of diutan, clarified diutan, a water-soluble derivative of diutan, and any combination thereof;
- (iii) a water-soluble oxidizer or source of a water-soluble oxidizer, wherein the concentration of the water-soluble oxidizer is in the range of 0.1% to 2% by weight of the water of the continuous phase;
- (iv) a water-soluble organic acid or source of a water-soluble organic acid, wherein the water-soluble organic acid has a pKa(1) in the range of 1 to 5 and the concentration of the water-soluble organic acid is in the range of 0.5% to 5% by weight of the water of the continuous phase; and
- (v) a water-soluble transition metal compound or source of a water-soluble transition metal compound, wherein the concentration of the water-soluble transition metal compound is in the range of 0.001% to 0.25% by weight of the water of the continuous phase; and

(B) introducing the treatment fluid into the treatment zone of the well;

wherein the treatment zone of the well has a design temperature that is less than 180 °F (82.2 °C);

wherein the continuous phase of the treatment fluid has or develops a viscosity in the range of 10 cP to 75 cP at the design temperature; and

wherein the treatment fluid has a cloud point and the step (A) of forming a treatment fluid comprises determining a concentration of the water-soluble organic acid that is less than the concentration that would lower the cloud point below a value that would cause the viscosity-increasing agent to salt out from the continuous aqueous phase at the design temperature.

2. The method according to claim 1, wherein the aqueous phase comprises inorganic salt dissolved in the continuous aqueous phase to the extent of at least 2% by weight of the water.
3. The method according to claim 1 or 2, wherein the aqueous phase comprises inorganic salt dissolved in the continuous aqueous phase to the extent of at least 5% by weight of the water.
4. The method according to any one of claims 1 to 3, wherein the viscosity-increasing agent is selected from the group consisting of diutan, clarified diutan, and any combination thereof.
5. The method according to any one of claims 1 to 4, wherein the viscosity of the treatment fluid is at least 20 cP.
6. The method according to any one of claims 1 to 5, wherein the oxidizer comprises a peroxide.
7. The method according to claim 6, wherein the oxidizer comprises t-butyl hydro peroxide.
8. The method according to any one of claims 1 to 7, wherein the organic acid is formic acid.
9. The method according to any one of claims 1 to 8, wherein the transition metal compound comprises a transition metal selected from the group consisting of manganese, vanadium, cobalt, and iron, wherein the transition metal further has a valence state of at least 2.
10. The method according to any one of claims 1 to 8, wherein the transition metal compound is a ferric compound.
11. The method according to any one of claims 1 to 8, wherein the transition metal compound is a ferric chloride.
12. The method according to any one of claims 1 to 11, wherein the pH of the continuous aqueous phase of the treatment fluid is in the range of about 3 to about 5.
13. The method of any one of claims 1 to 12, wherein the continuous aqueous phase of the treatment fluid further comprises a pH-adjuster other than the viscosity-increasing agent, the oxidizer, the organic acid, and the transition metal compound.

14. The method according to claim 13, wherein the continuous aqueous phase of the treatment fluid excludes a strong acid.
15. The method according to any one of claims 1 to 14, wherein the step of introducing is below a fracture pressure of the treatment zone of the well.
16. The method according to any one of claims 1 to 15, further comprising a step of flowing back the treatment fluid from the treatment zone of the well wherein the step of flowing back is in the range of 1 to 5 days of the step of introducing.
17. The method according to any one of claims 1 to 16, wherein the design temperature of the treatment zone of the well is between 140 °F (60 °C) and less than 180 °F (82.2 °C).
18. A method of gravel packing a treatment zone of a well, the method comprising the steps of:
 - (A) forming a treatment fluid including a continuous aqueous phase and gravel, wherein the aqueous phase comprises:
 - (i) water;
 - (ii) diutan;
 - (iii) oxidizer in the range of 0.1% to 2% by weight of the water;
 - (iv) organic acid in the range of 0.5% to 5% by weight of the water; and
 - (v) transition metal compound in the range of 0.001% to 0.25% by weight of the water; and
 - (B) introducing the treatment fluid into the treatment zone;
 - wherein the treatment zone has a design temperature that is less than 180 °F;
 - wherein the continuous phase of the treatment fluid has a viscosity in the range of 10 cP to 75 cP at the design temperature; and
 - wherein the treatment fluid has a cloud point and the step (A) of forming a treatment fluid comprises determining a concentration of the organic acid that is less than the concentration that would lower the cloud point below a value that would cause the diutan to salt out at the design temperature.

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30lb/Mgal DIUTAN GEL/BREAK TEST AT 140°F
[7% KCl; 12lb/Mgal IRON CHELATING AGENT; 0.15lb/Mgal BACTERICIDE; 0.15lb/Mgal MICROBIOCID; 20gal/Mgal SURFACTANT]

—X— 10 gpt FORMIC ACID + 5.0 gpt TBHP + 0.75 gpt FeCl3
--+-- 10 gpt FORMIC ACID + 10.0 gpt TBHP + 0.75 gpt FeCl3
---□--- 20 gpt FORMIC ACID + 5.0 gpt TBHP + 1.5 gpt FeCl3
—○— 20 gpt FORMIC ACID + 5.0 gpt TBHP + 0.75 gpt FeCl3
—◇— 10 gpt FORMIC ACID + 5.0 gpt TBHP + 0 gpt FeCl3
—△— 15 gpt FORMIC ACID + 5.0 gpt TBHP + 0.75 gpt FeCl3

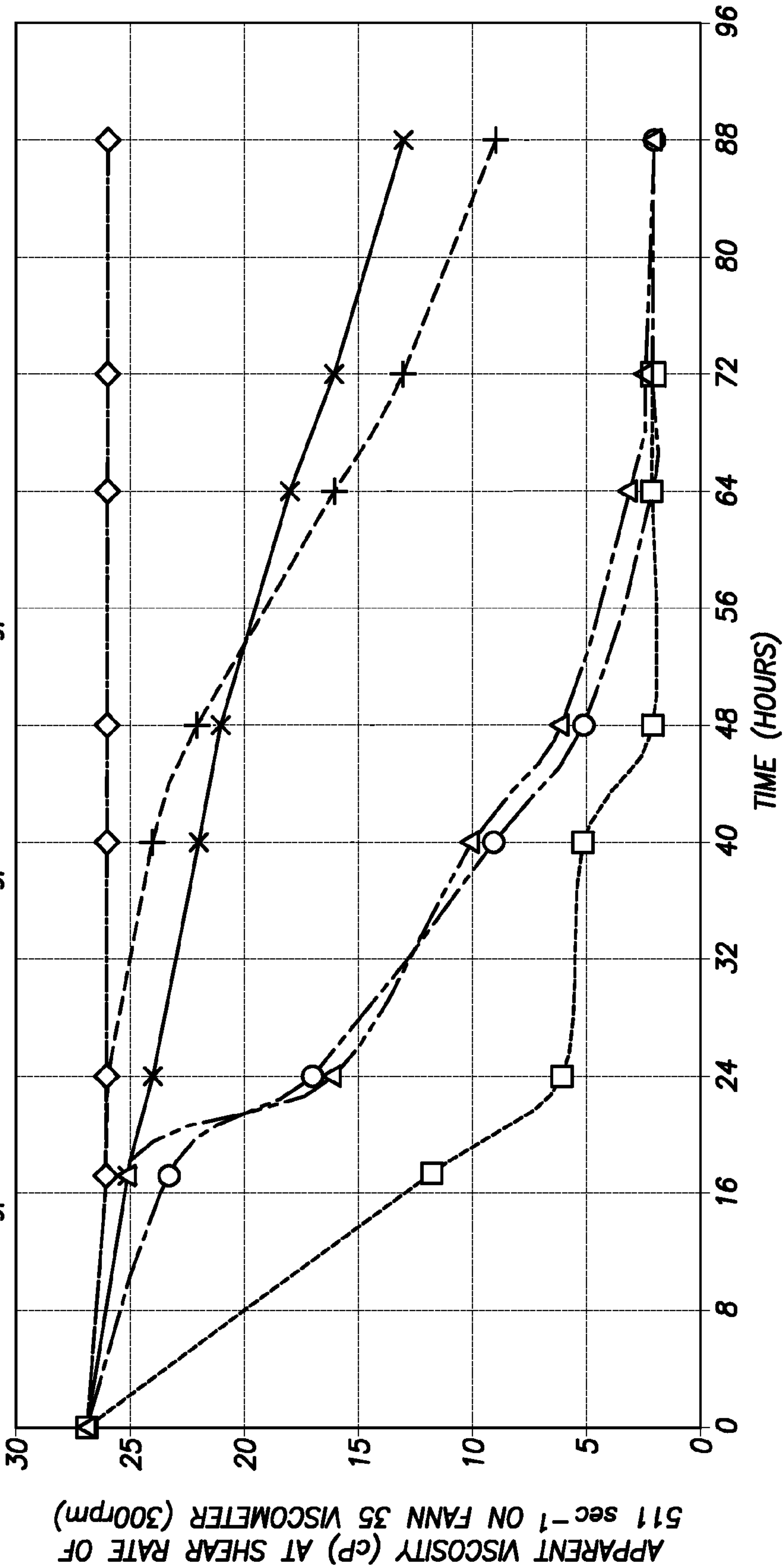


FIG.1

REGAIN PERMEABILITY TEST ON ALOXITE CORE 400 mD (AIR)

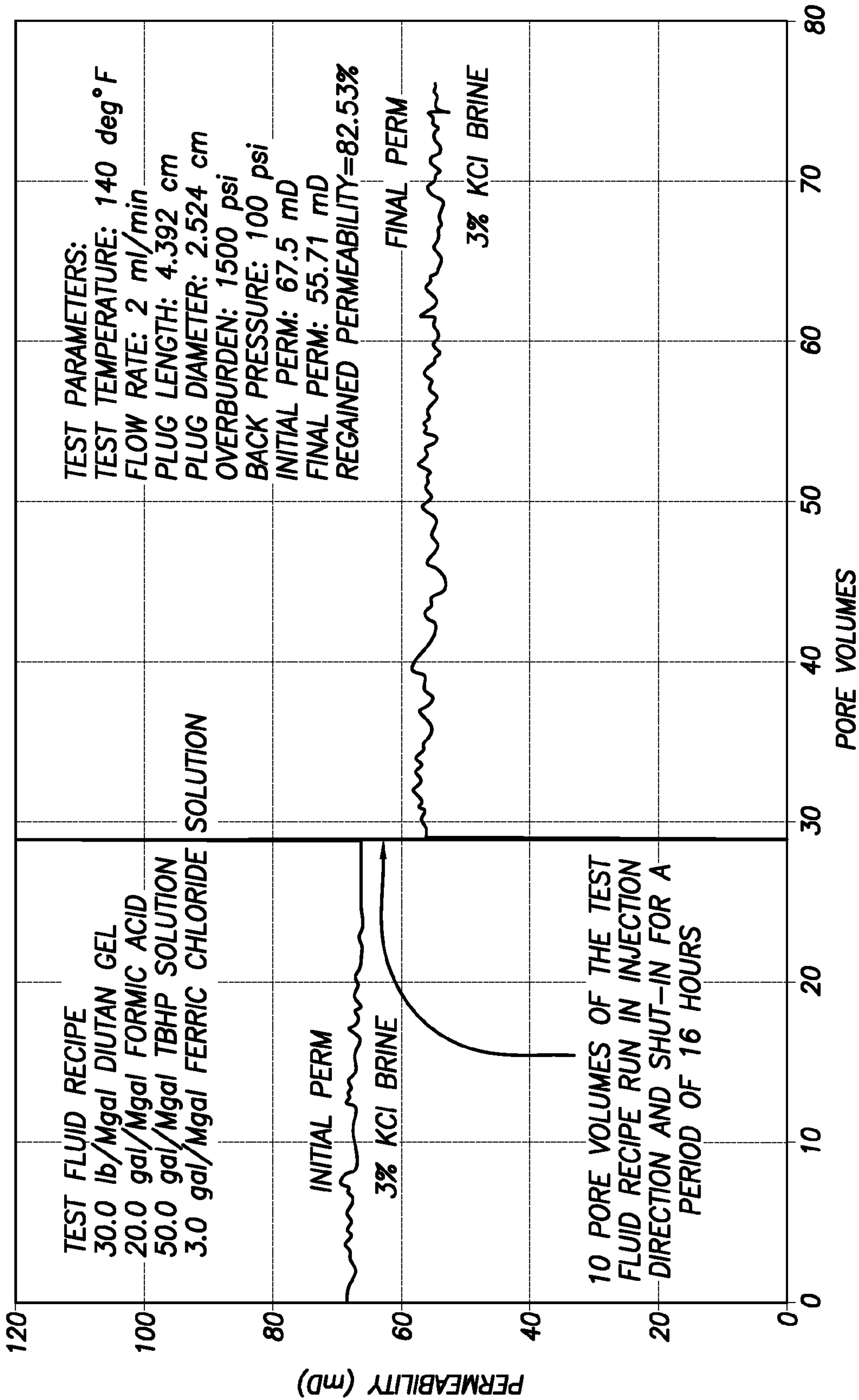


FIG.2

REGAIN PERMEABILITY TEST ON ALOXITE CORE 400 mD (AIR)

