(57) **Abstract:**
A method of using an organic peroxide containing composition as a gel breaker and a method of transporting the composition is disclosed, wherein the composition has a freeze point less than or equal to -10° C and a diluent which contains water and an organic solvent selected from ethylene glycol, methanol, ethanol and 1-propanol. During shipment, the amount of available oxygen in the composition is less than or equal to 1 weight percent.
ABSTRACT OF THE DISCLOSURE

A method of using an organic peroxide containing composition as a gel breaker and a method of transporting the composition is disclosed, wherein the composition has a freeze point less than or equal to \(-10^\circ\) C and a diluent which contains water and an organic solvent selected from ethylene glycol, methanol, ethanol and 1-propanol. During shipment, the amount of available oxygen in the composition is less than or equal to 1 weight percent.
APPLICATION FOR PATENT

TITLE: METHOD OF USING AND TRANSPORTING A NON-EMULSIFIED ORGANIC PEROXIDE-CONTAINING COMPOSITION

SPECIFICATION

Field of the Invention

The invention relates to a method of using and transporting a non-emulsified well treating composition.

5 Background of the Invention

In hydraulic fracturing, a fracturing fluid is injected into a wellbore under high pressure. Once the natural reservoir pressures are exceeded, the fracturing fluid initiates a fracture in the formation. The fracture usually continues to grow during pumping. Typically, treatment design requires the fracturing fluid to reach maximum viscosity as it enters the fracture since this affects fracture length and width. The fracturing fluid may include a proppant; the proppant being placed within the produced fracture. The proppant remains in the produced fracture to prevent the complete closure of the fracture and to form a conductive channel extending from the wellbore into the formation.

Viscosity affects the fluid’s ability to place proppant within the produced fracture.

In addition, fluid viscosity influences fracture geometry and minimizes fluid loss. The fracturing fluid's viscosity may principally be attributed to the presence of polymers, such as polysaccharides, in the fracturing fluid. To further enhance the viscosity, a crosslinking agent is frequently added to the fracturing fluid to gel the polymer.

The recovery of fracturing fluid from the formation is accomplished by reducing the viscosity of the fluid. Such reduction in viscosity should further be instrumental in retention of proppant within the fracture. Viscosity reduction may be accomplished by incorporating breakers into the initial fracturing fluid.

Many chemical agents have been reported in the literature for use as breakers. Conventional breakers have included oxidizers, acids and enzymes. In light of their reactivity and oxidative capacity, peroxides have been used as breakers for many years.

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For instance, U.S. Patent No. 5,447,199 reports the use of organic peroxides, slightly soluble in water (less than about 5% solubility), with water immiscible non-oxidizable organic solvents. Such peroxides render controlled viscosity reduction rate to the fracturing fluid after the fluid is pumped into the formation. The viscosity is controlled by the diffusion of the peroxide out of the oil phase and by the slow reaction of the peroxide and polymer. This allows for efficient recovery of the fracturing fluid from the formation.

In many instances, however, it is more desirable to use a water-soluble peroxide as the breaker composition. US Patent No. 3,922,173 discloses the use of t-butyl hydroperoxide in a gelled fluid as a breaker. However, no teaching is provided on the transport, storage and/or use of the product in cold weather environments.

In order for peroxides to be suitable at sub-freezing conditions, the breaker composition must exhibit a low freeze point. Dilution of water soluble organic peroxides with only water as diluent is unsuitable since the resulting composition is unacceptable for use at sub-freezing conditions.

Further, the difficulty in using organic peroxides in breaker compositions is compounded by stringent storage and transport regulations. Peroxides are typically prone to violent decomposition initiated by such external factors as mechanical agitation, friction and/or heat. Thus, handling and storage regulations as well as limits on container size have evolved in regards to the transport of such compounds. Such regulations have been implemented to reduce the risk of explosion which may, in turn, be caused by oxidation of peroxides in the presence of atmospheric oxygen.

A review of governmental transport and storage regulations appears in “Recommendations on the Transport of Dangerous Goods” Vol. 1, 14th revised edition, United Nations, New York and Geneva, 2005. While the regulations state that select organic peroxides may be diluted with a “suitable solvent”, defined as a “Type A solvent” having a boiling point greater than 150°C and which is compatible with the organic peroxide, no identification of a “suitable solvent” or a “Type A” is made. Thus, extensive testing is required in order to identify an acceptable solvent. Further, the regulations mandate a restricted container size and extensive explosion testing must be
undertaken in such containers to satisfy the stated criteria. Further, the diluted product must be stored in an isolated and controlled area. It therefore is desired to develop peroxide-containing breaker compositions having a freeze point which is acceptable for use in cold environments. It is also desired to develop peroxide-containing breaker compositions which may be stored and transported to their destination of use and thus used on-the-fly, wherein such breaker compositions exhibits a low decomposition rate. Furthermore, it is desired to develop peroxide-containing breaker compositions which would render unnecessary the need for explosion testing of shipping containers containing the compositions and allow the transport of the breaker without restrictions on container size.

**Summary of the Invention**

The organic peroxide containing composition used herein is outside of current governmental regulations relating to the transportation and storage of organic peroxides. The organic peroxide containing composition is a dilute composition of water and at least one water miscible solvent. The available oxygen content in the composition is less than 1 weight percent. Reduced safety hazards make the dilution process a very simple and convenient method of using organic peroxides as breakers for water based fracturing fluids. [Even in its diluted state (less than 1 wt% oxygen), the rate of addition of the diluted product to the fracturing fluid is typically less than 2%.] Since the organic peroxide containing composition is typically used in locations where ambient temperature conditions are less than 0°C, the diluent typically contains a suitable freeze point depressing solvent. The choice of freeze point depressing solvent may be made based on such factors as cost, effect on degradation rate of the peroxide, anticipated shelf life, degree of freeze point depression required and the effect of the solvent on the overall safety hazard of the diluted product. Typically, the breaker composition requires a freeze point which is at least less than or equal to -10° C. In preferred embodiments, the freeze point may be less than or equal to -20° C and in many cases less than or equal to -40° C. The breaker composition exhibits an available oxygen content of less than 1 weight percent and principally exists in a non-emulsified state.
The organic peroxide is substantially soluble in water. The diluent contains water and a water miscible solvent selected from ethylene glycol, methanol, acetone, ethanol and 1-propanol.

The amount of organic solvent in the breaker composition is between from about 0 to about 95 volume percent, preferably between from about 30 to about 70 volume percent.

In a preferred embodiment, the organic peroxide is t-butyl hydroperoxide and the organic solvent is ethylene glycol.

The concentration of organic peroxide in the breaker composition is such that the amount of available oxygen in the breaker composition is less than or equal to 1 weight percent. At such concentrations, explosion testing of shipping containers holding the compositions is unnecessary under regulations of certain jurisdictions.

The breaker compositions have a degradation of less than 20% over the expected storage life and storage temperature of the product.

The breaker compositions are extremely useful in the degradation of gels in subterranean formations. As such, the breaker compositions may be introduced into the formation with a fracturing fluid of an aqueous fluid and hydratable polymer and then pumped to a desired location within the wellbore under pressure sufficient to fracture the subterranean formation. The breaker is then capable of degrading the polymer to render a pumpable fluid.

**Detailed Description of the Preferred embodiments**

The breaker compositions for use in the method defined herein contain an organic peroxide and a diluent. The peroxide in the composition is dilutes such that less than 1 weight percent active oxygen is in the breaker composition.

The diluent in the breaker composition remains liquid and is stable at subfreezing conditions. As such, the breaker compositions have particular applicability for use in well treatment servicing when conditions are below freezing.

In particular, the use of the organic solvent provides excellent shelf-life freeze-proofing to the composition. For instance, the freeze point temperature of the breaker composition may be less than or equal to -10° C. In some cases, the freeze point of the
breaker composition is less than or equal to -20° C. In other cases, the freeze point of the breaker composition is less than or equal to -30° C. Still, in other cases, the freeze point of the breaker composition is less than or equal to -40° C. As such, the breaker composition exhibits excellent storage capabilities at very low temperatures.

The shelf-life of the breaker compositions defined herein is typically in excess of three months when stored or transported at a temperature of 25 °C or lower.

The breaker composition has an active oxygen content equal of less than 1 weight % and principally exists in a non-emulsified state.

The diluent contains water and/or an organic solvent acceptable for freeze-proofing. The organic solvent must be compatible with the organic peroxide. Compatibility may be measured by assaying the activity of the peroxide during storage. Preferably, the activity of the peroxide will not deteriorate by less than 20 % over a storage period of three months. Preferred organic solvents are those selected from the group consisting of ethylene glycol, methanol, ethanol, 1-propanol and acetone. Ethylene glycol is most preferred since it has been illustrated to provide very high stability to the resulting composition. Further, low molecular weight alcohols, as well as acetones, are generally less preferred in light of domestic and/or international shipping regulations.

The organic peroxide is substantially soluble in water so as to remain as a single homogeneous phase in the diluent. “Substantially soluble” is meant to mean up to a solubility of at least 10 weight %. Further, in order to conserve costs, the peroxide should be of relatively low molecular weight, typically less than or equal to approximately 200, in order to maximize available oxygen content.

Exemplary organic peroxides include t-butyl hydroperoxide, disuccinic acid peroxide, dipropionyl peroxide, diacetone alcohol peroxides, di-(2-methylbenzoyl) peroxide, and 3-chloroperoxybenzoic acid. Of these, t-butyl hydroperoxide is especially preferred. Commercially available t-butyl hydroperoxides are typically about 70% active in water and can be readily diluted in the organic solvents described herein. Such commercially available hydroperoxides include Trigonox A-W 70 of AKZO Nobel.

The amount of organic solvent in the breaker composition is between from about 0 to about 95 volume percent, preferably between from about 30 to about 70 volume percent.
In a preferred embodiment, the organic peroxide is t-butyl hydroperoxide and the organic solvent is ethylene glycol.

The maximum amount of organic peroxide employed in the breaker composition is that required to provide an available oxygen content of 1 weight percent. As such, the breaker compositions of the invention are preferably non-emulsified compositions. At such concentrations, the breaker composition may be transported in shipping containers without the need for conducting explosion tests on representative containers, under the regulations of some jurisdictions.

In addition to having low freeze points, the breaker compositions defined herein exhibit high flash points. Typically, the flash point of the breaker compositions is in excess of 37.8°.

Further, the breaker compositions display excellent compatibility with elastomers in conventionally employed pumping equipment, are readily miscible in water and demonstrate no adverse facts on crosslinked water gels.

In addition to exhibiting an acceptable freeze point, the breaker compositions for use herein do not exhibit separation into liquid phases nor does the precipitation of peroxide crystals occur at subfreezing conditions.

The breaker compositions are extremely useful in the degradation of gels in subterranean formations. As such, the breaker composition may be introduced into the formation with a fracturing fluid of an aqueous fluid, hydratable polymer and optional crosslinking agent. The aqueous fluid could be, for example, water, brine, aqueous based foams as well as mixtures of water and alcohol. Alternatively, the fracturing fluid introduced into the formation may by prepared by combining hydratable polymer, aqueous fluid, optional crosslinking agent with the organic peroxide and diluent described herein. Any suitable mixing apparatus may be used for this procedure.

The fluid may then be pumped to a desired location within the wellbore under pressure sufficient to fracture the surrounding subterranean formation. The breaker, as defined herein, degrades the polymer, whereby the fluid may be pumped from the subterranean formation to the well surface.

The hydratable polymer may be any of the hydratable polysaccharides that are conventionally employed in the well service industry. These polysaccharides may be
capable of gelling in the presence of a crosslinking agent to form a gelled based fluid. For instance, suitable hydratable polysaccharides are the galactomannan gums, guar, derivatized guar, cellulose and cellulose derivatives. Specific examples are guar gum, locust bean gum, fenugreek gum, caraya gum, xanthan gum, cellulose, and derivatives of these gums. The preferred gelling agents are guar gum, carboxymethyl guar, hydroxypropyl guar, carboxymethyl hydroxypropyl guar, cellulose, carboxymethyl cellulose, carboxymethyl hydroxyethyl cellulose and hydroxyethyl cellulose. The most preferred gelling agents are guar gum, hydroxypropyl guar, carboxymethyl hydroxypropyl guar, hydroxyethyl cellulose and carboxymethyl hydroxyethyl cellulose.

The polysaccharide of the fracturing fluid may further not be crosslinked. For instance, polysaccharides not requiring a crosslinking agent, such as starch, derivatized starch, xanthans and xanthan gums, may be used.

The fracturing fluids of the invention often include the crosslinking agent. The crosslinking agent can be any of the conventionally used crosslinking agents which are known to those skilled in the art. For instance, in recent years, gellation of the hydratable polymer has been achieved by crosslinking these polymers with metal ions including aluminum, antimony, zirconium, for example, zirconium chelates such as zirconium acetate, zirconium lactate, zirconium lactate triethanolamine and titanium containing compounds including organotitanates, for example, the titanium chelates such as triethanolamine titanates, titanium acetylacetonate and titanium lactate. See, for instance, U.S. Pat. No. 4,514,309.

Borate crosslinkers are further typically used. Such crosslinking agents are those capable of supplying borate ions in solution. For instance, such crosslinkers include those which are a convenient source of borate ions, for instance the alkali metal and the alkaline earth metal borates and boric acid. One such crosslinking additive is sodium borate decahydrate, the crosslinking agent described in Pat. No. 5,160,643. In a preferred embodiment of the invention, the fracturing fluid contains guar and a borate crosslinking agent. In such guar gels, the crosslinking additive is preferably present in the range from about 0.024% to in excess of 0.18% by weight of the fracturing fluid. Preferably, the concentration of crosslinking agent is in the range from about 0.024% to about 0.09% by weight of the fracturing fluid.
Any proppant known in the art may be added to the fracturing fluid. If a crosslinking agent is present in the fracturing fluid, the proppant is typically added to the fluid prior to the addition of the crosslinking agent. Suitable proppants include quartz sand grains, glass, ceramics, walnut shell fragments, aluminum pellets, nylon pellets and the like. The proppants are normally used in concentrations between about 1 to 18 pounds per gallon of fracturing fluid composition, but higher or lower concentrations can be used as required.

The fracturing fluid may also contain other conventional additives common to the well service industry such as surfactants and the like.

The following example illustrates the practice of the present invention in a preferred embodiment. Other embodiments within the scope of the claims herein will be apparent to one skilled in the art from consideration of the specification and practice of the invention as disclosed herein. It is intended that the specification, together with the example, be considered exemplary only, with the scope and spirit of the invention being indicated by the claims which follow.

EXAMPLES

Example 1. A solution of 8.5 volume % t-butyl hydroperoxide (70% in water) was prepared in a blend of 49.0 volume percent water and 43.5 volume percent ethylene glycol. The solution exhibited a flash point of 69.4° C. and a freeze point of -40° C. After storage at room temperature for 4 months the t-butyl hydroperoxide content was analyzed by a gas chromatograph equipped with an mass selective detector and the concentration was found to have degraded less than 5% compared to a new solution. This demonstrates the suitability of the ethylene glycol as a diluent in this invention.

From the foregoing, it will be observed that numerous variations and modifications may be effected without departing from the true spirit and scope of the novel concepts of the invention.
CLAIMS

What is claimed is:

1. A method of degrading a gel in a subterranean formation which comprises introducing into the formation a non-emulsified well treating composition comprising an organic peroxide and an organic solvent selected from the group consisting of ethylene glycol, acetone, methanol, ethanol and 1-propanol, wherein the well treating composition has a freeze point less than or equal to -10° C.

2. The method of Claim 1, wherein the well treating composition has a freeze point less than or equal to -20° C.

3. The method of Claim 1, wherein the organic peroxide is t-butyl hydroperoxide.

4. The method of Claim 1, wherein the organic solvent is ethylene glycol.

5. The method of Claim 4, wherein the amount of ethylene glycol in the well treating composition is between from about 10 to about 95 volume percent.

6. The method of Claim 1, wherein the amount of organic solvent in the breaker composition is between from about 10 to about 95 volume percent.

7. The method of Claim 6, wherein the amount of organic solvent in the breaker composition is between from about 30 to about 70 volume percent.

8. The method of Claim 1, wherein the composition has a self accelerating decomposition temperature greater than or equal to 55° C.

9. The method of Claim 1, wherein the amount of available oxygen in the composition is less than or equal to 1 weight percent.

10. A method of fracturing a subterranean formation surrounding a wellbore which comprises the steps of:

(a) introducing into the formation a fracturing fluid of an aqueous fluid, a hydratable polymer and a breaker;

(b) pumping the fracturing fluid to a desired location within the wellbore under pressure sufficient to fracture the surrounding subterranean formation; and

(c) allowing the breaker to degrade the polymer and produce a pumpable fluid
wherein the breaker is a composition comprising an organic peroxide which exhibits substantial solubility in water and a diluent selected from the group consisting of water, ethylene glycol, acetone, methanol, ethanol and 1-propanol.

11. The method of Claim 10, wherein the organic peroxide is t-butyl hydroperoxide.

12. The method of Claim 11, wherein the organic solvent is ethylene glycol.

13. A method of transporting an organic peroxide which exhibits substantial solubility in water, the method comprising:
   (a) preparing a dilute non-emulsified peroxide solution by mixing an organic peroxide with a sufficient amount of diluent in order to render a available oxygen content in the dilute peroxide solution in an amount less than or equal to 1 weight percent, wherein the diluent is a mixture of water and an organic solvent selected from the group consisting of ethylene glycol, acetone, methanol, ethanol and 1-propanol; and
   (b) transporting a receptacle containing the dilute peroxide solution to a desired location.

14. The method of Claim 13, wherein the activity of the peroxide will not deteriorate by less than 20% over a storage period of three months.

15. The method of Claim 13, wherein the freeze point of the dilute peroxide solution is less than or equal to -10° C.

16. The method of Claim 15, wherein the freeze point of the dilute peroxide solution is less than or equal to -20° C.

17. The method of Claim 16, wherein the freeze point of the dilute peroxide solution is less than or equal to -40° C.

18. The method of Claim 13, wherein the organic peroxide is t-butyl hydroperoxide.

19. The method of Claim 18, wherein the organic solvent is ethylene glycol.

20. The method of Claim 13, wherein the amount of organic solvent in the dilute peroxide solution is between from about 10 to about 95 volume percent.

21. In a method of transporting an aqueous organic peroxide solution in a shipping container, the improvement comprising shipping a dilute non-emulsified organic peroxide solution wherein the amount of available oxygen in the dilute organic peroxide
solution is less than or equal to 1 volume percent, the diluent being water and an organic solvent selected from the group consisting of ethylene glycol, acetone, methanol, ethanol and 1-propanol.

22. The method of Claim 21, wherein the freeze point of the dilute organic peroxide solution is less than or equal to -20°C.