GELLED OXIDIZING AGENTS, METHOD OF PREPARATION AND METHOD OF USE IN TREATING UNDERGROUND FORMATIONS

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ABSTRACT OF THE DISCLOSURE

(1) A method of selling concentrated HNO₃, fuming HNO₃, or a mixture of fuming H₂SO₄ and HNO₃, which consists of mixing with the acid between 0.5 and 25.0% by weight of a gelatin or other substance which is capable of forming an alkali cross-linked poly(N-vinylpyrrolidone); (2) the resulting gelled composition; and (3) a method of treating a subterranean formation by injecting the so gelled acid, as a component of an oxidizer and a liquid fuel explosive mixture, in the formation.

The invention concerns a novel gelled acid composition. It further concerns the use of such composition in controlled underground operations involving detonations and explosions including the treatment of fluid-bearing subterranean formations penetrated by a borehole for the purpose of stimulating fluid flow therefrom.

The composition of the invention employs an acidic oxidizing agent or oxidizer of high oxidation potential, having an oxidation potential at least as high as that of concentrated nitric acid. The oxidizers contemplated to be used in the invention are concentrated nitric acid, fuming nitric acid, and mixtures of fuming nitric acid and fuming sulfuric acids.

Such oxidizers are known to be highly useful as a component, together with a fuel or reducing agent in explosives. Uses for explosives are wide-spread and include underground operations employing such oxidizers and a fuel. The fuel employs one or two types: one which, when admixed with such oxidizer produces a hypergolic mixture, i.e., a mixture which spontaneously explodes or detonates when the oxidizer and fuel components of the mixture come into contact with each other, and a second type of fuel which requires substantially the same oxidizer but which is less reactive to the extent that it does not form a hypergolic mixture with the oxidizer upon mere contact but which requires (subsequent to the intermixing of the fuel and oxidizer components) an extrinsic detonating or igniting means. There are three principal types of such means: (1) a particularly reactive fuel or reducing agent which renders the resulting mixture hypergolic (sometimes referred to in the art as a chemical igniter), (2) a shock-inducing device, or (3) a high temperature igniter which raises the temperature of at least a small portion of the mixture above its ignition temperature which, when ignited, in turn ignites the balance of the mixture, much as a common fuel is ignited in the presence of elemental gaseous oxygen. Such high temperature igniters include a flame or spark provided, for example, by electricity, fuse, open flame, or such more sophisticated means as Primacord. It is quite possible, of course, to use combinations of shock and heat if desired. For purposes of the invention, when a fuel is employed which requires an extrinsic igniter to set off or ignite an admixture thereof with an oxidizer, the chemical igniter is preferred.

When a fuel which forms a hypergolic mixture with the oxidizer is selected from such chemical groups as amines, alkyl benzenes, sulfur-containing compounds such as mercaptans, aliphatic mono-alcohols, glycols, ketones, and certain highly branched and/or unsaturated hydrocarbon liquids. Any fuel which forms a hypergolic mixture with the oxidizing agent being employed at the temperature and pressure conditions existing at the place or site, e.g., the underground level where treatment is to be carried out, is acceptable for this type of explosive.

On the other hand, when a fuel is employed which does not form a hypergolic mixture with the oxidizer, but requires a chemical igniter or shock or high temperature igniting means for ignition or detonation, such fuel as a saturated or relatively unbranched and saturated hydrocarbon liquid, e.g., kerosene, nitropropane, or a mixture of such fuels, is commonly employed. The method of treating a formation employing an oxidizing agent which does not form a hypergolic mixture with the fuel employed, but is subsequently detonated by a chemical igniter, is described in U.S. Patent 3,075,463.

A test which may be employed to ascertain whether or not a particular fuel-oxidizer mixture is hypergolic for purposes of the invention is set out in S.N. 328,487, assigned to the same assignee as the instant application, and are filed Dec. 6, 1963, now U.S. Patent No. 3,266,572, as set out at pages 5 and 6 thereof.

The use of a hypergolic mixture offers certain advantages over a mixture which requires an extrinsic igniter and some encouraging progress has been made in providing improved oxidizers and fuel mixtures of the hypergolic type. However, several rather complicating problems have persisted. Among such problems associated with the use of hypergolic mixtures is the necessity of employing liquid components which must absolutely be maintained entirely unixed and out of contact with one another until they are in the formation where detonation or ignition is desired. Premature mixing clearly defeats the objectives and may culminate in serious personal injury and/or property damage. The fact that the oxidizing agent is fuming nitric acid, a mixture of fuming sulfuric acid and fuming nitric acid having the required oxidation potential, or concentrated nitric acid, any one of which is hazardous to personnel and equipment unless the utmost caution is exercised in transferring, mixing, and using the acid, as in injecting it into an underground formation, increases the gravity of the problem. When treating formations via a well, the liquid state of the acid presents particularly serious problems because of the relatively large volume capacity of the injection pipes, tubes, and the like of a wellbore and the relatively small volume of the components required to make the hypergolic mixture employed in treating formations. As a consequence, both components are usually in the wellbore at the same time and are, only after subsequent to the injection of both, displaced into the formation. Although a spacer liquid or spacer plug and preferably both, when most carefully used, have maintained the explosively reactive components safely spaced apart until they are back in the formation, maintaining two liquids so spaced apart is a more difficult task than maintaining a solid and a liquid spaced apart.

To lessen the dangers of handling the acid in use and to lessen the tendency of the reactive components to mix prematurely are existing needs. A further need in well treating operations employing liquid oxidizers is that of lessening the fluid loss thereof to the formation.

Advancements have been made which have alleviated, to some extent, the severity of these problems, among which are the gelation of some of the fuel components commonly used. A further advancement in the art of treating underground formations, desired, is usually spontaneous explosion composition is that described in the aforementioned S.N. 328,487, now U.S. Patent No. 3,266,572, wherein certain procedures, which describe a novel technique for maintaining the reactive components of a
hypergolic mixture spaced apart and out of contact with one another until they are in the formation, is described.

However, the problem of satisfactory handling of an acid of high oxidation potential and of lessening the fluid loss thereof to the formation has persisted because heretofore no method or composition is known which is effective for gelling the oxidizing mixtures of fuming sulfuric acid and fuming nitric, or concentrated nitric acid composition. Accordingly, the problem of gelling the oxidizing component present in either of the hypergolic or non-hypergolic explosive mixtures used in underground operations has heretofore remained unsolved and the need for a solution of the problem has persisted.

Prior to the instant invention, any gelling agent, when admixed with any one of the oxidizing acids, named above, was attacked by the acid and degraded, thereby destroying the gelation properties and defeating the attempt to congeal or gel the acid, often also rendering the so treated acid unusable for the purpose.

The principal object of the invention is to provide an effective method of gelling the above named acids and the resulting gelled acid composition and to provide an improved method of treating underground formations employing a gelled oxidizing component of either a hypergolic mixture or a non-hypergolic mixture composed of a fuel and oxidizer.

The invention comprises admixing with an oxidizing agent having an oxidation potential at least as high as that of concentrated nitric acid, illustrative of which are concentrated nitric acid, fuming nitric acid, and mixtures of fuming nitric acid and fuming sulfuric acid, between about 0.5 and about 25.0 percent by weight, based upon the weight of the resulting so treated acid, a cross-linked insoluble, acid-swellable and dispersible poly(N-vinylpyrrolidone). It further comprises a method of treating a fluid-saturated formation penetrated by a wellbore for stimulating fluid production therefrom.

The monomer usually employed to make the polymer is N-vinyl-2-pyrrolidone which may be represented by:

\[
\text{H}_2\text{C} - \text{CH} = \text{CH}_2
\]

\[
\text{N} - \text{C} = \text{O}
\]

\[
\text{CH} = \text{CH}_2
\]

Polymerization is effected through the vinyl group.

Although cross-linked poly(N-vinylpyrrolidone) has been known to gel certain liquid nitroalkanes and hydroxy compounds, as described in application S.N. 312,003, filed Sept. 27, 1963, now U.S. Patent No. 3,242,020, and in S.N. 312,008, filed Sept. 27, 1963, now U.S. Patent No. 3,242,032, its effectiveness and resistance to degradation in gelation of oxidizing agents of such high oxidation potential as fuming HNO₃, mixtures of fuming nitric and fuming sulfuric acids, or concentrated HNO₃ is completely unexpected.

The cross-linked polymer required in the practice of the invention is a recent discovery. It may be prepared either by use of a cross-linking agent and a chemical catalyst or by irradiation, or by a combination of both. In any case, N-vinylpyrrolidone, or a previously prepared linear polymer thereof, is cross-linked either in mass, i.e., without use of a liquid reaction medium, or in an aqueous or lower aliphatic mono-alkanol solution. It is preferable that the polymerization be carried out in an aqueous solution of at least about 5 percent concentration. Best results are obtained when a monomer or linear polymer in a concentration of between 20 and 90 percent in water (or usually between 25 and 50 percent), by weight of the reaction mixture, is employed. A chemical cross-linking agent is necessary when employing a chemical catalyst and is recommended when employing irradiation. The cross-linking agent is employed in an amount of between 0.02 and 10.0 percent (preferably between 0.2 and 5.0 percent), based on the weight of the reaction mixture. A reference which discusses the preparation of the polymer required for the invention may be found in U.S. Patent 2,810,716. Cross-linking agents which may be used in preparing the polymer for use in the practice of the invention include any of those which are not easily degraded by strong acids. Illustrative thereof are divinyl ether of ethylene glycol, divinyl benzene, and divinyl ether. The chemical catalyst, when employed, may be any of those known as free-radical catalysts of which water-soluble peroxides, peroxides, a,a'-azoisobutyronitrile, and the re-dox-type catalysts are illustrative.

When the cross-linked polymer is prepared by irradiation techniques, between 0.5 and 15.0 megardas are usually and preferably between 0.75 and 3.0 megards.

The extent of irradiation is that which produces a cross-linked poly(N-vinylpyrrolidone) which is insoluble but swellable in the acid to be gelled.

Care must be exercised in the polymerization to control the extent of cross-linking so as to provide one which is sufficiently cross-linked to be insoluble in the acid but which is insufficiently cross-linked to prevent it dispersing, swelling, and imbining large volumes of the aqueous medium.

A typical procedure for preparing cross-linked poly(N-vinylpyrrolidone) by irradiation is as follows: an aqueous solution, containing 50% by weight of N-vinylpyrrolidone, is irradiated with a dose of 0.805 megard from a 3000 curie cobalt-60 source of gamma rays at a dosage rate of 0.23 megard/hour. The polymer so made is separated from the reaction medium, dried in an oven for about 8 hours at a temperature of about 120° C, and then ground to a powder such that substantially all will pass through a 100 mesh screen.

As an alternative procedure for preparing the polymer is a mixture of 450 grams of N-vinylpyrrolidone, 0.9 gram of a,a'-azoisobutyronitrile (as a catalyst), 0.45 milliliter of 1-amino, 2-propanol, 2.25 grams of divinyl ether of diethylene glycol, and 1800 milliliters of water are placed in a suitable container and heated for about 8 hours under a protective blanket of nitrogen at from about 70° to 80° C. The polymer gel so formed is dried, e.g., by being placed in an oven at between 80° and 120° C, and then ground to a suitable size powder.

Illustrative of another procedure for preparing the polymer useful in the practice of the invention is a combination of the above two procedures which comprises irradiating N-vinylpyrrolidone together with a cross-linking agent to provide an initiating source of free radicals. As illustrative, a sample of N-vinylpyrrolidone containing 0.5 percent by weight of divinyl ether of diethylene glycol as cross-linker, is exposed to a dose of 0.24 megard gamma radiation from a cobalt-60 source.

The polymers formed by any of the suggested procedures are substantially equally effective and suitable in the practice of the invention.

The invention is practiced by admixing the pulverized polymer prepared by one of the above procedures with the high oxidation potential acid being employed in the preparation of explosive mixture. The exact mixing procedure is not highly critical, any of the known techniques for providing a substantially uniform dispersion of particulate material in a liquid being satisfactory. Relatively moderate to general agitation is usually provided until the gel begins to form (which is usually within 2 to 10 minutes) whereupon agitation is stopped.

The cross-linked poly(N-vinylpyrrolidone) prepared as described above is usually employed in an amount of between about 1 and 5 parts by weight of the explosive mixture. The admixture is usually allowed to stand for at least about 10 and preferably about 15 minutes. Longer standing is quite acceptable, however, since the gelled acid is known to be stable for a period of time up to a year and appears to be stable for much longer periods. However, no particular advantage resides in providing a prolonged gel time.
Examples 1 and 2 illustrate the preparation of the gelled acid composition of the invention.

**Example 1**

Cross-linked poly(N-vinylpyrrolidone) was admixed with red fuming nitric acid as follows: 3.12 parts by weight of the poly(N-vinylpyrrolidone) (which had been prepared by cross-linking with 0.7 percent by weight of divinyl ether of diethylene glycol, catalyzed with α,α'-azobisobutyronitrile) was admixed with 156 parts by weight of red fuming nitric acid. A stable particulate gel formed after 15 minutes. The viscosity of the resultant gel was 1100 centipoises as measured by a Brookfield viscometer, provided with a number 3 spindle rotating at 60 r.p.m.

**Example 2**

Example 1 was repeated employing white fuming nitric acid instead of the red fuming acid of Example 1. A gel formed as in Example 1.

The treatment of an underground formation, employing the gelled acid so formed is carried out, broadly, by placing the components of the explosive mixture in the ground via a shaft or tunnel, which may vary in depth or length from relatively shallow to very deep, or via a deep wellbore extending as much as many thousands of feet into the earth, and detonating the mixture in situ.

An improved method of injecting components of a hypergolic mixture into a formation penetrated by a well is described in aforementioned S.N. 328,487, now U.S. Patent No. 3,566,572. The present invention may be similarly practiced, if desired, employing the novel gelled acid as the oxidizer component. However, when employing a gelled acid, the dangers of premature mixing are very definitely lessened.

To carry out a treatment of a fluid-bearing subterranean formation penetrated by a wellbore for the purpose of fracturing and shattering portions of the formation to stimulate fluid production therefrom, the practice of the invention, employing components of a hypergolic mixture, is illustrated as follows: the gelled acid of the invention, e.g. that prepared in Example 1 or 2, is injected down a well penetrating the subterranean formation followed by a spacer liquid, e.g. water or brine, and then by a liquid fuel which forms a hypergolic mixture when in contact with the acid. It is recommended that a separatory snuggly fitting slidable plug be inserted ahead of the spacer liquid and a second such plug immediately behind it. If desired, the liquid fuel may be injected first followed by a spacer plug, spacer liquid, and then by the second plug and they in turn by the gelled oxidizing agent. However, it is usually preferred to inject the acid first. The thus injected but spaced-apart gelled acid and fuel are then forced from the wellbore, as by employing a displacing liquid, e.g. oil, water, brine, or a gelled or emulsified aqueous and/or oil composition into the formation where at least sufficient gelled acid and fuel are brought into intimate contact, whereupon those in contact with each other spontaneously ignite and explode, generating heat and creating turbulence which mixes and raises the temperature of the remaining components so that the explosions continue until either the fuel or the oxidizer is exhausted.

When the formation is to be treated by employing the less reactive type of fuel, i.e. that which does not form a hypergolic mixture with the gelled acid employed, the fuel and gelled components may be premixed and the resulting mixture injected; they may be injected simultaneously; or they may be injected successively. Thereafter, they are displaced into the formation by a displacing liquid and are then followed by an igniter means, most usually a liquid chemical igniter. To bring the liquid chemical igniter into contact with the fuel and gelled oxidizer, a small-diameter flexible line extending down the wellbore into the mixture is usually provided and the chemical igniter injected down through that line. Such procedure is illustrated in U.S. Patent 3,075,463.

The Example 3, below, illustrates a specific treatment of a subterranean formation penetrated by a deep well employing a fuel which makes a hypergolic mixture with the oxidizer.

**Example 3**

A fluid-bearing stratum at a level of between 11,020 feet and 11,235 feet penetrated by a wellbore which is provided with a 2" standard well tubing extending to the stratum is to be treated to stimulate the flow of fluid therefrom. The stratum to be treated is a tight or highly consolidated type and has not previously been fractured. Accordingly, a limited conventional fracturing job is performed on the stratum prior to treatment according to the invention. Such prefracture in brief, comprises the placing of a packer in the wellbore annulus just above the stratum to be treated and injecting a fluid down the tubing and into the stratum at sufficient pressure to create fractures in the stratum. Pressure is then released and the well allowed to back flow.

The treatment then proceeds as follows: 2 to 5 parts of cross-linked poly(N-vinylpyrrolidone) (prepared, for example, by subjecting a 50 percent aqueous solution of monomeric N-vinylpyrrolidone to about 1 megarad of radiation from a Coγ isotope in a radiation chamber and subsequently separating, drying and pulverizing the resulting polymer) is admixed with 100 parts by weight of red fuming nitric acid (98% nitric acid (balance water) containing dissolved therein from about 12 to about 14 percent by weight of gaseous nitrogen oxides, chiefly N2O5). The acid is thereby converted within minutes into a particulate pumpable gel. The gel is then injected down the wellbore followed by a resilient, tightly fitting but slidable plastic plug, then by a spacer liquid, e.g. gelled water or brine usually prepared by admixing a small amount of a gum, say 1 or 2 percent by weight of guar gum therewith. The gelled water was then followed by a second resilient plastic plug which also fits snugly but slidably in the tubing. A liquid fuel, consisting of a mixture by weight of about 20 percent furfuryl alcohol, about 20 percent xylene and between 40 and 50 percent of the two, is then injected into the tubing. The ratio of fuel to oxidizer may vary rather widely although it is clear that unless fuel is in the formation (as when treating an oil-bearing formation) the amounts of each will preferably be near the stoichiometric quantities.

It is understood that the fuel could have been 100 percent aniline, 100 percent furfuryl alcohol, or 100 percent mixture thereof. The use of the kerosene with the xylene was employed to show that a more economical fuel, to provide a hypergolic mixture may advantageously be used.

The total amount of the gelled acid and fuel employed varies with the job. For a particularly large scale treatment, as much as 3.0 or more barrels (42-gallons each) of the gelled acid may be used and an equivalent amount of fuel provided. However, from about 0.25 to about 2 barrels of the acid are commonly used for treating a subterranean fluid bearing formation. The amount of spacer liquid employed is usually sufficient to maintain a distance of separation between the fuel and the oxidizer of at least 2 or 3 vertical feet and more often about 8 or 10 feet.

A displacing liquid, e.g. oil, water, brine, or a prepared emulsion or gelled composition thereof, is then injected down the wellbore in an amount sufficient to displace the gelled acid and the fuel from the wellbore into the formation. It is recommended that a spacer plug be positioned just ahead of the displacing liquid to aid in preventing the displacing liquid from undesirably intermixing with the fuel.

The gelled acid enters the formation first. Because of its gelled state it exhibits a greatly reduced tendency...
to leak off into the formation (referred to in the art as fluid loss). The gelled acid is followed into the formation by a liquid which is then followed by the reactive fluid (which when in contact with the gelled acid forms a hypergolic mixture). A displacing liquid is then injected which forces the components of the hypergolic mixture into the formation whereupon explosions occur which propagate a throughout the fluid and oxidizer mixture as the fuel continues to move into the formation, being forced thereinto by the displacing liquid which is continued to be injected into the wellbore until at least substantially all the fuel is in the formation. A series of explosions, therefore, takes place in the formation, rubblizing and shattering the formation, and is manifested by relatively sharp rises in pressure (registered as back-pressure at the wellhead), oftentimes showing a pressure differential of as much as 1000 to 2000 p.s.i. followed by more gradual subsidence of pressure. Fluid communication through the formation is greatly enhanced by the treatment and production of fluids from the formation is stimulated.

Having described our invention what we claim and desire to protect by Letters Patent is:

1. The method of gelling an oxidizing agent having an oxidation potential at least as great as that of concentrated nitric acid which consists essentially of admixing with said oxidizing agent between about 0.5 and about 25.0 percent by weight, based on the weight of the resulting so treated oxidizing agent, of an acid-swellable insoluble cross-linked polymer of N-vinylpyrrolidone.

2. The method of gelling an oxidizing agent selected from the class consisting of fuming nitric acid, mixtures of fuming sulfuric acid and fuming nitric acid, and concentrated nitric acid which consists essentially of admixing with said oxidizing agent between about 0.5 and about 25.0 percent by weight, based on the weight of the resulting so treated acid, of an acid-swellable insoluble cross-linked polymer of N-vinylpyrrolidone.

3. The gelled composition consisting of an admixture of between about 0.5 and about 25.0 percent by weight of cross-linked polymer of N-vinylpyrrolidone and balance, to make 100 percent by weight, of an oxidizing agent having an oxidation potential at least as great as that of concentrated nitric acid.

4. The gelled composition consisting of an admixture of between about 0.5 and about 25.0 percent by weight of cross-linked polymer of N-vinylpyrrolidone and balance, to make 100 percent by weight, of an oxidizing agent selected from the class consisting of fuming nitric acid, mixtures of fuming nitric acid and fuming sulfuric acid, and concentrated nitric acid.

5. The method of rubblizing and shattering portions of an earthen stratum which consists of (1) admixing between about 0.5 and 25.0 percent by weight of an acid-swellable insoluble cross-linked polymer of N-vinylpyrrolidone with a sufficient amount of an oxidizing agent having high oxidation potential selected from the class consisting of fuming nitric acid, mixtures of fuming nitric acid and fuming sulfuric acid, and concentrated nitric acid to make 100 percent by weight of a gelled acid composition; (2) forcing the so gelled acid and a liquid fuel, which forms a hypergolic mixture with said gelled oxidizing agent when in intimate contact therewith, into the stratum to be so rubblized and shattered, said gelled acid and fuel being maintained out of contact with each other until they are in the formation, thereby providing a series of explosions in the formation to effect rubblizing and shattering of portions thereof.

6. The method of treating a stratum of a subterranean formation penetrated by a wellbore which consists essentially of (1) admixing between about 0.5 and 25.0 percent by weight of an acid-swellable insoluble cross-linked polymer of N-vinylpyrrolidone with a sufficient amount of an oxidizing agent having high oxidation potential selected from the class consisting of fuming nitric acid, mixtures of fuming nitric acid and fuming sulfuric acid, and concentrated nitric acid to make 100 percent by weight of a gelled acid composition; (2) positioning a spacer means into said wellbore; (3) injecting a fluid into said wellbore which forms a hypergolic mixture when in intimate contact with said oxidizing agent; (4) injecting a displacing liquid which is substantially unreactive with said fuel into the wellbore at sufficient pressure to force the oxidizing agent and at least some of said fuel from the wellbore into the formation and continuing to apply pressure on the displacing liquid until substantially all of the oxidizing agent and fuel are forced into the formation.

7. The method according to claim 6 wherein said oxidizing agent is fuming nitric acid.

8. The method of treating a stratum of a subterranean formation penetrated by a wellbore, which is provided with a casing having perforations at the stratum, a well tubing extending to the stratum, a packer positioned in the annulus between the casing and well tubing above the stratum, and a flexible line suspended down said tubing for injecting a liquid down the tubing and discharging it into the stratum, which consists essentially of:

(1) admixing between about 0.5 and 25.0 percent by weight of an acid-swellable insoluble cross-linked polymer of N-vinylpyrrolidone with a sufficient amount of an oxidizing agent having high oxidation potential selected from the class consisting of fuming nitric acid, mixtures of fuming nitric acid and fuming sulfuric acid, and concentrated nitric acid to form 100 percent by weight of a gelled acid; (2) injecting the so gelled acid and a fuel, which forms an explosive but non-hypergolic mixture when in intimate contact with said oxidizing acid, down the tubing; (3) injecting a displacing liquid which is substantially unreactive with said oxidizer and said fuel down the tubing at sufficient pressure to force substantially all of said oxidizing agent and said fuel from the wellbore into the formation; and (4) injecting a liquid chemical igniter down said line and into contact with at least a portion of said fuel and oxidizing agent thereby providing sufficient heat and turbulence to intermix substantially all the gelled acid and fuel and to provide a series of explosions until one of the components of the explosive mixture is substantially exhausted.

9. The method according to claim 8 wherein said oxidizing agent is fuming nitric acid.

10. The method according to claim 9 wherein the fuel is selected from the class consisting of at least about 50 percent by weight of furfuryl alcohol, aniline, and mixtures thereof, and balance, to make 100 percent of a fuel which makes a hypergolic mixture with said acid when admixed with said amount of furfuryl alcohol and aniline.

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