GELATION OF GALACTOMANNAN CONTAINING WATER-BEARING EXPLOSIVES

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7 Claims

ABSTRACT OF THE DISCLOSURE

The rate of gelling in aqueous compositions comprising a galactomannan crosslinked by chromium ions provided by a soluble chromate is accelerated by the addition of a soluble reducing agent to a hydrosol (colloidal solution) comprising the hydrated galactomannan prior to addition of the crosslinking agent. The accelerated crosslinking system is particularly suitable for use in blasting compositions comprising water, inorganic oxidizing salt and one or more fuels and/or sensitizers. Accelerating the rate of crosslinking finds special utility in the one-site formulation and mixing of these compositions, particularly in equipment known in the art as water gel trucks or slurry trucks.

Background of the invention

Recently, blasting explosive compositions have been developed which comprise one or more inorganic oxygen-supplying salts and one or more fuels and/or sensitizers which can be a self-explosive such as TNT, a metal such as aluminum or a carbonaceous, sulfurous or siliceous material, all dissolved or dispersed in an aqueous medium. These compositions have found wide acceptance and use in such applications as open-pit mining, quarrying and construction operations. They are relatively safe to use, economical, and, because high densities can be obtained in the borehole, very powerful.

While these aqueous, i.e., water-containing, blasting compositions have many advantages including ease of manufacture and relatively low ingredient costs, there are several inherent problems involved in their use. The compositions without modification tend to be more or less mobile fluids, a characteristic which can limit their usefulness to relatively dry, vertical boreholes or necessitate their being packaged in fluid-tight packages. Segregation of ingredients from the compositions is an even more serious problem, since such separation can lead to failures of initiation or detonation even when suitable primers are used or can lead to failure of a detonation to be propagated through a column of charge. Such segregation is further complicated by variations in temperatures to which the charges are exposed and the associated changes in component solubility in the aqueous medium. In wet boreholes, ground water can dilute the charges or leach away the soluble components unless the charges are in fluid containers, so that again failures of initiation or propagation can occur.

To overcome the foregoing problems, gelling agents or thickeners are commonly provided in the aqueous explosives. The most commonly used gelling agents are galactomannans, typically guar gum, which swell in water or other aqueous media to form viscous colloidal solutions (hydrosols, commonly referred to as “sols”). These thickeners tend to immobilize the insoluble and undissolved soluble components so that segregation is minimized, to protect the compositions from extraction by external water sources, and to permit wide variations in the consistency and fluidity of the explosive compositions. Additional variations in the type and extent of thickening or gelling action has been accomplished by the use of crosslinking agents, e.g., borax or potassium dichromate. The best of such crosslinking agents, in addition to permitting close control of product consistency, also serve to protect the galactomannan molecules against hydrolytic degradation and bacterial attack so that the compositions maintain the initial physical and explosive characteristics over long periods of time, even at elevated temperatures.

In areas where the volume of business is sufficient to justify the expense of loading equipment and support facilities, there has been increasing use of mobile, e.g., truck, service for on-site mixing and loading of these water-bearing blasting compositions. Such systems have in general depended upon the mixing of components to form a liquid, flowing mass, e.g., a slurry, and pumping this flowable mass through a delivery tube into a borehole. In most instances, particularly, for example in order to avoid friction within the pump and simplify materials handling, the compositions contain a gelling system in which crosslinking is delayed such that it begins to take effect as the composition is pumped but does not become fully effective until the composition is in the borehole. The effectiveness of the delayed action crosslinking agents also depends upon cooling which occurs in the borehole. Since the water resistance of the galactomannan (gums) without crosslinking is significantly lower than that in which the galactomannan is crosslinked for example by borate ions but most preferably by chromium ions, the use of a delayed crosslink system is satisfactory only for use in substantially dry boreholes or in boreholes which are provided with a water-resistant liner, e.g., of polyethylene, and is not suitable for use in boreholes containing relatively large amounts of water, i.e., in wet boreholes. Upon pumping of the composition into a wet borehole, water can begin degradative attack on the composition before crosslinking occurs, leaching away soluble components of the composition such that the effective explosive strength of the composition is decreased and, in some cases, the integrity of the column is weakened to such an extent that propagation of an explosive impulse throughout the length of the column of explosive cannot be assured. Still further, delay in crosslinking can allow the heavier components, e.g., TNT, aluminum or some carbonaceous fuels, to settle out of the composition or non-miscible phases to separate. Accordingly, misfires and failures to propagate occur even when the composition contains a gelling agent and delayed action crosslinking agent. These failures cause the blasting operator the expense and trouble of an interruption in the blasting schedule and necessitate removal and destruction of undetonated composition from the borehole and filling of the borehole with freshly prepared composition.

Recent developments in water gel trucks have made possible the formulation of water gel blasting compositions based upon a prethickened slurry comprised of a gelled solution of the inorganic oxidizing salt in which the galactomannan is hydrated, and crosslinking agent is incorporated as the composition is pumped. However, simply prehydrating the galactomannan does not increase the rate of gelling to provide sufficient water-resistance in the as-pumper compositions. Nor does increasing the quantity of crosslinking agent, i.e., source of chromium(+6) ions, significantly increase the crosslinking rate. Further, the rate of crosslinking in various solutions of inorganic nitrates vary according to the pH and composition of the solutions and especially the amount and nature of impurities present, many of these impurities causing an apparent decrease in the desired crosslinking effect.

Accordingly, there is a need for means to increase the rate of crosslinking galactomannans by chromium ions and to control this rate in order to minimize variations in rates from composition to composition.
Summary of the invention

In accordance with this invention by the use of a particular multicomponent crosslinking system and the incorporation of the components thereof in water-bearing explosives in a certain sequence there is obtained a marked increase in the rate and improvement of the control and reproducibility of gelation and crosslinking of water-bearing explosives. Thus, this invention provides an improvement in the method for making the conventional type of water-bearing explosives comprising inorganic oxidizing salt, fuel and water thickened with galactomannan. The improvement of this invention comprises first forming a hydrolosol of the galactomannan and at least part, and usually a major proportion, of the inorganic oxidizing salt and water and including therein a soluble reducing agent; and second incorporating a soluble chromate in the resulting hydrolosol containing explosive just prior to packaging or pumping into a borehole.

Details of the invention

BROADLY, the improvement of this invention can be applied to any of the known inorganic oxidizing salt types of water-bearing explosive compositions. Preferably, the compositions of this invention comprise at least one water-soluble inorganic oxidizing salt, about from 3 to 45%, and preferably 10 to 30% of water, based on the weight of the composition, and about from 0.1 to 5%, of the composition of the in situ formed gelling system of this invention. The compositions made in accordance with this invention can also contain, by weight, up to about 50% of a metallic fuel, up to about 40% of a solid organic explosive sensitizer, and up to about 25% of a nonexplosive, preferably carbonaceous, fuel, the compositions having an oxygen balance of about from -25 to +10% and preferably about from -10 to 0%.

In one preferred embodiment of this invention, explosives are prepared by incorporating the reducing agent, fuel, galactomannan and other additives such as gases and crystal habit modifier in a hot solution of the inorganic oxidizing salt component, then cooling the resulting product. As prepared, the oxidizing salt is usually substantially all in solution in the hot product. When the product cools, part of the salt crystallizes therein so that at ambient temperature 10 to 20% of the salt component may be undissolved, while at 40°F., as much as 50% or more of the salt may be crystallized.

The inorganic oxidizing salts employed in this invention can be any of the soluble salts conventionally used in water-bearing explosives including alkali metal, alkaline earth metal and ammonium nitrites, perchlorates and dichromates. In general, for economic reasons, ease of handling and overall sensitivity and other explosive properties compositions containing a salt component consisting essentially of at least 65% by weight of ammonium nitrate are preferred. Examples of other inorganic salts are sodium nitrate, calcium nitrate, potassium nitrate, magnesium nitrate, sodium perchlorate, potassium perchlorate, ammonium perchlorate and magnesium perchlorate. Of these, sodium nitrate is a preferred auxiliary salt used with ammonium nitrate, preferably in amounts up to 25% of the salt component.

In preparing the compositions of this invention the inorganic salt is preferably incorporated directly as hot "neutral liquor" or solution, preferably, e.g., one such as that obtained from the manufacturing of ammonium nitrate prior to grinding or prilling. The inorganic salts are chosen to be soluble in the hot liquor so that substantially all oxidizing agent is in solution at the time of manufacture. This is a boon in the preparation of blasting compositions at the blasting site, since the provision of heated storage tanks, the inorganic oxidants can be handled as a liquid minimizing the need for handling solids. Alternately, a portion of the salt component can be added as solid salt to the sol prior to addition of the chromate.

As stated above, the solution of inorganic oxidant is preferably based on hot, concentrated solution of ammonium nitrate, which usually contains about from 70 to 85% ammonium nitrate by weight. Such a solution is obtained from the neutralization step in the preparation of ammonium nitrate by the reaction of ammonia and with 40-60% nitric acid in a continuous process. Crystalization of the ammonium nitrate is prevented by keeping the temperature above the "crystallization point" of the liquor. This does not present particular problems since, for example, storage of hot, neutralized liquid in 10,000 gallon tanks normally is possible for 2 to 3 days without crystallization taking place and without the need for large amounts of additional heat. The crystalizing temperature of 70% liquor is 84°F. (29°C.), 80% solution will not crystalize out at about 136°F. (58°C.) and 85% solution will not crystalize out if maintained at temperatures above about 165°F. (74°C.). Since the liquor from commercial processes is well above 215°F. when it leaves the neutralizer, and in normal storage volume it cools slowly, stored liquor of even 85% strength normally will not begin to crystallize out for several days. However, during cold winter months, it usually is necessary to insulate the tanks and frequently is desirable to apply heat occasionally to prevent crystallization from the solutions below 70 to 85% concentration commonly employed. Means for supplying this heat are commonly provided on pump or slurry trucks. The neutral liquor desirably will maintain alkalinity of 0.01 to 0.05% NH₃. It is desired that the liquor retain this alkalinity in handling and storage so as to preclude corrosion of equipment, and prevent the contamination of blasting agent particularly with regard to ions such as iron, copper, zinc, and aluminum, which would inhibit or destroy a gelating system.

Although auxiliary oxidizing agents, in preferred oxidizing salts other than ammonium nitrate can be added as finely divided solids, preferably they are added in aqueous solution. When added in solution, the water content of the solution naturally will be included in determining the total water content of the composition. Usually, gelating or thickening agents as described in more detail hereinafter will be added with the preferred sodium nitrate auxiliary oxidizing agent to facilitate dispersion of ingredients.

The process of this invention is effective for crosslinking galactomannan gums, such as locust bean gum and particularly guar gum which are readily available commercially and also other galactomannans such as those from endosperms of leguminous plants including the sennas, brazilwood, tara, honey locust, paloverde and rattlesnake, alfalfa gum, clover gum and fenugreek gum. As indicated earlier, the galactomannan must be hydrated, i.e., swollen in the aqueous phase to form a hydrogel, before addition of the crosslinking chromate or dichromate. Reducing agents used in accordance with this invention should not retard or inhibit this hydration. The galactomannan usually comprises about from 0.1 to 5% by weight of the composition.

The reducing agent, which preferably is an at least readily soluble ammmonyl compound such as potassium ammnonyl tartrate, preferably is added to the aqueous phase of the composition in quantities comprising about from 10 to 30 p.p.m., and preferably about from 20 to 40 p.p.m. of the aqueous phase of the explosive. The addition can be to the sol in which the galactomannan has become hydrated, or to a solution of inorganic oxidizing salt before addition of galactomannan. Alternatively, the galactomannan and reducing agent can be added simultaneously and be dispersed in the aqueous phase of the blasting composition by the same mixing operation.

When the chromate is subsequently mixed with the hydrolosol, the reducing agent converts the chromium (+6) in the chromate into a form which virtually instantaneously crosslinks the galactomannan upon contact therewith. Therefore, as the reducing agent begins to react with the chromium compound, gelation proceeds very
rapidly resulting in firm gels shortly after the onset of gelation. Examples of reducing agents which can be used in the hydrodyes in accordance with this invention are inorganic sulfites including alkali, alkaline earth and ammonium sulfites and bisulfites including sodium sulfite, sodium bisulfite, potassium sulfite, potassium bisulfite, ammonium sulfite and ammonium bisulfite; soluble antimony compounds, i.e., compounds which provide soluble Sb(I) or [Sb(OH)](+) or a combination thereof, such as antimony trtarate, potassium antimony tartrate, potassium antimony citrate, antimony chloride, antimony fluoride, and potassium or sodium pyroantimonate, and soluble bismuth compounds such as bismuth citrate. Of the aforementioned reducing agents, alkali metal antimony salts of hydroxylated polybasic acids, particularly potassium antimony tartrate, are preferred because of their ready availability, solubility, inertness to ingredients other than chromates and their marked improvement in the speed, controllability and reproducibility in explosive products made therewith in accordance with this invention. Desirably, the reducing agent must be essentially inert in the sol base on aqueous solution of inorganic oxidizing salt in the absence of the chromate compound to preclude undesirable side reactions which could result in undesirable chromate-forming compounds or mixtures of such explosives, e.g., pentolite (PETN/TNT), Composition B or Cyclotol (RDX/TNT) and tetrytol (tetryl/TNT). For economic reasons, TNT alone or in combination with other self-explosive fuels is preferred for use in the compositions of this invention. The TNT or its mixtures can be introduced in the form of grains, crystals, pellets, flakes or any other form which allows ready dispersion thereof. In general up to 50% and preferably 10 to 45% by weight, based on the weight of the composition, of TNT will be used.

Examples of nonexplosive fuels which can be present include sulfuric fuel oxides including sulfur itself, siliceous fuels and carbonaceous fuels. Carbonaceous fuels, which are preferred, include finely divided coal and other forms of finely divided carbon, solid carbonaceous vegetable products such as starch, nut meals, wood and paper pulps, sugars, bagasse and the like; solid and liquid hydrocarbons such as powdered paraffin waxes and fuel oils; fatty oils; vegetable oils; and mixtures of two or more of the foregoing carbonaceous nonexplosive fuels. In general, up to about 25% and preferably about from 2 to 20% of such carbonaceous fuels are used. Up to about 10% of sulfuric fuels and up to about 5% of siliceous fuels are generally used.

Metallic fuels which can be present in accordance with this invention include, for example, light metals such as aluminum, magnesium, zinc, boron and silicon both singly and in combination and heavier metal alloys including ferrophosphorus and ferrosilicon, as well as mixtures of two or more of these metals and alloys. A preformed coating, e.g., of fatty acid and high viscosity oil, can be provided on particles of any of these types of metallic fuel. This preformed coating has been found of particular benefit for use with light metals and alloys thereof with minor amounts of each other and, for example, iron, manganese, silicon, copper, zinc or chromium, whose purity varies markedly from lot to lot.

The amount of metallic fuel used in the compositions of this invention naturally varies with the particular fuel used and can constitute up to 50% of the total composition. When the metallic fuel is aluminum, usually about from 1 to 25% by weight is used, whereas with heavier metal fuels, e.g., ferrophosphorus or ferrosilicon, about from 10 to 30% by weight is used.

The total weight of fuel, i.e., the weight of the combination of metallic, carbonaceous and/or self-explosive fuel, usually is adjusted so that the composition has an oxygen balance of about from -25 to +10% and excepting for those combinations containing the heavier metallic fuels such as ferrophosphorus and ferrosilicon, the oxygen balance is preferably about -10 to 0%.

Fuels and optional additives as well as solid oxidants can be blended with the hydrodyes during their preparation and before complete hydration of the galactomannan therein. However, optionally and preferably they are added to the hydrodyes either immediately after they are prepared or at some other time prior to use, but before addition of the chromate.

In the following examples, which further illustrate this invention, parts and percentages are by weight unless specified otherwise.

Examples 1-4

Blasting compositions of the formulation shown in the Table are prepared in a rotary mixer mounted on mobile equipment (a water gel truck) in the following sequence of steps:

1. Ammonium nitrate liquor ("neutral liquor" nominally 80% ammonium nitrate) and sodium nitrate are placed in the mixer and agitated.
2. Guar gum and potassium antimony tartrate as reducing agent are dispersed in the hot neutral liquor to form a sol.
3. Other fuels and sensitizers as specified are added
as the sol is transferred from a tank truck to the slurry truck.

(4) Sodium dichromate as crosslinking agent is added to the mixture as the mixture is pumped from the tank truck to the borehole. Crosslinking occurs as the composition is pumped at rates of up to 1100 lb./min., corresponding to crosslinking rates of less than 10 sec. All the compositions form firm gels having viscosities within the range of 2–4 million as measured with a TE spindle at 1 r.p.m. on a Brookfield Synchroelectric Viscometer.

Example

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<tr>
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<th>1</th>
<th>2</th>
<th>3</th>
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<tr>
<td>Ammonium nitrate liquor</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
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<tr>
<td>(N(\text{NO}_2))</td>
<td>48.5</td>
<td>48.5</td>
<td>48.5</td>
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<tr>
<td>Sodium nitrate</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>(Water)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Galactomannan</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Sodium dichromate</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Sodium aluminate</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
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</table>

Galactomannan is ground gum and is known by the trade name of "galactomannan." This ingredient is added to the mixture to improve its crosslinking properties.

For comparative purposes, the composition of Example 1 is prepared without the addition of potassium ammonium tartrate with the amount of sodium dichromate increased to 500 cc. of 5% Na\(\text{Cr}_2\text{O}_7\) per hundredweight of product. Five minutes for gel formation is observed.

In a like manner substantially improved rate control and reproductibility of crosslinking is obtained if an equivalent weight of sodium sulfite is substituted for the potassium ammonium tartrate used above.

1. In the process of making water-bearing explosives which comprises thickening a blend comprising inorganic oxidizing salt, fuel and water with galactomannan, the improvement which comprises:

(a) blending the ingredients of said explosive, exclusive of the chromate in (b) below, to form a hydrosol, said ingredients comprising inorganic oxidizing salt, fuel, water, galactomannan and at least one water-soluble reducing agent, said reducing agent having a solubility of at least about 1% in the aqueous phase of said explosive, and

(b) subsequently adding at least one water-soluble chromate to said hydrosol so formed.

2. A process of claim 1 wherein said galactomannan is guar gum, said reducing agent is selected from the group consisting of sulfites and antimony compounds soluble in said hydrosol, and said chromate is alkali-metal dichromate.

3. A process of claim 2 wherein said reducing agent is potassium antimonyl tartrate.

4. A process of claim 3 wherein said potassium antimonyl tartrate is present in the amount of about from 10 to 50 p.p.m. of said hydrosol and said chromate is present in the amount of about from 0.1 to 5% based on the weight of said guar gum, the weight ratio of gram atoms of antimony to gram atoms of chromium being about from 0.1:1 to 0.5:1.

5. A process of claim 1 wherein said fuel and the remainder of the ingredients of said hydrosol are all blended together at substantially the same time.

6. A process of claim 1 wherein said fuel is added to a preformed blend of said oxidizing salt, said water, said galactomannan and said reducing agent.

7. A process of any one of claims 1 to 6 wherein said chromate is added to said explosive comprising said hydrosol as said explosive is pumped into boreholes.

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<tr>
<th>Number</th>
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<th>Classification</th>
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