United States Patent Office 3,734,864
Patented May 22, 1973

3,734,864

AQUEOUS GEL FOR SLURRY EXPLOSIVES COMPOSITION AND METHOD OF PREPARING SAID GEL

William Allan Craig, Glasgow, Scotland, assignor to Imperial Chemical Industries Limited, London, England

No Drawing. Filed Nov. 8, 1971, Ser. No. 196,797
Claims priority, application Great Britain, Nov. 30, 1970, 56,694/70
Int. Cl. B01j *13/00*
U.S. Cl. 252—315 8 Claims

ABSTRACT OF THE DISCLOSURE

Aqueous gel for slurry explosive composition containing at least one inorganic oxygen-supplying salt and as a thickener, a macromolecular compound containing vicinal cis-hydroxyl groups (e.g., guar gum) cross-linked with compound of tellurium VI. Aqueous gel is prepared by method in which the macromolecular compound dissolved in water is cross-linked with the compound of tellurium VI and mixed with the inorganic oxygen-supplying salt(s). The aqueous gels are useful as general binding and thickening agents.

This invention relates to thickened aqueous gels suitable for slurry explosives, to the preparation of such gels and slurry explosives containing such gels. The aqueous gels are also valuable general binding and thickening agents.

Explosive compositions comprising an oxygen-supplying salt, for example ammonium nitrate, a solvent or carrier for the said salt, a thickener and a fuel are well known. These compositions are commonly referred to as slurry explosive compositions or, more generally, slurry explosives. Such slurry explosives may range in degree of firmness or consistency from highly viscous, plastic-like extrudable compositions to less viscous, pumpable or pourable fluid-like mixtures.

Slurry explosives of the aforementioned types normally contain as essential ingredients widely known power-enhancing materials and fuels such as, for example finely divided light metal or finely divided carbon. In some cases it is advantageous to include in the composition a self-explosive fuel ingredient such as particulate TNT, PETN or smokeless powder to further improve the sensitivity and/or strength, thereby ensuring detonation and propagation. A wide range of such compositions is now known to the art.

Of most important commercial interest are the water-bearing explosive slurry compositions wherein water comprises the greater proportion of the fluid carrier or disperser for the solid ingredients of the explosive mixture. While these water-bearing slurry explosives possess many advantages such as economy in manufacture and use and reduced hazard, they are, however, generally susceptible to the segregation of the solid and liquid ingredients, both when packaged in containers and when placed directly into a borehole. These slurry explosives are also subject to dilution by water which may be present in the borehole, which water may leach out water-soluble ingredients and result in possible detonation failure. To overcome the problems of water attack and penetration, manufacturers of water-bearing explosive slurries have employed a wide range of thickening agents as essential components of the slurries for the purpose of cohering together the ingredients in the form of non-segregating gels which will resist attack by excess water and so overcome the aforementioned difficulties.

Many thickening or gelling agents are known which have been employed with varying degrees of success, either alone or in combination, in water-bearing explosive slurries. Thus macromolecular compounds containing

vicinal cis-hydroxyl groups are commonly employed and these are advantageously cross-linked by cross-linking agents which attach to the cic-hydroxyl groups. For example, the most widely used of these thickening agents have been the galactomannans, particularly guar gum, and these have been cross-linked with, for example, sodium dichromate, potassium dichromate, zinc chromate or potassium antimonate. These slurry explosives have not, however, been completely successful because of syneresis on storage, especially at elevated temperatures and with explosive compositions containing calcium nitrate.

It is an object of the present invention to provide a gel suitable for thickening aqueous slurry explosive, which gel will be stable at elevated temperatures even in the presence of calcium nitrate.

It has now been found that improved aqueous gels suitable for slurry explosives thickened with certain cis-hydroxylated compounds can be prepared by cross-linking the thickener with an oxide, acid or salt of tellurium VI. Gels of a tough, rubbery consistency may thus be readily prepared.

Thus, in accordance with this invention an aqueous gel suitable for use in a slurry explosive composition comprises, as thickener, an aqueous solution of a macromolecular compound containing vicinal cis-hydroxyl groups cross-linked with an oxide of tellurium VI or an acid produced from the said oxide or a salt of the said acid. The macromolecular thickener may conveniently comprise a galactomannan gum, a glucomannan gum, a glucoxylgalactan gum or a xylogalactan gum, for example guar gum, locust bean gum, tara gum, Ilesmannan gum, tamarind gum or psyllium seed gum. The cross-linking agent in advantageously telluric oxide, telluric acid or an alkali metal salt of telluric acid, for example sodium tellurate.

For use in a slurry blasting explosive the gel may advantageously contain at least one inorganic oxygen-supplying salt.

A preferred aqueous gel for use in slurry explosive compositions contains from 15 to 83 parts by weight of at least one inorganic oxygen-supplying salt, from 10 to 30 parts by weight of water and from 0.2 to 10 parts by weight of cross-linked cis-hydroxylated macromolecular thickener wherein the cross-linking agent is used in amounts in the range 1 to 30% by weight of the colloid.

The inorganic oxygen-supplying salt may conveniently comprise a nitrate or perchlorate of ammonia, sodium, potassium, barium, magnesium or calcium or a mixture of two or more of these compounds. The gels of the invention exhibit a very high degree of tolerance to electrolytes and may be formed in saturated solutions of any of these salts or mixtures thereof.

The slurry explosives of the invention comprise the aforedescribed gel containing inorganic oxygen-supplying salt with a sensitising fuel mixed therewith. Preferably the fuel constitutes from 5 to 55% by weight of the explosive.

The fuel may be water-soluble or water-insoluble, explosive or non-explosive fuel. Insoluble fuels conveniently comprise particulate light metal or metalloid, for example finely divided aluminium, aluminium alloy, silicon, ferrosilicon, ferrophosphorus, particulate organic explosives, sulphur or carbonaceous material.

Useful particulate organic explosives which may be used in the compositions include, for example, TNT, PETN, cyclotrimethylenetrinitramine (RDX), Composition B (mixture of TNT and RDX), Pentolite (mixture of PETN and TNT), smokeless powder, nitrocellulose, nitrostarch and mixtures of these.

Suitable soluble fuels comprise glycol, diethylene glycol, dioxan, methyl Cellosolve, methyl Carbitol, sucrose, urea

or thiourea. Monomeric soluble fuels should preferably not comprise compounds containing cis-hydroxyl groups (e.g. glycerol) since these compounds could react with the cross-linking agent.

The compositions may also contain modifiers, for example density control agents. Thus it is generally advantageous to incorporate a gassing agent, for example sodium nitrite, into a composition which contains no self-explosive sensitiser.

The invention also includes a method of preparing an aqueous gel suitable for use in a slurry explosive wherein a macromolecular thickening compound containing vicinal cis-hydroxyl groups dissolved in water is cross-linked with an oxide of tellurium VI, or an acid produced from the said oxide, or a salt of the said acid.

In one convenient method the macromolecular compound is dispersed in a non-solvent liquid medium, for example diethylene glycol, and added to a solution of the cross-linking agent in the water which may have the inorganic oxygen-supplying salt also dissolved therein. Alternatively, it is also convenient to disperse the macromolecular compound and the cross-linking agent in a non-solvent liquid medium and to add the dispersion to water or an aqueous solution of oxygen-supplying salt. A few hours after the thickener and cross-linking agent are dissolved in water the cross-linking action is complete and the solution has changed to a rubbery gel.

The cross-linking agent may be added as such to the thickened gel composition or formed in situ in the composition, during mixing of the composition, by adding a tellurium compound containing tellurium in a low valent oxidation state and an oxidising agent to convert the tellurium to the required high oxidation state. Thus, a compound containing tellurium IV and hydrogen peroxide, chromic oxide or an alkali metal dichromate, peroxide or permanganate can be added to the composition to form a cross-linking agent containing tellurium VI.

The cross-linking action is faster when the solution is slightly acidic so it is advantageous to acidify the slurry.

The aqueous gels and slurry explosives of the invention have greatly enhanced stability at elevated temperatures and over prolonged storage periods. They are stable over a range of pH values from below 4 to above 10 and are very water-resistant.

The invention is further illustrated by the following examples in which all parts and percentages are by weight.

EXAMPLES 1–4

These examples were aqueous gels containing guar gum cross-linked to different degrees.

In preparing these examples, four solutions containing varying amounts of telluric acid were prepared and to these were added dispersions of guar gum in diethylene glycol. In each case a paste was initially formed but after several hours gel formation occurred to varying degrees of rigidity, as described in Table 1.

TABLE 1

Example number	Guar gum in gel, percent	Telluric acid in gel, percent	pH	Result
1	5.0	1.5	5.3	Rubbery gel. Not deformable.
2	5.0	0.15	5.8	Rubbery gel. Deforms under its own weight.
3	2.0	0.06	6.4	Lightly cross-linked gel.
4	2.0	0.02	6.7	Very lightly crosslinked.

EXAMPLES 5–9

These examples were aqueous gel bases containing dissolved inorganic oxidising salt. The compositions were as given in Table 2. In preparing the gels the ammonium nitrate, calcium nitrate, water and tellurium compound were mixed together and the pH was adjusted, by nitric acid addition, to 4.5–6.0, the normal pH of slurry explosive. The guar was then added as a dispersion in the diethylene glycol.

After storage at 50° C. for 12 hours a firm, rubbery gel was produced in each case which remained stable at 50° C. for at least 3 months.

TABLE 2

Example number	5	6	7	8	
Composition (parts):					
Ammonium nitrate	1,600	1,600	1,600	1,600	1,600
Calcium nitrate	800	800	800	800	800
Guar gum	40	40	40	40	40
Diethylene glycol	50	50	50	50	50
Water	800	800	800	800	800
Telluric acid	1	1	1		
Sodium tellurate				1	
Telluric oxide					1
pH	5.9	5.4	4.8	5.4	5.5

EXAMPLES 10–13

These examples were slurry explosives having the following compositions and properties shown in Table 3. In preparing the compositions a mixture containing the oxygen-supplying salts, water and guar gum (predispersed in the ethylene glycol) was acidified to pH 5.0 with acetic acid, heated to 50° C., and maintained thereat for about 3 hours until the guar gum had completely dissolved. An aqueous solution or suspension of the telluric compound was added, followed by a blend of atomised aluminum and sensitising fuel. Example 12 was sensitised by aeration with sodium nitrite which was added terminally to the mixture. In each case, after 12 hours a cross-linked rubbery gel, which was very stable and resistant to water, was produced. No syneresis was detectable after storage of the explosives compositions for 6 months at 50° C. The minimum initiator and the velocity of detonation were measured on samples fired in 6 mm. thick mild steel tubes.

TABLE 3

Example	10	11	12	13
Composition (parts):				
Ammonium nitrate	42.4	53.0	42.3	32.4
Sodium nitrate	3.3	5.0	3.3	3.3
Calcium nitrate	27.4		27.4	27.4
Diethylene glycol	8.0	1.2	8.0	8.0
Water	8.3	15.0	8.3	8.3
Guar gum	0.6	0.8	0.6	0.6
Atomised aluminium	7.5	5.0	10.0	5.0
Paint-fine aluminium	2.5			
PETN		20.0		
TNT				25.0
Sodium nitrite			0.10	
Telluric acid	0.012	0.012		
Sodium tellurate			0.012	
Telluric oxide				0.012
Properties:				
Density, g./cc	1.35	1.40	1.10	1.50
Minimum initiator in—				
5 cm. diameter	(1)	(2)		
12.5 cm. diameter			(3)	(3)
Velocity of detonation, km./s. in—				
5 cm. diameter	3.5	5.5		
12.5 cm. diameter			3.0	5.0

[1] No. 6 detonator.
[2] 3 g. Pentolite.
[3] 220 g. Pentolite.

EXAMPLE 14

The composition of this example was the same as that of Example 10 except that the telluric acid was replaced by 0.01 part of tellurium IV oxide and, after all the ingredients were mixed as described in Example 10, 0.007 part of potassium permanganate were added to oxidise the tellurium IV oxide to tellurium VI oxide. The properties of the explosive composition were the same as those of Example 10.

EXAMPLE 15

This example had the same composition and was prepared in the same manner as Example 14 except that the oxidising agent used was 0.007 part of sodium dichromate. The properties were the same as those of Example 10.

What we claim is:

1. An aqueous gel for a slurry explosive composition, which gel comprises 15 to 83 parts by weight of at least one inorganic oxygen-supplying salt, from 10 to 30 parts by weight of water and from 0.2 to 10 parts by weight of cross-linked cis-hydroxylated macromolecular thicken-

er wherein the cross-linking agent is used in amounts in the range 1 to 30% by weight of the colloid, the macromolecular thickener being a galactomannan gum, a glucomannan gum, a glucoxylgalactan gum or a xylogalactan gum and the cross-linking agent being an oxide of tellurium VI or an acid produced from the said oxide or a salt of the said acid.

2. A gel as claimed in claim 1 wherein the macromolecular thickener comprises guar gum, locust bean gum, tara gum, Ilesmannan gum, tamarind gum or psyllium seed gum.

3. A gel as claimed in claim 1 wherein the cross-linking agent comprises telluric oxide, telluric acid or an alkali metal salt of telluric acid.

4. A gel as claimed in claim 1 wherein the inorganic oxygen-supplying salt comprises a nitrate or perchlorate of ammonia, sodium, potassium, barium, magnesium or calcium or a mixture of two or more of the said compounds.

5. A method of preparing an aqueous gel as claimed in claim 1 in which method said macromolecular thickener dissolved in water is cross-linked with an oxide of tellurium VI, or an acid produced from the said oxide, or a salt of the said acid and mixed with said inorganic oxygen-supplying salt.

6. A method as claimed in claim 5 wherein the cross-linking agent is formed in situ in the composition, during mixing of the composition, by adding a tellurium compound containing tellurium in a low valent oxidation state and an oxidising agent to convert the tellurium to the required high oxidation state.

7. A method as claimed in claim 6 wherein a compound containing tellurium IV and an oxidising agent comprising hydrogen peroxide, chromic oxide, or an alkali metal dichromate, peroxide or permanganate, is added to the composition to form a cross-linking agent containing tellurium VI.

8. A method as claimed in claim 5 wherein the composition is acidified to accelerate the cross-linking action.

References Cited

UNITED STATES PATENTS

3,251,781 5/1966 Jordan ---------- 252—316

RICHARD D. LOVERING, Primary Examiner

U.S. Cl. X.R.

106—208; 149—29, 32; 252—316