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SLURRY EXPLOSIVES

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ABSTRACT OF THE DISCLOSURE

Slurry explosives comprising as thickener a Xanthomonas hydrophilic colloid cross-linked with an oxide of an element in a pentavalent or hexavalent state, for example antimony V, tellurium VI or chromium VI or an acid produced from the oxide or an alkali metal salt of such acid, the acid produced from the oxide having a dissociation constant $K<1.0$ in 0.1 to 0.01 N aqueous solution.

This invention relates to thickened aqueous gels suitable for slurry explosive, to the preparation of such gels and slurry explosives containing such gels.

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 fluidlike 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 (trinitro toluene), PETN (pentaacrythritol tetranitrate) or smokeless powder to further improve the sensivity 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. The most widely used of these thickening agents have been the galactomannans, particularly guar gum. Advantageously these have been cross-linked with cross-linking agents such as, for example, sodium dichromate, potassium dichromate or zinc chromate.

Slurry explosives thickened with cross-linked galactomannans have not, however, been completely successful because of syneresis on storage especially at elevated temperatures. In U.S. patent specification No. 3,326,733 slurry explosives thickened with a Xanthomonas hydrophilic colloid cross-linked with a water-soluble borate salt were proposed. Although these explosives were superior to the previous slurry explosives, they still had a tendency to exhibit syneresis on prolonged storage, especially when the gel was acidic.

It is an object of the present invention to improve the thickening of aqueous slurry explosive thickened with a Xanthomonas hydrophilic colloid.

It has now been found that improved aqueous slurry explosives can be prepared when the aqueous slurry is thickened by a Xanthomonas hydrophilic colloid cross-linked with an oxide, acid or salt of an element in a pentavalent or hexavalent oxidation state, which element in this oxidation state gives acids having a dissociation constant $K<1.00$ in 0.1 to 0.01 N aqueous solution.

Thus in accordance with this invention a gel suitable for use in a slurry explosive composition comprises at least one oxygen-supplying inorganic salt, water and, as thickener, a Xanthomonas hydrophilic colloid cross-linked with an oxide of an element in a pentavalent or hexavalent state, or an acid produced from the said oxide or an alkali metal salt of the said acid, in which acid or salt the said element is present in a pentavalent or hexavalent state, the acid produced from the said oxide having a dissociation constant $K<1.0$ in 0.1 to 0.01 N aqueous solution.

Preferred blastiing slurry explosive compositions of this invention contain 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 2.5 parts by weight of cross-linked Xanthomonas hydrophilic colloid wherein the cross-linking agent is used in amounts in the range 2 to 10% by weight of the colloid.

Suitable cross-linking agents include the oxides of antimony V, tellurium VI and chromium VI, the acids from these oxides and the sodium or potassium salts of these acids. With chromium VI compounds the rate of gelation is markedly increased by including a reducing agent, for example thiourea, sodium thiosulphate or tannic acid.

The inorganic oxygen-supplying salt may conveniently comprise a nitrate or perchlorate of ammonium, sodium, potassium, barium or calcium, or a mixture of two or more of said nitrates.

The slurry explosives of the invention comprise the aforedescribed gel 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 (mixtures 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 advan-

tageous 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 Xanthomonas hydrophilic colloid is dissolved in an aqueous solution of an inorganic salt and the colloid is cross-linked with an oxide of an element in a pentavalent or hexavalent state, or with an acid produced from the said oxide or with an alkali metal salt of the said acid in which acid or salt the said element is present in a pentavalent or hexavalent state, the acid produced from the said oxide having a dissociation constant $K<1.0$ in 0.1 to 0.01 N aqueous solution.

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 the element, as a compound in a low valent oxidation state, and an oxidising agent to convert it to the required high oxidation state. Thus a compound containing Sb III and an alkali metal peroxide or permanganate, for example potassium permanganate, can be added to the composition to form a cross-linking agent containing Sb V. The cross-linking action is faster when the colloid solution is slightly acidic so it is advantageous to acidify the slurry.

The slurry explosives of the invention have greatly enhanced stability at elevated temperatures and over prolonged storage periods, even when the slurry is acidic.

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

EXAMPLES

Examples 1 and 2 are non-explosive aqueous gels having the compositions shown in Table 1. In making these gels the ammonium nitrate was mixed with the water and the pH of the resulting slurry was adjusted to 5.2 by addition of a small amount of zinc nitrate. The Xanthomonas hydrophilic colloid and the cross-linking agent were mixed with the glycol and the mixture mixed into the slurry. The slurry was heated in a water bath to 50° C. and maintained thereat. After 12 hours the slurry of both examples had set to a stiff rubbery gel. The gels were stored for 6 months at 50° C., during which time no syneresis occurred and gel rigidity was only slightly reduced.

TABLE 1

Example	1	2
Composition parts):		
Ammonium nitrate	77.5	77.5
Water	20	20
Glycol	1.5	1.5
Xanthomonas hydrophilic colloid	1.0	1.0
Potassium antimonate	0.05	
Sodium dichromate		0.025

Examples 3 to 7 were slurry explosives having the compositions and properties shown in Table 2. In making these explosives the ammonium and sodium nitrates were mixed with the water and the pH of the slurry adjusted to 5.4 with nitric acid. The solid fuels were then incorporated, followed by a dispersion of the Xanthomonas colloid and cross-linker in glycol (Examples 3 and 4) or water (Examples 5, 6 and 7). After storage at 50° C. for 12 hours (2 hours for Example 6) the slurry explosives had set to a stiff rubbery gel and this gel consistency was retained throughout 6 months storage. The sensitivity of the explosives was not significantly reduced after storage for 6 months.

TABLE 2

Example	3	4	5	6	7
Composition (parts):					
Ammonium nitrate	52.96	62.86	62.88	62.88	65.36
Sodium nitrate	5.0	5.0	5.0	5.0	5.0
Aluminium	5.0	10.0	10.0	10.0	10.0
PETN	20.0				
Dinitrotoluene		5.0			
Sulphur			5.0	5.0	
Pelleted pitch					2.5
Glycol	1.2	1.2	1.2	1.2	1.2
Water	15.0	15.0	15.0	15.0	15.0
Xanthomonoas hydrophilic colloid	0.8	0.8	0.8	0.8	0.8
Sodium nitrite (gassing agent)		0.1	0.1	0.1	0.1
Potassium antimonate	0.04	0.04			
Sodium dichromate			0.02	0.02	
Telluric acid					0.04
Thiourea				0.02	
Properties:					
Density g./cc.	1.35	1.25	1.25	1.25	1.25
Initiation in 5 cm. diameter polythene	(1)				
Initiation in 12.5 cm. diameter×6 mm. thick mild steel		(2)	(2)	(2)	(2)
Velocity of detonation:					
Fresh, K m/s.	5.5	3.5	3.0	3.5	3.5
After 6 months at 50° C., K m./s.	5.3	3.0	2.8	2.8	3.0
Gel condition after 6 months at 50° C	(3)	(3)	(3)	(3)	(

[1] Fired 3 g. Pentolite pellet.
[2] Fired 125 g. Pentolite.
[3] Rubber, no synersis.

What we claim is:

1. An aqueous slurry explosive composition comprising a thickened aqueous gel and a sensitising fuel, said gel comprising at least one oxygen-supply inorganic salt, water and, as thickener, a Xanthomonas hydrophilic colloid cross-linked with an oxide of an element in a pentavalent or hexavalent state, or an acid produced from the said oxide or an alkali metal salt of the said acid, in which acid or salt the said element is present in a pentavalent or hexavalent state, the acid produced from the said oxide having a dissociation constant $K<1.0$ in 0.1 to 0.01 N aqueous solution.

2. A slurry explosive composition as claimed in claim **1** wherein the fuel comprises particulate light metal or metalloid, particulate organic explosive, sulphur or carbonaceous material.

3. A slurry explosive composition as claimed in claim **1** wherein the fuel comprises aluminum, aluminum alloy, silicon, ferrosilicon, ferrophosphorus, trinitrotoluene, pentaecrythritol tetranitrate, cyclotrimethylene-trinitramine, smokeless powder, nitrocellulose, nitrostarch, glycol, diethylene glycol, dioxan, methyl Cellosolve, methyl carbitol, sucrose, urea or thiourea or a mixture of two or more of the said fuels.

4. A slurry explosive composition as claimed in claim **1** including a density control agent.

5. A slurry explosive composition as claimed in claim **4** wherein the density control agent comprises sodium nitrite.

6. An aqueous slurry explosive composition as claimed in claim **1** wherein said gel comprises 15 to 83 parts by weight of at least one inorganic-supplying salt, from 10 to 30 parts by weight of water and from 0.2 to 2.5 parts by weight of cross-linked Xanthomonas hydrophilic colloid wherein the cross-linking agent is used in amounts in the range 2 to 10% by weight of the colloid.

7. An aqueous slurry explosive composition as claimed in claim **1** wherein the cross-linking agent includes an oxide of antimony V, tellurium VI and chromium VI, an acid derived from one of the said oxides or a sodium or potassium salt of one of the said acids.

8. An aqueous slurry explosive composition as claimed in claim **7** wherein the cross-linking agent comprises a chromium VI compound and a reducing agent.

9. An aqueous slurry explosive composition as claimed in claim 8 wherein the reducing agent comprises thiourea, sodium thiosulphate or tannic acid.

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