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[54] **AQUEOUS SLURRY EXPLOSIVE CONTAINING A THICKENER OF CROSS-LINKED GALACTOMANNAN WITH PSYLLIUM FLOUR**  
**7 Claims, No Drawings**

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**ABSTRACT:** A thickening agent for an aqueous slurry explosive composition comprises the combination of a cross-linked galactomannan with psyllium flour in specific proportions, which thickener provides good fluidity and reduced tackiness.

# **AQUEOUS SLURRY EXPLOSIVE CONTAINING A THICKENER OF CROSS-LINKED GALACTOMANNAN WITH PSYLLIUM FLOUR**

This invention relates to water-bearing explosive compositions comprising essentially an inorganic oxygen-supplying salt, a fuel, a thickener and water. In particular, the invention relates to a means whereby the thickening of such explosive compositions may be substantially improved.

Explosive compositions comprising an oxygen-supplying salt such as, for example, ammonium nitrate, and a fuel together with a fluid solvent, disperser or carrier such as water, are known. These compositions are commonly referred to as slurry explosive compositions or, more generally, as slurry explosives.

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, finely divided carbon and the like. In some cases, it is advantageous to include in the compositions a self-explosive fuel ingredient such as particulate TNT, PETN, or smokeless powder to further improve the sensitivity and/or strength, thereby insuring detonation and propagation. A wide range of such compositions are 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 carried 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 at the same time generally susceptible to the segregation of the solid and liquid ingredients both when packaged in containers and when placed directly into the 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 nonsegregating gels which will resist attack by excess water and so overcome the difficulties mentioned heretofore.

Many thickening or gelling agents are known which have been employed with varying degrees of success, either along or in combination, in water-bearing explosive slurries. Amongst these may be mentioned galactomannan polysaccharide guar gum, pregelatinized starches, hydroxyethylcellulose, carboxymethylcellulose, tamarind seed flour and hydrophilic vinyl polymers, such as, for example, polyacrylamide. The most widely used of these thickening agents have been the galactomannans, particularly guar gum. While the uncross-linked galactomannans have enabled the production of slurry explosives of improved homogeneity and resistance to water penetration, these have not been completely successful per se in producing a slurry explosive of optimum physical characteristics since relatively large percentages of thickener are required to prevent segregation and the resulting compositions are unduly tacky or adherent to contacting surfaces. Water resistance is also less than complete. When an improved type of cross-linked galactomannan is employed as a thickener, water resistance is improved, adhesiveness is reduced and segregation is more conveniently prevented but at the same time the resultant slurry may frequently range from one which is overly stiff in consistency and cannot easily be poured into boreholes to one which is still unduly soft and tacky. Additionally because of either the high resistance to flow or the tackiness of slurries made with the cross-linked galactomannans, great difficulty is often experienced in preventing adherence of material to the package wall and thus removing all of the explosive from the package.

It has now been found that a water-bearing explosive slurry composition may be provided which will not segregate over long periods of storage, is highly water resistant and yet may

be poured or pumped with little or no adherence to container walls or delivery hoses.

It is therefore the primary object of this invention to provide a sensitive slurry explosive composition which combines the features of water resistance, nontackiness, and nonsegregation with improved fluidity. Additional objects will appear hereinafter.

The improved explosive composition of this invention comprises essentially at least one inorganic oxygen-supplying salt, a fuel, water and a thickener, the thickener comprising the combination of cross-linked galactomannan with psyllium flour, the ratio of galactomannan to psyllium flour being from about 1:20 to 5:1 and preferably from 1:10 to 2:1.

By "psyllium flour" is generally meant the carbohydrate gum of psyllium seed husks, which husks have preferably been ground to a powdery consistency. Additionally, the gum may be obtained by water extraction of the psyllium seed or husks, dried and ground. Whereas the gum of psyllium seed husks has been referred to as a xylogalactan, chemical analysis has shown variations in chemical composition depending on the plant species from which the seed husks are taken. *Plantago ovata* is the most common species from which seed husks are harvested in India but *P. arenaria*, *P. lanceolata* and *P. psyllium* yield similar gums. North American species such as *P. wrightiana*, *P. inflexa*, *P. rhodosperma*, *P. helleri*, *P. aristata* and *P. purshii* provide similar material. Analysis of the seed husks from the various species of the Plantaginaceae family show the presence of xylose, arabinose and galacturonic acid. Some species additionally show the presence of galactose and rhamnose in minor amounts. To all of these the commercial generic name of "psyllium" is commonly applied. Generally, psyllium may be further characterized as a mucilaginous material when in solution.

The galactomannan suitable for use in the composition of the invention is preferably guar gum but other galactomannans such as, for example, locust bean gum, honey locust gum, gum gatto, Kentucky coffee bean guar, Tara and Paloverde gums, etc. may also be usefully employed. Guar gum of the self-cross-linking type may be used. Non-self-cross-linking guar gum when used may be cross-linked by employing any of the well-known conventional cross-linking agents such as, for example, sodium dichromate, potassium dichromate and potassium pyroantimonate as disclosed, for example, in Canadian Pat. No. 729,555 issued on March 8, 1966. The faster acting cross-linking agents are especially preferred in plant manufacture and the dichromates are particularly useful either alone or as the first addition of a two-step cross-linking process with antimony salt solutions.

It is thus now possible to prepare useful and powerful water-bearing slurry explosive compositions which resist segregation and water penetration, yet which flow with ease from containers or which may be effectively pumped through loading hoses into boreholes even of small diameters.

Preferred blasting slurry explosive compositions of this invention contain from 15 percent to 83 percent by weight of at least one inorganic oxygen-supplying salt, from 12 percent to 30 percent by weight of water, from 0.2 percent to 2.5 percent by weight of thickener and from 5 percent to 55 percent by weight of fuel. All the slurries of this invention are possessed of a pseudoplastic (shear-dependent) characteristic and the pourable types exhibit viscosities in the ranges shown below in table I when measured at about 72° F. on a Brookfield viscometer, Model RVF equipped with a No. 6 spindle.

TABLE I

Spindle Speed	Viscosity
4 r.p.m.	16,000-80,000 cps., typically 40,000 cps.

10 r.p.m.

10,000-45,000 cps., typically 22,000 cps.

20 r.p.m.

6,500-25,000 cps., typically 15,000 cps.

This pseudoplastic nature contributes greatly to preventing the sedimentation of suspended particles under static conditions yet permitting ready pourability and high flow rates with low to moderate increases in shear stress.

A preferred solvent or carrier for the oxidizing salt is water. However, less than half of the water may be replaced by organic solvents such as formamide, dimethyl sulfoxide and the lower glycols and alcohols. These solvents are polar liquids, readily miscible with water in all proportions and are effective solvents for ammonium nitrate and other inorganic salts and tend to function as fluidizing agents in the mixture.

The fuels employed in the composition of the invention may be, for example, energetic metals such as aluminum or aluminum alloys, metalloids such as silicon, particulate self-explosive fuels, nonexplosive carbonaceous material such as finely divided carbon or mixtures of these.

Where employed as fuel, the aluminum or aluminum alloy or other energetic metal or metalloid such as silicon, must be in finely divided form and may most suitably range from a fine dust to a form not coarser than that which will pass through a size 6 Tyler mesh screen. For example, relatively inexpensive air-atomized powder, shredded foil or granules made from reclaimed scrap are suitable types of aluminum. Where silicon is employed, the fine powder form is used.

Useful particulate self-explosives which may be used as fuel in the explosive composition include, for example, trinitrotoluene (TNT), pentaerythritol tetranitrate (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 carbonaceous fuels include, for example, finely divided coal or carbon, vegetable products such as woodmeal, sugar, ground nut husks, and the like, hydrocarbon oils and similar oleaginous material, urea and mixtures of these.

The explosive composition may be prepared by processes well known in the art employing simple mixing procedures. In general, the polysaccharide ingredients are hydrated in a mixture of the nitrate salts and water with pH adjustment into the range of 3.1 to 5.5. A mix procedure is adopted which allows good hydration of the guar component before cross-linking becomes too advanced and mixing is usefully carried out at an elevated temperature to reduce the time of hydration. More specific items of procedure are described in the examples. The composition may similarly be employed where a slurry explosive composition is prepared for use at the blasting site by means of the now well-known slurry mix truck although in this case a supply of warm prethickened nitrate salt liquor would be necessary to accomplish practical discharge rates.

The degree of thickening or gelling and hence the viscosity and fluidity of the slurry explosives compositions of the invention is dependent on the quantity and kind of galactomannan and psyllium employed and on the quantity and type of cross-linking agent used. It will be obvious that variations are possible which will permit the manufacture of explosive slurries having a wide range of gel characteristics. The preferred slurry composition however, is one which is easily pourable or pumpable yet which retains all the water-resistant and antisegregation properties of a thick or dense gel. Slurry explosives of high viscosity may be obtained through the use of a larger percentage by weight of galactomannan and/or a larger quantity of cross-linking agent. The psyllium component of the thickener is only very mildly cross-linked by conventional cross-linking agents and hence the psyllium functions to provide fluidity to the gelled mixture and reduce tackiness.

The mild response of psyllium to cross-linking additives is demonstrated in example 1.

## EXAMPLE 1

A solution was prepared comprising 30 parts by weight of ammonium nitrate, 12 parts by weight of sodium nitrate and 15 parts by weight of water. The solution was adjusted to a pH of 4.4 with acetic acid and one part by weight of ground psyllium seed husks was added. The ingredients were stirred together for 15 minutes and allowed to stand for 20 hours at 23° C. A second mixture was prepared except that 0.2 part by weight of sodium dichromate cross-linking agent was added. The viscosities of both mixtures were measured with a Brookfield RVT viscometer, No. 6 spindle at 10 r.p.m. and 72° F. The viscosity of the non-cross-linked mixture was 9,000 cps. and the viscosity of the cross-linked mixture was 13,000 cps. With 5.0 parts of technical grade calcium nitrate, the viscosity increased from 9,000 cps. to 11,000 cps. and even with 0.1 part of potassium pyroantimonate, a relatively high amount of an extensive cross-linker, the resulting mixture still exhibited the characteristic of flow. In contrast, similar mixtures containing 0.5 part of guar gum thickener cross-linked with 0.02 part of potassium pyroantimonate or with 0.2 part of sodium dichromate resulted in gelled, immobile masses which could not be poured.

The reduced response of psyllium to cross-linking additives coupled with a characteristic ability to form smooth, stringy elastic solutions provides for effective plasticizing action when combined with the more drastically cross-linked thickeners such as the galactomannans. This characteristic permits the formulator of slurry explosives wide latitude in producing smooth-flowing solutions or gels of a consistency not heretofore possible. Additionally, the presence of small amounts of bivalent or polyvalent metal ions which may inadvertently be present in the explosive mixture and which may affect the viscosity of the slurry has little or no effect on thickened explosive slurries containing psyllium. Polyacrylamide which has been disclosed as useful thickening agent for explosives slurries in U.S. Pat. No. 3,097,120 issued July 9, 1963 and in U.S. Pat. No. 3,355,336 issued Nov. 28, 1967 is effectively gelled in the presence of small amounts of these ions as recorded in the earlier patent. On the other hand, relatively large amounts of the order of 2 percent to 20 percent by weight of a bivalent metal salt such as calcium nitrate, especially in the presence of a more highly ionized salt such as sodium nitrate provides a desirable and controllable enhancement in thickening without any evidence of immobile gel formation. These factors together with the greater economy found in the comparison between psyllium and the hydrophilic vinyl polymers provides for explosives slurry compositions of extended utility and application.

## EXAMPLES 2-6

Water-bearing explosive slurry compositions were prepared from the ingredients shown below in table II. The mixing was performed as follows:

## Mix procedures

A blend of the nitrate salts (except calcium nitrate where present) was first prepared in a jacketed ribbon mixer together with the psyllium husk four, fumaric acid and urea. Water was then added and steam heating was begun. Consecutive additions were then made of 2-ethylhexanol, formamide, aluminum powder, TNT pellets and guar/glycol slurry. Differing procedures were used depending on the rate of cross-linking reaction and were applied according to the following guidelines:

- Potassium pyroantimonate was added in the guar/glycol slurry and mixing was continued for about 15 to 20 minutes at 75° to 85° F.
- Premixed solutions of antimony salts and strong oxidizers, e.g., dichromate, hypochlorite, peroxide, were regarded as solutions of antimonate and added a few minutes after the guar/glycol slurry.

c. Additions of faster cross-linkers such as dichromate or consecutively added dichromate and antimony salt solutions were delayed to allow hydration of the guar for about 10 to about 20 minutes at 75° to 85° F. with a postaddition mixing time of about 5 minutes.

The remaining ingredients, e.g., calcium nitrate and oil, were added 3 to 5 minutes before the end of mixing. Mixing was terminated when stable suspension of the TNT pellets had been achieved. Final pH range was 3.1 to 5.5; preferably 3.8 to 4.8.

TABLE II

Example.....	2	3	4	5	6
Ammonium nitrate.....	27.6	27.63	27.72	25.0	47.0
Sodium nitrate.....	20.0	21.0	11.0	13.5	11.4
Potassium nitrate.....				9.0	
Calcium nitrate.....	2.5			0.4	
Zinc nitrate (pH reducer).....	0.4			0.4	0.2
Zinc chromate.....					0.12
Psyllium husk flour.....	0.6	0.9	0.8	0.8	0.6
Fumaric acid (pH reducer).....		0.01	0.02		
Dissolved urea.....				2.0	
Formamide.....		1.6	1.6		
Guar flour (high viscosity grade).....	0.16	0.16	0.16	0.16	0.15
Ethylene glycol (guar dispersant).....	0.24	0.30	0.30	0.24	
Potassium pyroantimonate.....		0.003	0.003		0.03
Sodium dichromate (10% solution).....	0.2				
Sodium dichromate (4% solution).....				0.1	
Potassium antimony tartrate (4% solution).....				0.1	
Ammonium lignosulphonate.....		0.10	0.10		2.0
Trichloroethylene (sensitizer).....					7.5
TNT pellets.....	30.0	30.0	25.0	30.0	
Aluminum powder.....			15.0		15.0
Water.....	18.0	18.3	18.3	18.0	16.0
Light paraffin oil (parting agent).....	0.3			0.3	
2-ethylhexanol (defoamer).....	(1)	(1)	(1)	(1)	
Test results after 1-2 days at about 70° F.:					
Velocity in 2½ in. diameter (m./s., unconfined).....	4,500	4,500	4,200	3,500	3,500
Density in g./cc.....	1.45	1.45	1.45	1.46	1.20
Viscosity in cps. at 72° F. (Brookfield, No. 6 spindle at 4 r.p.m.).....	45,000	45,000	18,000	38,000	59,000

<sup>1</sup> 3 ml./100 lb.

All the mixes shown in table II flowed cleanly and evenly, left little or no deposit on container walls and showed no signs of segregation after 4 weeks storage at 90° C. In example 6 the dry ingredients were blended in an unheated ribbon mixer (rotation speed 36 r.p.m.) and trichloroethylene mixed in for about 2 minutes. Water was then added and mixed in for 10 minutes to achieve a density of about 1.2 g./cc. The latter mixing time may be varied to produce compositions of differing

densities.

## EXAMPLE 7

A composition similar to that of example 4 was prepared except that the aluminum was replaced by silicon powder. The resultant composition was easily poured into a 6-inch-diameter metal can and was detonated effectively.

What we claim is:

1. An aqueous slurry explosive composition comprising at least one inorganic oxygen-supplying salt, a solvent or carrier for the inorganic oxygen-supplying salt, a fuel and a thickener, said thickener comprising the combination of cross-linked galactomannan with psyllium flour, the ratio of galactomannan to psyllium flour being from about 1:20 to about 5:1.

2. An explosive composition as claimed in claim 1 wherein the ratio of galactomannan to psyllium flour from 1:10 to 2:1.

3. An aqueous slurry explosive composition comprising from about 15 percent to about 83 percent by weight of an inorganic oxygen-supplying salt, from about 12 percent to about 30 percent by weight of a solvent or carrier for the inorganic oxygen-supplying salt, from about 5 percent to about 55 percent by weight of a fuel and from about 0.2 percent to about 2.5 percent by weight of a thickener, said thickener comprising the combination of cross-linked galactomannan to psyllium flour of from about 1:20 to about 5:1.

4. An explosive composition as claimed in claim 1 wherein the inorganic oxygen-supplying salt is selected from the group consisting of the nitrates of ammonium, sodium, potassium, barium, calcium and mixtures thereof.

5. An explosive composition as claimed in claim 1 wherein the fuel is selected from the group consisting of finely divided aluminum, finely divided aluminum alloys, silicon, ferrosilicon, ferrophosphorus, finely divided carbonaceous nonexplosives, oleaginous hydrocarbons, particulate trinitrotoluene, particulate pentaerythritol tetranitrate, particulate cyclotrimethylenetrinitramine, particulate mixtures of trinitrotoluene and cyclotrimethylenetrinitramine, particulate pentolite, smokeless powder, nitrocellulose, nitrostarch and mixtures thereof.

6. An explosive composition as claimed in claim 1 wherein the solvent or carrier for the inorganic oxygen-supplying salt is water.

7. An explosive composition as claimed in claim 6 wherein less than half of the water is replaced by a polar solvent for the inorganic oxygen-supplying salt selected from the group consisting of formamide, dimethyl sulfoxide, the lower glycols, the lower alcohols and mixtures thereof.

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