United States Patent

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[54] **WATER-BEARING EXPLOSIVES THICKENED WITH A PARTIALLY HYDROLYZED ACRYLAMIDE POLYMER**

1 Claim, No Drawings

[52] **U.S. Cl.** **149/109,** 149/38, 149/39, 149/43, 149/44, 149/60

[51] **Int. Cl.** **C06b 1/00**

[50] **Field of Search** 149/38, 39, 43, 44, 60, 109

[56] **References Cited**

UNITED STATES PATENTS

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ABSTRACT: Water-bearing explosives thickened with polyacrylamide containing at least 10 percent by weight of carboxylate (-COO-) moieties and having a molecular weight of about from 3 to 15 million.

WATER-BEARING EXPLOSIVES THICKENED WITH A PARTIALLY HYDROLYZED ACRYLAMIDE POLYMER

CROSS REFERENCE TO PRIOR APPLICATION

This is a divisional application of applicant's copending application Ser. No. 573,206, filed Aug. 18, 1966, Pat. No. 3,355,336.

This invention relates to improvements in water-bearing explosive compositions and more particularly, to improvements in water-bearing explosive compositions thickened with galactomannan.

Considerable commercial interest has developed in the use of water-bearing explosives in recent years. Generally, water-bearing explosive compositions comprise an aqueous solution or slurry of inorganic oxidizing salts mixed with organic or metallic fuels and sensitizing agents which can also act as fuels.

While these water-bearing explosive compositions have many inherent advantages such as a wide range of explosive properties, and better safety characteristics and economy, both in manufacture and use, there are likewise many difficulties encountered in their use. Among the major problems encountered in the use of water-bearing-explosive compositions are dilution of the explosive composition by water which may be present in the borehole and the leaching out of the dissolved and undissolved, but water-soluble, oxidizing salts thus leading to changes in composition which result in losses in explosive power or even in failures to detonate. In addition, even in dry boreholes segregation of components can take place under certain conditions so that solid components separate into layers above or below the aqueous salt solutions to the extent that gross inhomogeneity occurs, again leading to loss of strength and failure to propagate. Many attempts have been made in the art to overcome the aforementioned difficulties.

Galactomannans, particularly guar gum, have found wide utility as thickening or gelling agents in improving the water-resistance of water-bearing explosives. However, if the galactomannans are not highly cross-linked, such products gradually segregate and do not meet the stringent water-resistance requirements of current commercial explosives. On the other hand, guar compositions sufficiently cross-linked for good water-resistance yield relatively immobile gelled masses which, in some cases, are disadvantageous and difficult to handle and load into boreholes. For example, stiff, nonpourable gels tend to spread and plug boreholes partially filled with water when they strike the surface of the water. Also, such compositions are somewhat more inconvenient to remove from contains than more pourable products and do not spread to fill the available space in the borehole leaving voids which could present propagation of detonation. The foregoing problems become progressively greater as the diameter of the borehole is reduced.

Substantially linear, water-soluble or water-dispersible vinyl polymers also have been proposed to gel or thicken water-bearing explosives. However, unless these polymers are cross-linked, as in U.S. Pat. No. 3,097,120, or are present in high concentration, they give very little body to the explosives. Furthermore, such polymers are relatively expensive.

This invention provides thickened water-bearing explosives which do not segregate and are water resistant over a wide range of viscosities. Preferred compositions of this invention have a unique combination of pourability and fluidity coupled with resistance to water and segregation which makes them particularly suitable in small diameter holes and in holes partially filled with water.

Accordingly, this invention provides water-bearing explosive compositions comprising inorganic oxidizing salt, fuel and water, which improvement comprises thickening said compositions with the combination of polyacrylamide and cross-linked galactomannan, the weight ratio of said polyacrylamide to galactomannan being from about 0.1:1 to 10:1, and preferably 1:1 to 5:1. "Thickened" as used herein refers to compositions in which the viscosity of the aqueous phase has been increased, e.g., to 10,000 centipoises or more, as well as to gelled products, including those gels which are cross-linked.

The polyacrylamide used is a preformed polymer which has a molecular weight of 1 to 25, and especially 3 to 15 million. Molecular weight can be determined from the relation:

$$V=3.73\times10^{-4}(m.w.)^{0.66}$$

wherein V is the intrinsic viscosity of the polymer in dl/grams and m.w. is its molecular weight. Intrinsic viscosity can be determined in the conventional manner from inherent viscosity measured in dilute solutions in water at 30° C. with an Ostwald Fenske Viscometer. Preferred polymers have a pH as a 1 percent by weight solution in water at 30° C. of about from 6 to 8, and preferably 6.5 to 7.5. Preferably, the polymer contains at least 10 percent by weight of carboxylate (-COO-) moieties neutralized with alkali, alkaline earth metal or ammonium bases.

Galactomannans which can be used in this invention include, e.g., guar gum and locust bean gum, and also other galactomannan gums which include those from endosperm seeds of leguminous plants such as the sennas, brazilwood, tara, honey locust, paloverde, rattlebox, alfalfa gum, clover gum and fenugreek gum. Of these, guar gum is particularly preferred because of its ready availability, stability and general compatibility with aqueous solutions of inorganic oxidizing agents.

The galactomannans are cross-linked in the aqueous solution of the inorganic oxidizing salt to form stable gelled products at relatively low concentrations of preformed polyacrylamide and galactomannan and to impart greater strength, cohesiveness and water-resistance to the resulting compositions. Any of the known cross-linking agents conventionally employed for galactomannans can be used including potassium and sodium dichromate; sodium tetraborate as described in U.S. Pat. No. 3,072,509; soluble antimony and bismuth compounds at a pH of from about 6 to 13 as in U.S. Pat. No. 3,202,551; and transition metal compounds as in Ser. No. 343,140, filed Feb. 6, 1964, the teachings of each of which is included herein by reference. Systems, especially those comprising soluble antimony and bismuth compounds plus oxidizing agents are preferred for forming water-resistant, pourable compositions. The terms "soluble antimony and bismuth compounts" as used herein refer to antimony or bismuth in ionic form, preferably as Sb^{+3}, Bi^{+3}, SbO^{+1} or BiO^{+1} or a combination thereof, in the gelation system, for example, in aqueous or aqueous nitrate containing solutions of galactomannan gum during the gelatin reaction. In general, the foregoing is fulfilled by antimony or bismuth compounds soluble to the extent of at least about 1 part per million in the gelatin system. Examples of antimony or bismuth compounds which can be used in the process of this invention include oxides and organic and inorganic salts of bismuth and antimony such as antimony oxide, antimony chloride and antimony oxychloride, antimony sulfate, antimonyl sulfate, antimony tartrate, potassium antimonyl tartrate, sodium pyroantimonate, antimony fluoride, antimony citrate, bismuth oxide, bismuth chloride, bismuth citrate, sodium bismuthate, bismuth nitrate and mixtures thereof. Alkali metal antimony salts of hydroxylate polybasic acids, particularly potassium antimony tartrate, are preferred. Oxidizing agents used in combination with the above include hydrogen peroxide, alkali and alkaline earth peroxides, and alkali, alkaline earth and ammonium permanganates, chromates and dichromates. However, alkali metal dichromates, e.g., sodium and potassium dichromates are especially preferred.

In the process of this invention the particularly preferred cross-linking agent is potassium antimony tartrate and the particularly preferred oxidizing agent is alkali metal, especially sodium or potassium dichromate. The concentration of antimony or bismuth cross-linking agent based on the amount of galactomannan is about from 1 to 15 percent, preferably 2 to 10 percent by weight of potassium antimony tartrate or an equivalent and about from 0.2 to 5 percent, preferably 0.5 to 3 percent by weight of potassium dichromate.

The rate of gelation and final viscosity of the gelled compositions of this invention is related to the kind and concentration of the galactomannan, the molecular weight and concentration of the preformed polyacrylamide, and the kind and concentration of the cross-linking agent. Thus, it will be apparent that the variables are interrelated and conveniently are adjustable to provide a gel having the desired properties during manufacture, storage, shipping and use. As indicated earlier, a particularly preferred composition of this invention is a pourable, water-resistant, water-bearing explosive composition containing a ratio of polyacrylamide to guar gum of about from 1/1 to 5/1, most preferably 2/1 to 3/1, the total amount of guar gum and polyacrylamide employed being less than about 2 percent, and preferably less than 1 percent, by weight of the total explosive composition. The cross-linking agent, used in the quantities set forth above, will react with the guar gum to form a gel in the aqueous phase of the blasting composition, the polyacrylamide functioning primarily as a thickening agent. Thicker, i.e., more viscous, less pourable compositions can be obtained by employing a larger weight percentage of galactomannan (guar) and/or polyacrylamide, by employing a higher ratio of cross-linking agent to galactomannan, by using polyacrylamide of higher molecular weight, and/or by providing a cross-linking system which will provide a more highly cross-linked, stable structure with the galactomannan.

In its broad aspects the improvement of this invention can be applied to any of the known general types of water-bearing explosives fluid at room temperature having a continuous phase comprising water. The compositions of this invention usually contain at least about 20 percent by weight of an inorganic oxidizing salt. Such salts include ammonium, alkali metal and alkaline earth metal nitrates and perchlorates as well as mixtures of two or more of such salts. Examples of such salts are ammonium nitrate, ammonium perchlorate, sodium nitrate, sodium perchlorate, potassium nitrate, potassium perchlorate, magnesium nitrate, magnesium perchlorate and calcium nitrate. Preferably, the inorganic oxidizing salt component contains at least 45 percent of at least one salt which is highly soluble in water at room temperature, that is, at least as soluble as ammonium nitrate, and preferably, the aqueous phase in the composition contains a substantial portion of ozidizing salt, for example, 40 to 70 percent by weight thereof. Inorganic oxidizing salt mixtures containing at least about 50 percent by weight of ammonium nitrate and at least about 50 percent by weight of sodium nitrate are particularly preferred.

The fuels employed in the compositions of this invention can be, for example, self explosive fuels, nonexplosive carbonaceous and metallic fuels, or mixtures of the aforementioned types of fuels. The fuel or fuels used in the compositions of this invention can be varied widely, provided that in the composition in which any particular fuel is used, the fuel is stable, that is, prior to detonation, during preparation and storage, the fuel is chemically inert with the system. "Self-explosive" fuel as used herein refers to a substance which by itself is generally recognized in the art as an explosive. Examples of selfexplosive fuels include organic nitrates, nitro compounds, and nitramines such as TNT, pentaerythritol tetranitrate (PETN), cyclotrimethylenetrinitramine (RDX), cyclotetramethylenetetranitramine (HMX), tetryl, nitrostarch, explosive-grade nitrocellulose and smokeless powder, as well as mixtures of the aforementioned self-explosive fuels such as, for example, pentolite (PETN/TNT), Composition B (RDX/TNT) and tetratol (tetryl/TNT). The self-explosive fuel can be, for example, in any of the conventional flake, pelleted or crystalline forms. The amount of fuel varies with the particular fuel employed. In general, up to 40 and, preferably, 10 to 40 percent by weight based on the weight of composition of self-explosive fuel is used.

Examples of carbonaceous nonexplosive fuels include finely divided coal and other forms of finely divided carbon; solid carbonaceous vegetable product such as cornstarch, woodpulp, sugar, ivory nut meal and bagasse; organic liquids such as hydrocarbon oils, fatty oils and vegetable oils; urea; and mixtures of two or more of the aforementioned carbonaceous fuels are employed.

Metallic fuels include, for example, alumina and iron, and alloys of such metals such as aluminum-magnesium alloys, ferrosilicon, ferrophosphorous, as well as mixtures of the aforementioned metals and alloys. Although, as disclosed in U.S. Pat. No. 2,836,484, up to about 50 percent by weight of metallic fuel can be employed in water-bearing compositions, usually on the order of 1 to 20, and preferably 1 to 8 percent by weight of metals such as aluminum, and on the order of about 10 to 30 percent by weight of heavier metallic fuels such as ferrophosphorus and ferrosilicon are employed.

Preferably, the total amount of fuel is adjusted so that the total composition has an oxygen balance of from about −30 to +10 percent and, excepting for those compositions containing the aforementioned heavier metallic fuels such as ferrophosphorus and ferrosilicon, preferably the oxygen balance is between about −15 to 0 percent.

To further enhance fluidity of the compositions of this invention, particularly at low temperatures, they can contain 0.25 to 10 percent, and preferably 1 to 5 percent, based on the total weight of composition of fluidizing agent as described in U.S. Pat. No. 3,190,777, which is incorporated herein by reference. Preferred fluidizing agents include dimethyl sulfoxide, methanol, formamide and methyl cellosolve.

As previously indicated, the composition of this invention contain at least about 5 percent by weight of water. The water-bearing compositions to which this invention is directed generally contain less than about 45 percent by weight of water and, preferably on the order of about 10 to 30 percent by weight of water based on the total composition.

In general, the explosive compositions of this invention can be prepared by the conventional formulating techniques used for preparing galactomannan or cross-linked galactomannan aqueous explosives. Preferably, however, the galactomannan, mixed with soda, preformed polyacrylamide and fuels is added to a hot (100°–200° F.) concentrated solution containing the major proportion of oxidizing salt, then the cross-linking agents are added, the solution is mixed and the product packed. It has been found particularly advantageous for improved uniform dispersion to add approximately one-third of the ammonium nitrate liquor first, then to add the remaining ingredients, and finally, after about 30 seconds, add the balance of the ammonium nitrate liquor.

This invention provides a means for making water-bearing explosive compositions having excellent water-resistance in products varying in characteristics from pourable fluids to moldable, tough plastic masses. The compositions of this invention have excellent cohesiveness over a wide range of viscosities. Furthermore, the improvement of this invention alters the crystal growth of inorganic salts, reduces crystal size, and improves sensitivity. When measured at 25° C. in the aqueous phase without solids, the preferred fluid compositions have a viscosity of about from 100,000 to about 400,000 centipoises, preferably 150,000 to 300,000 centipoises, as measured on a Brookfield Synchrolectric viscometer, Model RVT with a helipath attachment using a TC spindle at 1 r.p.m. These fluid compositions are particularly outstanding in their ease of packing and loading and the facility with which they fill boreholes yet resist segregation, leaching and dilution in the presence of water. Such fluid products are also eminently suited for rapid loading in small diameter holes giving ease in borehole loading which has heretofore only been obtainable with products blended in situ at the blasting site, e.g., in slurry trucks, but economically infeasible for use in smaller blasting operations.

As previously indicated, the explosive compositions of this invention can vary from pourable fluids to moldable, tough plastic masses, all having excellent water-resistance and excellent cohesiveness. Particularly preferred compositions of this invention are pourable explosive compositions having a viscosity of 150,000 to 300,000 centipoises, and containing,

by weight, 20 to 60 percent ammonium nitrate alone or in combination with 10 to 40 percent sodium nitrate; 15 to 40 percent fuel, preferably TNT; 10 to 30 percent water; 0.1 to 0.5 percent guar gum; 0.2 to 1.0 percent preformed polyacrylamide; and, based on the weight of galactomannan, about from 0.5 to 3 percent of oxidizing agent, preferably an alkali metal dichromate such as sodium or potassium dichromate and 2 to 10 percent of an antimony compound soluble in the system, preferably potassium antimony tartrate.

The compositions of this invention possess greater fluidity, homogeneity, resistance to disintegration or leaching by water and stability, i.e., resistance to degradation and settling out of components, than compositions which contain only substantially linear, water-soluble or water-dispersible vinyl polymers or those which contain only cross-linked galactomannans. This greater fluidity, homogeneity, stability and water-resistance is particularly advantageous when the compositions are to be used in wet locations, since disintegration and leaching of a composition by water, if such occurs, can lead to failures to detonate or to propagate a detonation throughout the length of an explosive column. If the explosive structure degrades, i.e., by virtue of disintegration of the gel structure, subsequent segregation of components, particularly undissolved (solid) fuels and sensitizers, can occur under the force of gravity, and the components in a borehole, whether in a container or cartridge, shucked therefrom, or simply poured into a borehole will become so heterogeneous that complete failure of detonation or propagation of detonation through the entire length of the column of the explosive charge will occur. Further, the compositions can be packaged in contains compatible with the ammonium nitrate liquor employed, e.g., of polymeric materials, and stored until time of use without deterioration or separation of components. Even when freed from the container these compositions retain an optimum degree of resistance to disintegration and leaching by water which may be already present in the borehole or which may enter the borehole after the compositions are loaded. With the compositions of this invention, bottom of the hole loading is not required. Likewise, the material will not block a borehole as a conventional water gel very often does. The higher loading per foot of borehole and speed of loading compared to either cartridged products or normal water gels are significant advantages which are manifest in the compositions of this invention.

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

EXAMPLES 1 TO 5

Water-bearing explosive compositions of this invention are prepared from the materials noted in table I. The formulations are prepared in a rotary mixer in the following sequence of steps:

1. One-third of 65 percent ammonium nitrate solution at 150°–170° F., is placed in the mixer, and to the ammonium nitrate solution, with continuous agitation, is added 6 to 8 mesh pelleted TNT or smokeless powder, hydrocarbon oil ("-Corvus" oil), metal fuels and/or sulfur as indicated in the Table.

2. A premixed composition of sodium nitrate, polyacrylamide and galactomannan is added and the contents of the resulting mixture are agitated for 15 seconds.

3. The balance of the ammonium nitrate liquor and formamide, where used, are added and the contents of the mixture are agitated for 3–½ minutes.

4. The oxidizing agent is added and incorporated in the blend by agitating for 15 seconds.

5. Cross-linking agent is added and the blend is mixed 30 seconds more.

6. Contents of mixer are discharged into polyethylene bags.

TABLE I

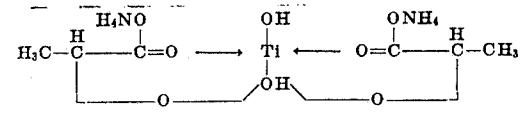
Example	1	2	3	4	5
65% AN liquor	50	57	50	42	30
(Ammonium nitrate)	(32.5)	(37)	(32.5)	(27.3)	(20)
(Water)	(17.5)	(20)	(17.5)	(14.7)	(10)
Sodium nitrate	20.0	18.0	20.0	21.0	20.0
TNT	30.0	25.0	.....	20.0	42.0
Smokeless powder	.....	.....	30.0	.....	.....
Aluminum	.....	.....	.....	12.0	6.0
Ferrophosphorus	.....	.....	.....	5.0	.....
Sulfur	.....	.....	.....	.....	2.0
The compositions also contain per hundred weight:					
Corvus oil, lbs	0.25	0.25	0.25	0.25	.....
Formamide	2.0	2.0	2.0	2.0	.....
Guar gum, lbs	0.2	0.3	0.2	0.2	0.2
Polyacrylamide,[1] lbs	0.5	0.8	0.5	0.4	1.0
5% solution, $K_2Cr_2O_7$, cc	25	25	10	10	30
5% PAT,[2] cc	100	100	45	45	60
Velocity, m./sec., 70° F	[3] 4,104	[4] 3,900	[3] 4,104	[5] 4,200	[3] 4,800
Density, g./cc	1.4	1.5	1.4	1.65	1.45

[1] Molecular wt.: 5–6 million; pH of 1% solution in H_2O~7; neutralized carboxylate>10%.
[2] Potassium antimony tartrate.
[3] Tested in 3-inch diameters in air.
[4] Tested in 4-inch diameters in air.
[5] Tested in 5-inch diameters in air.

In examples 1 to 4, the finished compositions are pourable, water-resistant gels having a density of from about 1.45 to about 1.65 g/cc. and a pH of about 7 to 9. The viscosity of the compositions is from about 100,000 to 400,000 cps. The composition in example 5 is a stiff water-gel suitable for use in mudcapping operations. All the compositions in table I are uniform in appearance and composition, and undissolved components remain uniformly dispersed. Even when the compositions are dropped approximately 40 or more feet into water, no evidence of breakdown of the gel structure is noted. No evidence of incompatability with water-filled boreholes is found. Deliberate attempts to plug a borehole with compositions of examples 1 to 4 are not successful. The formulations in examples 1 to 4 will flow through a 1-inch-diameter funnel at 70° F., and have sufficient water-resistance whereby bottom of the hole loading is not required. The compositions are not capsensitive but can be detonated by a conventional 25 g RDX primer and detonate with a velocity of about 4100 meters/second in a 2-inch-diameter column.

In the foregoing examples, similar results are obtained when a bismuth compound or a transition metal compound, especially TYZOR LA*, is employed in place of the potassium antimony tartrate as the cross-linking agent for the galactomannan.

*Titanium-antimonium lactate E. I.



available from E. I. du Pont de Nemours & Company

EXAMPLES 6–10

In order to evaluate the stability of the gelled water-bearing explosive compositions of this invention and to compare them with compositions containing only polyacrylamide or only guar gum, a sample of each composition, described in table II, and prepared by the general procedure of examples 1 to 5 is placed in a tightly closed glass container in a chamber maintained at 20° F. The composition in example 7 which contains only guar gum becomes hard at this temperature, is not pourable, and separation of the ingredients occurs in a matter of hours. All the other compositions are pourable, water-resistant compositions at this temperature. About four weeks later, the compositions in examples 6, 8, 9, and 10, which are still pourable, coherent, water-resistant gels, are transferred to a chamber maintained at 100° F. This is representative of a moderately high temperature which might be experienced in a field storage magazine or a service truck. The compositions stored at 100° F. are inspected at intervals for evidence of deterioration such as obvious softening and clumping of gel

structure, visible segregation of liquid (syneresis) or insoluble high density material such as TNT, foaming and development of tackiness and stickiness in compositions which were originally pourable, water-resistant gels. As illustrated in table II, the composition in example 6 which contains only polyacrylamide has started to deteriorate whereas compositions of the instant invention containing a combination of polyacrylamide and guar gum do not break down of noticeably deteriorate in 12 weeks or more of storage at 20° F. or 100° C.

TABLE II

Example No.	Composition, percent by wt.			Composition, per hundred weight						Time for deterioration
	65% AN liquor	TNT	Sodium nitrate	Formamide, lbs.	Guar gum, lbs.	Polyacrylamide, lbs.	"Corvus" oil, lbs.	PAT, cc.	$K_2C_2O_7$, cc.	
6	50.0	30.0	20.0	3.0		0.6	0.25	80.0	25.0	5 weeks.
7	57.0	25.0	18.0	3.0	0.75		0.25		10.0	12 hours.
8	57.0	25.0	18.0	3.0	0.3	0.6	0.25	100.0	25.0	12 weeks.
9	57.0	25.0	18.0	3.0	0.6	0.3	0.25	100.0	25.0	Do.
10	57.0	25.0	18.0	3.0	0.27	0.8	0.25	100.0	52.0	Do.

I claim:

1. In thickened water-bearing explosives comprising inorganic oxidizing salt, fuel and water, the improvement which comprises said explosives thickened with polyacrylamide containing at least about 10 percent by weight of carboxylate moieties and having a molecular weight of about from 3 to 15 million determined from the relation

$V=3.73\times10^{-4}(m.w.)^{0.66}$, wherein V is intrinsic viscosity in dl/grams and m.w. is molecular weight, said explosive additionally containing guar gum cross-linked with the combination of a soluble antimony compound and alkali metal dichromate, said carboxylate moieties are alkali metal base salts.

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