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**WATER-BEARING EXPLOSIVE COMPOSITIONS
GELLED WITH POLYMERIC AMIDE-ALDE-
HYDE AND METHOD OF MAKING SAME**

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ABSTRACT OF THE DISCLOSURE

A water-bearing explosive composition comprising a mixture of water, fuel, inorganic oxidizing agent and a gelling agent. The gelling agent is present in an amount of about from 0.1 to 5% by weight of the explosive composition and said gelling agent is an aldehyde-crosslinked substituted or unsubstituted poly(acrylic amide). The explosive composition is made by mixing water, fuel, inorganic oxidizing agent and gelling agent. The gelling agent added is composed of about 0.5 to 10%, by weight, based on the weight of the aqueous phase of the composition, of a soluble polymer comprising units of an aliphatic acrylic amide, e.g., acrylamide, crosslinked by about from 0.2 to 5%, by weight, based on the weight of the amide of an aliphatic aldehyde, e.g., formaldehyde. The acrylic amide can be added as polymer, or an acrylic amide monomer can be added to the mixture and said monomer polymerized to the corresponding poly(acrylic amide), then crosslinked.

BACKGROUND OF THE INVENTION

It is known that explosives composed of an aqueous solution or suspension of at least one inorganic oxidizing agent, at least partly soluble in water, together with one or more sensitizer or fuel components generally have greater work potential per unit weight than comparable compositions substantially free of water. This finding has led to the development of a variety of new water-containing blasting explosives. Among the sensitizer or fuel components commonly specified for use in such explosives have been metallic and metalloid elements or mixtures thereof, one or more solid self-explosives such as TNT, pentaerythritol tetranitrate (PETN), cyclotrimethylenetrinitramine (RDX), cyclotetramethylenetetranitramine (HMX), nitrostarch, explosive grades of nitrocellulose or smokeless powders, etc. and/or one or more nonexplosive and generally carbonaceous combustibles, e.g., solid and liquid hydrocarbons and fractions, mono- and dinitro-substituted aromatic hydrocarbons, powdered carbons and coals, crude and refined carbohydrate products, fatty acids and oils, organic amines, amides, hydroxy compounds and sulfur.

While these slurry blasting agents have many advantages including simplicity of manufacture and relatively low ingredient and production costs, there are several inherent problems involved in their storage and use. The compositions without modification tend to be more or less mobile fluids, a characteristic that can limit their use to substantially vertical boreholes, unless the charges are in suitable fluid-tight packages. Segregation of the ingredients from the initially substantially uniform mixtures is an even more serious problem because segregation of the charge components can lead to failure in initiation of detonation even when suitable primers are used or can result in failure in propagation of detonation through a column of charge once initiations has occurred. Such segregation is accentuated by variations in the temperatures to which the charges are exposed in storage or in the boreholes and the concomitant changes in component solu-

bility, particularly of the inorganic oxidizing salts, in the aqueous medium. A related situation exists in wet boreholes where ground water can act to dilute the charges or leach their soluble components and, therefore, failure in initiation or propagation of the charge can occur.

To overcome the foregoing problems, gelling agents or thickeners are commonly incorporated in aqueous explosive compositions. The gelling agents usually employed are natural hydroxylated polymers, e.g., natural polysaccharide materials, often called gums, and their chemically modified derivatives, which swell in water or other aqueous media to form viscous colloidal solutions (sols) or mucilages. The polysaccharides and derivatives most commonly used as gelling or thickening agents are the galactomannan gums, locust bean gum and especially guar gum. These gelling agents tend to immobilize the insoluble and undissolved soluble components so that segregation of the ingredients is minimized. They also aid in protecting the soluble components from extraction by external water sources. They further permit wide variations in the consistency and fluidity of the aqueous explosives, which can range from fluids that can be pumped by slurry trucks, to thick, rigid or flexible masses, suitably transferred by extrusion or similar methods. Additional variation in the type and extent of gelling action has been accomplished by use of appropriate crosslinking agents, e.g., borax, for the hydroxylated polymer-thickeners. The best of such crosslinking agents, in addition to permitting close control of product consistency, also serve to protect the polysaccharide molecules against hydrolytic degradation and bacterial attack, so that the product maintains its initial physical and explosive characteristics over long periods of time, even under conditions of elevated temperature, e.g., of 100° F. or above. However, gelling systems based on the galactomannan gelling agents, particularly guar gum, have not proved entirely satisfactory. For example, such gelling systems often require careful control of pH during formulation in order to produce gel structures which remain stable over periods of several months or more. When storage of the water-bearing explosive composition is under heated conditions, e.g., at 100° F. and above, the lack of stability of such galactomannan system commonly employed, for example, the borax crosslinked systems mentioned above, is even more apparent. Furthermore, stable pourable, relatively thin blasting compositions cannot be prepared using crosslinked guar gum as the gelling agent without significantly reducing water resistance of the product, particularly after storage, to such an extent that, in wet boreholes, soluble components are easily leached away. Recently, there has been increasing effort to provide such pourable, water-resistant explosive compositions since compositions of this nature offer advantages of ease in loading and handling by manual means to the small operators; these properties have heretofore been available only with slurry trucks, which truck are economical only if large volumes of blasting composition are to be handled. With the currently used gelling systems, however, this has not been achievable.

Then, too, in recent years there has been a revival of interest in the so-called Sprengel-type explosive compositions comprising concentrated nitric acid and a fuel as basic components. Such compositions also must be converted to a form which can be safely and readily handled, i.e., the liquid phase made less mobile. Thickening of such compositions by such means as silicas, clays and linear polyacrylates, as suggested heretofore, has not been satisfactory since water-resistant compositions have not been provided. The gelling action of polysaccharides such as used in compositions based on inorganic nitrates is too sensitive to pH variations to permit their use in compositions based on nitric acid. Accordingly, there is still a need for a gelling system for water-containing blasting composi-

tions which can be used in various water-containing explosive compositions to give stable products ranging from pourable, yet cohesive, water-resistant gels to rigid, firm cohesive gels. This invention fills such a need.

SUMMARY OF THE INVENTION

This invention is directed to novel water-bearing explosive compositions and methods for making the same. The explosive compositions of the present invention are prepared by mixing water, fuel, inorganic oxidizing agent and a gelling agent; the improvement comprises adding as gelling agent about from 0.5 to 10%, and preferably 1 to 5%, by weight, based on the weight of the aqueous phase of the explosive composition, of aliphatic acrylic amide or preformed poly(acrylic amide), both being soluble in the system, and about from 0.2 to 5%, and preferably about from 0.3 to 4%, based on the weight of the acrylic amide, of lower aliphatic aldehyde having up to 5 carbon atoms, that is soluble in the system. If the aliphatic acrylic amide is added in monomeric form it must be polymerized to the corresponding polymer in situ. However, if desired, preformed polymer can be added as such to the mixture. The term polymeric aliphatic acrylic amide refers both to homopolymers and to copolymers comprising at least about 5% of units derived from an acrylic amide and the balance copolymerizable units such as other acrylic monomers or vinyl pyridines, provided the copolymer is soluble and stable in the system.

In any event, the lower aliphatic aldehyde acts as a crosslinking agent for the poly(acrylic amide) through the amide functions, thus forming an insoluble, crosslinked poly(acrylic amide) as gelling agent in the water-bearing explosive composition. Accordingly, the resulting novel water-bearing explosive composition comprises fuel, water, inorganic oxidizing agent and gelling agent, said gelling agent being present in an amount of about from 0.1 to 5% by weight of the total water-bearing explosive composition and composed of at least one polymeric aliphatic acrylic amide crosslinked by aliphatic aldehyde having up to 5 carbon atoms. The water-bearing explosive compositions made according to the present invention are stable and have excellent water-resistant properties so that when these compositions are used in wet boreholes, especially those compositions that are readily pourable, the soluble components therein are not leached out and the compositions are reliably detonated and easily handled.

The poly(acrylic amide) and the lower aliphatic aldehyde used in gelling the aqueous phase of the water-bearing explosive compositions each must have sufficient solubility, e.g., at least about 5% for the polymer and monomer and 1% for the aldehyde, at ambient temperature (20–25° C.) in the particular aqueous solution of inorganic oxidizing agent to permit their dispersion and interaction. As mentioned above, the reaction between said poly(acrylic amide) and aldehyde at ambient temperature or by, for example, heating to about 30 to 80° C., forms a crosslinked structure which is a gel rather than a solid precipitate. This crosslinked structure swells in the aqueous phase of the explosive composition holding said aqueous phase and said structure is of substantially constant composition throughout. The gelled crosslinked structure of aldehyde-poly(acrylic amide) contains a fairly low ratio of polymer solids to liquid phase, e.g., less than about 1:10, this ratio being roughly equal to the weight ratio of gel components to other components making up the liquid phase, in contrast to precipitates or agglomerates in which there is a relatively high ratio of solids to liquid phase.

The explosive compositions of the present invention and the components therein are stable. By stable is meant, unless otherwise indicated, the absence of significant degradation of reactants or their reaction products in the aqueous phase of the novel explosive composition. Since prolonged stability is commonly of significance in gelled explosive compositions, stability refers particularly to

the absence of appreciable degradation in samples containing the gelling system when they are subjected to accelerated thermal stability tests involving heating of the material in question in the aqueous solution of oxidizing agent at temperatures of about 100° F., for example, for 8 to 12 hours.

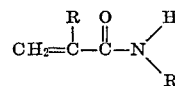
PREFERRED EMBODIMENTS

This invention is directed to water-bearing explosive compositions containing in addition to water inorganic oxidizing agent, such as contained for example in Sprengel-type explosives, i.e., explosives predominantly containing nitric acid as the inorganic oxidizing agent, and in the more conventional slurry type explosive compositions wherein the oxidizing agent is an inorganic salt such as ammonium nitrate; a fuel including self-explosives, non-explosive, sulfurous, siliceous or metallic fuels; and 0.1 to 5% gelling agent composed of an aldehyde crosslinked poly(acrylic amide), either substituted or unsubstituted, wherein the lower aliphatic aldehyde is the crosslinking agent and contains up to 5 carbon atoms.

The preferred compositions of this invention usually contain at least about 20% to 90%, by weight, of an inorganic oxidizing agent. Any of the conventional oxidizing agents used in explosive compositions including ammonium, alkali metal and alkaline earth metal nitrates, chromates, dichromates, chlorates, and perchlorates, as well as mixtures of two or more such salts can be used in the compositions of this invention. Representative examples of these salts are ammonium nitrate, ammonium perchlorate, ammonium chromate, ammonium dichromate, ammonium chlorate, sodium nitrate, sodium perchlorate, potassium nitrate, potassium perchlorate, potassium dichromate, magnesium nitrate, magnesium perchlorate, and calcium nitrate. Preferably, the inorganic oxidizing salt contains at least 65% of at least one salt which is highly soluble in water at room temperature, i.e., at least as soluble as ammonium nitrate, and preferably the aqueous phase in the compositions contains a substantial proportion of oxidizing salt, e.g., 40 to 70% by weight thereof. Inorganic oxidizing salt mixtures containing up to about 65% by weight of ammonium nitrate and up to about 40%, by weight, of sodium nitrate are particularly preferred. The compositions of this invention contain about 5 to 45%, and preferably 10 to 30%, by weight of water. The inorganic oxidizing agent can also be nitric acid alone or in combination with an inorganic oxidizing salt, particularly a nitrate.

The polymer-aldehyde crosslinked gelling agent used in the explosive composition is present in an amount of about from 0.1 to 5% by weight of said composition. The gelling agent ingredients added to the composition comprises about from 0.5 to 10%, based on the weight of the aqueous phase, of an aliphatic acrylic amide or the preformed poly(acrylic amide), soluble in the system, and about from 0.2 to 5%, based on the weight of the acrylamide, of a lower aliphatic aldehyde having 1 to 5 carbon atoms that is soluble in the system.

Particularly effective poly(acrylic amides) which are used in the invention include polymers of acrylic amides composed of the units



where R and R' are independently selected from the group consisting of hydrogen, lower alkyl or hydroxyalkyl, both having 1 to 4, and preferably 1 to 2, carbon atoms or mixtures thereof. Homopolymers of acrylamide are particularly preferred because of their ease of dissolution in the aqueous phase of the explosive composition even over a wide range of concentrations of inorganic oxidizing agent. Representative of other preferred poly(acrylic amides) are homopolymers of methacrylamide, N-substituted derivatives such as N-methyl acrylamide, N-ethyl

acrylamide and N-methyl methacrylamide and hydroxy-alkyl acrylamides such as, 2-hydroxyethyl acrylamide and -hydroxymethyl acrylamides. However, copolymers comprising at least about 5% and preferably at least 10% of amide units as defined in the formula above and the balance copolymerizable units are also suitable, provided the copolymers meet the specifications of solubility and stability set forth above. Examples of copolymers which are particularly useful in gelling aqueous solutions of inorganic oxidizing agents, particularly nitrates, especially ammonium nitrates in accordance with this invention from the viewpoint of solubility and availability at reasonable cost include copolymers of acrylamide with other monomers such as amides such as methacrylamide and N-methyl acrylamide; hydroxymethyl derivatives of amides such as, 2-hydroxymethylacrylamide; acrylic acids such as acrylic acid and methacrylic acid; salts of acrylic acids such as sodium, potassium and ammonium acrylate; and monovinyl pyridines. In aqueous nitric acid, solubility considerations permit the use of a wide range of copolymers; particularly preferred copolymers comprise at least 5% acrylamide, the balance of the polymer being derived from one or more of copolymerizable monomers including acrylic nitriles such as acrylonitrile and methacrylonitrile; acrylic acids such as acrylic acid and methacrylic acid; alkali metal or ammonium salts of such acrylic acids; hydroxy alkyl acrylates, e.g., hydroxymethyl acrylate; cyanokyl acrylics such as 2-cyanoethylacrylonitrile and cycloalkyl substituted acrylics, e.g., cyclohexyl methacrylate.

The poly(acrylic amide) used in preparing the gelled structure has, preferably, a molecular weight of about from 50,000 to 6,000,000. Although the preformed polymer can be added as such and incorporated in the explosive composition, an aliphatic acrylic amide monomer can be added to the explosive mixture for in situ polymerization of the monomer to the corresponding polymer. The preferred aliphatic acrylic amides are represented by the formula given hereinabove and the acrylic amides especially preferred are recited above. It might be mentioned that the acrylic amide monomers employed need not be highly purified. For example crude acrylamide sulfate obtained by the hydrolysis of the corresponding nitrile, e.g., acrylonitrile, in the presence of concentrated mineral acid, e.g., sulfuric acid, can be used directly without purification. The presence of residual amounts of mineral acid in the crude monomer catalyzes the cross-linking of the polymer, thus resulting in faster gel times. Additional acid, such as sulfuric acid, can be added in amounts of about from 0.5 to 5% to the explosive composition and these acids serve a positive catalyst function, thus hastening gelling of the aqueous phase of the water-bearing explosive composition. The pH of the aqueous phase of the explosive composition is usually less than about 6 and preferably less than about 5.5. When the aliphatic acrylic amide monomer is added to the mixture and polymerized in situ polymerization promoters are added to the mixture.

The polymerization promoters are generally soluble to the extent of at least about 0.1%, by weight, in the aqueous phase of the explosive composition. Representative free-radical polymerization promoters include sodium, potassium and ammonium salts of inorganic peracids such as persulfates, perborate and pervanadates; hydrogen peroxide; and organic peroxide and azo catalysts such as azobis(isobutyronitrile), α, α' -azobis (α, γ -dimethyl- γ -methoxyvaleronitrile), tertiary butyl hydroperoxide, methylvinyl ketone peroxide, benzoyl peroxide and peracetic acid. Persulfates are usually preferred. The persulfate ions which are introduced as a soluble persulfate salt, can be used alone in the solution of inorganic oxidizing salt to promote the copolymerization reaction or an added reducing agent can also be employed to form a redox couple. Redox systems that utilize a source of persulfate ion ($S_2O_8^{2-}$) as one component can be used throughout a range of concentrations of inorganic oxidiz-

ing agents. Reducing agents that can also be used, if desired, include nitrogen bases such as hydroxylamine, carbonylhydrazide, and, particularly hydrazine; bisulfites; thiosulfates; ferrous ion and nitrilo-tris-propionamide. If needed, higher rates of polymerization are achieved at lower temperatures when the polymerization system also includes a minor amount, e.g., a few parts per million up to about 1%, of metal ion, usually a Group I-B or transition metal ion. These metal ions are generally introduced as soluble inorganic or organic salts, e.g., as the nitrates, sulfates, or acetates.

In general, the total amount of promoter used varies with the particular promoter and monomers, and increases proportionately with the desired speed of polymerization, but usually is at least 0.002% and preferably within the range of about from 0.002 to 3% based on total weight of aqueous phase containing amide monomers to be polymerized, although large excesses of promoter have no detrimental effect on the gel structure. The optimum concentration of the preferred persulfate ions, based on total amide monomers, can vary considerably depending on the particular polymerization system, the desired consistency of the gel, and the presence or absence of supplementary promoter components, but in general will be about from 0.005 to 2% by weight of the aqueous phase. Chain transfer agents, e.g., isopropyl alcohol or aliphatic thiols or thio acids, which are commonly used for this purpose, can be used to control the molecular weight of polyamide.

When the acrylic amide polymer is to be formed in situ the rate of polymerization, and, in some instances, product consistency can be adversely affected by the presence of nitrogen oxides and oxygen, either in dissolved form or as the gases, and by the presence of large amounts of compounds conventionally used to inhibit free-radical polymerizations of the monomers. Compensations for these variations can be provided, when necessary, by simply increasing the concentrations of polymerization promoters. An alternative and generally more economical expedient, however, is to reduce the concentrations of these polymerization-retarding components prior to the polymerization. In the case of nitrogen oxides and oxygen, this can be accomplished by carrying out the polymerization under a blanket of an inert gas, typically nitrogen. To further eliminate polymerization inhibiting concentrations of nitrogen oxides and/or oxygen the components of the explosive composition, particularly the aqueous solution of inorganic oxidizing salt, can be sparged with the inert gas. When preformed polymer is used there is no need to sparge the components.

Lower aliphatic aldehydes having up to 5 carbon atoms are used as crosslinking agents for the polymer in the water-bearing explosive composition. Representative aliphatic aldehydes used in the gelling system of this invention are mono- or polyfunctional aldehydes, particularly those soluble in the aqueous phase of the explosive composition to the extent of at least about 1%. Specifically preferred aldehydes for use in accordance with this invention are, for example, formaldehyde, paraformaldehyde, formalin, acetaldehyde, propionaldehyde, butyraldehyde, glyoxal, trioxane and acrolein. Formaldehyde is especially preferred since it is readily soluble in aqueous solutions of inorganic salts generally used in water-bearing explosive compositions and is readily available. In comparison to the aliphatic acrylic amide monomer or polymer, only relatively minor amounts of lower aliphatic aldehydes are required to be used to crosslink the polymer and thus form gelled products of satisfactory consistencies and stabilities. In general, about from 0.2 to 5%, by weight, based on the weight of the amide monomer or polymer, is used. The particular concentration employed is influenced by the particular aliphatic aldehyde chosen, and the exact amount of aldehyde used will depend upon the type gel product desired. Weak, pourable gels require less aldehyde than firm, rigid gels,

quantities of other components remaining the same. The aldehyde comprises about from 0.005 to 0.5% by weight of the aqueous phase of the water-bearing explosive composition.

By the process of the present invention the aqueous phase of the explosive composition is converted from a liquid, water-like consistency to a gel characterized by the presence of an aqueous phase and a solid phase substantially uniformly distributed or dispersed therein. The gels are substantially homogeneous down to substantially colloidal dimensions and resist finite shear forces. Thus, the crosslinked polymers form a continuous or semicontinuous matrix in the gelled compositions, at least a portion of the continuity being due to crosslinking of polymeric amide chains by the aldehydes. A broad spectrum of product consistencies is readily available varying from pourable, cohesive, water-resistant masses to moderately stiff or very stiff gelatin-like masses, that often are resilient, elastic and even rigid, shapable products.

Various self-explosive fuels, non-explosive fuels such as carbonaceous, sulfurous or siliceous fuels or various combinations of mixtures of these types of fuels can also be present in the composition. The fuel used in the explosive compositions can be varied widely provided that it is stable, e.g., chemically inert, in the system in which it is employed, during preparation and storage prior to detonation. "Self-explosive" fuel refers to a substance which by itself is generally recognized in the art as an explosive. Some examples of self-explosive fuels that can be used in the composition include organic nitro compounds, nitrates and nitramines, such as TNT, dinitrotoluene, pentaerythritol tetranitrate (PETN), tetranitromethylaniline (tetryl), cyclotrimethylenetrinitramine (RDX), cyclotetramethylenetetranitramine (HMX), nitrostarch, explosive-grade nitrocellulose, smokeless powder, and mixtures of such explosives, e.g., pentolite (PETN/TNT), Composition B or cyclotol (RDX/TNT), and tetrytol (tetryl/TNT). 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 thereof, can be introduced into the compositions in the form of crystals, grains, pellets, flakes of any other particulate form which allows ready dispersion thereof. In general, up to 50% and, preferably 10 to 45% by weight, based on weight of the composition, of self-explosive fuel is used. TNT and other fuels as desired will usually be dispersed in the aqueous phase of the composition before gelling is initiated.

Examples of nonexplosive fuels which can be present in the explosive compositions include sulfurous fuels, including sulfur itself, siliceous fuels and particularly carbonaceous fuels. Examples of carbonaceous fuels which are preferred are finely divided coal and other forms of finely divided carbon, solid carbonaceous vegetable products such as starch, ivory nut meal, wood and paper pulps, sugar, bagasse and the like; solid and liquid organic 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 25% and preferably, about from 2 to 20% by weight of such carbonaceous fuels are used. Sulfurous fuels are generally used in the explosive composition in amounts of up to about 10% and siliceous fuels up to about 5%.

The metallic fuels which can be present in the novel explosive composition include, for example, light elements such as aluminum, magnesium, zinc, boron and silicon both singly and in combination, and heavier metallic alloys including ferrophosphorus and ferrosilicon, as well as mixtures of two or more of these metals or 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 fuels. Such a coating has been found to be of particular benefit for use with light elements and alloys thereof with minor amounts of each other and, for exam-

ple, iron, manganese, silicon, copper, zinc or chromium, whose composition and degree of purity varies markedly from lot to lot.

The quantity of metallic fuel used in the compositions of this invention naturally varies with the particular fuel employed and can constitute up to 50% by weight of the total composition. When the metallic fuel is aluminum, usually about from 1 to 25% by weight is used whereas with heavier metallic fuels, such as ferrophosphorus and ferrosilicon, about from 10 to 30% by weight is used. The average particle size of the metals can vary, for example from -325 mesh to +15 mesh, but preferably is on the order of +100 to -18 mesh.

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 total composition has an oxygen balance of about from -30 to +10%, and excepting for those combinations containing the heavier metallic fuels such as ferrophosphorus and ferrosilicon, the oxygen balance is preferably between about -10 to 0%.

To impart fluidity to the water-bearing gelled explosive compositions, particularly at temperatures of lower than about -10° F., the composition can also contain about from 0.25 to 10%, and preferably about 1 to 5%, by weight, based on the total composition, of a winter fluidizing (antifreezing) agent as described in U.S. Patent 3,190,777, the teachings of which are incorporated herein by reference. Examples of suitable fluidizing agents are methanol, formamide, dimethyl sulfoxide and methyl Cellosolve. These fluidizing agents can be considered as a portion of the fuel contained in the explosive composition.

A preferred embodiment for preparing the gelled explosive compositions of this invention comprises mixing water, fuel, an inorganic oxidizing agent and gelling agent. The gelling agent can be a preformed poly(acrylic amide) or an aliphatic acrylic amide monomer that is polymerized in the explosive mixture in situ by means of a polymerization promoter. The mixture containing the inorganic oxidizing agent together with the amide monomer can be reacted at room temperature to effect simultaneously both polymerization of the aliphatic acrylic amide monomer and crosslinking of the resulting polymer by the aliphatic aldehyde. Although the mixture reacts at room temperature, preferably it is heated at elevated temperatures of the order of about from 30° to 80° C., because gel is formed more rapidly when the aqueous phase is heated than when the reaction is carried out at about room temperature. However, when the oxidizing agent is a strong oxidizer, particularly nitric acid, heating to temperatures above about 30° C. should be avoided to preclude degradative oxidation of the aldehyde. The aliphatic acrylic amide monomer or poly(acrylic amide) can be, if desired, dissolved in a small amount of water and then added to the mixture. The order of addition of ingredients is not critical. However, when aliphatic monomeric acrylic amide is used, the polymerization promoter is added last, and all the ingredients uniformly dispersed prior thereto. Agitation used for blending the ingredients usually is continued until after the composition is gelled, particularly when added fuels or sensitizers are solids, such as TNT, smokeless powder, ferrophosphorus, ferrosilicon or aluminum, which ingredients must be uniformly distributed throughout the gel matrix. In some instances when, for example, the explosive composition is to contain a high percentage of solids which inhibit polymerization, e.g., TNT, all the ingredients except such additives can be mixed and gelled and subsequently the additives blended with finished gel.

Reference is now made to the following detailed examples wherein parts and percentages are by weight unless otherwise indicated.

In the following examples, the terms noted describing the product characteristics designate the following:

Very firm: Viscosity of about from 3 million to 10 mil-

lion centipoise as measured with a TF¹ spindle at 0.5 r.p.m.¹ on the Brookfield Synchroelectric Viscometer.

Firm: Viscosity of about from 1 million to 3 million centipoise measured with a TE¹ spindle at 1.0 r.p.m.¹ on a Brookfield Synchroelectric Viscometer, Model RVT, with helipath attachment.

Medium firm: Viscosity of about from 400,000 to 1 million centipoise using the same conditions of measurement on the Viscometer.

Weak: Viscosities generally less than about 400,000 centipoise, generally 200,000 to 400,000 centipoise.

Examples 1-18

Gelled 65% aqueous solutions of ammonium nitrate are prepared from the materials noted in Table I, these aqueous solutions being suitable for providing the aqueous phase of a blasting composition. In preparing the gelled compositions the formation of the poly(acrylic amide) and its in situ crosslinking by the aldehyde is effected simultaneously. The acrylic amide in the amount indicated is dissolved in the aqueous solution of the inorganic oxidizing salt at the temperature indicated. Then

Example 19

To a 65% aqueous solution of ammonium nitrate at 60° C. is added 4%, based on the weight of the aqueous phase, of acrylamide. Polymerization of the acrylamide in situ is catalyzed by the addition of 0.14% of (NH₄)₂S₂O₈ as a polymerization promoter. After 10 minutes, 3.75% of formaldehyde, based on the weight of acrylamide, is added as a 3.7% aqueous solution. A firm gel is formed in 13 minutes. When TNT is present in the composition, and comprises 30% by weight of the total composition, the gelled composition is explosive and detonates reliably when actuated by a 100 g. RDX primer.

Examples 20-28

A preformed polymer of acrylamide (molecular weight, 5-6 million; commercially available as "Cyanomer"-P-250 from American Cyanamid Co.) in the amount indicated in Table II is mixed with 65% ammonium nitrate liquor. Mixing is begun and continued for 30-120 minutes to assure uniform dispersion of the polyacrylamide. Formaldehyde in the amount indicated in Table II is added as a 3.7% aqueous solution. Time of gel forma-

TABLE II

Example	Polyacrylamide, percent based on aq soln.	Formaldehyde, percent based on polyacrylamide	Other additives, percent of aq soln.	Temperature, ° C.	Product characteristic, gel time
20.....	4	3.75	65	Firm gel in 21 sec.
21.....	4	3.75	H ₂ SO ₄ , 4%.....	65	Firm gel in 15 sec.
22.....	2	4	65	Firm gel in 125 sec.
23.....	2	2	65	Very weak gel in 21 min.
24.....	3	2.6	30	Do.
25.....	3	2.6	80	Medium firm gel in 8 sec.
26.....	2	0.75	65	Weak gel in 4 min., stronger on standing.
27.....	1.6	0.94	H ₂ SO ₄ , 0.8%.....	65	Weak gel in 14 min.
28.....	1.2	1.25	H ₂ SO ₄ , 0.8%.....	65	Very weak gel in 26 min.

When TNT is present in the compositions above, comprising 30% by weight of the total composition, the gelled compositions are explosive and detonation thereof is actuated by a 100 g. RDX pellet primer.

the aldehyde is added as an aqueous solution (ca. 3.7% concentration). The polymerization promoter system (NH₄)₂S₂O₈ (0.14% by weight of aqueous solution) is added last and mixing continued. Gelation time refers to the time expired between the addition of the last component to the reaction mixture and the first appearance of gelled product in the reaction mass. None of the gel products show visible indication of deterioration at ambient temperature (ca. 25° C.) over times of a week or more, the maximum period of observation.

tion is determined from the time of the formaldehyde addition.

Example 29

To a 65% ammonium nitrate liquor at 65° C. are added, by weight of the aqueous solution, 1% of acrylamide, 2% of 4-vinyl pyridine and 0.044% formaldehyde. Ammonium persulfate (0.14% by weight based on ammonium nitrate liquor) is then added as polymerization promoter. A weak gel suitable for the aqueous phase of

TABLE I

Example	(a) Amide, percent by weight of aq NH ₄ HO ₃ soln.	(b) Aldehyde, percent of (poly)amide (a)	Other components added	Temperature, ° C.	Product characteristic
1.....	Acrylamide, 4%.....	Formaldehyde, 5%.....	60	Firm gel in 50 sec.
2.....	Acrylamide, 3%.....	Formaldehyde, 3.3%.....	60	Firm gel in 141 sec.
3.....	do.....	do.....	H ₂ SO ₄ , 4%.....	60	Firm gel in 21 sec.
4.....	do.....	do.....	60	Firm gel in 38 sec.
5.....	do.....	do.....	40	Firm gel in 8 min.
6.....	do.....	do.....	80	Firm gel in 13 sec.
7.....	Acrylamide, 1.36%.....	Formaldehyde, 2.9%.....	60	Weak gel in 8.5 min.
8.....	Acrylamide, 2%.....	Formaldehyde, 2.2%.....	H ₂ SO ₄ , 3.6%.....	65	Very firm gel in 121 sec.
9.....	do.....	do.....	H ₂ SO ₄ , 3.6%.....	65	Very firm gel in 113 sec.
10.....	Acrylamide, 1%.....	Formaldehyde, 3.0%.....	H ₂ SO ₄ , 3.6%.....	65	Weak, flowing gel in 8 min.
11.....	Acrylamide, 1.6%.....	Formaldehyde, 1.5%.....	H ₂ SO ₄ , 1.6%, NaNO ₃ , 20%.....	65	Weak gel in 4 min.
12.....	do.....	do.....	H ₂ SO ₄ , 1.6%, NaNO ₃ , 20%.....	65	Do.
13.....	Acrylamide, 4%.....	Propionaldehyde, 10%.....	60	Weak gel.
14.....	do.....	do.....	H ₂ SO ₄ , 4%.....	60	Firm gel in 80 sec.
15.....	do.....	Glyoxal, 3%.....	H ₂ SO ₄ , 4%.....	60	Firm gel in 38 sec.
16.....	Acrylamide, 3%.....	Glyoxal, 1.2%.....	H ₂ SO ₄ , 4%.....	60	Medium firm gel in 19 min.
17.....	do.....	Glyoxal, 0.8%.....	H ₂ SO ₄ , 4%.....	65	Weak gel in 6 min.
18.....	Acrylamide, 4%.....	Paraformaldehyde, 10%.....	60	Firm gel in 30 min.

¹ Added as crude acrylamide sulfate.

When TNT is present in the above-listed gelled compositions with a weight ratio of gelled composition to TNT of 70/30, the gelled aqueous compositions are explosive compositions which detonate reliably when actuated by a 100 g. RDX primer.

a water-bearing explosive composition is formed 25 minutes after addition of the ammonium persulfate.

Examples 30-36

To 70% nitric acid is added, with stirring, acrylamide in the amount indicated in Table III. After the acrylamide is dispersed, polymerization initiators consisting

¹ Change in spindle and r.p.m. needed to obtain accurate readings.

of, by weight of the aqueous nitric acid, 0.14% $(\text{NH}_4)_2\text{S}_2\text{O}_8$, 0.04% $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 0.0018% hydrazine hydrate are added. Polymerization is allowed to proceed for 10 or 15 minutes. The formaldehyde in the quantity indicated is added as a 3.7% aqueous solution. Gel time refers to the time elapsed between the addition of the formaldehyde and observance of a gel.

TABLE III

Example	Acrylamide, percent of aq. HNO_3	Formaldehyde, percent of acrylamide	Other additives, percent of aq. NH_4NO_3	Temp. ($^{\circ}\text{C}$)	Product characteristic, gel time
30.....	4	3.75	20	Firm gel, 4-12 hrs.
31.....	6	3.75	20	Very firm gel, overnight.
32.....	4	2.0	20	Firm gel, overnight.
33.....	4	3.75	20	Weak gel in 4 hrs, became firmer on standing.
34.....	4	3.75	NH_4NO_3 , 4%.....	20	Firm, foamed gel.
35.....	4	3.75	NH_4NO_3 , 12%.....	20	Very weak gelatin 3 hrs, firmer on standing.
36.....	4	5	NH_4NO_3 , 30%.....	25	Firm gel, 3 hrs.

The gelled compositions of Examples 30-36 are converted to Sprengel-type explosive compositions by the addition of refined mineral oil and starch as fuels to form oxygen-balanced compositions.

Example 37

To 70% nitric acid at 30 $^{\circ}$ C. is added 2% of a copolymer comprising 10% acrylamide and 90% acrylonitrile, formed by emulsion polymerization as described in Interscience Publisher's Encyclopedia of Polymer Science and Technology, vol. I, p. 400. After the polymer is dispersed, formaldehyde (3.7% by weight of polymer) is added as aqueous solution. A weak gel is formed in 10 minutes.

Similar results are obtained when the copolymer comprises at least 5% acrylamide and the balance sodium or ammonium acrylate, methyl acrylate α -hydroxyethylacrylate, or acrylic acid, in the general amounts and by the procedure shown above.

Example 38-40

Explosive compositions of the formulations shown in Table 4 are prepared in which the liquid phase is gelled by the in situ formed polyacrylamide crosslinked by formaldehyde.

To aqueous ammonium nitrate solution at 65 $^{\circ}$ C. are added sodium nitrate and monomeric acrylamide. Mixing is begun and continued about three minutes to assure uniform dispersion of ingredients. A 50% aqueous solution of ammonium persulfate is then added to initiate polymerization of the acrylamide in situ.² After about ten minutes pellets of TNT are blended into the composition until complete incorporation and dispersion thereof is observed. Formaldehyde is then added as crosslinking agent for the polyacrylamide. Gel formation is observed in about 5 minutes. The firm gelled compositions are transferred into 5-inch-diameter polyethylene bags (25 lb./bag). When detonation is initiated in air by two conventional commercially available boosters, each comprising 1 lb. (454 g.) of cast TNT, the compositions detonate at the velocities shown in Table IV.

² The combining of ingredients and particularly the in situ formation of polyacrylamide are conducted under a blanket of nitrogen.

TABLE IV

Example.....	Percent		
	38	39	40
Water.....	22.5	17.04	18.12
Ammonium nitrate.....	41.77	31.65	33.64
Acrylamide.....	2.06	1.55	1.45
$(\text{NH}_4)_2\text{S}_2\text{O}_8$	0.98	0.62	0.79
HNO_3 , 75% concn.....	0.32	0.24	0.26
Sodium nitrate.....	12.86	19.49	20.71
TNT.....	19.28	29.23	24.85
Formaldehyde, 37% concn.....	0.23	0.17	0.19
	100.00	100.00	100.00
Detonation velocity, m. sec.....	2,890	4,880	4,880

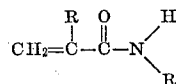
Similar results are obtained when compositions are prepared wherein the fuel is aluminum, sulfur, dinitrotoluene, or coal provided to give formulations having an oxygen balance of -10% to 0%.

I claim:

1. In a water-bearing explosive composition comprising fuel, water, inorganic oxidizing agent selected from the

group consisting of inorganic oxidizing salts and nitric acid, and gelling agent, the improvement which comprises gelling agent composed of at least one polymeric aliphatic acrylic amide crosslinked with aliphatic aldehyde having up to 5 carbon atoms.

2. The explosive composition of claim 1 wherein the polymeric aliphatic acrylic amide is composed of polymerized units of:



wherein R and R' are independently selected from the group consisting of hydrogen, alkyl or hydroxyalkyl having 1 to 4 carbon atoms or mixtures thereof.

3. The explosive composition of claim 2 wherein said polymer is polyacrylamide.

4. The explosive composition of claim 2 wherein the aldehyde is formaldehyde.

5. The explosive composition of claim 2 wherein the aldehyde is paraformaldehyde.

6. The explosive composition of claim 2 wherein the aldehyde is glyoxal.

7. The explosive composition of claim 2 wherein the aldehyde is propionaldehyde.

8. The explosive composition of claim 2 containing about from 0.1 to 5% by weight gelling agent.

9. The explosive composition of claim 2 wherein the oxidizing agent is nitric acid.

10. The explosive composition of claim 3 wherein the aldehyde is formaldehyde.

11. The explosive composition of claim 10 wherein the oxidizing agent is ammonium nitrate.

12. In a water-bearing explosive compositions comprising fuel, 20 to 90% by weight inorganic oxidizing agent selected from the group consisting of inorganic oxidizing salts and nitric acid, 5 to 45% by weight water and gelling agent consisting essentially of about 0.1 to 5% by weight polyacrylamide crosslinked with formaldehyde.

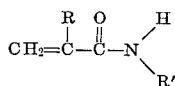
13. The explosive composition of claim 12 wherein the oxidizing agent consists essentially of up to 65% by weight ammonium nitrate and up to 40% by weight sodium nitrate and the composition contains 10 to 30% water.

14. In a process for making water-bearing explosive compositions which comprises mixing water, fuel, inorganic oxidizing agent selected from the group consisting of inorganic oxidizing salts and nitric acid, and gelling agent, the improvement which comprises incorporating in said compositions aliphatic acrylic amide soluble therein,

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polymerizing the acrylic amide, and crosslinking the resulting polymer with aliphatic aldehyde having up to 5 carbon atoms and soluble in said compositions.

15. The process of claim 14 wherein the aliphatic acrylic amide is:



wherein R and R' are selected from the group consisting of hydrogen, alkyl or hydroxyalkyl of 1 to 4 carbon atoms or mixtures thereof.

16. The process of claim 15 wherein about from 0.5 to 10%, by weight amide, based on the weight of the aqueous phase and 0.2 to 5%, by weight aliphatic aldehyde, based on the weight of amide, are added to said compositions.

17. The process of claim 16 wherein the aliphatic acrylic amide is polymerized in situ by the addition thereto of a polymerization promoter.

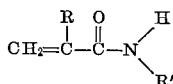
18. The process of claim 17 wherein the R and R' represent hydrogen.

19. The process of claim 18 wherein the aliphatic aldehyde is propionaldehyde.

20. The process of claim 18 wherein the aliphatic aldehyde is formaldehyde.

21. In a process for making water-bearing explosive compositions which comprises mixing water, fuel, inorganic oxidizing agent selected from the group consisting of inorganic oxidizing salts and nitric acid, and gelling agent, the improvement which comprises adding as gelling agent: (a) aliphatic acrylic amide polymer soluble in said compositions and (b) aliphatic aldehyde having up to 5 carbon atoms that is soluble in said compositions and crosslinking said polymer with said aldehyde.

22. The process of claim 21 where the acrylic amide polymer is composed of polymerized units of:



wherein R and R' are independently selected from the

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group consisting of hydrogen, alkyl or hydroxyalkyl of 1 to 4 carbon atoms or mixtures thereof.

23. The process of claim 22 wherein about from 0.5 to 10% by weight amide polymer, based on the weight of the aqueous phase and about from 0.2 to 5% by weight aliphatic aldehyde, based on the weight of polymer, are added to the composition.

24. The process of claim 23 wherein the R and R' represent hydrogen.

25. The process of claim 23 where the aliphatic aldehyde is propionaldehyde.

26. The process of claim 23 wherein the aliphatic aldehyde is formaldehyde.

27. In a process for making water-bearing explosive compositions which comprises mixing fuel, 5 to 45% water, 20 to 90% inorganic oxidizing agent selected from the group consisting of inorganic oxidizing salts and nitric acid, and gelling agent, the improvement which comprises adding as gelling agent: (a) about from 0.5 to 10% by weight polyacrylamide, based on the weight of the aqueous phase, (b) about from 0.2 to 5% by weight formaldehyde, based on the weight of the polyamide, and crosslinking said polyacrylamide with formaldehyde.

28. The process of claim 27 wherein the oxidizing agent consists essentially of up to 65% by weight ammonium nitrate and up to 40% by weight sodium nitrate and the composition contains 10 to 30% water.

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