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THICKENED AQUEOUS INORGANIC OXIDIZER SALT EXPLOSIVE COMPOSITION CONTAINING DISSOLVED PROTEINACEOUS MATERIAL

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ABSTRACT OF THE DISCLOSURE

Water-bearing explosive compositions containing inorganic oxidizing salt, fuel, thickener, water and a proteinaceous material which is soluble in the aqueous explosive composition of pH 3 to 10 and, preferably, foamable therein. Procedurely, the aqueous inorganic oxidizing salt can be added to a mixer at a temperature between about 150°-170° F., fuel, proteinaceous material and thickening agents are added thereto and agitated until mixed.

BACKGROUND OF THE INVENTION

The advent of explosive compositions comprising an aqueous solution of an inorganic oxidizing salt, at least partially dissolved in water, together with one or more fuels and a gelling agent provided blasting operations with a variety of new explosive compositions having many desirable advantages such as a wide variety of explosive properties, and better safety characteristics and economy, both in manufacture and use. In addition, aqueous explosive compositions free of self-explosives, e.g., TNT and/or metallic fuels, e.g., aluminum, have been proposed which offer added safety features and low cost. However, despite their inherent advantages, aqueous explosive compositions possess certain drawbacks with regard to their physical and explosive properties, particularly at low temperatures, e.g., 32 to 40° F. (0 to 5° C.). After standing for a period of time, often as short a time as several hours, whether in storage or in open boreholes prior to detonation, water gels tend to separate or settle into layers and/or "harden" or solidify, instead of remaining soft and pliable.

In actual practice, it is not uncommon for blasting agents to "sit" in magazine storage or, during field operations, e.g., blasting of taconite ore, to remain loaded in wet boreholes for 4 to 6 weeks, or even longer, prior to use. The separation and/or hardening which invariably occurs and the resulting inhomogeneity causes difficulties in handling and loading and adversely affects the sensitivity of the explosive compositions. As a result, the gels fail to detonate. While the two problems, i.e., separation and hardening, are often related in actual experience, they need not co-exist and are best considered separately since experience suggests that a solution to one problem does not necessarily correct the other. Separation, as used herein, is defined as the tendency of a water-bearing explosive composition to separate or settle into layers, each layer containing different proportions of the various components. Such separation can occur under either hot or cold temperature conditions and is generally a result of a lack of mutual solubility of the various components. On the other hand, "hardening," which may occur concommitantly with, or independently of, separation, is defined as the tendency of a water-bearing explosive composition to become stiff and hard and concurrently to exude liquid. Such hardening, which may occur at ambient temperatures but is more pronounced at lower temperatures, is a result of the "salting out" of crystals from the saturated inorganic oxidizing salt solution. The separation problem is somewhat counteracted by the addition of various thickening or gelling agents either alone or in combination with suitable cross-linking agents which serve to increase the viscosity of the explosive composition and thereby reduce the tendency of the less soluble components to settle out. Although various agents have been proposed as solutions to the separation and hardening problems, e.g., the combination of urea and cross-linked polyacrylamide as described in Can. 712,981, no truly satisfactory agent is known which will not only successfully prevent "hardening" but also insure reliable detonation at low temperatures. For maximum commercial utility, it is highly desirable that aqueous blasting agents be sufficiently sensitive to propagate detonation in a continuous unconfined and usually narrow column, generally, not exceeding 10 inches in diameter. Accordingly, there is a definite need for blasting agents which will provide stable, soft aqueous explosive compositions capable of reliable detonations even at low temperatures in small diameter holes, e.g., about 2 to 10 inches and usually diameters of 6 inches or less.

SUMMARY OF THE INVENTION

The present invention provides an improvement in water-bearing explosive compositions comprising inorganic oxidizing salt, fuel, thickener and water, the improvement comprising using a soluble proteinaceous material, said proteinaceous material being soluble in the aqueous explosive composition of pH 3 to 10. The amount of proteinaceous material, i.e., protein or protein derivative, can vary within a rather wide range but at least about 0.01 percent by weight proteinaceous material is used. Although larger amounts can be used, no beneficial effect results when quantities greater than about 10 percent by weight proteinaceous material are incorporated in the explosive composition, and generally, less than about 3 percent by weight protein is sufficient. The resulting water-bearing explosive compositions are rendered soft and pliable and consistently sensitive to detonation at low temperatures due primarily to the presence of the proteinaceous material. Furthermore, these water-bearing explosive compositions retain their valuable properties at low temperatures even when used in boreholes having very small diameters, e.g., 2 inches due to the presence of proteinaceous material. The improvement of the present invention is further characterized in that the use of a soluble proteinaceous material that is also foamable in aqueous explosive compositions can result in the incorporation of small gas bubbles in the gel structure when the mixture is sufficiently agitated thus providing further sensitivity to the explosive composition. A proteinaceous material is herein defined as any protein or protein derivative, such as those obtained by hydrolysis, amidation, acylation or other chemical reaction applied to a protein. By soluble is meant at least about 10% by weight of the porteinaceous material added to the aqueous explosive composition having a pH of 3 to 10 dissolves therein, the balance of the proteinaceous material being either water-soluble or water-dispersible. By foamable is meant the protein or protein derivative in the explosive composition is capable of at least minimum observable foaming, i.e., increases the volume of the explosive composition at least about 5 percent when agitated by mechanical means in any conventional type of mixer.

In the process of preparing aqueous explosive compositions based on the use of a hot aqueous inorganic oxidizing salt "neutral liquor," e.g., a solution such as that obtained from the manufacture of ammonium nitrate prior to graining or prilling, the fuel and other additives such as thickening agent and crosslinking agent are generally added to the hot liquor at about 150–170° F. with mixing and the resulting solution cooled. The use of proteinaceous material does not alter the process procedures; any of the mixing procedures and order of mixings normally employed in explosive gel formulation can be used in the present invention. The soluble proteinaceous material can be added to the mixture at any step in the process, preferably prior to or at the same time as the thickener is added. The addition of the proteinaceous material is preferably accompanied by mixing, and an additional mixing time of about 0.5 to 5 minutes may be required depending on the type and operating speed of the mixer employed as well as the amount of material to be mixed and the foamability of the particular proteinaceous material. For example, in using egg albumin in a high-speed turbine-type mixer, only a short period of mixing, e.g., about 30 to 60 seconds, is necessary. To preclude the possibility of coagulation or degradation of a number of the proteins or derivatives thereof it is advisable to effect their addition to the hot inorganic oxidizing salt liquor, e.g., ammonium nitrate liquor, at temperatures of about 150° F. or below. However, the addition of one or more of the other ingredients, e.g., fuels, prior to the addition of the proteinaceous material will serve to adequately cool the mixture and lower the reaction temperature to an acceptable level.

DESCRIPTION OF PREFERRED EMBODIMENTS

The water-bearing explosive compositions of the present invention comprise an inorganic oxidizing salt, fuel, thickener and a proteinaceous material that is soluble in the aqueous explosive composition of pH 3 to 10.

The inorganic oxidizing salt, usually comprising at least about 20% by weight of the total composition, can be any of the soluble salts conventionally used in aqueous explosive compositions including alkali metal, alkaline earth metal and ammonium nitrates, chromates, dichromates, chlorates, perchlorates as well as mixtures of two or more such salts. 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 component contains at least 45% 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 oxidizing salt, for example, 30 to 70% by weight thereof. It should be understood, however, that compositions employing substantial amounts of undissolved oxidizing salts, e.g., 20 to 70% ammonium nitrate prills, are also within the scope of the present invention. Sodium nitrate is a preferred auxiliary salt; in a preferred embodiment of the invention the explosive composition contains about 20 to 70% ammonium nitrate and about 5 to 25% sodium nitrate by weight based on the total weight of the composition.

The fuels employed in the compositions of this invention can be, for example, self-explosive fuels, non-explosive fuels and metallic fuels, as well as 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, i.e., chemically inert with the system employed, during storage and preparation prior to detonation. "Self-explosive" fuel refers to a substance which by itself is generally recognized in the art as an explosive. Examples of self-explosive fuels include certain organic nitrates, nitrocompounds, and nitramines such as TNT, pentaerythritol tetranitrate (PETN), tetranitro - N - methylaniline (tetryl), cyclotrimethylene - trinitramine (RDX), cyclotetramethylenetetramine (HMX), nitrostarch, explosive-grade nitrocellulose, smokeless powder, and mixtures of such explosives, e.g., pentolite (PETN/TNT), cyclotol (RDX/TNT), and tetryltol (tetryl/TNT). The self-explosive fuel can be, for example, in any of the conventional flaked, pelleted, grained, crystalline or other particulate forms. In those compositions employing a self-explosive fuel, up to 50% and preferably about 10 to 40% by weight, based on the weight of the composition is used.

Non-explosive fuels include, for example, certain nitro aromatic hydrocarbons which provide sensitizing action when combined with the oxidizing salt, e.g., ammonium nitrate. Examples of such fuels include the mono- and di - nitrobenzenes and the mono- and di - nitrotoluenes. Such fuels may replace a part or all of the high-explosive fuel employed in the compositions of this invention. For example, some water-bearing explosive compositions contain no high explosive fuel and are prepared by dispersing a liquid nitro aromatic hydrocarbon in the gelled composition with a dispersing agent, as described in copending application Ser. No. 609,330, filed Jan. 16, 1967 the teachings of which are incorporated herein by reference.

Examples of other nonexplosive fuels which can be used include sulfurous fuels including sulfur itself, siliceous fuels and carbonaceous fuels. Examples of preferred carbonaceous fuels are finely divided coal and other forms of finely divided carbon, solid carbonaceous vegetable products such as starch, wood and paper pulps, sugar, ivory nut meal and bagasse; solid and liquid organic hydrocarbons such as powdered paraffin waxes and fuel oils, including nitrogen-containing liquid organic hydrocarbons such as urea, formamide and other amides; fatty oils; vegetable oils; and mixtures of two or more of the foregoing carbonaceous nonexplosive fuels. In general, up to about 25%, and preferably from 2 to 20% by weight of such carbonaceous fuels are used. Up to about 10% of sulfurous fuels and up to about 5% of siliceous fuels are generally used.

The metallic fuels which can be present include, for example, light elements such as aluminum, magnesium, zinc, boron and silicon both singly and in combination and heavier metallic compounds and 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 as described in copending application Ser. No. 441,319, filed Mar. 19, 1965, now Patent No. 3,297,502, 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 example, iron, manganese, silicon, copper, zinc, or chromium whose composition and purity vary considerably from lot to lot. The amount of metallic fuel used varies with 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 ferrosilicon or ferrophosphorus, usually about from 10 to 30% by weight is used. The average particle size can vary, for example, from −325 mesh to +15 mesh, but preferably is on the order of −100 to −18 mesh.

Preferably the total amount of fuel, usually about 5 to 50% by weight, i.e., the weight of the metallic, nonexplosive, and/or self-explosive fuel, alone or in combination, is usually adjusted so that the total composition has an oxygen balance of −30 to +10%, and excepting for those compositions containing the aforementioned heavier metallic fuels such as ferrophosphorus and ferrosilicon, preferably the oxygen balance is between −10 to 0%.

The compositions of this invention generally containing 5 to 30% water, and preferably about 10 to 20%, are thickened by any of the thickeners conventionally used in water-bearing explosive compositions. "Thickened" as used herein refers to compositions in which the viscosity of the aqueous phase has been materially increased, e.g., to 20,000 c.p.s. or more, as well as gelled products including those gels which are crosslinked. The composition can vary in consistency from pourable, pumpable semifluid solutions, slurries and dispersions to moldable, tough plastic masses. Such thickeners are used in amounts ranging from about 0.2 to 5%. Suitable examples of thickeners include tree exudates such as gum arabic, ghatti, karaya and tragacanth; seaweed colloids such as agar-agar, Irish moss, carrageenin and the alginates; seed extracts such as locust bean, locust kernel, guar and quince seed gums; starches and modified starches such as dextrins, hydroxyethyl starch and British gums; water-dispersible derivatives of cellulose such as methylcellulose, sodium carboxymethylcellulose and sodium sulfoethylcellulose; gelatin; casein, polyvinyl alcohol; polyacrylamides; high molecular weight polyethylene oxides; exocellular heteropoly saccharides made by fermenting starch-derived sugars, silica gels as well as mixtures of two or more of the above thickening agents. Of these, galactomannans such as guar and locust bean gum, and particularly guar gum, are preferred.

When a galactomannan, particularly guar gum, is used as the gelling agent, about from 0.25 to 2% of the galactomannan is usually employed. The galactomannan can be a self-complexing guar gum, e.g., EX-FC-50 and EX-FC-DP supplied by Stein-Hall Co. or a noncomplexing guar gum such as Stein-Hall's Jaguar 100 in which no crosslinking agent is incorporated. When a noncomplexing guar gum is used, small amounts, i.e., about 0.001 to 1% by weight of the total composition, of crosslinking agents, e.g., borax, sodium or potassium dichromate, for the gelling agent can be employed. Other suitable crosslinking agents are soluble antimony and bismuth compounds at a pH of 6 to 13 as described in USP 3,202,556 and transition metal compounds as in S.N. 343,140, filed Feb. 6, 1964, now Patent No. 3,301,723, the teachings of which are incorporated herein by reference.

Still further suitable thickening agents or gelling systems are those described in copending U.S. application Ser. No. 579,852, filed Sept. 16, 1966, which are formed by polymerizing in situ a monoethylenically unsaturated monomer, e.g., acrylamide, with polyethylenically unsaturated monomer, e.g., methylenebisacrylamide.

The proteinaceous material, which includes both protein and protetin derivatives, used in the present invention must be soluble in the aqueous explosive composition having a pH of from 3 to 10. Soluble proteinaceous material means at least about 10% by weight of the amount of said proteinaceous material added to the aqueous explosive composition dissolves therein and the remainder of the proteinaceous material is either water-soluble or water-dispersible. As mentioned above, at least 0.01 percent proteinaceous material is incorporated into the water-bearing explosive composition in order to realize beneficial results. Although relatively large amounts of proteinaceous material can be incorporated in the explosive composition, no added advantages result from the use of more than about 10%, and usually less than about 3% is adequate. Representative proteinaceous materials that are used in the invention include: simple proteins, that is proteins that yield, on complete hydrolysis, chiefly alpha amino acids; conjugated proteins, that is, compounds of a protein with some other molecule or molecules referred to as a prosthetic group; and protein derivatives, i.e., derived proteins, namely, products formed by the action of heat or other physical forces, or by hydrolytic agents, such as denatured proteins or peptides. Preferably, the molecular weight of the proteinaceous material is generally within the range of from about 5000 to 200,000 and, most preferably, not over 100,000.

As is evident from the above and the specific examples that follow, the particular source of proteinaceous material is not critical. Whether the protein is naturally occurring or a derivative is immaterial, provided it is soluble in the explosive composition. Representative simple proteins that are used in the invention are albumins such as ovalbumin and lactalbumin, occurring respectively, in egg white and milk; globulins such as ovoglobulin and lactoglobulin, conjugated proteins such as the glycoprotein mucin. Representative protein derivatives that are incorporated into the explosive composition are partially hydrolyzed milk protein and extracted collagen derivatives. Other suitable naturally occurring animal and vegetable proteins that can be used in the explosive compositions are, for example, cottonseed protein, fishmeal protein, soybean and nonfat milk solids. Examples of some specific commercially available proteinaceous materials that can be used in the invention are Fluid Colloids 2225 and 2226 and Colloid 5V (dry) manufactured by Swift & Co., which are extracted and refined proteins of a collagen source, having a molecular weight of at least 20,000 and a pH of about 6 as well as the N-Z amines, pancreatic digests of casein, manufactured by Sheffield Chemical. A large number of protein derivatives are commercially available and with consideration of solubility and preferably at least a minimum degree of observable foamability as mentioned above, such proteins and derivatives thereof are applicable for use in the described aqueous explosive compositions. Of those described egg albumin is especially preferred due to its wide range of solubility and its exceptional ability both in producing and maintaining a foamed structure. For ease of handling, dry powdered egg whites manufactured by Henningson & Co. are particularly suitable for incorporation in the explosive compositions of the present invention. Preferably, the proteinaceous material is foamable, i.e., the volume of the explosive composition is increased at least 5%, and generally not more than about 50%, when agitated with said material. However, it should be understood that foaming of the protein is not absolutely necessary. Even if the proteinaceous material is not foamed or if foaming action is kept at a minimum by minimal mixing, the proteinaceous materials of this invention are still found to improve the properties of aqueous blasting agents so that they are soft and pliable and capable of detonation at low temperatures. Yet, the foaming action produced by the combination of the proteinaceous material and mixing as described herein, or by any of the conventional agitation methods used in the manufacture of water-bearing explosive compositions, serves to introduce and entrain small bubbles of a gas, commonly air, in the gel structure, thus making the explosive composition especially sensitive to detonation. Quite surprisingly then, the proteinaceous material can also function as an effective foaming agent for the water-bearing explosive composition. The dimensions of the gas bubbles are small, e.g., they have a diameter not larger than about 3.5 mm. and are substantially uniformly distributed throughout the composition so as to preclude any discontinuities which might result in failures in detonation. The foaming which results from the agitation or turbulent mixing of the proteinaecous material in the explosive composition precludes the necessity of introducing an additional gas into the composition or even to forego the use of more expensive high speed mixers. It is understood, however, that any of these supplementary methods for introducing air or other gas into the compositions, as well as the use of low-density fuels as described herein, which serve to lower the product density to a desired level, can be employed in formulating the explosive compositions of this invention. About 5 to 50%, and preferably about 10 to 40%, by volume, of the composition will comprise gas, e.g., air, entrained in small cavities or bubbles with the density of the explosive composition being about 1.0 to 2.0 g./cc. and preferably about 1.1 to 1.7 g./cc.

While the use of soluble proteinaceous materials is beneficial to all types of aqueous blasting agents, the foaming ability of the proteinaceous materials is particularly beneficial in formulating water-bearing explosive compositions containing nonexplosive fuels, i.e., free of self-explosives and/or metallic fuels. These explosive compositions known as Nitro-Carbo-Nitrates, or "NCN" gels tend to become insensitive to detonation at high density, usually densities above about 1.4–1.5, depending on the particular composition of the NCN gel. The use of high cost ingredients such as TNT or aluminum, can be avoided and the sensitivity to detonation maintained if the density of the NCN gel can be lowered to about 1.1 to 1.4 g./cc. without sacrificing the composition ingredients. Employing proteinaceous materials, e.g., egg albumin, NCN gels having densities of about 1.1 to 1.4 g./cc. are prepared which are sensitive to detonation, even at low temperatures, e.g., of the order of 20° to 40° F.

The addition of a soluble, foamable proteinaceous material, particularly egg albumin, to the explosive compositions of the present invention is found to provide an additional advantage in formulating those compositions which contain a finely divided form of a metallic fuel, e.g., fine flake aluminum. The use of small quantities of proteinaceous material is found to minimize the "dusting" problem which arises when incorporating a fine aluminum powder into a slurry-type explosive composition. It is believed that on foaming a composition by mixing in the proteinaceous material the fine metal particles are entrapped in the gas bubbles being formed thus eliminating metal "dust" and providing better dispersion of the metal throughout the gel composition.

The soluble proteinaceous materials described herein act to improve the properties of all types of water-bearing explosive compositions by reason of their ability to act as crystal habit modifiers for the predominant explosive ingredient, namely, the inorganic oxidizing salt, e.g., ammonium nitrate. In the presence of the soluble proteinaceous materials of this invention, the particle size of crystallized oxidizing salt is altered and the resultant particle sensitivity enhanced.

In the explosive compositions of this invention, at ambient temperatures, up to 50% of the inorganic oxidizing salts, predominantly ammonium nitrate, are crystallized and even higher concentrations of crystallized salts are present at low temperatures. In the absence of a habit modifying material the crystallized salt on recrystallizing from aqueous solutions, forms long, large, acicular crystals having a hard and brittle texture. While it is not intended that the present invention be limited by theory, it is believed that when soluble proteinaceous materials, e.g., egg albumin, are added to a solution of the inorganic oxidizing salt at a temperature above the crystallization point of the oxidizing salt in solution, crystals of, for example, ammonium nitrate, having smaller particle size and larger specific surface are formed than those formed in the absence of the crystal habit modifier. Addition of the crystal habit modifier after crystallization has occurred will not enhance the sensitivity of the blasting composition by crystal habit modification. The crystals formed in the presence of the habit modifier are found to be in a more sensitive habit and are small, fine particles similar in appearance to the "hedgehog" dendritic habit described by Buckley, Crystal Growth, John Wiley & Sons, New York, p. 487. It is believed, therefore that the incorporation of a soluble proteinaceous material, in altering crystal size, shape and texture results in the salt being in a more sensitive habit and by eliminating the conventional long, brittle crystals it allows the gelled structure to remain soft and pliable. In addition to the habit modifying properties, it is believed that the proteinaceous materials may also act as so-called "crystal lubricants." The proteinaceous materials described in this invention are generally complex, high molecular weight, e.g., in the range of 5,000 to 200,000, organic materials, many of which are oily- viscous-, or slippery-type fluids themselves or in solution. Even when used in relatively small quantities, the proteins may act as lubricants, perhaps reducing friction between crystal faces, thus enabling individual crystals to slide easily over one another and allowing the encompassing gel structure to remain soft, even at low temperatures where a considerable proportion of the inorganic salt may be out of solution.

In the following examples, parts, unless otherwise indicated, are by weight. In the Tables 1–5, "PAT" refers to potassium antimony tartrate.

EXAMPLES 1–6

Water-bearing explosive compositions are prepared in a turbine-type slurry mixed from the materials shown in Table 1 by the following sequence of steps:

(1) Ammonium nitrate "liquor" (78–80% concentration, pH adjusted to 4.5–5.0 by addition of nitric acid) at 150–170° F. is placed in the mixer and potassium antimony tartrate crosslinking agent added while agitation is begun.

(2) A soluble carbonaceous fuel is added and mixed until the temperature drops to 150° F. or below.

(3) The soluble proteinaceous material is added and mixed therein for about 1 minute.

(4) Formamide and dinitrotoluene are added and mixed in for about 1 minute.

(5) A premixed composition of sodium nitrate and guar gum is added and mixed for about 4 to 5 minutes, or until thickening is observed.

(6) Ammonium nitrate prills and/or solid carbonaceous fuels (if specified) are added and mixed in.

(7) Crosslinking agent (sodium dichromate) is added while the composition is pumped from slurry truck.

The compositions of Examples 2 and 3 are loaded into 6 inch diameter, 32 feet deep boreholes filled with 10 to 18 feet of water. Stemming consists of about 20 feet of sand. The composition of Example 2 remains loaded for a period of 5 days before shooting; the composition of Example 3 for 4 days prior to shooting. The composition of Example 4 is loaded into a 9 inch diameter, 50 feet deep borehole filled with 27 feet of water. The compositions of Examples 1, 4, 5 and 6 are packaged in 6-inch, 40-lb. polyethylene bags. One bag of each composition is shot unconfined in air and the others placed in hot (ca. 100° F.) and cold (20° F.) storage. Likewise, the composition of Example 1 without the addition of a soluble, foamable proteinaceous material is prepared and packaged as previously described and placed in hot and cold storage. No separation or hardening is observed, in the compositions of Examples 1, 5 and 6 containing the proteinaceous material even after 6 weeks storage, the maximum period of observation. The composition without the proteinaceous material gave evidence of hardening after 3 days storage and failed to detonate when shot unconfined in 6 inch diameter at 40° F.

The compositions are initiated at the temperatures designated in Table 1 by conventional primers, e.g., 2 lb. (908 g.) of cast TNT. The detonation velocity measurements are given in meters/second, "D" indicates the composition propagates a detonation.

TABLE 1

Example	1	2	3	4	5	6
78% AN liquor	48.4	48.4	61.2	48.4	48.4	48.4
Ammonium nitrate	37.8	37.8	47.8	37.8	37.8	37.8
Water	10.6	10.6	[1] 16.1	10.6	10.6	10.6
Ammonium nitrate (AN) prills	19.8	19.8		18.6	18.6	18.6
Sodium nitrate	13.9	13.9	18.1	14.0	14.0	14.0
DNT (26°) [2]	7.9	[3] 10.9	11.0	11.0	11.0	11.0
Formamide	4.9	1.9	1.8	2.0	2.0	2.0
Sugar (granulated)	4.9	4.9	5.0	5.0	5.0	5.0
Bagasse pith				0.8	0.8	0.8
Egg albumin	0.2	0.2	0.2	0.2		
Extracted collagen					0.2	
Hydrolyzed milk protein						0.2
The compositions also contain per hundred weight:						
Guar gum, lbs	1.0	1.0	1.0	1.0	1.0	1.0
5% $Na_2Cr_2O_7$, cc	300	300	400	300	300	300
PAT, g	1.25	1.25	1.25	1.25	1.25	1.25
Velocity, m./sec.:						
76° F	4,150					[4] 4,150
56° F		5,100	5,100		3,915	[5] 3,950
40° F	2,915				3,100	
33° F				4,150		
20° F				D		
Density, g./cc	1.32	1.29	1.22	1.32	1.31	1.32

[1] Approx. 3 lbs. of H_2O added to AN liquor.
[2] Dinitrotoluene oil 26° technical.
[3] Dinitrotoluene oil technical, 30±5° C.
[4] Tested at 70° F.
[5] Tested at 50° F.

The compositions of the preceding examples, particularly Examples 2 and 3, are foamed by agitation of the proteinaceous material. The composition of Example 2 is also loaded in dry boreholes and after 4 days standing, is detonated at a velocity of 4920 m./sec. The composition of Example 2 is packed in polyethylene bags as described for the compositions of Examples 1, 4 and 5 and is detonated in air unconfined in 6" diameter at 76° F. at a velocity of 4500 m./sec. and at 40° F. at a velocity of 4000 m./sec.

The composition of Example 1 with 0.8 part bagasse pith added was also evaluated as a seismic blasting agent by packaging in 4½-inch-diameter, 20 lb. metal cans and shooting underwater at a depth of 6 feet and a temperature of about 70° F. Five different shots recorded velocities of 4000–4400 m./sec. when primed with an 18.5 g. charge of RDX.

The composition of Example 2 when formulated at a density of 1.41 g./cc. detonated in air unconfined in 6-inch-diameter at 76° F. at a velocity of 3400 m./sec. and at 40° F. at 3915 m./sec.

When 56° C. DNT is substituted for 26° C. DNT in the composition of Example 2, the composition has a density of 1.29 and detonates in a wet 6-inch-diameter, 32 feet deep borehole under conditions previously described for the composition of Example 2. Similar results are obtained when about 0.3% of an enzyme-modified soy protein or about 0.3% of an enzymatic digest of lactalbumin is substituted for the hydrolyzed milk protein in the composition of Example 6.

EXAMPLES 7–10

Water-bearing explosive compositions are prepared in a rotary mixer from the materials shown in Table 2 by the following sequence of steps:

(1) Ammonium nitrate liquor (about 80% ammonium nitrate) at 150–170° F. is placed in the mixer and agitation is begun.

(2) A soluble non-explosive carbonaceous fuel is added and mixing is continued until the temperature drops to 150° F. or less.

(3) A soluble, foamable proteinaceous material is added and mixed for about 1–5 minutes.

(4) A premixed composition of sodium nitrate and guar gum is added and mixed for about 4–5 minutes, or until thickening is observed.

(5) A solid, carbonaceous fuel (if specified) is added.

(6) Crosslinking agents (sodium dichromate and potassium antimony tartrate) are added; the compositions mixed for several minutes and discharged into 6-inch-diameter, 50 lb. polyethylene bags, except the composition of Example 10 which is packaged in 5-inch-diameter, 50 lb. bags. After being subjected to both hot and cold storage for 6 weeks, the compositions are examined and found to be soft and pliable and completely homogeneous. The compositions are detonated in air, unconfined in 2 1 lb. cast TNT primers. Detonation velocity measurements are given in meters/second.

TABLE 2

Example	7	8	9	10
77–80% AN liquor	70.0	70.0	65.3	30.0
Ammonium nitrate	55.2	54.0	51.0	23.6
Water	[1] 16.1	[1] 15.7	[1] 15.6	[2] 6.4
AN prills				46.4
Sodium nitrate	20.9	20.4	20.0	7.6
Sugar (granulated)	6.6	7.8	3.8	7.3
Urea			7.8	
Coal (fine)				4.0
Bagasse pith		1.9	1.6	
Egg albumin	0.2	0.2	0.2	0.1
The compositions also contain per hundred weight:				
Guar gum, lbs	1.0	1.0	1.0	1.0
5% $Na_2Cr_2O_7$, cc	400	400	400	100
5% PAT, cc	200	200	200	300
Velocity, m./sec.:				
76° F	[3] 3,000	4,400	4,250	[4] 3,600
40° F	4,200	3,820	3,500	3,400
Density, g./cc	1.42	1.23	1.13	1.25

[1] 1–2 lbs. of H_2O added to AN liquor.
[2] 3.6 lbs. of H_2O added to AN liquor.
[3] Tested at 100° F.
[4] Tested at 60° F.

EXAMPLES 11–14

The following compositions (in Table 3) of this invention are prepared in a bench-type agitating mixer by the general procedures described in the preceding examples and discharged into 3½-inch-diameter polyethylene bags.

After 5 days recycling in hot and cold storage, the compositions, still soft and pliable, are detonated in air, unconfined with 35 g. of pressed "Pentolite" (50/50 PETN/TNT). Velocity measurements could not be recorded; in the table, "D" indicates the composition propagates a detonation at the specified temperatures.

TABLE 3

Example	11	12	13	14
77–80% AN liquor	66.2	60.0	64.6	60.0
Ammonium nitrate	53.0	48.0	51.7	48.0
Water	[1] 16.1	[1] 16.0	[1] 16.0	[1] 16.0
Sodium nitrate	20.3	18.0	20.0	18.0
Sugar (granulated)	7.7	4.9		5.0
Urea		8.0	12.1	7.8
Formamide				5.0
Coal (coarse)		4.9		
Coal (fine)	2.7			
Egg albumin	0.2	0.2	0.2	0.2
The compositions also contain per hundred weight:				
Guar gum, lbs	0.7	0.7	0.7	0.7
5% $Na_2Cr_2O_7$, cc	60	60	60	60
5% PAT, cc	200	200	200	200
Detonation Results:				
80° F	D	D	D	D
40° F	D	D	D	D
Density, g./cc	1.3–1.5	1.3–1.5	1.3–1.5	1.3–1.5

[1] 2–4 lbs. of H_2O added to AN liquor.

EXAMPLES 15–19

Water-bearing explosive compositions are prepared in a rotary mixer from the materials shown in Table 4 by the general procedures described in the preceeding examples. Aluminum is added after the addition of the premixed sodium nitrate and guar gum, at the same time as other optional solid, insoluble fuels and mixed into the composition. After addition of the specified cross-linking agents and additional mixing as heretofore described, the products of Table 4 are discharged into 2, 2½, 3 and 4 inch diameter polyethylene bags. The compositions are detonated in air, unconfined with 140 g. of pressed pentolite.

TABLE 4

Example	15	16	17	18	19
78.5% AN liquor	61.0	48.4	54.9	60.8	58.5
Ammonium Nitrate	47.9	37.8	43.1	47.7	45.9
Water	[1] 16.1	[2] 13.3	[3] 23.5	[2] 16.4	[4] 18.2
AN prills		15.8			
Sodium nitrate	15.8	11.9	12.7	15.9	15.8
DNT (26°)	11.0	8.0	10.7	10.9	10.9
Fine flake aluminum	2.0	2.0	2.9	2.0	2.0
Sugar (granulated)	5.0	5.0		3.0	2.0
Formamide	2.0	5.0	2.0	2.0	2.0
Coal (fine)			4.9	2.0	3.0
Bagasse pith		1.0			
Egg albumin	0.2	0.2	0.2	0.2	0.2
The compositions also contain per hundred weight;					
Guar gum, lbs	1.0	1.0	1.0	1.0	1.0
5% $Na_2Cr_2O_7$, cc	100	100	100	100	100
5% PAT, cc	200	200	250	200	250
Velocity, m./sec.;					
60° F-4"	4,600	4,450	3,820	4,400	4,250
60° F-3"	4,150	3,400	3,700	4,000	3,650
72° F-2-1/2"	4,000	4,100	3,700	3,900	3,600
72° F-2"	3,820	3,700	3,550	3,800	3,400
Density, g./cc	1.24	1.15	1.14	1.20	1.13

[1] 2.7 lbs. H_2O added to AN liquor.
[2] 3.4 lbs. H_2O added to AN liquor.
[3] 11.7 lbs. H_2O added to AN liquor.
[4] 5.6 lbs. H_2O added to AN liquor.

The compositions of the preceding examples are foamed to varying degrees, as evidenced by the variation in density.

EXAMPLE 20

Water-bearing explosive composition of the formulation shown below is prepared in a rotary mixer by adding to the mixer 70 parts ammonium nitrate prills, 8.8 parts sodium nitrate, 7 parts sugar, 4 parts fine coal, 1 part guar gum, and 0.05 part powdered egg albumin. After mixing for about 30 seconds, 9.15 parts water is added and the mixture agitated for 4–5 minutes. Sodium dichromate is added and mixed in for about 15 seconds, followed by the addition of potassium antimony tartrate and an additional mixing time of 30 seconds more. The composition, having a density of 1.30 g./cc., is discharged into 5-inch-diameter polyethylene bags. The overall composition is:

Ammonium nitrate prills	70.00
Water	9.15
Sodium nitrate	8.80
Sugar	7.00
Coal	4.00
Egg albumin	0.05
Guar gum [1]	1.00
	100.00

[1] Crosslinked by 100 cc./cwt. of 5% aqueous sodium dichromate and 300 cc./cwt. of 5% aqueous potassium antimony tartrate.

The composition detonates at a velocity of 3350 m./sec. at 60° F. and 3200 m./sec. at 42° F.

EXAMPLES 21–22

Water-bearing explosive compositions of the formulations shown below are prepared in a rotary mixer by the following sequence of steps:

(1) 65% ammonium nitrate liquor at 150–170° F. is placed in the mixer and to the solution is added flaked TNT. The mixture is agitated until the temperature drops to about 150° F.

(2) A soluble, foamable protein and a premixed composition of sodium nitrate and guar gum are added and mixed for about 3½ minutes.

(3) Sodium dichromate is added and incorporated into the blend by agitating for 30 seconds.

(4) Potassium antimony tartrate is added and the blend mixed for an additional 45 seconds.

(5) The contents are discharged into polyethylene bags.

TABLE 5

Example	21	22
65% AN Liquor	56.95	56.80
Ammonium nitrate	37.00	37.00
Water	19.95	19.80
Sodium nitrate	18.00	18.00
TNT (flaked)	25.00	25.00
Egg albumin	0.05	-----
Extracted collagen	-----	0.20
The compositions also contain per hundred weight:		
Guar gum, lbs	1.0	1.0
5% $Na_2Cr_2O_7$, cc	50	50
5% PAT, cc	250	250
Velocity, m./sec., 70° F	4100	4050
Density, g./cc	1.37	1.36

I claim:

1. In a water-bearing explosive composition comprising inorganic oxidizing salt, fuel, thickener and water, the improvement which comprises said explosive composition containing at least about 0.01 percent proteinaceous material selected from the group consisting of albumin, extracted collagen and soybean protein at least 10 percent of which is dissolved in the aqueous explosive composition having a pH of 3 to 10.

2. A composition of claim 1 wherein the proteinaceous material is an albumin.

3. A composition of claim 1 wherein the proteinaceous material is egg albumin.

4. A composition of claim 3 wherein the fuel is a nonexplosive.

5. A composition of claim 3 wherein the fuel is metallic.

6. A composition of claim 3 wherein the fuel is explosive.

7. A composition of claim 1 wherein the proteinaceous material is extracted collagen.

8. A composition of claim 1 wherein the proteinaceous material is soybean protein.

9. A composition of claim 1 wherein the protein is lactalbumin.

10. A composition of claim 1 wherein the molecular weight of the protein is within the range of from about 5000 to 200,000.

11. A composition of claim 1 wherein the explosive is in a foamed condition.

12. A composition of claim 1 comprising, by weight, based on the total composition from about 20 to 70 percent ammonium nitrate, from about 5 to 25 percent sodium nitrate, from about 5 to 50% fuel, from about 5 to 30 percent water, from about 0.2 to 5 percent thickener, and from about 0.01 to 10 percent egg albumin.

13. A composition of claim 12 having 0.1 to 3 percent egg albumin.

14. A composition of claim 13 containing a nonexplosive fuel.

15. A composition of claim 13 containing a metallic fuel.

16. A composition of claim 13 containing an explosive fuel.

17. A composition of claim 12 wherein the explosive is in a foamed condition.

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