EXPLOSIVE COMPOSITION CONTAINING COATED METALLIC FUEL

Joseph D. Chrisp, Claymont, Del., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

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This invention relates to improvements in explosive compositions and, more particularly, to improvements in aqueous explosives based on inorganic oxidizing salt and particular metallic fuel.

The finding that explosives composed of an aqueous solution or suspension of inorganic oxidizing salt(s), 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 has led to the development of a variety of new blasting explosives in recent years. Among the sensitizer or fuel components commonly specified for use in such explosives have been the metallic and metalloid elements, mixtures, and alloys, particularly the lighter elements such as aluminum, zinc, boron, and silicon, both singly and in combination, and the heavier metallic alloys, including ferroalloy silicon and ferrophosphorus. Combinations of the light metals and the heavier alloys also are suitable. In some formulations, the metallic fuels have been used alone, whereas in others, they have been employed together with one or more solid self-explosives such as TNT, dinitrotoluene, pentaerythritol tetranitrate (PETN), cyclohexylmethylene-trinitramine (RDX), nitroaromatic, explosive grades of nitrocellulose or smokeless powders, etc., and/or with one or more nonexplosive and generally carbonaceous combustibles, e.g., solid and liquid hydrocarbons and fractions, powdered carbons and coals, crude and refined carbohydrate products, fatty acids and oils, organic amines, amides and hydroxy compounds, sulfates, etc.

While these aqueous solution or 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, in that separation of the charge components can lead to failures in initiation of detonation even when suitable primers are used, or can result in failures in propagation of detonation through a column charge once initiation has occurred. Such segregation is accentuated by variations in the temperatures to which the charges are exposed in storage or during travel. The resultant comminution changes in component solubility, particularly of the inorganic oxidizing salts, in the aqueous medium. A related situation exists in wet blast holes, where ground water can act to dilute the charges or leach their soluble components unless such charges are in fluid-tight containers, so that again failures in initiation or propagation can occur.

To overcome the foregoing problems, it has become common practice to employ gelling agents or thickeners in the aqueous explosives. The thickeners usually employed are natural hydroxylated polymers, e.g., natural polysaccharide materials, and their chemically modified derivatives, that swell in water or other aqueous media to form viscous colloidal solutions (sols) or mucilages. (These natural polysaccharide materials are often known as "gums.") Among the polysaccharides and derivatives, the galactomannan gums, locust bean gum and especially guar gum, have been found to give superior thickening action on a unit weight basis and hence often are specified as preferred thickening or gelling agents. These thickeners tend to immobilize the insoluble and undissolved soluble components, so that segregation 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 thin yet nonsegregating fluids that can be poured or pumped, e.g., by slurry trucks, to thick, rigid or flexible masses, suitably transferred by extrusion or similar methods. Additional variation in the type and extent of thickening or gelling action has been accomplished by use of appropriate crosslinking agents 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 (\(>100^\circ\text{F.}\)).

One problem associated with the aforesaid aqueous explosives that has not yet been well-recognized concerns the combination of aqueous solutions of inorganic oxidizing salts with metallic fuels. The inorganic oxidizing salt principally employed in the aqueous explosives is ammonium nitrate, either alone or in combination with other at least partly soluble oxidizing salts, such as the alkali and alkaline-earth metal nitrates, chlorates, and perchlorates. Concentrated aqueous ammonium nitrate solutions or liquids tend to be somewhat acidic, i.e., generally have a \(\text{pH}\) in the 4.5—7 range. Such acidity may not be of major significance when the metallic fuels combined therewith are of high purity and/or low reactivity, i.e., do not readily displace hydrogen from the resulting suspension. However, when reactive light metals and particularly when low-cost light metal mixtures and alloys of varying and often unknown composition and purity are used, the production of flammable hydrogen and the consequent swelling and "gassing," i.e., entrapment of gas bubbles, of the aqueous explosives can both be serious problems. In addition, the cations produced by such reactions of the metallic fuels can have a deleterious effect on the aforementioned thickened or gelled aqueous explosives, either by interfering with the swelling action of the hydrophilic colloid thickener in the aqueous medium, or by preventing or reducing the extent of crosslinking, or both. Consequently, the desired consistency and stability in the thickened explosives often are not achieved in the presence of reactive metals.

Several soluble salt-type additives for protecting metallic fuels against attack in ammonium nitrate liquors are known, but not all of these are suitable for use in aqueous explosives, especially when the aforesaid thickeners and...
crosslinking agents are employed. It is also known from U.S.P. 2,894,864 that aluminum powder for use in explosives by removing the natural oxide surface film; heating in an oxygen-containing gas atmosphere at 400–600° C. to reform a uniform oxide coating on the powder particles; suspending the oxide-coated product in a solvent solution of higher fatty acid, and finally drying the product. While this method of protection, which involves both the naturally resistant aluminum oxide film and the fatty acid, provides some inhibition of attack on aluminum, the procedure is inherently uneconomical in requiring prolonged heating to high temperature to give a uniform oxide surface on the particles. Also, U.S.P. 2,894,864 indicates, the protective coating is not reliably effective above 60° C. (140° F.), which is below the temperature of up to 160° F. often encountered in preparing the aforementioned aqueous explosives from hot concentrated ammonium nitrate liquors.

This invention therefore provides aqueous explosives based on inorganic nitrate oxidizing agent and containing particulate metallic fuel wherein the fuel particles are easily and reliably protected against attack in said aqueous explosives. The invention further provides aqueous explosives based on inorganic nitrate oxidizing agent and containing particulate metallic fuel and hydrophilic polysaccharide thickening agent wherein deleterious effects on the action of the thickening agent and any crosslinking agent used therefor are substantially avoided.

More particularly, this invention provides aqueous explosive compositions, usually having an oxygen balance of from about 30 to +10%, comprising water, inorganic oxidizing agent and metallic fuel particles in which the metallic fuel particles are provided with a continuous, preformed coating composed of from about 10 to 90%, preferably 70 to 85% by weight of a normally liquid oil having a viscosity of about from 30 to 400 Saybolt Universal seconds at 100° F. and about from 10 to 90% and preferably 15 to 30% by weight of aliphatic monocarboxylic acid, preferably fatty acid, containing about from 8 to 22, and preferably about from 16 to 22, carbon atoms in the molecule. The preformed continuous coating constitutes about from 1 to 10% by weight of the metallic fuel particles.

Broadly, the improvement of this invention can be applied to any of the known types of water-borne explosive compositions containing metallic fuels. Preferably, however, the preformed, continuous coating of aliphatic monocarboxylic acid, preferably fatty acid, and oil is provided on metallic particles to be used in amounts of about 50% in compositions at least one water-soluble, inorganic oxidizing salt, about from 5 to 50% and preferably 10 to 30% of water, based on the total weight of the composition, and from about 25 to 2% of a hydrophobic polysaccharide thickener such as a galactomannan gum and from 0 to 1% by weight of a crosslinking agent for the gum. In addition to the metallic fuel the composition can also contain about from 0 to 40% of a solid organic explosive sensitizer and about from 0 to 25% of a carbonaceous fuel. In general, the water-containing gelled explosives are of conventional types and contain at least about 20% by weight of the inorganic oxidizing salt or salts including one or more of ammonium, alkali metal, or alkaline earth metal nitrates and perchlorates. Preferably the inorganic oxidizing salt is composed of about from 65 to 100% by weight of ammonium nitrate and about from 35% to 1% of a salt or salts such as sodium nitrate, potassium nitrate, or calcium nitrate that are dissolved in the solution of the composition to form a substantially saturated solution. If desired, the explosive composition also can contain one or more other optional additives which do not substantially change the basic and novel character of the claimed compositions, for example, for example on the order of 0.25 to 10%, and preferably 1 to 5%, by weight based on the total composition of an anti-freezing (fluidizing) agent.

The metallic fuels which are provided with the continuous, preformed coating in accordance with this invention include, for example, light elements such as aluminum, magnesium, zinc, boron and silicon both in combination, and heavier metallic alloys including ferrophosphorus and ferrosilicon, as well as mixtures of two or more of these metals or alloys. Although the preformed coating can be provided on particles of any of these types of metallic fuels, it has been found that particles of light elements and alloys thereof with minor amounts of each other and, for example, iron, manganese, silicon, copper, zinc or chromium, for example impure aluminum alloys and ground aluminum scrap, such as the EXXO 90–30 aluminum alloy, supplied by ALMEG Corp. of Kansas City, Mo., whose composition and degree of purity varies markedly from lot to lot. Unless otherwise indicated, when reference is made herein and in the appended claims to elements, e.g., "aluminum," alloys of the elements with minor amounts, e.g., 20% by weight or less, of other elements, e.g., one or more of those specified above, are included.

The coated metallic fuel particles of this type allows the production of consistently good explosive products of the gelled, aqueous type in spite of inherent differences in lots of metallic fuel. The preformed continuous coating of oil and acid inhibits corrosion reaction of the metallic fuel particles with the aqueous solution and thus precludes the formation of flamable hydrogen and "gassing" and swelling of the aqueous explosive formulation. The coating is particularly effective in inhibiting the corrosive reaction of aluminum and metallic impurities of varying and unknown identity, for example, in the aforementioned EXXO 90–30 aluminum alloy. The coating minimizes solvolyis of metal impurities in aluminum allowing the formation of more uniformly good gels. This is of particular importance when the gelling agent is a self-complexing guar gum. Further the protective, continuous, preformed coating serves to inhibit significant increases in pH caused by the reaction of metallic fuel particles, allowing more uniform, consistently good crosslinking of the gelling agent.

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, e.g., the EXXO 90–30 aluminum alloy previously mentioned, 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 about 325 mesh to +15 mesh, but preferably is on the order of 18 to 100 mesh.

As mentioned above, the aliphatic mono- and polycarboxylic acid employed in coating the metallic fuel particles is one containing from about 8 to 22 and preferably from 16 to 18, carbon atoms in the molecule. The acid, which comprises from about 10 to 50% of the preformed coating on the metallic fuel particles, is believed to form, owing to the oriented (polar) nature of the acid, a layer on the particles of metallic fuel in which HO-group of the acid becomes closely bound to the surface of the metallic particles, perhaps with the formation of small amounts of a metallic salt of the fatty acid, and the paraffinic hydrocarbon radicals of the acid extend radially outward from the particles in a loosely packed layer. A layer of hydrocarbon radicals presents a protective sheathing which is hydrophobic but oleophilic. Accordingly, the oil, which comprises about from 50 to 90% and preferably 70 to 85% of the preformed coating is attracted to the oleophilic layer of hydrocarbon radicals to present a further layer to protect the metallic particles from the aqueous phase of the explosive composition.
Examples of fatty acids containing about from 8 to 22 carbon atoms and preferably 16 to 18 carbon atoms which can be used in providing a preformed coating on the metallic fuel particles include, but are not limited to, those in the following group.

**Straight Chain Saturated Acids:**
- Caprylic acid, $C_8H_{16}O_2$
- Palmitic acid, $C_{16}H_{31}O_2$
- Capric acid, $C_{10}H_{21}O_2$
- Undecylic acid, $C_{11}H_{23}O_2$
- Lauric acid, $C_{12}H_{25}O_2$
- Tridecanoic acid, $C_{13}H_{27}O_2$
- Myristic acid, $C_{14}H_{29}O_2$
- Pentadecanoic acid, $C_{15}H_{31}O_2$
- Palmitic acid, $C_{16}H_{33}O_2$
- Margaric acid, $C_{17}H_{35}O_2$
- Stearic acid, $C_{18}H_{37}O_2$
- Nonadecanoic acid, $C_{19}H_{41}O_2$
- Arachidic acid, $C_{20}H_{43}O_2$
- Henicosanoic acid, $C_{21}H_{45}O_2$
- Behenic acid, $C_{22}H_{47}O_2$

**Branches Chain Saturated Acids:**
- 2-ethylhexanoic acid, $C_7H_{15}O_2$

**Unsaturated Acids:**
- 10-tetradecylenic acid, $C_{14}H_{23}O_2$
- Petroselinic acid, $C_{16}H_{31}O_2$
- Oleic acid, $C_{18}H_{31}O_2$
- Elaidic acid, $C_{18}H_{31}O_2$
- Vacuum acid, $C_{18}H_{31}O_2$
- Erucic acid, $C_{22}H_{41}O_2$
- Brassidic acid, $C_{20}H_{39}O_2$
- Linoleic acid, $C_{18}H_{32}O_2$
- Linolenic acid, $C_{18}H_{34}O_2$
- Linoleic acid, $C_{18}H_{32}O_2$
- Elaidolinolenic acid, $C_{20}H_{38}O_3$
- Palmeistsenic acid, $C_{18}H_{32}O_2$
- Elaeostearic acid, $C_{18}H_{34}O_2$
- Arachidonic acid, $C_{20}H_{42}O_2$

Mixtures of two or more of any of these fatty acids can also be used. Of these fatty acids, oleic acid and stearic acid and mixtures of fatty acids, e.g., tall oil, which comprises oleic, stearic, linoleic, linolenic and palmitic acids in admixture with rosin acids, are particularly preferred for use in providing the preformed coating on the metallic fuel particles. These fatty acids or mixtures thereof such as the commercial grades of oleic and stearic acids and the above mentioned tall oils are low in cost and readily available. Oleic acid, which is probably the most abundant of the naturally occurring fatty acids, is usually employed as the commercial grade, which contains in addition to about 75% oleic acid about equal parts of linoleic acid, palmitic, and stearic acids. The commercial grade of oleic acid is fluid at ambient conditions of temperature and pressure and thus can be easily applied to the metallic particles without any preheating of this fatty acid or of its mixture with oil. Whereas the oleic acid is suitable for providing a coating on relatively pure metallic fuel particles, for impure metallic fuel particles such as the EXXO 90–30 aluminum whose purity and composition of impurities can vary widely from lot to lot, more consistent protection is usually achieved when stearic acid is employed. However, stearic acid itself and the commercial (USP) grade of stearic acid, which comprises a mixture of stearic and palmityl acids (45% stearic, 55% palmityl, are waxy solids at room temperature and require that the fatty acid or the oil mixture he heated above the melting point of the stearic acid (60–70°C, or 157–158°F) or the commercial grade (55°C, 131°F) to impart sufficient fluidity for the stearic acid to flow about and coat the individual particles of metallic fuel.

Tall oil, which are a byproduct of the wood pulp industry and thus are a low-cost source for the fatty acid, are liquid at room temperature and thus do not require preheating before they are used to coat the metallic fuel particles.

As mentioned above, the oil employed in this invention in conjunction with the fatty acid is one which has a viscosity of about from 30 to 400 seconds at 100°F., and preferably from 35 to 150 SUS, as determined by the Saybolt Universal method (“Corvus” oil has viscosity of 70 Saybolt Universal seconds at 100°F.). Oils within this range of viscosities adhere closely to the film of fatty acid on the metallic fuel particles to protect the metallic particles from the aqueous phase of the explosive composition. Oils having a viscosity below 35 seconds fluid and limit the thickness of the protective film, whereas oils of viscosity greater than about 400 seconds are too resistant to flow to permit uniform coating of the particles of metallic fuel. Oils having a viscosity above 150 SUS usually must be heated before they are applied. The oil may be either paraffinic, naphthenic, or aromatic base providing it contain no substituent or impurities which cause corrosion of the metallic fuel particles or interfere with crosslinking of the aqueous phase of the explosive compositions. Hydrocarbon oils are preferred. Examples of oils which are normally liquid at room temperature and which have viscosities within the specified range of from about 30 to 400 Saybolt Universal seconds (SUS) at 100°F. include, but are not limited to, “Corvus” oil, (70 SUS at 100°F.), numbers 2, 4, 5, and 6 fuel oil (all have SUS’s of less than 125); transformer oil (65 SUS); light grade cable oils (100 SUS); “Ebony P” oil (300 SUS at 150°F.); S.A.E. 30 crankcase oil (about 300 SUS); kerosene (32 SUS); dormant and verdant tree-spray oils (80–125 SUS and 40–80 SUS, respectively); light liquid petroleum (70–110 SUS); light weight hydraulic oils (100 SUS); and low-velocity nonmisible cutting oils (40–150 SUS). (Each of the viscosities indicated above are determined at 100°F.) “Corvus” oil and number 2 fuel oil are particularly preferred oils for use in forming the desired protective coatings on the metallic fuel particles since these oils are inexpensive, readily available and have viscosities at 100°F., i.e., 70.5 and about 36, respectively, which permit the formation of a continuous protective film about the metallic fuel particles.

“Corvus” oil, which is commercially available from Texas Oil Co., is a light bodied, straight mineral product which contains no additives and which is accordingly neutral and noncorrosive.

As mentioned above, sufficient quantity of the protective oil/fatty acid coating is provided when the coating comprises about from 1 to 10% by weight of the fatty acid/oil mixture based on the weight of the metallic fuel. Of this protective coating, about 50 to 90% by weight is the oil and about 10 to about 50% is the fatty acid. Naturally variations are possible within the ranges set forth based on the thickness of the coating required, cost of the individual components, and the nature of the fatty acid and oil employed and the surface area of the metallic particles. For example, a coating particularly suitable for aluminum comprises 80% “Corvus” oil and 20% oleic acid employed in proportions of 8.34 pounds combined weight of coating (6.67 pounds oil, 1.67 pounds oleic acid) per 100 pounds of aluminum. When stearic acid is used as the fatty acid an effective coating on a commercial basis is provided when the coating is 70 to 85% “Corvus” oil and 15 to 30% stearic acid.

The preformed continuous coating of fatty acid and oil can be provided on the metallic fuel particles well before the particles are to be incorporated in the explosive formulation and the coated particles subsequently stored until ready to formulate the explosive composition, the coating protecting the particles from changes of moisture and temperature changes in storage. When such is the case the coated particles of metallic fuel can be added to the formulation in the course of conventional formulating steps, used in preparing gelled, aqueous explosive compositions. In an embodiment of this invention pre-
ferred for convenience in preparing the compositions of this invention, however, the particles of metallic fuel are provided with the coating of fatty acid and oil immediately before their incorporation with the other components of the explosive compositions. This coating of fatty acid/oil on the particles can be prepared on the particulate metallic fuel in the mixer before the addition of other components of the explosive formulation. In a particularly preferred method of preparing gelled, aqueous explosive compositions of this invention, the particles of metallic fuel are added to, i.e., blended with or folded into, a mixture of the fatty acid and oil in a rotating mixer and the contents of the mixer rotated for 0.5 to 5 minutes to allow the particles of metallic fuel to become thoroughly coated with the fatty acid and oil. When the particles are thoroughly coated, the organic explosive sensitizer is added, and subsequently a concentrated, preferably saturated, solution of the inorganic oxidizing salt or salts, e.g., ammonium nitrate or a mixture of ammonium nitrate and sodium nitrate, is added. To the resulting mixture in the mixer are added premixed gelling agent and cross-linking agent, additional oxidizing salts, if employed, and, if desired, fluidizing agent.

As stated earlier, the compositions of this invention usually contain at least about 20% 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 such salts. Examples of these 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 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 at least about 50% by weight of ammonium nitrate and at least about 5% by weight of sodium nitrate are particularly preferred.

The compositions of this invention contain about 5% to 45% by weight of water, and preferably 10% to 30% of water. As mentioned above, in the preparation of the explosive compositions, it is particularly convenient to use concentrated aqueous solutions of ammonium nitrate commonly known as ammonium nitrate liquors. In such cases, the water for the matrix is provided by the aqueous phase of the aqueous solution of ammonium nitrate, and this aqueous phase thickened or gelled to provide compositions which can vary in consistency from pourable, pumpable semifluid solutions, slurries and dispersions to moldable, tough, plastic masses.

Preforming of a protective oil/fatty acid coating on the particles of metallic fuel is of particular benefit in thickened and particularly gelled compositions. Thickening and gelling agents which can be used in these compositions include tree exudates such as gum arabic, ghatti, karaya, and tragacanth; seaweed colloids such as 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 methyl cellulose, carboxymethylcellulose, sodium cellulose sulfate, methyl hydroxyethyl cellulose and sodium sulfocetyl cellulose; gelatin; casein; polyvinyl alcohol; polycryliclamides of high molecular weight and modified polycryliclamides of high molecular weight and modified polycryliclamides containing up to 5 mole percent carboxylic acid salt groups; high molecular weight polyethylene oxide; ("Carbowaxes"); exocellular heteropoly saccharides such as B-1459 made by fermenting starch-derived sugars, as well as mixtures of two or more of the above thickening and gelling agents.

Of these, galactomannans such as locust bean gum and guar gum, and particularly guar gum, are preferred because of their ready availability, their stability and their compatibility with aqueous solutions of inorganic oxidizing agents. Generally, about from 0.1 to 10% and preferably 0.5 to 5% of such thickening and gelling agents based on the total weight of composition are employed depending upon the particular agent selected and the consistency of explosive composition desired. When the gelling agent is a galactomannan, particularly guar gum, about from 0.25 to 2% of the galactomannan will be employed.

The provision of a continuous, preformed coating of oil and fatty acid on the particles of metallic fuel is of particular benefit in aqueous explosive compositions based on inorganic oxidizing salts and gelled by a galactomannan, since the provision of this coating has been shown to permit the formation of (1) consistently good gelled products in spite of the impure nature of the metallic fuel and (2) firmer gelled products with the same amount of gelling agent than are obtained when the particles of metallic fuel are not provided with a preformed coating and (3) equivalent firmness of gelled product when less gelling agent is used.

The galactomannan can be a self-complexing guar gum, e.g., EX-FC-50 and EX-FC-DP supplied by Steinel Hall Co. Or the guar gum can be a non-complexing guar gum such as Stein Hall's Jupiter 100 or Jupiter 10 in which no crosslinking agent is incorporated. When a non-complexing guar gum is used, small portions, e.g., 0.001-1% by weight of the total composition, of crosslinking agents, e.g., borax and potassium dichromate, for the thickening or gelling agents can be employed.

To impart fluidity to the water-bearing thickened or gelled explosive compositions, particularly at temperatures of lower than about -10° F., the composition can 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. Suitable fluidizing agents can be selected from at least one of the group consisting of compounds of the formula

$$\left[\left(\begin{array}{c} -\text{CH}_2 \\ -\text{O} \\ -\text{H} \\ -\text{N} \\ -\text{R} \\ -\text{H} \end{array}\right)\right]$$

wherein x plus y equals about 2 and R is oleyl; caprylamine; sodium alkylaryl polyether alcohol sulfonates such as the compound

$$\text{CH}_2\text{(CH}_3\text{)}_2\text{CH}_2\text{-O}-\text{CH}_2\text{-O}(\text{CH}_3\text{)}_2\text{-O}-\text{CH}_2\text{-OH}$$

in which x has an average value of about 20; stearyl dimethyl benzyl ammonium chloride; polyoxyethylated fatty alcohols; compounds of the formula

$$\left[\left(\begin{array}{c} -\text{CH}_3 \\ -\text{Cl} \\ -\text{H} \\ -\text{R}_1 \\ -\text{R}_2 \end{array}\right)\right]$$

wherein R1 and R2 are selected from the group consisting of 12 to 18 carbon atom alkyl radicals; dimethyl formamide; glycerol monooleate, 1-hydroxy-2-methoxy-4-allyl benzene; calcium cyanamid; formamide; dimethyl sulfoxide; ethylene carbonate; glycerol; acetonitrile; acetic acid; glycolic acid, methyl Cellosolve (i.e., ethylene glycol monomethyl ether); methanol; ethanol; formic acid; dihydric glycol; sodium acetate; hexamethylenetetramine; acrylonitrile; acetic acid; glycine, tetraethylsilicate; ammonium formate; acrylamide; N,N-dimethylacetamide; and dioxane. Of these fluidizing agents, methanol, formamide, dimethyl sulfoxide and methyl Cellosolve yield compositions having particularly unique, desirable low temperature properties. These fluidizing agents permit the formulation of compounds which are fluid, i.e.,
3,297,502 capable of being deformed continuously and permanently in any direction without rupture, and retain their desirable handling properties even at temperatures lower than about -10°F. These fluidizing agents and their use in water-bearing, thickened or gelled explosive compositions are discussed more completely in copending, common U.S. patent applications Serial No. 277,087, in the names of C. J. Breza, J. D. Chirris, and H. H. Fassnach, filed May 1, 1963, the teachings of which patent applications are incorporated in this application by reference.

In addition to the metallic fuels employed in the explosive compositions of this invention, various self-explosive fuels or non-explosive carbonaceous fuels or various combinations of mixtures of these types of fuels can also be present. The fuel or fuels used in the compositions of this invention can be varied widely provided that the fuel is stable, i.e., chemically inert with the system in which it is employed, during preparation and storage prior to detonation. “Self-explosive” fuels refer to a substance which by itself is generally recognized in the art as an explosive and which has a negative oxygen balance with respect to conversion to carbon dioxide, water, and nitrogen. Examples of self-explosive fuels include organic nitro compounds, nitrates and nitramines, such as TNT, dinitrotoluene, pentaerythritol tetranitrate (PETN), tetranitromethaniline (tetryl), cyclotrimethylenetraminitrime (RDX), cyclotetramethylenetetranitramine (HMX), nitrostarch, explosive-grade nitrocellulose, and mixtures of such explosives, e.g., pentolite (PETN/TNT), Composition B (RDX/TNT), and tetryl (tetryl/TNT). For economic reasons, TNT or in combination with other self-explosive fuels is preferred for use in the compositions of this invention. The TNT or its mixtures can be introduced into the compositions in the form of crystals, grains, pellets, flakes or any other particulate form which allows ready dispersion thereof. In general, up to 40% and, preferably, 10 to 35% by weight, based on weight of the composition, of self-explosive fuel is used.

Examples of nonexplosive, carbonaceous fuels which can be present include finely divided coal and other forms of finely divided carbon, solid carbonaceous vegetable products such as starch, 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 2 to 20% by weight of such carbonaceous fuels are used.

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 ferroalum, the oxygen balance is preferably between about -10 to +10%.

In the following additional detailed examples, parts and percentages are by weight unless otherwise indicated.

EXAMPLES 1 TO 6

The following Table 1 illustrates several types of aqueous explosive formulations in which particles of metallic fuel are provided with a preformed, continuous coating of oleic acid before their inclusion in the formulation. The general procedure used to prepare these formulations is carried out in a rotary mixer in the following sequence of steps;

(1) 65% ammonium nitrate solution, at 130–150°F, placed in a mixer; mixing started.

(2) TNT, formamide as fluidizing agent, and premixed coating composition of sodium nitrate and guar gum added. Contents of mixture agitated for 4 minutes.

(3) Add particles of aluminum and ferrophosphorus (if called for) which are provided with a preformed coating of oleic acid and “Corvus” oil in proportions of 1.67 pounds of oleic acid and 6.67 pounds of “Corvus” oil per 100 lbs. of metallic particles. Contents of mixer are agitated until all metal particles are incorporated in blend. (4) K$_2$Cr$_2$O$_7$, as a crosslinking agent, is added; and the blend is mixed one minute.

(5) Contents of mixer are discharged into a cartrigging machine from which it is extruded into polyethylene bags.

Table 1

<table>
<thead>
<tr>
<th>Examples</th>
<th>NH$_4$NO$_3$</th>
<th>H$_2$</th>
<th>NaNO$_3$</th>
<th>TNT</th>
<th>Precoated AI</th>
<th>FeP</th>
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<td>32.7</td>
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</tr>
<tr>
<td>5</td>
<td>27.5</td>
<td>14.7</td>
<td>32.0</td>
<td>32.0</td>
<td>15.0</td>
<td>3.0</td>
</tr>
<tr>
<td>6</td>
<td>27.5</td>
<td>14.7</td>
<td>32.0</td>
<td>32.0</td>
<td>15.0</td>
<td>3.0</td>
</tr>
</tbody>
</table>

The formulations of Table 1 also contain small proportions of Jaguar 100 guar gum crosslinked by a 5% solution of K$_2$Cr$_2$O$_7$, and small proportions (3% based on total weight of the composition) of formamide. Each of the formulations has an oxygen balance in the range of -30 to +10%.

The aluminum used in the above examples has an average particle size of about 30 mesh and is an alloy of about 90% of aluminum with minor amounts of manganese, iron, magnesium, silicon, copper, zinc and chromium, the amount varying from lot to lot.

All the compositions of Table 1 have a thickened, gelled consistency such that all the ingredients remain uniformly dispersed and show no evidence of "gassing", i.e., entrapment of gas bubbles, or swelling.

Evaluation of the compositions is made at 100°F, an elevated temperature that can exist both during transport of the compositions and in field storage. The test samples are kept at 100°F in tightly closed containers and are examined periodically for degradation as evidenced by visible segregation, "gassing" and swelling. All the test samples remain intact without those signs of degradation for a period of several weeks.

For comparative purposes, formulations are prepared that are substantially the same in composition as the formulations of Table 1 except that the metallic fuel particles are not protected, i.e., not provided with a coating of oleic acid and "Corvus" oil. These compositions tend to segregate with "gassing" and swelling and in many cases show no evidence of gelling in the as-made state. All of the samples show visible signs of deterioration, as judged by the foregoing criteria after one to two days in the 100°F, storage stability test.

Similar results are obtained when No. 2 fuel oil is substituted for the "Corvus" oil and when commercially available tall oils are substituted for the oleic acid, each on an equimolar basis, in performing the continuous coating on the particles of aluminum and ferrophosphorus.

EXAMPLES 7–9

A premixed sol is prepared comprising:

<table>
<thead>
<tr>
<th>Parts</th>
<th>80% ammonium nitrate solution</th>
<th>78.9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>4.2</td>
<td></td>
</tr>
<tr>
<td>Sodium nitrate</td>
<td>16.0</td>
<td></td>
</tr>
<tr>
<td>Jaguar 100 guar gum</td>
<td>0.9</td>
<td></td>
</tr>
</tbody>
</table>

Particles of aluminum similar to that described in the preceding example are provided with a preformed condition of sodium nitrate-80% "Corvus" oil and 20% oleic acid. (8.34 parts coating consisting of 6.67 parts "Corvus" oil and 1.67 parts oleic acid is used to coat 100 parts of aluminum.)
Formulations of the compositions indicated in Table II below are prepared in a slurry truck adapted to mix components of an explosive formulation in the field.

Table II

<table>
<thead>
<tr>
<th>Examples</th>
<th>Premixed</th>
<th>Pelletol</th>
<th>Precocated</th>
<th>Aluminum</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Scoria</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>75.0</td>
<td>20.0</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>70.0</td>
<td>20.0</td>
<td>10.0</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>65.0</td>
<td>20.0</td>
<td>15.0</td>
<td></td>
</tr>
</tbody>
</table>

A small proportion of K$_2$Cr$_2$O$_7$, as crosslinking agent, is added to each formulation near the end of the mixing cycle.

All of the formulations form well-crosslinked gels which can be pumped from the slurry truck into the borehole, even at elevated temperatures. When compositions are prepared of the same formulation except that the mentioned aluminum and 5 parts ferrophosphor are not provided with the preformed continuous coating of “Corvus” oil and oleic acid, most of the formulations show evidence of no or only weak crosslinking of the guar gum to thicken and gel the composition, accordingly the formulations segregate, particularly at temperatures above 80° F.

EXAMPLE 10

In a rotating mixer 15 parts of aluminum, similar to that described in Examples 1 to 6, and 5 parts ferrophosphor are brought into contact with 1.25 parts of a mixture comprised of 20% oleic acid and 80% “Corvus” oil. The blend is agitated for 30 seconds to provide a continuous coating of oleic acid and “Corvus” oil on the metallic particles. The agitation is continued while 20 parts of pelleted TNT are added. The contents of the mixer are then agitated for 15 seconds and then there are added 42 parts of 65% ammonium nitrate solution, heated to 180° F. Agitation is continued fifteen seconds before adding 17 parts sodium nitrate premixed with a mixture of 0.7 part of commercial self-complexing guar gum. The contents of the mixer are then stirred an additional three minutes to obtain a substantially homogeneous mixture which is then extruded into 3-inch diameter polyethylene bags which are aged for one day at ambient room temperature. Representative bags are placed in storage at controlled low temperature and at controlled high temperature for designated periods of time after which the composition is tested as described below. The composition as-made is a thick but pourable gel which shows no separation of solids.

For comparison purposes, a composition is prepared by the following series of steps. In a rotating mixer, about 21 parts of a 65% ammonium nitrate solution heated to 180° F. is combined with 15 parts of the aforementioned aluminum and 5 parts ferrophosphor with continuous agitation. Subsequently a mixture comprising 0.25 part of oleic acid and 1.00 part of “Corvus” oil is added to the contents of the mixer, followed by the addition of an additional 21 parts of the ammonium nitrate solution. The mixture is agitated for 10 seconds. TNT (20 parts) is then added, and the blend mixed for 30 seconds. After this, premixed commercial, self-complexing guar gum (0.7 part), 17 parts sodium nitrate and 3.0 parts formamide are stirred into the mixture. The mixture is then stirred for 3 minutes to obtain a substantially homogeneous composition. This composition is then packaged and placed in storage as is the composition containing metallic fuel particles provided with a preformed continuous coating of oleic acid and “Corvus” oil.

For further comparison, a control composition is formulated containing the same proportions of ingredients except that no “Corvus” oil or oleic acid are included in the formulation.

It is noted both of the latter two formulations in which the metallic fuel particles are not provided with a preformed, continuous coating of oleic acid and “Corvus” oil tend to have, in the as-made state, a thin, runny, consistency from which solids tend to segregate. These formulations are also placed into 3-inch diameter bags for one day at ambient room temperature. Representative bags are also placed in storage at controlled low and high temperatures as are the formulations having a preformed coating of oleic acid and “Corvus” oil on the metallic fuel particles.

After the formulations have aged a few hours, the formulations in which the metallic fuel particles have a preformed coating of oleic acid and “Corvus” oil show evidence of extensive crosslinking, this crosslinking beginning soon after the formulations are bagged. These compositions have a high surface tension, a high water resistance and can be easily “shucked,” i.e., removed from the bag without parts thereof on the composition by the bag. The compositions show significant resistance to rupture or tearing when deformed and are non-tacky. In the comparative formulations in which the particles of metallic fuel are not provided with a preformed coating of oleic acid and “Corvus” oil, there is no crosslinking at best, insufficient crosslinking may occur. In the latter case the product is stringy, tacky, and has a low surface tension. The formulation is non-elastic, i.e., ruptures or tears when deformed. Part of the formulation remains in the bag when attempts are made to “shuck” the composition.

In order to evaluate the stability of the formulations at elevated temperature, samples of each type formulation are placed in a chamber maintained at 100° F. This is representative of moderately high temperatures which can be encountered in field storage magazines or a service truck, i.e., a slurry truck. The formulations stored at 100° F are inspected at 24-hour intervals for evidence of deterioration such as softening and slumping of the gel structure, visible segregation of liquid or of insoluble high density components (TNT), foaming, and development of tackiness and stickiness which were originally good gels. Formulations in which the aluminum particles are precoated by oleic acid and “Corvus” oil do not break down in several weeks of storage. In the comparative compositions in which the oleic acid/“Corvus” oil are incorporated into the formulation during the mixing and which contain no oleic acid or “Corvus” oil show evidence of deterioration in a few days storage at 100° F.

The formulations described above are also stored at -10, -15, and -20° F. The compositions containing metallic fuel particles which had been provided with the preformed coating of oleic acid and “Corvus” oil deform when squeezed by hand without fracture, i.e., rupture or tearing, and remain soft at temperatures down to -20° F. The formulations made for comparative purposes become rigid and hard at about 0° F, and are not subject to deformation without fracture under hand pressure at each of such low temperatures at which they are stored.

EXAMPLE 11

Formulations are prepared as in Example 10 except in this case the metallic fuel particles are provided with a preformed coating consisting of 0.25 part stearic acid and 1.00 part “Corvus” oil. The compositions contain 0.8 part of self-complexing guar gum. No antifreeze (antifreezing) agent is provided. The formulation is uniform, non-tacky gel in the as-made state. The viscosity and strength of the gel composition increases appreciably during the first hour after being bagged, showing that
crosslinking is continuing. The mixture is uniform in appearance and composition and undissolved components remain uniformly dispersed without signs of deterioration or gassing even when the formulations are stored at 100° F. for several weeks. The formulation can be easily shucked from the polyethylene bag. In storage at --10° F. the composition remains soft and pliable and can be deformed by hand without rupture.

The practical significance of the stability of the compositions of this invention as compared to conventional crosslinked gels and as illustrated above is easily appreciated. Crosslinked, gelled, water-bearing blasting explosive compositions have a high degree of utility in the field. Sometimes these are stripped from the containers and loaded directly into the borehole. Such a “shucking” operation is practicable only if the composition retains its original non-tacky characteristics. Even when freed from the container, the crosslinked compositions should retain a high degree of resistance to disintegration and leaching by water which may be present or may enter the borehole after the blasting composition is loaded therein. Disintegration and leaching, if they do occur, may lead to failure of the compositions to explode or failures of propagation of a column of explosive through a section which has been exposed to water. The crosslinking compositions in which a preformed continuous coating of oil and fatty acid is provided on the metallic fuel particles are remarkably free from failures of this kind. Finally, if the gel structure deteriorates, segregation of components, especially undissolved fuels and oxidizing agents, can take place under the force of gravity, and compositions whether still in the cartridge, or “shucked” therefrom, will become so heterogeneous that complete failures of detonation or failures to propagate detonation through the full length of the charge column will occur. The instant inventive process and the blasting agent compositions produced thereby minimize and essentially overcome the deficiencies of heretofore known crosslinked gelled blasting agent compositions.

What is claimed is:

1. Aqueous explosive compositions comprising water, inorganic oxidizing salt, and metallic fuel particles, said particles having a continuous, preformed coating composed of about from 10 to 90% by weight of a normally liquid oil having a viscosity of from 30 to 400 Saybolt Universal seconds at 100° F. and about from 90 to 10% by weight of monocarboxylic aliphatic acid containing about from 8 to 22 carbon atoms.

2. A composition of claim 1 wherein said metallic fuel is particulate light metal coated with a mixture of fatty acid and said oil.

3. A composition of claim 2 wherein said composition is gelled with crosslinked polysaccharide.

4. A composition of claim 3 wherein said metallic fuel is particulate aluminum.

5. A composition of claim 4 wherein said particulate aluminum is coated with a continuous preformed coating of about from 70 to 85% of said normally liquid oil and about 15 to 30% of 16 to 22 carbon atom fatty acid.

6. A stable, gelled, water-bearing explosive composition having an oxygen balance of about from -30 to +10% comprising, based on the total weight of composition:

(a) at least 20% of inorganic oxidizing salt at least 65% which is ammonium nitrate and 0 to 35% of which is sodium nitrate;
(b) about from 1 to 30% of particulate metallic fuel consisting essentially of aluminum;
(c) about from 10 to 30% of water; and
(d) about from 0.25 to 2% of gelled galactomannan gum,

the particles of metallic fuel being coated with about from 1 to 10%, based on the weight of said fuel of a continuous preformed coating composed of about from 10 to 90% by weight of a normally liquid oil having a viscosity of about from 30 to 400 Saybolt Universal seconds at 100° F. and about from 90 to 10% by weight of 8 to 22 carbon atom fatty acid.

7. A composition of claim 6 wherein said metallic fuel includes particulate ferrophosphorus.

8. A composition of claim 6 additionally containing from about 10 to 35% of trinitrotoluene.

9. A composition of claim 6 additionally containing from about 2 to 20% of nonexplosive carbonaceous fuel.

10. A composition of claim 6 wherein said fatty acid is oleic acid.

11. A composition of claim 6 wherein said fatty acid is stearic acid.

12. A composition of claim 6 wherein said fatty acid is tall oil.

13. In the process for preparing aqueous explosive compositions which comprises blending inorganic oxidizing salt, particulate metallic fuel and water, the improvement which comprises precoating the particles of said metallic fuel with about from 1 to 10% by weight thereof of a continuous coating of about from 10 to 90% by weight of a normally liquid oil having a viscosity of about from 30 to 400 Saybolt Universal seconds at 100° F. and about from 90 to 10% by weight of 8 to 22 carbon atom fatty acid.

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L. DEWAYNE RUTLEDGE, Primary Examiner.
S. J. LECHERT, Jr., Assistant Examiner.