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# [54] AQUEOUS SLURRY EXPLOSIVES HAVING IMPROVED OXIDIZER-FUEL SYSTEM AND METHOD OF MAKING

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[57] **ABSTRACT**

Aqueous slurry-type inorganic oxidizer salt explosive containing a defined nitrate salt fuel-oxidizer system imparting unpredicted low-aqueous aqueous solution precipitation temperatures, which, in turn, provide for improved sensitivity, detonation rate, available energy and fluid properties at temperatures as low as −60° C. and lower.

Method for manufacture of the explosives under ambient temperature conditions utilizing two separate solutions each having a crystallization temperature below the ambient temperature, is provided, thus eliminating need for elevated mixing, and solution, temperatures utilized heretofore.

**23 Claims, No Drawings**

# AQUEOUS SLURRY EXPLOSIVES HAVING IMPROVED OXIDIZER-FUEL SYSTEM AND METHOD OF MAKING

This invention relates to inorganic oxidizer salt explosives of the aqueous slurry type containing an improved oxidizer-fuel system. In one aspect this invention relates to such explosives having high energy, sensitivity, fluidity and detonation rate properties at unexpectedly low temperature levels. Other aspects will be apparent in light of the accompanying disclosure and the appended claims.

Inorganic oxidizer salt explosives of the aqueous slurry type have had extensive use in the explosive industry in recent years. These explosives comprise an inorganic oxidizer salt, water, a fuel, a separate sensitizer if needed, and a thickener. They are generally gelled by the presence of a gelatin agent, as a thickener, often cross-linked by a suitable cross-linking agent incorporated into the formulation.

Exemplary ingredients of such slurry type explosives are flaked aluminum, smokeless powder, self-explosives such as TNT, PETN, and the like, as sensitizers; ethylene glycol, hydrocarbon oils, powdered coal, particulate aluminum, particulate silicon, and the like as fuels; guar gum, hydroxyethyl cellulose, acrylic type polymers, and the like, as gel-forming agents; and ammonium nitrate alone or with one or more other inorganic oxidizer salts, exemplary of which are alkali, and alkaline earth, metal nitrates and perchlorates. Although generally insensitive to detonating action of a No. 8 commercial blasting cap, these explosives are detonatable by conventional "booster" charges such as PETN (pentaerythritol tetranitrate), RDX (cyclotrimethylene trinitramine), Pentolite (PETN–TNT, 50/50), tetryl, Composition B (RDX-TNT, 60/40), and the like.

Although sensitivity of the above explosives is suitably regulated over a broad range at ambient temperatures, say of from 50° to 80° F., and higher, sensitivity at lower temperatures has been impaired by precipitation of significant proportions of the oxidizer salt from the aqueous solution phase to form a separate crystalline mass, to thus deplete the solution phase of its salt content with accompanying impairment of sensitivity, fluidity, detonation rate and energy properties of the explosive, particularly at temperatures near the freezing point of water and lower.

By way of example, an aqueous slurry explosive at 60° F., containing on a weight basis about 67 percent ammonium nitrate/sodium nitrate inorganic oxidizer salt, about 17 percent water, about 15 percent particulate aluminum, and about 1 percent guar gum as a gelation agent in cross-linked form, has an inorganic oxidizer salt content in the aqueous solution phase of about 69 percent and is readily detonatable by action of a 20-gram PETN-booster charge. On the other hand, at the same diameter but at a lower detonating temperature, say 20° F., the precipitation of oxidizing salt, of the same explosive, is so extensive that about only 59 percent inorganic oxidizer salt remains in the solution phase, and the explosive, at that temperature level, is insensitive to detonating action of 500-gram PETN booster charge; and, of course, associated properties of fluidity, available energy, and detonation rate are correspondingly impaired at the lower temperature.

This invention is concerned with inorganic oxidizer salt explosives of the aqueous slurry type containing a combination of nitrate salts as an improved oxidizer-fuel system imparting unpredicted low solution precipitation temperatures thereto, which in turn provides for improved sensitivity, detonation rate, available energy and fluid properties at temperatures as low as −40° F. and lower.

In accordance with the invention, inorganic oxidizer salt explosives of the aqueous slurry type are provided, which, on a weight basis, contain from 12 to 30 percent water and as a nitrate salt oxidizer-fuel system from 18 to 70 percent of a Group II (Periodic System) metal nitrate oxidizer component selected from the group consisting of calcium nitrate, strontium nitrate, cadmium nitrate, a mixture of any of said nitrates, and magnesium nitrate together with at least one of said calcium, strontium and cadmium nitrates in a weight ratio thereto not exceeding about 1:1, in combination with from 10 to 60 percent of an amine nitrate fuel component selected from the group consisting of lower alkyl amine nitrates containing from 1 to 8 alkyl carbon atoms, alkanol amine nitrates containing from 2 to 9 alkanol carbon atoms and hexamethylene tetramine nitrate (HMTN).

The oxidizer-fuel system of the explosive compositions of the invention often constitutes substantially the sole fuel-oxidizer salt content, although one or more suitable supplementary oxidizer salts and/or fuels, are often utilized. Exemplary supplemental fuels include hydrocarbon oils, aluminum, silicon, iron-silicon alloys, ground coal, ethylene glycol and the like; and exemplary supplemental oxidizer salts include ammonium nitrate, ammonium nitrate-sodium nitrate mixtures, ammonium perchlorate, sodium perchlorate and the like.

Exemplary amine nitrates of the oxidizer-fuel system of the invention include monomethylamine nitrate, dimethylamine nitrate, trimethylamine nitrate, monoethylamine nitrate, diethylamine nitrate, triethylamine nitrate, monopropylamine nitrate, dipropylamine nitrate, monooctylamine nitrate, monoethanolamine nitrate, diethanolamine nitrate, triethanolamine nitrate, monopropanolamine nitrate, dipropanolamine nitrate, tripropanolamine nitrate, hexamethylenetetramine nitrate and any combination of such nitrates. Now preferred amine nitrate fuels, in practice of the invention are alkylamine nitrates containing from 1 to 3 alkyl carbon atoms and alkanolamine nitrates containing from 2 to 3 alkanol carbon atoms.

Generally the amount of any supplemental inorganic oxidizer salt, or supplemental fuel, utilized, is any suitable proportion up to about 40 percent, and 30 percent, respectively, based on the weight of the finished explosive.

Any suitable supplementary explosive sensitizer can be utilized such as a particulate aluminum, DNT oil, TNT, smokeless powder, and the like, often advantageously in combination with one or more fuels such as above described. The amount of any supplemental sensitizer utilized is any suitable proportion generally up to about 30 weight percent of the finished explosive.

Although any suitable material can be utilized as a thickener component, a highly purified guar gum in cross-linked form is now preferred. Further exemplary of other suitable, and often utilized thickener materials are hydroxyethyl cellulose, generally in cross-linked form, and acrylic-type thickeners as for example an acrylamide-alkali metal acrylate copolymer. The proportion of any thickener utilized is generally any suitable thickening amount up to about 5 weight percent of the finished explosive; from about 0.5 to 2.5 weight percent more often being utilized.

In preferred practice, density of the explosive compositions of the invention is generally not greater than about 1.40 grams/cc., although higher densities can be utilized when desired. Although density of the explosive compositions may often be at a suitable level due to inherent aeration during mixing, it is generally preferred to regulate the density to a desired predetermined level by the action of a suitable aeration agent in the formulation.

Now preferred compositions of the invention comprise (weight basis) from 20 to 60 percent of the amine nitrate fuel, generally mono-, di- or trimethylamine nitrate, in combination with from 25 to 70 percent of the Group II metal nitrate oxidizer, generally calcium nitrate in at least major proportion; from 12 to 25 percent water; from 0 to 10 percent of one or more carbonaceous supplemental fuels such as ethylene glycol, powdered coal, a hydrocarbon oil, and the like; from 0 to 30 percent of one or more particulate metal energizer and/or sensitizer ingredients, often aluminum, silicon, silicon alloys, and the like; and a thickening amount of a suitable gelation agent, generally in cross-linked form. Often from 5 to 40, generally from 10 to 35 percent of a supplemental oxidizer salt is utilized, preferably ammonium nitrate alone or in major proportion with another supplementary oxidizer salt, often sodium nitrate.

Further exemplary of metal nitrate oxidizer amine nitrate fuel systems of the invention are those of the following tabulation, each of which can be incorporated as aqueous solution phase with the remaining ingredients required for the finished explosive.

TABLE 1

| Metal Nitrate | Supplemental Inorganic Oxidizer Salt | Amine Nitrate |
|---|---|---|
| $Ca(NO_3)_2$ | | $CH_3NH_3NO_3$ |
| $Ca(NO_3)_2$ | | $(CH_3)_2NH_2NO_3$ |
| $Ca(NO_3)_2$ | | $(CH_3)_3NHNO_3$ |
| $Ca(NO_3)_2$ | | Mixed methylamine nitrates |
| $Ca(NO_3)_2$ | $NH_4NO_3$ | $CH_3NH_3NO_3$ |
| $Ca(NO_3)_2$ | $NaNO_3$ | $CH_3NH_3NO_3$ |
| $Ca(NO_2)_2$ | $NH_4NO_3$ | $(CH_3)_2NH_2NO_3$ |
| $Ca(NO_3)_2$ | | ($C_2$-$C_8$ alkylamine) nitrate |
| $Ca(NO_3)_2$ | $NH_4NO_3$ | ($C_2$-$C_8$ alkylamine) nitrate |
| $Ca(NO_3)_2$<br>$Mg(NO_3)_2$ | | $CH_3NH_3NO_3$ |
| $Ca(NO_3)_2$<br>$Mg(NO_3)_2$ | $NH_4NO_3$ | $CH_3NH_3NO_3$ |
| $Ca(NO_3)_2$<br>$Mg(NO_3)_2$ | | ($C_1$-$C_8$ alkylamine) nitrates |
| $Ca(NO_3)_2$<br>$Mg(NO_3)_2$ | $NH_4NO_3$ | ($C_1$-$C_8$ alkylamine) nitrates |
| $Sr(NO_3)_2$ | | $CH_3NH_3NO_3$ |

This invention is based on the further discovery that when the proportion of Group II metal nitrate, of the oxidizer-fuel system of the invention is above a certain minimum, the aqueous solution phase undergoes glass formation at low temperatures sufficiently to form a glass which is stable to ingredient separation at temperatures below the freezing point of water and as low as −60° C. and lower. For example, when the fuel-oxidizer system is calcium nitrate and monomethylamine nitrate, glassing takes place at a calcium nitrate content (based on the aqueous solution phase) in the order of 30 to 40 percent, and higher. By way of further example, when the aqueous solution phase contains, on a weight basis, from 45 to 55 percent of the metal nitrate oxidizer in combination with from about 25 to 45 percent of monomethylamine nitrate, glassing is obtained throughout a temperature range extending to as low as −60° C., and in some instances lower.

The invention is based on the still further discovery that the composition of a suitably oxygen balanced aqueous solution of oxidizer-fuel system of the invention approximates that of the eutectic mixture of the ingredients thereof, i.e., the particular ingredients of the aqueous solution, at a given water content, require substantially the lowest of the possible temperatures for precipitation of any mixture of those ingredients; and hence the concentrations of those ingredients most satisfactory for their function as a fuel-oxidizer system also provide substantially for glassing, i.e., nonprecipitation, of those salt ingredients at their maximum low temperature capability generally from 50 to 100° C. below the precipitation temperatures predicted from a phase study of the nonglassing mixtures of these ingredients.

Although I have noted that the above described glass formation occurs at oxidizer metal nitrate solution concentrations generally not less than 30 percent, I have found that when higher molecular weight amine nitrate fuels are utilized, it is necessary in most instances that the minimum oxidizer metal nitrate concentration in the solution be greater in order that a suitable oxygen balance be maintained for the finished explosive. For example, when the alkyl amine nitrate ingredient is dimethylamine nitrate, and calcium nitrate is the oxidizer metal nitrate salt, the concentration of calcium nitrate in the solution phase is generally at least about 45 percent, and greater when still higher molecular weight alkyl amine nitrates are utilized.

In a series of tests, several solution phase components for explosive compositions of the invention were prepared and crystallization and glass temperatures were observed. The solution in each case consisted of calcium nitrate, monomethylamine nitrate (MAN) and water. Each temperature shown is that at which crystallization, or glassing, was initially observed; hence fluidity, or glass stability, of the solution was in each case retainable to still lower temperature levels. The results of the tests are summarized in Table 2 following.

TABLE 2

| | Weight percent | | | | |
|---|---|---|---|---|---|
| Test No. | Calcium nitrate | MAN | Water | Temp. °C. | Remarks |
| 1 | 20.0 | 50.0 | 30.0 | −7 | Normal crystallization. |
| 2 | 20.0 | 55.0 | 25.0 | 1 | |
| 3 | 20.0 | 60.0 | 20.0 | 16 | |
| 4 | 30.0 | 40.0 | 30.0 | −20 | |
| 5 | 30.0 | 45.0 | 25.0 | −8 | |
| 6 | 30.0 | 50.0 | 20.0 | 5 | |
| 7 | 30.0 | 55.0 | 15.0 | 17 | |
| 8 | 40.0 | 30.0 | 30.0 | −22 | Nonprecipitating glass formation. |
| 9 | 40.0 | 45.0 | 15.0 | −8 | |
| 10 | 50.0 | 30.0 | 20.0 | 8 | |
| 11 | 50.0 | 35.0 | 15.0 | 15 | |

As shown in the above tabulation, at those calcium nitrate concentrations shown below 40 percent (based on the solution component) normal crystallization took place at temperatures of from 17° to −20° C., and at the higher calcium nitrate concentrations, nonprecipitating glass formation was initially observed. The glasses thus formed, are stable at temperatures markedly lower than those at which they are initially formed to thereby preclude precipitation of the salt-fuel system at temperatures as low as −60° C., and in some instances lower.

A series of tests similar to those summarized in Table 2 was conducted except that the amine nitrate was dimethylamine nitrate (DMAN). The results of the tests are summarized in Table 3 following.

TABLE 3

| | Weight percent | | | | |
|---|---|---|---|---|---|
| Test No. | Calcium nitrate | DMAN | Water | Initial crystallization, or glass, temp. °c. | Remarks |
| 1 | 20.0 | 50.0 | 30.0 | −45 | Normal Crystallization |
| 2 | 20.0 | 55.0 | 25.0 | −30 | |
| 3 | 20.0 | 60.0 | 20.0 | −21 | |
| 4 | 30.0 | 40.0 | 30.0 | — | Formed nonprecipitating glass (initial temperature not recorded) |
| 5 | 30.0 | 45.0 | 25.0 | — | |
| 6 | 30.0 | 50.0 | 20.0 | — | |
| 7 | 30.0 | 55.0 | 15.0 | — | |
| 8 | 30.0 | 60.0 | 10.0 | — | |
| 9 | 40.0 | 35.0 | 25.0 | — | |
| 10 | 40.0 | 40.0 | 20.0 | — | |
| 11 | 40.0 | 45.0 | 15.0 | — | |
| 12 | 40.0 | 50.0 | 10.0 | — | |
| 13 | 50.0 | 20.0 | 30.0 | 8° | Formed nonprecipitating glass |
| 14 | 50.0 | 25.0 | 25.0 | 22° | |
| 15 | 50.0 | 30.0 | 20.0 | 35° | |
| 16 | 50.0 | 35.0 | 15.0 | 45° | |
| 17 | 50.0 | 40.0 | 10.0 | 60° | |

The data of Table 3 demonstrate low initial crystallization temperatures at calcium nitrate concentration of 20 percent; and nonprecipitating glass formation at calcium nitrate contents of 30 percent and higher when the water content is 10 to 30 percent.

A solution phase for each of four explosive compositions of the invention, containing calcium nitrate in proportions greater than 50 percent, and diethylamine nitrate (DEAN) in proportions in excess of 20 percent was prepared and observed for glass formation at various low temperature levels. The weight of each solution was 25 grams. The results are set forth in Table 4 following.

TABLE 4

| Weight percent | | | Glass formation, temp., ° C. | | |
|---|---|---|---|---|---|
| Calcium nitrate | DEAN | Water | Initial formation (some thickening) | Viscous, pourable | Solid* |
| 61.7 | 23.3 | 15.00 | 75 | 45 | −5 |
| 50.3 | 24.7 | 25.00 | 35 | 5 | −45 |
| 53.6 | 26.4 | 20.00 | 60 | 30 | −25 |
| 57.0 | 28.0 | 15.00 | 80 | 50 | −10 |

*An immovable glass devoid of the presence of crystalline material.

The above data show the formation of glass, in each test, stable at temperatures at least as low as −45° C.

In a series of tests similar to those of Table 4, a solution phase for each of five explosive compositions of the invention containing in excess of 50 percent calcium nitrate and at least 20 percent isobutylamine nitrate (IBAN) was prepared and observed for glass formation at various temperature levels. The weight of each solution tested was 25 grams. The results are set forth in Table 5 following.

TABLE 5

| Weight percent | | | Glass formation, temp., ° C. | | |
|---|---|---|---|---|---|
| Calcium nitrate | DEAN | Water | Initial formation (some thickening) | Viscous, pourable | Solid* |
| 54.4 | 20.5 | 25.0 | 40 | 17 | −35 |
| 61.6 | 23.3 | 15.0 | 85 | 40 | −5 |
| 50.2 | 24.7 | 25.0 | 35 | −3 | −40 |
| 53.6 | 26.4 | 20.0 | 55 | 25 | −25 |
| 56.7 | 28.0 | 15.0 | 80 | 35 | −10 |

*An immovable glass devoid of the presence of crystalline material.

The above data show the formation of glass, in each test, stable at temperatures at least as low as −40° C.

In a series of tests similar to those of Table 5, a solution phase for each of three explosive compositions of the invention containing at least 45 percent calcium nitrate and at least 29 percent monoethanolamine nitrate (MEOAN) was prepared and observed for glass formation at various temperatures. The weight of each solution was 25 grams. The results are set forth in Table 6.

TABLE 6

| | Weight percent | | | Glass formation, temp., ° C. | | |
|---|---|---|---|---|---|---|
| Test No. | Calcium nitrate | MEOAN | Water | Initial formation (some thickening) | Viscous, pourable | Solid* |
| 1 | 45.20 | 29.80 | 25.00 | 15 | −10 | −60 |
| 2 | 48.25 | 31.75 | 20.00 | 20 | −5 | −50 |
| 3 | 51.30 | 33.70 | 15.00 | 50 | +10 | −25 |

*An immovable glass devoid of the presence of crystalline material.

The above data show the formation of glass, in each test, stable at temperatures at least as low as −60° C.

In a series of tests similar to those summarized in Tables 5 and 6 solution phases, for four explosive compositions of the invention, containing 55 to 65 percent calcium nitrate and from 10 to 25 percent hexamethylenetetramine nitrate were observed for glass formation. The weight of each solution was 50 grams. The results are tabulated as follows.

TABLE 7

| | Weight percent | | | Glass formation, temp., ° C. | |
|---|---|---|---|---|---|
| Test No. | Calcium nitrate | HMTAN | $H_2O$ | Initial formation (some thickening) | Solid* |
| 1 | 65.0 | 10.0 | 25.0 | 70 | −10 |
| 2 | 65.0 | 15.0 | 20.0 | 85 | 15 |
| 3 | 65.0 | 20.0 | 15.0 | 115 | 40 |
| 4 | 55.0 | 25.0 | 20.0 | 90 | 0 |

*An immovable glass devoid of the presence of crystalline material.

The above data show the formation of glass initially at temperatures in the order of 70° to 115° C. at concentrations of HMTAN in the order of from 10 to 25 percent and solid glass formation at temperatures of from −10° to 40° C. Each of the glasses formed is, however, stable at temperatures as low as −40° F. and lower. The tabulation demonstrates glass formation utilizing HMTAN as an amine nitrate fuel component in accordance with the invention albeit temperatures in excess of 40° C., and somewhat higher, are often required for pumping the resulting formulation to emplacement where final glass formation takes place, and hence nonprecipitation, at temperatures substantially below the borehole temperature.

In another series of tests similar to those of Table 7 solution phases for each of a series of explosive compositions of the invention containing calcium nitrate in proportions in excess of 50 percent together with various amine nitrates containing 3–8 carbon atoms were prepared for observation of glassing temperatures. The weight of each solution was 25 grams. The results of the test are tabulated as follows.

TABLE 8

| Weight percent | | | Glassing temperature, ° C. | | |
|---|---|---|---|---|---|
| Calcium Nitrate | Amine nitrate | Water | Thickens | Pourable | Solid* |
| 51.1 | 23.8 (mono n-propylamine nitrate) | 25.0 | 35 | 10 | −40 |
| 54.6 | 25.4 (mono n-propylamine nitrate) | 20.0 | 55 | 15 | −25 |
| 58.0 | 26.9 (mono n-propylamine nitrate) | 15.0 | 70 | 30 | −10 |
| 54.4 | 20.5 (diethylamine nitrate) | 25.0 | 35 | 10 | −40 |
| 58.0 | 21.9 (diethylamine nitrate) | 20.0 | 55 | 25 | −20 |
| 54.4 | 20.6 (monoisobutylamine nitrate) | 25.0 | 40 | 17 | −35 |
| 58.0 | 22.0 (monoisobutylamine nitrate) | 20.0 | 60 | 30 | −15 |
| 61.6 | 23.3 (monoisobutylamine nitrate) | 15.0 | 85 | 40 | −5 |
| 57.9 | 17.1 (triethylamine nitrate) | 25.0 | 45 | 16 | −25 |
| 61.8 | 18.2 (triethylamine nitrate) | 20.0 | 70 | 30 | −5 |
| 65.7 | 19.3 (triethylamine nitrate) | 15.0 | 100 | 70 | 15 |
| 60.0 | 15.0 (di-n-propylamine nitrate) | 25.0 | 60 | 19 | −30 |
| 64.0 | 16.0 (di-n-propylamine nitrate) | 20.0 | 75 | 29 | −15 |
| 68.0 | 17.0 (di-n-propylamine nitrate) | 15.0 | 85 | 40 | −5 |
| 59.8 | 15.2 (tert-octylamine nitrate) ** | 25.0 | 65 | ---------- | −20 |
| 63.8 | 16.2 (tert-octylamine nitrate) ** | 20.0 | 85 | 48 | 0 |
| 67.8 | 17.2 (tert-octylamine nitrate) ** | 15.0 | 100 | 85 | 15 |

*An immovable glass devoid of the presence of crystalline material.

**In each of these tests (calcium nitrate-tert-octylamine nitrate) some precipitation was noted during, and after, cooling and glass formation.

In a series of tests similar to those of Table 8, solution phases, for a series of explosive compositions of the invention, containing cadmium nitrate-DMAN and strontium nitrate-MAN, fuel-oxidizer systems were prepared and observed for glassing at various temperature levels. Similar tests utilizing barium nitrate-MAN as a fuel-oxidizer system were also conducted. The results of these tests are set forth in the following table.

TABLE 9

| Weight Percent | | | Glassing ° C. | | |
|---|---|---|---|---|---|
| $Cd(NO_3)_2$ | DMAN | Water | Thickens | Pourable | Solid* |
| 50 | 30 | 20 | 15 | −28 | −70 |
| 40 | 40 | 20 | 10 | −39 | −76 |
| 30 | 50 | 20 | −10 | −50 | −71 |

| | | | | | |
|---|---|---|---|---|---|
| $Sr(NO_3)_2$ | MAN | | | | |
| 35.4 | 39.5 | 25 | −23 | — | — |
| 37.8 | 42.2 | 20 | −26 | — | — |
| 40.2 | 44.8 | 15 | −15 | — | — |
| $Ba(NO_3)_2$ | | | | | |
| 39.5 | 35.5 | 25 | —** | | |
| 42.1 | 37.8 | 20 | —** | | |
| 44.7 | 40.2 | 15 | —** | | |

*An immovable glass devoid of the presence of crystalline material.

**Separate $Ba(NO_3)_2$ solid salt phase at 100° C.

The above data show the formation of glass in each of the tests for cadmium nitrate at least as low as −76° C. and for the strontium nitrate solutions at temperatures as low as −26° C.; and demonstrate inoperability of barium nitrate as a metal salt oxidizer component of the invention.

In a series of tests similar to those summarized in the foregoing tables, solution phases for each of either explosive compositions of the invention, containing calcium nitrate in proportions in excess of 45 percent together with amine nitrate mixtures of monomethylamine nitrate (MAN) with each of isobutylamine nitrate (IBAN) and diethylamine nitrate (DMAN) in a proportion exceeding 25 percent and were observed for glass formation temperature levels. The weight of each solution was 25 grams. The results are tabulated as follows.

TABLE 10

| Weight percent | | | | | Glass formation, Temp., ° C. | | |
|---|---|---|---|---|---|---|---|
| Calcium nitrate | MAN | IBAN | DMAN | Water | Initial formation (some thickening) | Pourable | Solid* |
| 48.8 | 10.6 | 15.6 | | 25.0 | 25 | 0 | −45 |
| 55.3 | 12.1 | 17.6 | | 15.0 | 85 | 55 | −15 |
| 47.4 | 11.3 | 16.3 | | 25.0 | 35 | 0 | −45 |
| 50.6 | 12.0 | 17.4 | | 20.0 | 60 | 34 | −25 |
| 53.7 | 12.8 | 18.5 | | 15.0 | 75 | 40 | −5 |
| 48.8 | 10.6 | | 15.6 | 25.0 | 38 | 0 | −45 |
| 52.0 | 11.4 | | 16.6 | 20.0 | 65 | 15 | −30 |
| 55.3 | 12.1 | | 17.6 | 15.0 | 80 | 35 | −10 |

*An immovable glass devoid of the presence of crystalline material.

Each of the metal salt oxidizer-amine nitrate salt solution phases of the invention illustrated in the foregoing Tables 4–10 showed no tendency to crystallize after standing several hours at the solid glass temperature (except for some crystallization noted at Table 8); and each was suitably balanced for use as a solution phase of an explosive composition of the invention.

The compositions of the invention containing a solution component, as above illustrated, can be handled at temperatures above the glass-forming level and then emplaced in a low temperature shooting zone without substantial loss in sensitivity even after an extended period of emplacement. The explosive compositions, thus formulated, remain stable for extended period of emplacement at temperatures far below those at which the normally expected crystallization would take place.

A series of glass-forming oxidizer fuel system components, all shown in association with 20 percent water, as an aqueous solution phase for explosive compositions of the invention are illustrated in Table 11 with reference to temperature at which glassing was observed. Each solution was prepared by adding the ingredients in the indicated ratio in an amount totaling 25 grams and stirring the resulting admixture with a 1-inch magnetic stirring bar. Each solution was then gradually cooled while stirring with the magnetic bar and the crystallization or glassing characteristics noted. In the Table, "Initial Glassing" or thickening, indicates the first observation of glassing; "Sufficient Glassing For No Stirring" was that observed to impart sufficient viscosity to the admixture for it to resist, and stop, the action of the magnetic stirrer, albeit the admixture at that stage remained stirrable by other means, and "Sufficient Glassing For Solidification" was that observed to impart substantially complete solidification to the solution. The solid glass in each test was devoid of the presence of crystalline material.

TABLE 11

| | Aqueous oxidizer-fuel components | | | | Temperature, ° C. | | |
|---|---|---|---|---|---|---|---|
| Test No. | Metal nitrate salt | Weight percent | Amine nitrate | Weight, percent | Initial glassing | Sufficient glassing for no-stirring | Sufficient glassing for solidification |
| 1 | $Ca(NO_3)_2$ | 34 | $CH_3NH_3NO_3$ | 46 | 5 | −4* | |
| 2 | $Ca(NO_3)_2$ | 48 | $(CH_3)_2NH_2NO_3$ | 32 | 30 | 15 | −45 |
| 3 | $Ca(NO_3)_2$ | 55 | $(CH_3)_3NHNO_3$ | 25 | 50 | 20 | −25 |
| 4 | $Ca(NO_3)_2$ | 52 | $CH_3NH_3NO_3$<br>$(C_2H_5)_2NH_2NO_3$ | 11<br>17 | 65 | 15 | −30 |
| 5 | $Ca(NO_3)_2$ | 52 | $CH_3NH_3NO_3$<br>$i\text{-}C_4H_9NH_3NO_3$ | 11<br>17 | 60 | 26 | −30 |
| 6 | $Ca(NO_3)_2$<br>$Mg(NO_3)_2$ | 25<br>22 | $(CH_3)_2NH_2NO_3$ | 33 | 55 | 33 | −25 |

*Glassing started at +5° C.; precipitation at −4° C., and no glassing thereafter.

In accordance with one procedure for preparation of the explosives of the invention, the metal nitrate oxidizer of the oxidizer-fuel system, and any supplementary inorganic oxidizer salt is added to the water component and dissolved therein, and the pH of the resulting solution is adjusted for subsequent aeration and cross-linking of gelation agent, generally by the addition of acetic acid or fumaric acid; the gelation agent, dispersed in ethylene glycol, is admixed with the aqueous solution, and all remaining formulation ingredients other than the cross-linking and aeration agents are then added—all under continuous agitation conditions. The cross-linking and gelation agents are then added separately, or together, after which gas particles are dispersed throughout the resulting admixture for regulation of density, and gelation and cross-linking is initiated and completed. When guar gum is the gelation agent, the metal nitrate oxidizer component may, in some instances, be somewhat reactive with the guar gum to impair the extent and rate of its hydration; and in those instances it is advantageous to initially add a limited portion of the contemplated metal nitrate oxidizer to the water component and add the remaining portion after hydration of the guar gum is in progress, or substantially completed, but, of course, prior to any substantial degree of cross-linking.

In preferred practice, the gas particles are produced in situ from sodium nitrite, as an aeration agent, the gas generation rate being regulated when desired, by the presence of a sulfamate and/or sulfamic acid. These aeration procedures are well known and are disclosed in U.S. Pat. No. 3,390,031 of Albert and in U.S. Pat. No. 3,442,729 of Knight et al. The resulting mixture of explosive ingredients prior to completion of the cross-linking, is pumpable and is in that state for a sufficient length of time for it to be pumped to emplacement for final cross-linking for shooting.

The explosive, in emplacement, contains substantially all metal nitrate and amine nitrate, of the fuel-oxidizer system, dissolved in the aqueous solution phase with substantially no crystallization taking place at the lower temperature levels. The solution phase, under such low-temperature conditions, therefore, remains substantially free from solid crystals of metal nitrate and/or amine nitrate of the fuel-oxidizer system. In this manner there has been no dilution of aqueous phase by precipitation of those nitrates; and the low-temperature sensitivity of the thus emplaced explosive, which ordinarily would be lowered as a consequence of precipitation of the inorganic oxidizer salt component, is retained and the composition is thus available for detonation at high-detonation rate and improved available energy levels, and is fluid for handling at temperatures significantly lower than possible heretofore.

It is within the scope of the invention to form the oxidizer-fuel system of the invention from mixtures of the above-described amine nitrates, and/or metal nitrates, particularly those amine nitrate mixtures which are formed inherently in any of the well-known amine nitrate forming reactions, and those metal nitrate mixtures naturally occurring in various minerals. For example, magnesium nitrate can be present as a natural occurring ingredient of lime or limestone. By way of further example, mixed methylamine nitrates may be formed from any suitable amine mixture with or without fractionation, as desired, of final product to obtain the amine nitrate to be utilized. In other instances, final amine nitrate product from neutralization of an amine may contain small proportions of other amine nitrates, or ammonium nitrate, present as byproduct and is utilizable in that form as a fuel ingredient in the oxidizernfuel system of the invention.

Four explosive compositions of the invention, summarized in Table 12 following, were prepared and stored at various temperature levels and thereafter examined microscopically (at 25 X) for crystal growth.

TABLE 12

| Example | Parts by Weight<br>1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Water | 18.5 | 18.5 | 15.0 | 15.0 |
| Calcium Nitrate | 21.2 | 42.4 | 34.2 | 58.3 |
| Ammonium Nitrate | 21.2 | 0.0 | 24.1 | 0.0 |
| Monomethylamine Nitrate | 34.5 | 31.5 | 0.0 | 0.0 |
| Dimethylamine Nitrate | 0.0 | 0.0 | 22.1 | 22.1 |
| Ethylene Glycol | 3.0 | 3.0 | 3.0 | 3.0 |
| Guar Gum | 1.5 | 1.5 | 1.5 | 1.5 |
| Cross-linking Agent | 0.04 | 0.04 | 0.04 | 0.04 |
| Fumaric Acid | 0.06 | 0.06 | 0.06 | 0.06 |
| $NaNO_2$ | 0.02 | 0.02 | 0.02 | 0.02 |
| Aluminum (particulate) | 10.0 | 10.0 | 10.0 | 10.0 |
| Totals: | 110.0 | 110.0 | 110.0 | 110.0 |

As noted (Table 12), Examples 1 and 3 contain significantly less than 40 percent calcium nitrate and did not form glasses. However, they gelled with guar gum satisfactorily. After storage at 0° C. about one hour, all formulations were microscopically examined. A small amount of crystals (less than 1 percent of the total) was noted in the formulation of Example 3. All other formulations were clear of crystals. The formulations of Examples 2 and 4, each clear of crystals, formed glasses at 0° C.

The formulations of Table 12 demonstrate that even in the presence of aluminum, gums, cross-linking agents, sodium nitrite, and indeed other conventional ingredients of explosives of the inorganic oxidizer salt aqueous slurry type, the solution precipitation temperatures are not affected and are substantially the same as those of the isolated salt solution such as of the preceding tables. Hence the above complete formulations can be retained in a state of high sensitivity in low-temperature emplacement zones without substantial loss in sensitivity, inasmuch as substantially no crystallization of the solution phase ingredients takes place and there is therefore insufficient loss in sensitivity to render the explosive nondetonatable under those low-temperature conditions.

The invention is further illustrated with reference to the examples of Table 13 showing formulations of a series of finished explosive compositions of the invention and associated detonation data.

The examples of Table 13 illustrate low-temperature sensitivity and hence low-shooting temperatures, provided in accordance with the invention as a result of low-temperature crystallization and/or glassing that takes place. Thus the formulation of Example 1 contained 32.0 percent calcium nitrate as the only inorganic oxidizer salt in combination with 44.1 percent monomethylamine nitrate as substantially the only fuel; it was suitably oxygen balanced at a density of 1.16 and was detonated by a conventional booster charge at a detonation rate of 5,900 meters per second (m./sec.) at −40° F. Substantially no crystallization of either of the two nitrate salts took place at that low temperature and hence there could be no depletion of salt content of the aqueous phase to impair sensitivity of the explosive. Examples 2 and 3, substantially the same as Example 1 except for higher density of Example 2 and the presence of guar gum and Reten A-11 respectively in lieu of Natrosol 250 as the thickener, similarly demonstrate the low temperature crystallization of the two nitrate salts, with detonations (m./sec.) at 5,520 (−20° F.) and 5,150 (−40° F.) respectively. All shots of Examples 1, 2 and 3 were confined.

Example 4 illustrates the presence of ammonium nitrate as a supplementary inorganic oxidizer salt ingredient, with detonation at a rate of 3,600 m./sec. at 0° F. (unconfined). Sensitivity of the formulation of Example 4 is somewhat less than that of the formulations of Examples 1–3 which is attributable to the crystallization of some of the ammonium nitrate from the aqueous solution phase and the significantly higher formulation density. Example 5, similar to Example 4 except for Reten A-11 as a thickener component in lieu of guar gum, and having a lower density, demonstrates under those conditions a higher detonation rate at a lower temperature, even with the same proportions of ammonium nitrate in the formulation.

Examples 6, 7 and 8 illustrate formulations containing monomethylamine nitrate in suitable proportions for the oxidizer-fuel system of the invention but with ammonium nitrate present in lieu of the calcium nitrate oxidizer salt. As shown, even at the low densities, the formulations of Examples 6, 7 and 8 failed to detonate at 20° F., −20° F. and 40° F. respectively. At 0° F., formulation 7 showed a detonation of only 2,150 m./sec. which for operational purposes is considered to be a failure.

Examples 8 and 9 further illustrate that even at low content of methylamine nitrate (22.2) a failure at 40° F. was obtained in the absence of a metal nitrate oxidizer component of the invention (Ex. 8) whereas at substantially the same total inorganic oxidizer salt content, but including 37.2 percent calcium nitrate, a high detonation rate, i.e., 4,000 m./sec. at 0° F. was obtained. Examples 7–9 demonstrate the critical need for the metal nitrate salt oxidizer component of the fuel-oxidizer system in practice of the invention.

Examples 10 and 11 show formulations similar to those of Example 2 except that the formulation of Example 10 contains 7.7 percent particulate aluminum and the formulation of Example 11 contains 5.9 percent Fe/Si each as an energizer. In each instance, the formulation detonated at a temperature of −20° F. at about the same density and at about the same rate thus demonstrating that the compositions of the invention can contain supplemental fuel ingredients without impairing low temperature sensitivity.

TABLE 13

| | Parts by weight | | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Example | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 |
| Water | 20.95 | 20.85 | 20.85 | 16.7 | 16.7 | 16.7 | 16.7 | 16.7 | 16.7 | 19.26 | 19.33 | 16.8 | 15.0 | 15.0 | 15.0 | 17.7 | 17.5 | 19.4 | 19.4 | 16.0 | 16.0 | 19.1 |
| Calcium nitrate | 32.0 | 31.9 | 31.9 | 23.5 | 23.5 | | | | 37.2 | 29.3 | 29.9 | 33.0 | 34.2 | | | 24.9 | | 33.0 | 33.4 | | | |
| Strontium nitrate | | | | | | | | | | | | | | | | | | | | | 39.5 | 31.3 |
| Magnesium nitrate | | | | | | | | | | | | 0.5 | | | | | | 0.4 | | | | 10.0 |
| Barium nitrate | | | | | | | | | | | | | | | | | | | | 39.5 | | |
| Sodium nitrate | | | | | | | | | | | | | | 53.0 | 14.0 | | 15.7 | | | | | |
| Ammonium nitrate | | | | 20.2 | 20.2 | 46.7 | 43.7 | 57.8 | 20.2 | | | 2.0 | 24.1 | | 49.9 | 40.3 | 52.1 | 23.1 | 23.1 | | | |
| Monomethylamine nitrate | 44.1 | 43.9 | 43.9 | 35.9 | 35.9 | 33.3 | 35.9 | 22.2 | 22.2 | 40.4 | 40.4 | | | | | | | | | 40.0 | 40.0 | 35.0 |
| Dimethylamine nitrate | | | | | | | | | | | | 43.4 | 22.1 | 27.4 | 16.5 | | | | | | | |
| Trimethylamine nitrate | | | | | | | | | | | | | | | | | | 19.8 | 19.8 | | | |
| Ethylene glycol | 2.8 | 2.8 | 2.8 | 2.4 | 2.4 | 2.0 | 2.4 | 2.0 | 2.4 | 2.8 | 2.8 | 2.8 | 3.0 | 3.0 | 3.0 | 15.6 | 13.2 | 2.8 | 2.8 | 3.0 | 3.0 | 3.0 |
| Thickeners: | | | | | | | | | | | | | | | | | | | | | | |
| Guar gum [1] | | 1.4 | | 1.2 | | 1.2 | | 1.2 | | 1.4 | 1.4 | 1.4 | 1.5 | 1.5 | 1.5 | 1.4 | 1.4 | 1.4 | | 1.4 | 1.4 | 1.5 |
| Reten A-11 [2] | | | 1.2 | | 1.2 | | 1.2 | 0.04 | 1.2 | | | | | | | | | | 1.2 | | | |
| Natrosol 250 [3] | 0.8 | | | | | | | | | | | | | | | | | | | | | |
| Crosslinking agent [4] | 0.1 | 0.04 | 0.03 | 0.04 | 0.03 | 0.04 | 0.03 | | 0.03 | 0.04 | 0.04 | 0.04 | 0.04 | 0.04 | 0.04 | 0.04 | 0.04 | 0.04 | 0.03 | 0.04 | 0.04 | 0.04 |
| Aluminum | | | | | | | | | | 7.7 | | | | | | | | | | | | |
| Fumaric acid | | 0.06 | | 0.06 | | 0.06 | | 0.06 | | 0.06 | 0.06 | 0.06 | 0.06 | 0.06 | 0.06 | 0.06 | 0.06 | 0.06 | | 0.06 | 0.06 | 0.06 |
| $NaNo_2$ | 0.05 | 0.03 | 0.05 | 0.02 | 0.03 | 0.02 | 0.03 | 0.02 | 0.05 | 0.03 | 0.03 | 0.03 | 0.02 | 0.02 | 0.02 | 0.03 | 0.03 | 0.03 | 0.05 | 0.04 | 0.04 | 0.04 |
| Ammonium sulfamate | 0.2 | | 0.2 | | 0.2 | | 0.2 | | 0.2 | 0.40 | 0.40 | | | | | | | | 0.2 | | | |
| FeSi alloy [5] | | | | | | | | | | | 5.9 | | | | | | | | | | | |
| Oxygen balance percent | −2.9 | −3.5 | −3.9 | −1.1 | −1.6 | −5.9 | −9.0 | +0.1 | +10.9 | −11.6 | −5.3 | −20.7 | −0.6 | −1.0 | −1.3 | −1.6 | −0.9 | −5.3 | −5.6 | −7.1 | −4.3 | −0.3 |
| Specific gravity | 1.16 | 1.24 | 1.12 | 1.29 | 1.22 | 1.21 | 1.18 | 1.21 | 1.17 | 1.27 | 1.25 | 1.22 | 1.35 | 1.36 | 1.22<br>1.26 | 1.28<br>1.21 | 1.21 | 1.23 | 1.12 | 1.36 | 1.28 | 1.27 |
| Detonation (500 grams pentolite, booster Charge): | | | | | | | | | | | | | | | | | | | | | | |
| Rate, m./sec. | 5,900 | 5,550 | 5,150 | 3,600 | 5,400<br>4,250 | Failed | Failed<br>2,150 | Failed | 4,000 | 5,550 | 5,700 | 4,350 | 3,600 | Failed | Failed<br>4,900 | Failed<br>5,700 | Failed | 5,700 | 4,750 | 4,550 | 4,000 | 3,900 |
| Temp., ° F. | −40 | −20 | −40 | 0 | −40<br>−40 | 20 | −20<br>0 | 40 | 0 | −20 | −20 | −20 | 30 | 60 | 60<br>50 | 40<br>80 | 70 | −20 | −20 | 50 | −20 | 0 |
| Diameter, inches: | | | | | | | | | | | | | | | | | | | | | | |
| Confined | 5 | 5 | 5 | | 5<br> | | | | | 5 | 5 | 5 | | | <br>5 | 5<br>5 | 5 | 5 | 5 | 5 | 5 | 5 |
| Unconfined | | | | 5 | <br>5 | 5 | 5<br>5 | 5 | 5 | | | | 5 | 5 | 5<br> | | | | | | | |

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[1] High purity guar gum. "J2S1" manufactured by Steinhall Co.

[2] Sodium acrylate-acrylamide copolymer. Acrylamide: Sodium acrylate wt. ratio, about 9:1. See U.S. 3,442,729 Manufactured by Hercules Incorporated.

[3] A hydroxyethyl cellulose. Manufactured by Hercules Incorporated. See NATROSOL (Hercules Powder Co., 1965).

[4] Potassium pyroantimonate for the guar gum; hexamethoxymethyl melamine for the Natrosol 250; basic aluminum acetate for the Reten A-11.

[5] Fe:Si=85:15 (wt.).

The formulation of Example 12 is similar to that of Examples 2 and 4 except that the amine nitrate fuel ingredient is dimethylamine nitrate in place of the monomethylamine nitrate of Example 2. The formulation as in Example 2 shot at a high rate at −20° F. The low temperature sensitivity of the formulation of Example 12 thus further illustrates the class of amine nitrate fuel ingredients of the invention.

The formulation of Example 13 is similar to that of Example 12 except that the aeration therefor was regulated to provide for a density of 1.35 grams/cc. Even at that high density and with considerable dilution of the system with ammonium nitrate at the expense of dimethylamine nitrate, the formulation illustrates the function of the combined metal nitrate oxidizer-amine nitrate fuel system of the invention to impart improved low-temperature sensitivity.

The formulations of Examples 14 and 15 are similar to those of Examples 12 and 13 except that sodium nitrate alone (Example 14) and ammonium nitrate/sodium nitrate (Examples 15), was each in lieu of calcium nitrate. As shown, detonation failed at 60° F. in each instance, thus indicating precipitation of crystals from the aqueous solution phase of each formulation with corresponding loss in sensitivity.

Example 16 illustrates the effect on low-temperature sensitivity of the absence of an amine nitrate fuel ingredient even though calcium nitrate as the metal nitrate oxidizer salt is present in a substantial proportion. Hence at a density of 1.26, the formulation of Example 16 detonated at a rate of 4,900 m./sec. at substantially a minimum temperature of 50° F. (failed at 40° F.), again demonstrating that the results of the invention are not accomplished in the absence of one of the ingredients of the fuel-oxidizer system.

The formulation of Example 17 similarly illustrates the function of the oxidizer-fuel ingredient of the invention being devoid of both ingredients, i.e., calcium nitrate and an amine nitrate and even at a low density of 1.21 grams/cc. having shot at 80° F. with failure at 70° F., again demonstrating the inadequate low-temperature sensitivity that results in the absence of a fuel-oxidizer system of the invention.

The formulation of Examples 18 and 19 demonstrates trimethylamine nitrate as an ingredient of the fuel-oxidizer system of the invention, in each instance the explosive composition exhibiting high sensitivity at −20° F.

The formulations of Examples 20 and 21 each containing 40 percent monomethylamine nitrate demonstrate that barium nitrate (Example 20) is not operable as a metal salt oxidizer of the oxidizer-fuel system of the invention, i.e., to impart, with the amine nitrate ingredient, an improvement in low temperature sensitivity. Thus, as shown in Example 20, substantially a minimum temperature of 50° F. was required for detonation of the formulation of Example 20 thus demonstrating that crystallization of barium nitrate, with accompanying loss in low-temperature sensitivity, took place. In contrast, the formulation of Example 21 containing strontium nitrate as the metal nitrate ingredient of the oxidizer-fuel system underwent substantially no crystallization at −20° C. as indicated by the detonation obtained at that temperature level and hence the improved low-temperature sensitivity of that formulation.

Example 22, similarly to Example 21, illustrates a mixture of magnesium nitrate and strontium nitrate as a metal salt oxidizer of the fuel-oxidizer system, the detonation of that formulation having been accomplished at 0° F.

In the manufacture of aqueous slurry type ammonium nitrate explosives heretofore, it has often been necessary to maintain the aqueous ammonium nitrate solution phase at an elevated temperature, say at 120° to 175° F., in order to maintain the solution above its crystallization temperature and thus retain the ammonium nitrate in solution during manufacture and use of the explosive. However, it is a feature of the invention that due to the low-crystallization temperature properties of the aqueous solution phase, in the compositions of the invention, those elevated temperature requirements are unnecessary.

Thus, in one such embodiment, an aqueous solution phase of metal nitrate oxidizer-amine nitrate fuel system of the invention is formed for mixing with a separate, and second, water solution of supplemental oxidizer salt ingredients to form the final explosive product. The total water content of the two separate solutions is that of the final slurry product; and the water contents of the two solutions are adjusted so that the crystallization temperature of each solution is below the ambient mixing temperature. Generally, the water content of the stock solution is limited so as to provide the supplemental salt solution with an adequate proportion of water as a solvent, and a diluent, for maintaining the desired low-crystallization temperature of the solution.

Any desired number of supplemental solutions of suitable composition can be formed and mixed with requisite portions of stock solution, together with subsequent addition of remaining ingredients such as gelation agent, supplemental fuel, cross-linking agents, and the like. Due to the low-crystallization temperature of the two initially formed solutions, and of the solution phase product of the final explosive composition, there is no need for elevated mixing, and separate solution, temperatures. Further, the embodiment provides for use of the stock solution in the manufacture of explosives, utilizing any one of several separate supplemental oxidizer salt solutions of predetermined composition to provide for variance of composition of the final slurry explosive product for the particular need.

Further exemplary of the above embodiment, are the following separate stock and supplementary oxidizer salt solutions, each formed and stored at ambient temperature, say at 15° C., and then admixed under such temperature conditions, to form an aqueous ammonium nitrate solution phase for a slurry explosive having a low-crystallization temperature in accordance with the invention.

| | Weight, percent | | |
|---|---|---|---|
| | Stock solution | Supplemental salt solution | Aqueous solution phase for slurry explosive product * |
| Calcium nitrate | 50.0 | | 40 |
| Methylamine nitrate | 35.0 | | 28 |
| Ammonium nitrate | | 60 | 12 |
| Water | 15 | 40 | 20 |

*Stock solution mixed in weight ratio to supplemental salt solution of 4:1.

The aqueous solution phase product forms a glass stable at −60° C. and lower.

It will be evident to those skilled in the art, various modifications can be made or followed, in light of the foregoing disclosure and discussion without departing from the spirit or scope of the disclosure or from the scope of the claims.

What I claim and desire to protect by Letters Patent is:

1. An inorganic oxidizer salt explosive of the aqueous slurry type containing a nitrate salt oxidizer - fuel system imparting improved stability to aqueous solution precipitation at low temperatures, comprising, on a weight basis, from 12 to 30 percent water and, as said nitrate salt oxidizer - fuel system, from 18 to 70 percent of a Group II (Periodic System) metal nitrate oxidizer selected from the group consisting of calcium nitrate, strontium nitrate, cadmium nitrate, a mixture of any of said nitrates, and magnesium nitrate together with at least one of said calcium, strontium and cadmium nitrates in a weight ratio thereto not exceeding about 1:1, in combination with from 10 to 60 percent of an amine nitrate fuel component selected from the group consisting of lower alkylamine nitrates containing from 1 to 8 alkyl carbon atoms, alkanolamine nitrates containing from 2 to 9 alkanol carbon atoms, and hexamethylenetetramine nitrate (HMTAN).

2. A composition of claim 1 containing a thickening amount of a thickener therefor.

3. A composition of claim 2 containing at least 25 percent of said metal nitrate oxidizer and at least 20 percent of said amine nitrate fuel.

4. A composition of claim 3 containing an alkylamine

nitrate having from 1 to 3 alkyl carbon atoms, as an amine nitrate fuel.

5. A composition of claim 3 containing calcium nitrate as a metal nitrate oxidizer and monomethylamine nitrate as an amine nitrate fuel.

6. A composition of claim 3 containing an alkanolamine nitrate having from 2 to 3 alkanol carbon atoms, as an amine nitrate fuel.

7. A composition of claim 3 containing hexamethylenetetramine nitrate as an amine nitrate fuel.

8. A composition of claim 1 containing a sufficient proportion of said metal nitrate oxidizer for the formation of a glass, in the aqueous solution phase, stable at temperatures below the freezing point of water.

9. A composition of claim 8 containing at least 40 percent calcium nitrate as a metal nitrate oxidizer.

10. A composition of claim 9 containing at least 25 percent dimethylamine nitrate and at least 45 percent calcium nitrate, as said fuel-oxidizer system.

11. A composition of claim 1 wherein said amine nitrate fuel is selected from the group consisting of mono-, di-, and trimethylamine nitrates, and said metal oxidizer salt is calcium nitrate in at least major proportion; and said composition containing from 12 to 25 percent water, from 0 to 10 percent of a carbonaceous fuel, from 0 to 30 percent of a particulate metal energizer, from 5 to 40 percent of a supplemental inorganic oxidizer salt, and from 0.5 to 2.5 percent of a gelation agent in cross-linked form.

12. A composition of claim 11 containing an alkylamine nitrate having from 1 to 3 alkyl carbon atoms as said amine nitrate fuel.

13. A composition of claim 12 in which said alkylamine nitrate is methylamine nitrate.

14. A composition of claim 11 containing up to about 10 percent ethylene glycol as a supplementary fuel.

15. A composition of claim 11 containing a particulate metal as a supplementary fuel.

16. A composition of claim 15 containing a particulate silicon as a supplementary fuel.

17. A composition of claim 15 containing a particulate aluminum as a supplemental fuel.

18. A composition of claim 11 containing from 10 to 35 percent of a supplemental inorganic oxidizer salt.

19. A composition of claim 18 in which ammonium nitrate is at least a major proportion of said supplemental inorganic oxidizer salt.

20. A composition of claim 11 containing a sufficient proportion of said metal nitrate oxidizer for the formation of glass, in the aqueous solution phase, stable at temperatures below the freezing point of water.

21. A composition of claim 20 containing at least 40 percent calcium nitrate as said metal nitrate oxidizer, and monomethylamine nitrate as said amine nitrate fuel.

22. In a process for the manufacture of an aqueous slurry inorganic oxidizer salt type explosive, the improvement providing for the formation of an aqueous solution phase therefor without need for elevated temperatures comprising forming, under ambient temperature conditions, a separate solution of each of (1) a combined fuel-oxidizer system for said explosive in a portion of the total water component for said explosive, and (2) a supplemental inorganic oxidizer salt for said explosive in the remainder of said water component; regulating the water content of each said solution to maintain crystallization temperature of each at a level below said ambient temperature, and maintaining the total inorganic oxidizer salt content of said supplemental salt solution at a level not exceeding about 40 percent of the weight of said explosive; said fuel-oxidizer comprising from 18 to 70 percent of a Group II (Periodic System) metal nitrate oxidizer selected from the group consisting of calcium nitrate, strontium nitrate, cadmium nitrate, a mixture of any of said nitrates, strontium nitrate, cadmium nitrate, a mixture of any of said nitrates, and magnesium nitrate together with at least one of said calcium, strontium and cadmium nitrates in a weight ratio thereto not exceeding about 1:1, in combination with from 10 to 60 percent of an amine nitrate fuel component selected from the group consisting of lower alkylamine nitrates containing from 1 to 8 alkyl carbon atoms, alkanolamine nitrates containing from 2 to 9 alkanol carbon atoms, and hexamethylenetetramine nitrate (HMTAN); and admixing the separately formed fuel-oxidizer, and supplemental salt, solutions under ambient temperature conditions to form the resulting admixture as said aqueous solution phase.

23. In a process of claim 22, forming said solution of fuel-oxidizer system from calcium nitrate and monomethylamine nitrate; and forming said supplemental salt solution from ammonium nitrate.

* * * * *

PO-1050
(5/69)

# UNITED STATES PATENT OFFICE
# CERTIFICATE OF CORRECTION

Patent No. 3,645,809 Dated February 29, 1972

Inventor(s) Frederic S. Stow, Jr. (Case 3)

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 5, line 27 of printed patent; page 11, line 27 of spec.
TABLE 5 "DEAN" should be -- IBAN --

Col. 7, line 19 of printed patent; page 16, line 2 of spec.
"either" should be -- eight --

Col. 7, line 50 of printed patent; page 16, line 15 of spec.
TABLE 15 under column: Initial Formation
<u>(some thickening)</u>
"25" should be -- 35 --

Col. 9, line 40 of printed patent; page 20, line 30 of spec.
"oxidizernfuel" should be -- oxidizer-fuel --

Col. 11 & 12 of printed patent; page 23 of spec. - TABLE 13

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after "idizer" insert -- system --

Col. 16, line 26-27 of printed patent; Claim 22 of spec.
after "said nitrates," delete

-- strontium nitrate, cadium nitrate, a mixture of any of said nitrates, --

Signed and sealed this 19th day of September 1972.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

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