United States Patent

Fee et al.

[15] **3,653,992**

[45] **Apr. 4, 1972**

[54] AQUEOUS SLURRY SALT TYPE EXPLOSIVES CONTAINING NITRATO-ALKANOL AS SENSITIZER COMPONENT AND MANUFACTURE THEREOF

[72] Inventors: **Harry R. Fee,** Hopatcong; **Eldon K. Hurley,** Wharton, both of N.J.

[73] Assignee: **Hercules Incorporated,** Wilmington, Del.

[22] Filed: **Mar. 5, 1970**

[21] Appl. No.: **16,939**

[52] **U.S. Cl.** **149/2,** 149/38, 149/41, 149/43, 149/44, 149/46, 149/47, 149/60, 149/74, 149/88, 149/92

[51] **Int. Cl.** **C06b 19/00**

[58] **Field of Search** 149/2, 46, 38, 60, 74, 41, 149/60, 92, 43, 44, 88

[56] **References Cited**

UNITED STATES PATENTS

3,507,721	4/1970	Nakagawa et al.	149/88 X
3,523,808	8/1970	Gold et al.	149/88 X

Primary Examiner—Carl D. Quarforth
Assistant Examiner—Stephen J. Lechert, Jr.
Attorney—S. Grant Stewart

[57] **ABSTRACT**

Aqueous slurry salt type explosives containing, as a sensitizer component, a nitrato-alkanol, soluble, and dissolved, in sensitizing amount in the aqueous solution phase.

An aqueous solution phase for explosives of the invention and containing the nitrato-alkanol formed in situ, is provided by reacting a suitable epoxide with aqueous excess HNO_3 to form the nitrato-alkanol, and then neutralizing the excess HNO_3 to form a resulting aqueous salt and nitrato-alkanol product solution, as said aqueous solution phase; and, in a separate embodiment, admixing the remaining ingredients for the explosive with the entire aqueous product solution, to form the slurry explosive product. The nitrato-alkanol, in each method embodiment, is formed and handled without need for isolation of same; and excess HNO_3, which enhances equilibrium of the nitrato-alkanol-forming reaction is readily removed by the neutralization which concomitantly provides in situ formation of the salt for incorporation into the explosive product without need for associated separation or isolation steps.

28 Claims, No Drawings

AQUEOUS SLURRY SALT TYPE EXPLOSIVES CONTAINING NITRATO-ALKANOL AS SENSITIZER COMPONENT AND MANUFACTURE THEREOF

This invention relates to aqueous slurry type salt explosives containing one or more nitrato-alkanols dissolved in the aqueous phase as a combined fuel, sensitizer and fluidizer component. In one aspect this invention relates to aqueous salt explosives above described having improved sensitivity at high density levels with accompanying increase in detonation velocity and volume energy yield. In another aspect this invention relates to process for the manufacture of the above described aqueous slurry type explosives including steps for in situ formation of the nitratro-alkanol in an aqueous solution phase for the explosive. In still another aspect this invention relates to process for the manufacture of an aqueous solution of a nitrato-alkanol and a salt for use in an aqueous slurry type salt explosive, as aqueous phase component, to provide the nitrato-alkanol as a combined fuel, sensitizer and fluidizer without the need for handling same in isolated form. Other aspects will be apparent in light of the accompanying disclosure and the appended claims.

Salt type explosives of the aqueous slurry type include the salt, water and sensitizer components, often with a thickener and one or more of supplemental fuel, salt and energizing ingredients, and have had extensive use in recent years.

In such slurry type explosives, the sensitizer is generally smokeless powder, a high explosive such as TNT or PETN, or a nonexplosive such as particulate aluminum, DNT oil and the like; and, in numerous instances, gas bubbles are present to enhance sensitivity. A separate fuel component is often utilized for suitable oxygen balance and available energy properties. Generally, the explosive contains a gelation agent as a thickener component, often in crosslinked form and in at least a sufficient amount to cause the slurried ingredients to be retained in aqueous suspension. The salt component is of the inorganic oxidizer and/or oxidizer-fuel types, exemplary of which are alkali metal, ammonium, and alkaline earth metal nitrates, and alkylamine nitrates, respectively.

These aqueous slurry explosives are in some instances cap-sensitive, although they are generally insensitive to initiation by the detonating action of No. 8 commercial blasting cap and hence are considered in the art to be cap-insensitive although they readily detonate in response to action of a suitable booster charge. However, at the higher density levels, and particularly at lower temperatures, sensitivity of the aqueous slurry type explosives is relatively low and in some instances the explosive is not detonatable by action of a 500 gram PETN booster.

Pourability of the aqueous slurry type salt explosives is of major importance to the handling and emplacement of the explosive at maximum loading density. However, at temperatures say in the order of 60° F. and lower, the oxidizer salt component often undergoes crystallization to cause sufficient precipitation to impair pourability even at temperatures above those at which the aqueous solution component would normally freeze.

The incorporation of large amounts of entrained gas bubbles into the slurry salt type explosive in control of density involves control problems often leading to excess or insufficient aeration and lack of sufficient precision for attaining the desired density in any particular instance.

This invention is concerned with aqueous slurry type salt explosives containing a nitrato-alkanol(s) which serves as a novel fluidizer-fuel-sensitizer component, imparting improved sensitivity and detonation velocities, particularly at the higher density levels, with accompanying increase in energy yield, and improved pourability — without a requirement for extensive aeration, and, when desired, without need for particulate metal, and high explosive, sensitizers, particularly nitroglycerin and/or ethylene glycol dinitrate with attendant toxic and safety hazards involved in their use. The invention is further concerned with manufacture of such aqueous slurry explosives, including steps eliminating the need for handling the nitrato-alkanol as the fuel-sensitizer-fluidizer component, in isolated form; and with manufacture of nitrato-alkanol-containing reaction product for incorporation in toto into the explosive as aqueous solution phase therefor.

In accordance with the invention, salt explosives of the aqueous slurry type are provided which contain, as a sensitizer component, a nitrato-alkanol, soluble, and dissolved, in sensitizing amount in the aqueous solution phase.

Further in accordance with the invention, a method is provided for manufacture of an aqueous solution phase for a salt explosive of the aqueous slurry type, which comprises reacting aqueous nitric acid with an epoxide reactable therewith to form a nitrato-alkanol, as a sensitizer for said explosive and soluble in sensitizing amount in said aqueous solution phase, when said aqueous nitric acid contains HNO_3 in stoichiometric excess of said epoxide; and neutralizing excess HNO_3 in the resulting reaction mixture to form a water-soluble salt for said explosive and thereby provide the resulting neutralized solution as said aqueous solution phase. Still further, the invention provides for manufacture of an aqueous slurry explosive of the invention, by forming the above described aqueous solution phase and then admixing therewith the remaining ingredients for the explosive to form resulting explosive product.

The aqueous slurry explosives of the invention generally require a small amount of aeration in order to have a satisfactory degree of sensitivity. In those instances, however, the degree of aeration required is substantially lower than that required heretofore in aerated aqueous slurry type salt systems. Often, the proportion of gas particles, or bubbles, required for suitable sensitivity is that which will hold, or maintain, the absolute density of the slurry explosive at a level not exceeding about 99 percent of the theoretical and generally, within a range of from 70 to 98 percent of the theoretical. Generally, the slurry explosive contains gas bubbles in any suitable amount (volume basis) up to about 60 percent, often at least about 1 percent, and more often from 5 to 50 percent. The sensitizing proportion of dissolved nitrato-alkanol can be as low as about 1 weight percent of the finished explosive, often in the range of from about 5 to 75 percent and usually not exceeding about 50 percent. The water, salt and thickener components are present in the finished explosive in any suitable proportions, generally (weight basis) within the range of from 3 to 40 percent water, 10 to 80 percent salt, and 0.2 to 10 percent thickener.

In preferred practice the sensitizer component is ethylene glycol mononitrate dissolved in the aqueous phase in a proportion, based on the finished explosive, in the order of from 5 to 50 weight percent, although proportions outside that range are often advantageously utilized. Now preferred slurry compositions of the invention comprise from about 12 to about 30 weight percent water, a thickening amount of a suitable thickening agent, from 30 to 80 weight percent of the salt, and the dissolved mononitrato-alkanol sensitizer component, generally ethylene glycol mononitrate. The sensitizer component although often a single nitrato-alkanol can, when desired, constitute any suitable mixture of such nitrato-alkanols.

Any nitrato-alkanol of which a sensitizing amount, for the explosive, is soluble in the aqueous solution phase thereof can be used as a sensitizer component in the practice of the invention. Exemplary nitrato-alkanol sensitizer components are: 1-hydroxy-2-propylnitrate and 2-hydroxy-1-propylnitrate; 3-chloro-1-hydroxy-2-propylnitrate and 3-chloro-2-hydroxy-1-propylnitrate; glycerol 1- and 2-mononitrates; and glycerol dinitrate.

Ethylene glycol mononitrate is substantially completely water-soluble in all proportions and constitutes a preferred sensitizer component of the invention. However, nitrato-alkanols having a water-solubility of at least 4 percent at 25° F. are advantageously utilized and are generally dissolved in the aqueous phase of the explosive in a proportion of at least 1 percent, based on the finished explosive. Thus, by way of illustration, propylene glycol mononitrate exhibits a water-solu-

bility of about 10 percent at 25° F. and is dissolved in the aqueous solution phase often as high as 3 to 4 percent (based on the finished explosive) and in some instances higher, dependent upon the particular formulation. Similarly, glycerol mononitrate, highly water-soluble, is dissolved in the aqueous solution phase in suitable proportions.

Exemplary salt components of the invention include inorganic oxidizer salts such as alkali metal and alkaline earth metal nitrates and perchlorates such as, for example, sodium nitrate, magnesium nitrate, calcium nitrate, potassium nitrate, barium nitrate, sodium perchlorate, ammonium perchlorate, calcium perchlorate and magnesium perchlorate; and organic salt components such as nitrogen based oxidizer fuel salts including hexamethylene-tetramine mono- and di-nitrates, primary, secondary and tertiary alkyl, and alkanol, amine nitrates, generally containing one to four carbon atoms in each alkyl, or alkanol group, as for example, monomethylamine nitrate, dimethylamine nitrate, trimethylamine nitrate, monoethylamine nitrate, diethylamine nitrate, triethylamine nitrate, monopropylamine nitrate, dipropylamine nitrate, tripropylamine nitrate, monobutylamine nitrate, dibutylamine nitrate, tributylamine nitrate, monoethanolamine nitrate, diethanolamine nitrate, triethanolamine nitrate, and the like. Particle size of the salt ingredients, which are normally solid, is generally not critical. For example, ammonium nitrate can consist of prills such as used in fertilizers or it can be granular and in form varied from coarse to fine, and when desired, all or any portion of it can be added to the slurry formulation in aqueous solution. The salt component can be solely inorganic, or organic, as above illustrated, or it can constitute a mixture of organic and inorganic salts either one of which can be in major proportion.

A thickener component can be utilized in any suitable proportion and can be of any of those well known in the art including such as Karaya gum, water-soluble starches, mannogalactans, preferably guar gum in crosslinked form, locust bean gum, cereal products, hydroxyethylcellulose, generally crosslinked, acrylic type thickeners such as a sodium acrylate-acrylamide copolymer, and the like. The proportion of thickener does not generally exceed about 10 weight percent, an amount up to about 2 percent being often sufficient, particularly when the thickener is a crosslinked gelation agent. When the thickener content is within the range of from about 0.2 to 0.5 percent, there is generally sufficient thickening to prevent settling of the composition ingredients although additional thickener is often utilized in order to impart a greater degree of cohesiveness.

In some instances, the proportion of nitrato-alkanol may influence the choice of thickener. For example, at concentrations of ethylene glycol mononitrate of at least about 30 weight percent, hydroxyethylcellulose, in crosslinked form, is advantageously utilized, whereas an acrylic type thickener is often less suitable. On the other hand, at ethylene glycol mononitrate concentrations not exceeding about 30 percent an acrylic, or guar gum, type thickener is often preferred.

It is advantageous from the standpoint of oxygen balance to, at times, include in the formulation one or more of supplemental fuels, sensitizers and fluidizers. By way of example, suitable and now preferred supplemental fuels are particulate silicon and silicon alloys, and particulate metals such as aluminum, although any suitable supplemental fuel(s) such as ground coal, ethylene glycol, sugar, and the like, can be advantageously utilized; supplemental sensitizers include such as TNT, smokeless powder, particulate aluminum, DNT oil, and the like, and are preferably those which are not per se self-explosives; and ethylene glycol is a now preferred supplemental fluidizer. The total amount of each of such supplemental fuel and sensitizers does not generally exceed 35 weight percent of the finished composition, often being within the range of from about 5 to 25 percent.

The aqueous slurry type compositions of the invention are characterized by high sensitivity at densities (grams/cc.), after aeration as described, often as high as 1.4 and somewhat higher, such densities in the range of from about 1.00 to 1.40 being generally preferred. Detonation velocities at these density levels are often within the range of from 4000 to 7000 meters per second (m/s) to provide available energy approximating, in many instances, the energy delivered by conventional dynamite type explosives.

A specific aeration step for regulation of density to desired levels in the range of about 1.00 to 1.40 is often not required, inasmuch as, generally, sufficient aeration is inherent during mixing of ingredients in an open air atmosphere. However, in the event that aeration steps are required, such can be accomplished by any of well-known procedures such as aeration disclosed in U.S. Pat. Nos. 3,390,031, 3,390,032 and 3,449,181. Direct aeration or in situ generation by other means can be utilized when desired. Other suitable means for aeration include incorporation of hollow gas-filled plastic spheres known in the art as "microballons" or hollow gas-filled microglass spheres which serves as enclosed inert gas bubbles.

The aqueous slurry explosives of the invention can be prepared in accordance with any suitable mixing procedure. In one embodiment the aqueous solution phase is first formed from the nitrato-alkanol, oxidizer salt, and water components, followed by addition of the remaining ingredients in any suitable sequence, any thickener and/or aeration agent often being last added.

In now preferred manufacture of aqueous slurry explosives of the invention, the nitrato-alkanol component is formed in situ, in an aqueous product solution which is then admixed, as aqueous solution phase component, with the remainder of the required ingredients for the finished explosive. In this manner, the nitrato-alkanol is formed and incorporated into the finished formulation, substantially free from unreacted nitric acid and epoxide reactants without the need, at any time, for being handled in isolated form. The in situ formulation of the nitrato-alkanol is the result of reaction of an epoxide with aqueous nitric acid containing HNO_3 in stoichiometric excess of the epoxide, and a salt for the explosive is formed in the resulting in situ reaction mixture as product of neutralization of the excess HNO_3 therein.

Reaction of ethylene oxide and aqueous nitric acid for the formation of ethylene glycol mononitrate, as a sensitizer component, is the now preferred in situ reaction utilized, together with neutralization of the excess HNO_3 with ammonia and/or an amine such as an alkyl or alkanol amine to form corresponding nitrate salt ingredient for the explosive.

In one embodiment of now preferred manufacture of aqueous slurry explosives, 55–75 weight percent nitric acid is admixed with ethylene oxide in a stoichiometric excess weight ratio thereto, say up to 2:1, to produce ethylene glycol mononitrate, and the excess nitric acid is then neutralized with ammonia and/or an alkyl, or alkanol amine, to produce ammonium, or the corresponding amine, nitrate, as a salt component for the explosive. The in situ reaction is exothermic, and with the neutralization, can be carried out under suitable temperature control conditions at ambient temperature, say from 30° to 140° F., or outside that range if desired. The proportions and amounts of aqueous nitric acid and ethylene oxide are predetermined so as to form total resulting aqueous product for use as aqueous solution phase of the explosive composition. The process can be carried out on batch or continuous basis, as desired.

The presence of a small amount of nitrate anions in the in situ reaction mixture often enhances the equilibrium of the in situ reaction to the nitrato-alkanol product side and hence, for that purpose, a small proportion of a suitable nitrate salt, advantageously a small preformed amount of the desired salt product of neutralization, is generally incorporated into the in situ reaction mixture concurrently with addition of the epoxide and aqueous nitric acid reactants. The presence of a stoichiometric excess of HNO_3 in the in situ reaction mixture also enhances the reaction equilibrium to the nitrato-alkanol product side; and accordingly, the neutralization step provides for use of excess HNO_3 for suitable in situ reaction equilibrium

and for substantial removal of the excess HNO_3 from the system, while concommitently providing salt product for incorporation into the finished explosive.

It is a feature of the invention that in the use of the above procedure for the formation of ethylene glycol mononitrate, a minor proportion of ethylene glycol is formed as by-product, often in amount of from about 1 to 6 percent, based on the final explosive composition. In this manner, the ethylene glycol as a water-soluble supplemental fuel, is compatible with the ethylene glycol mononitrate fuel-sensitizer to maintain high sensitivity and fluidity of the slurry product and to be substantially oxygen balanced with the concurrently formed ammonium nitrate. The remaining ingredients of the explosive composition are then added to the resulting solution under agitation conditions, and the gelation agent, aeration agent and crosslinking agents are last added in that order. In all other embodiments of manufacture, corresponding glycol type by-product is formed which in all instances serves as a fuel ingredient, often being highly soluble in the aqueous product solution.

The invention is further illustrated with reference to the following examples in which all percentages are on a weight basis unless indicated otherwise.

EXAMPLE 1

679 Grams of vaporous ethylene oxide was passed into an admixture of 2020 grams of 70 percent HNO_3 and 142 grams ammonium nitrate under continued agitation conditions. 170 Grams vaporous ammonia was passed into the resulting reaction mixture to neutralize the excess nitric acid. The total resulting reaction product solution had the following composition:

Ingredient	Parts by weight
Ethylene glycol mononitrate	41.1
Ammonium nitrate	31.3
Water	18.4
Ethylene glycol	6.2

To 4000 grams of total reaction product solution prepared in accordance with the above procedure (this example) were added 527 grams calcium nitrate, 350 grams additional ammonium nitrate, 50 grams of hydroxyethylcellulose as a gelation agent, together with 23 grams of hexamethoxymethyl melamine as a cross-linking agent therefor, and 50 grams of glass microballons to regulate finished product density to the desired level. The resulting formulation was a gelled aqueous slurry explosive product having the following composition:

Ingredient	Parts by weight
Water	16.3
Ammonium nitrate	32.0
Ethylene glycol mononitrate (EGM)	35.3
calcium nitrate	9.0
Ethylene glycol	5.0
Gelling agent	1.0
Crosslinking agent	0.5
Glass microballoons	1.0
Density, grams/cc.	1.31

A portion of the above finished explosive composition was detonated, confined in a 3 × 28 inch black iron pipe, utilizing 225 grams pentolite as the booster charge. The detonation rate was 6650 m./sec. The test was repeated except that the charge was maintained unconfined in a 3 × 28 inch polyethylene bag, and the resultant detonation rate was 5550 m./sec. Both shots were made at 75° F.

EXAMPLE 2

An aqueous slurry explosive having the following composition was prepared in accordance with the general procedure of Example 1, i.e., the same procedure with obvious variation in ingredients and ingredient proportions.

Ingredients	Parts by weight
Water	14.7
Ammonium nitrate	39.5
Ethylene glycol mononitrate	35.2
Ethylene glycol	5.0
Gelling agent (hydroxyethylcellulose)	1.0
Crosslinking agent (hexamethoxymethol melamine)	0.5
Glass microballoons	4.0

The resulting slurry composition had a density of 1.25 grams per cc. and was detonated at 40° F., confined, by action of a commercial No. 8 blasting cap, thus demonstrating cap-sensitive explosives of the invention.

EXAMPLE 3

400 Grams of cap-sensitive, aqueous slurry explosive was formed in accordance with the general procedure of Example 1, and was utilized as a cap-sensitive booster charge for detonation of a cap-insensitive aqueous ammonium nitrate explosive. The cap-sensitive booster and the cap-insensitive main explosive are summarized as follows:

Ingredients	Parts by weight: Cap-sensitive Booster	Cap-insensitive Main Charge
Water	18.6	17.8
Ammonium nitrate	38.2	46.9
Sodium nitrate	—	14.1
Ethylene glycol mononitrate	33.5	—
Ethylene glycol	4.2	3.10
Gelling agent		
Hydroxyethylcellulose	1.0	—
Guar gum	—	0.70
Crosslinking agent		
Hexamethoxymethyl melamine	0.5	—
Potassium pyroantimonate	—	0.04
Aluminum	—	17.0
Glass microballoons	4.0	—
Fumaric acid	—	0.10
Sodium nitrite	—	0.07
Ammonium sulfamate	—	0.20
Pine oil	—	0.05

The cap-sensitive booster charge was initiated in response to action of a No. 8 commercial blasting cap and the main charge slot at a rate of 4150 m./sec. For control purposes, the same main charge was initiated in response to booster action of a 500-gram pentolite charge, and the resultant detonation rate was 4100 m./sec., thus demonstrating that explosive compositions of the invention can be made cap-sensitive with excellent booster properties. The detonation temperature for each test was 63° F.

EXAMPLE 4

A formulation of the invention, and a control, were prepared and tested for detonation rate at various aeration levels. Each formulation was aerated by incorporation of sodium nitrite therein and generation of the gas bubbles by reaction of the sodium nitrite (with ammonium cation) for regulation of density, and hence sensitivity, of the explosive. The formulations tested were as follows:

Ingredients	Parts by weight Formulation* of the Invention	Formulation**
Water	17.0	17.0
Ammonium nitrate	42.6	54.6
Calcium nitrate	14.3	18.3
Ethylene glycol mononitrate	20.0	—
Ethylene glycol	2.5	2.5
Coal	2.0	6.0
Thickening agent	1.5	1.5
Sodium nitrite	0.0–0.1	0.1

*Prepared in accordance with general procedure of Example 1.

**Prepared in accordance with conventional mixing of water and ammonium nitrate solution, followed by addition of the remaining ingredients to the aqueous ammonium nitrate admixture.

Detonation rate of the two compositions at the various aeration agent levels are summarized as follows:

Formulation	Formulation of the invention 1	2	3	4	5	6	7	8	Control formulation 9
Sodium nitrite, parts by weight	0.1	0.06	0.03	0.02	0.01	.005	.002	0.0	0.1
Density, gm./cc.	0.94	1.08	1.20	1.27	1.30	1.34	1.34	1.41	1.03
Gas bubbles, volume percent	35	26	17	12	10	7	7	3	30
Detonation rate,[1] m./sec.	[2] 4,150	4,550	5,000	5,000	4,750	4,350	3,550	([3])	([3])

[1] Except as shown, all shots were unconfined, 3 x 27-inch bag; 225 grams pentolite booster; detonation temperature 65°–70°F.
[2] Cap-sensitive, unconfined, (initiated by No. 8 commercial blasting cap).
[3] Failed.

The above summary demonstrates that when aeration is required for the compositions of the invention, the requirement is low. Thus the formulation No. 7 containing 7 volume percent gas bubbles detonated at a rate of 3550 m./s. and higher, whereas the control formulation (without the ethylene glycol mononitrate) failed to shoot even through it contained 30 volume percent gas bubbles, thus demonstrating the strong sensitivity function of the ethylene glycol mononitrate.

EXAMPLE 5

Three aqueous slurry formulations of the invention containing ethylene glycol mononitrate in different proportions were tested for detonation characteristics. A fourth formulation, without ethylene glycol mononitrate, was tested for comparative purposes. The formulations and results of the tests are summarized as follows:

Formulation*	Parts by weight 1	2	3	4
Water	17.0	17.0	17.0	17.0
Ammonium nitrate	42.0	45.0	48.0	54.0
Calcium nitrate	14.0	15.0	16.0	18.0
Ethylene glycol mononitrate(EGM)	20.0	15.0	10.0	0.0
Ethylene glycol	2.5	2.5	2.5	2.5
Coal	2.0	3.0	4.0	6.0
Thickening agent	1.5	1.5	1.5	1.5
Glass microballons (for substantially enclosed gas bubbles, see below)	1.0	1.0	1.0	1.0
Density, grams/cc.	1.34	1.37	1.34	1.35
Oxygen balance	−3.0	−2.8	−2.5	−2.1
Gas bubbles, volume	8	5.5	24	27
Detonation Rate [a] (m./sec.)	5,900	5,250	3,400	Failed

*Formulations 1, 2 and 3 were prepared in accordance with general procedure of Example 1. Formulation 4 was prepared in accordance with conventional mixing procedure involving formation of aqueous ammonium nitrate and admixture of remaining ingredients therewith.

(a) 3" × 27" bags confined in a 3" diameter pipe; 67° F.

As demonstrated, at a concentration of the ethylene glycol mono-nitrate as low as 10 percent a detonation rate of 3400 m/s was obtained (500-gram pentolite booster), whereas under the same shooting conditions but in the absence of the ethylene glycol mononitrate the shot failed. However, although lower concentration of ethylene glycol mononitrate can be utilized (lower than 10.0 percent), often as low as 1 percent, the generally preferred minimum content is in the order of say 5 percent and up to any suitable maximum proportion, often from 50 to 60 percent.

EXAMPLE 6

500 Grams of aqueous solution, on a weight percent basis, of water (25), ammonium nitrate (32.3), ethylene glycol mononitrate (37.3), and ethylene glycol (5.2), formed in accordance with the general (solution formation) procedure of Example 1, was admixed with 500 grams of methylene chloride and then, upon standing, separated into two layers. The weight of the lower and methylene chloride-rich layer was 630 grams and was separated from the top layer by gravitation. The methylene chloride was then evaporated from the lower, and separated, layer to provide ethylene glycol mononitrate of 94 percent purity, as residual product, for incorporation, in its thus isolated form, into a slurry explosive of the invention.

EXAMPLE 7

Three formulations of the invention, each containing glycerolmononitrate as a sensitizer component, were made in accordance with the general procedure of Example 1 utilizing reaction of glycidol as the epoxide reactant. The finished formulations were then tested for detonation properties. The foregoing is summarized in the following tabulation:

Formulation	Parts by weight 1	2	3
water	18.0	18.0	18.0
Ammonium nitrate	56.0	56.0	56.0
Calcium nitrate	15.0	15.0	15.0
Glycerol mononitrate	1.0	2.0	10.0
Glycol and glycerine	3.0	3.0	5.0
Coal	5.0	5.0	3.0
Guar gum	1.1	1.1	1.1
Crosslinker (potassium pyroantimonate)	0.06	0.06	0.06
Sodium nitrite	0.07	0.07	0.07

Buffer*	0.5	0.5	0.5
Pine oil	0.1	0.1	0.1
*Sodium acetate:acetic acid 1:1			
Density, grams per cc.	1.07	1.06	1.02
Detonation			
Temperature, °F.	120	120	120
Booster, grams pentolite			
25	shot		
10	failed	shot	shot
5		shot	
2		failed	shot
Electric blasting cap			
No. 8			shot
No. 6			shot
F			shot
E			failed

EXAMPLE 8

Two aqueous slurry formulations, the same except that one (B) contained TNT, and the other (A) contained ethylene glycol mononitrate as a sensitizer component, were prepared and tested for sensitivity, as summarized in the following tabulation:

Formula	Parts by weight A*	B**
Water	18.0	18.0
Ammonium nitrate	27.0	27.0
Calcium nitrate	27.0	27.0
TNT	—	18.0
Ethylene glycol mononitrate	18.0	—
Ethylene glycol	7.0	8.0
Coal	1.0	—
Guar gum	1.1	1.1
Crosslinking agent Potassium pyroantimonate	0.06	0.06
Ammonium sulfamate	0.2	0.2
Sodium nitrite	0.01	0.01
Buffer***	0.5	0.5
Density	1.35	1.37
Detonation, m/s		
Temperature, °F.	40	75
4" unconfined	5,900	
Booster(pentolite)	225	
3" unconfined	shot	failed
Booster(pentolite, g.)	10	225

*Formed in accordance with general procedure of Example 1.

**Formed in accordance with conventional mixing procedure involving formation of aqueous ammonium nitrate and admixture of the remaining ingredients therewith.

***Sodium acetate:acetic acid, 1:1.

The above data demonstrate ethylene glycol mononitrate as a sensitizer in practice of the invention, together with failure of TNT as a sensitizer, even in response to a manifold stronger booster, under otherwise comparable conditions.

EXAMPLE 9

Several formulations of slurry explosives of the invention were made up in accordance with the general procedure of Example 1, containing ethylene glycol mononitrate (EGN), or propylene glycol mononitrate (PGM), in varying sensitizer amounts, and the formulations were tested for sensitivity. The foregoing is summarized in the following tabulation:

	Parts by weight 1	2	3	4	5	6	7	8
Water	18.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0
Ammonium nitrate	57.0	56.0	55.0	54.0	53.0	52.0	56.0	55.0
Calcium nitrate	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0
EGM	0	1.0	2.0	3.0	4.0	5.0	.....	.....
PGM	0	.....	.....	.....	.....	.....	1.0	2.0
Ethylene glycol	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
Coal	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Guar gum	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1
Potassium pyroantimonate	.06	.06	.06	.06	.06	.06	.06	.06
Ammonium sulfamate	.2	.2	.2	.2	.2	.2	.2	.2
Buffer	.5	.5	.5	.5	.5	.5	.5	.5
$NaNO_2$	.07	.07	.07	.07	.07	.07	.07	.07
Density	1.07	1.0	1.0	1.0	1.0	1.07	1.07	1.07
Temperature,[1] °F.	120	100	100	100	100	120	120	120
Detonation, m/s, Booster (pentolite) grams:								
25	(2)	(3)	.....	.....	.....	.....	(3)	.....
10	.....	(3)	.....	.....	.....	.....	(3)	(3)
5	(2)	(2)	(3)	.....	.....	.....	(2)	(3)
Electric blasting cap:								
Army	.....	.....	.....	(3)	(3)	.....	.....	.....
#8	.....	.....	.....	(2)	(2)	.....	.....	.....
#6	.....	.....	.....	.....	.....	(3)	.....	.....

[1] Detonation temperature.
[2] Failed.
[3] Shot.

The tests demonstrate sensitizing amounts of ethylene glycol mononitrate and propylene glycol mononitrate as low as 1 percent; and that with 3 percent ethylene glycol mononitrate, the formulation was cap-sensitive.

EXAMPLE 10

The following formulation was prepared in accordance with the general procedure of Example 1 and was tested for detonation, and was pourable at low temperature, as summarized in the following tabulation:

Formulation	Parts by weight
Water	18
Ammonium nitrate	42
Methylamine nitrate	16
Ethylene glycol mononitrate	18
Ethylene glycol	2.3
Thickener*	1.5
Crosslinking agent**	0.05
Glass microballoons	1.0

*Sodium acrylate-acrylamide copolymer.Acrylamide:sodium acrylate weight ratio, about 9:1.

**Chromium acetate

Density, grams per cc.	1.27
Detonation	
Booster, grams pentolite	225
Temperature, °F.	30
Rate m/s	4,250

The above slurry explosive composition was readily flowable at the shooting temperature (30° F.); and, as shown, it detonated at a rate of 4250 meters per second at 30° F. and at a density of 1.27.

In all formulations of the invention, specifically illustrated herein (Examples 1–10), the nitrato-alkanol compound was dissolved, in its entirety, in the aqueous solution phase.

Ethylene glycol mononitrate, the now preferred sensitizer component, is, per se, a class B explosive, and, as such, imparts safety in handling of the finished explosive, not possible in aqueous slurry explosive systems containing high (class A) explosives such as TNT, PETN and the like.

As 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 we claim and desire to protect by Letters Patent is:

1. In a salt explosive of the aqueous slurry type, the improvement comprising a nitrato-alkanol, as a sensitizer component, soluble, and dissolved, in sensitizing amount in the aqueous solution phase.

2. An explosive of claim **1** containing gas bubbles in sufficient amount to maintain the absolute density of said explosive at a level not exceeding about 99 percent of the theoretical.

3. An explosive of claim **2** containing a thickening amount of a thickener and at least 1 volume percent of said gas bubbles.

4. An explosive of claim **3** containing an aeration agent in amount sufficient to generate said gas bubbles in said explosive.

5. An explosive of claim **3** containing gas filled hollow spheres as said gas bubbles.

6. An explosive of claim **3** containing, on a weight basis, from 3 to 40 percent water, from 1 to 75 percent of said nitrato-alkanol, from 10 to 80 percent of said salt, and not more than about 10 percent of said thickener.

7. An explosive of claim **3** containing a mononitrato-alkanol as said sensitizer component.

8. An explosive of claim **7** containing ethylene glycol mononitrate as said sensitizer component.

9. An explosive of claim **8** containing on a weight basis from 30 to 80 percent of said salt, from 12 to 30 percent water, and at least 5 percent of said ethylene glycol mononitrate.

10. An explosive of claim **9** containing a sufficient amount of gas bubbles to maintain its absolute density within the range of from 70 to 98 percent of the theoretical.

11. An explosive of claim **9** wherein said salt is inorganic in at least major proportion.

12. An explosive of claim **11** wherein said inorganic salt comprises ammonium nitrate in at least major proportion.

13. An explosive of claim **12** containing at least one of an alkylamine nitrate, an alkanolamine nitrate, and calcium nitrate, as a supplemental salt.

14. An explosive of claim **9** wherein said salt is organic in at least major proportion.

15. An explosive of claim **14** wherein said organic salt comprises at least one of the group of alkylamine nitrates and alkanolamine nitrates in at least major proportion, and said alkylamine nitrates and said alkanolamine nitrates respectively containing from 1 to 4 carbon atoms in the alkyl and alkanol groups.

16. An explosive of claim **7** wherein said mononitrato-alkanol nitrate is propylene glycol mononitrate.

17. An explosive of claim **7** wherein said mononitrato-alkanol is glycerol mononitrate.

18. An explosive of claim **9** containing from 5 to 50 weight percent of said ethylene glycol mononitrate.

19. An explosive of claim **9** containing a supplementary fuel.

20. An explosive of claim **19** in which said supplemental fuel is particulate and is at least one of the group of aluminum, silicon, and silicon alloys.

21. An explosive of claim **9** wherein the proportion of said ethylene glycol mononitrate is at least about 30 percent, and said thickener comprises at least one of the group of guar gum and an acrylic type thickener.

22. An explosive of claim **9** wherein the proportion of said ethylene glycol mononitrate does not exceed about 30 percent and said thickener is hydroxylethylcellulose in crosslinked form.

23. A method for the manufacture of an aqueous solution phase for a salt explosive of the aqueous slurry type, said method comprising reacting aqueous nitric acid with an epoxide reactable therewith to form a nitrato-alkanol, as a sensitizer for said explosive and soluble in sensitizing amount in said aqueous solution phase, when said aqueous nitric acid contains HNO_3 in stoichiometric excess of said epoxide; and neutralizing excess HNO_3 in the resulting reaction mixture to form a water-soluble salt for said explosive and thereby provide the resulting neutralized solution as said aqueous solution phase.

24. A method of claim **23** wherein said epoxide is ethylene oxide, and wherein said excess HNO_3 is neutralized with at least one of ammonia, an alkylamine, and an alkanolamine, to form said salt.

25. A method for the manufacture of a salt explosive of the aqueous slurry type containing, as a sensitizer component, a nitrato-alkanol, soluble, and dissolved, in a sensitizing amount in the aqueous solution phase of said explosive, said method comprising forming an aqueous solution of said nitrato-alkanol by reacting aqueous nitric acid with an epoxide reactable therewith to form said nitrato-alkanol, when said aqueous acid contains HNO_3 in stoichiometric excess of said epoxide; neutralizing excess HNO_3 in the resulting reaction mixture to form a water-soluble salt for said explosive, whereby an aqueous product solution of said nitrato-alkanol and said water-soluble salt is formed; and admixing the remaining ingredients for said explosive with said product solution to form said slurry type explosive.

26. A method for the manufacture of a salt explosive of the aqueous slurry type containing ethylene glycol mononitrate as a sensitizer component, including manufacture and incorporation of said ethylene glycol mononitrate into said explosive without isolation of same from the reaction mixture in which it is formed, said method comprising introducing vaporous ethylene oxide into contact with aqueous nitric acid in an HNO_3:ethylene oxide stoichiometric weight ratio up to about 2:1, and then reacting said ethylene oxide and said HNO_3 to form ethylene glycol mononitrate, whereby an aqueous solution of said ethylene glycol mononitrate and excess HNO_3 is formed; introducing a basic reactant of the group of ammonia, an alkylamine, and an alkanolamine into said aqueous solution in proportions for neutralizing said excess HNO_3 therein; and incorporating the remaining ingredients for said explosive into the resulting neutralized solution to form said aqueous slurry type explosive.

27. A method of claim **26** wherein said aqueous nitric acid contains from 55 to 75 weight percent HNO_3.

28. A method for the manufacture of an aqueous solution of ethylene glycol mononitrate and a salt for incorporation into a salt type explosive of the aqueous slurry type as aqueous solution phase therefor, comprising passing gaseous ethylene oxide through a body of aqueous nitric acid containing from 55–75 weight percent HNO_3, in an HNO_3:ethylene oxide stoichiometric excess weight ratio up to about 2:1, whereby said ethylene oxide and said HNO_3 react to form ethylene glycol mononitrate and a total resulting aqueous solution of same with excess HNO_3; introducing at least one of ammonia, and alkylamine and an alkanolamine into said total aqueous solution to neutralize said excess HNO_3 and thereby from an aqueous solution of ethylene glycol mononitrate and said salt as said aqueous solution phase.

* * * * *

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,653,992 Dated April 4, 1972

Inventor(s) Harry R. Fee and Eldon K. Hurley (Case 1)

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

Col. 7, line 38 of printed patent; page 16, line 6 of spec.

"through" should be -- though --

Col. 12, line 46 of printed patent; claim 26, line 7 of spec.

insert -- excess -- before "weight"

Signed and sealed this 26th day of September 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,653,992 Dated April 4, 1972

Inventor(s) Harry R. Fee and Eldon K. Hurley (Case 1)

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

Col. 7, line 38 of printed patent; page 16, line 6 of spec.

"through" should be -- though --

Col. 12, line 46 of printed patent; claim 26, line 7 of spec.

insert -- excess -- before "weight"

Signed and sealed this 26th day of September 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents