

1

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**WATER-BEARING EXPLOSIVE CONTAINING
NITROGEN-BASE SALT AND METHOD OF
PREPARING SAME**

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ABSTRACT OF THE DISCLOSURE

Water-bearing explosives comprising nitrogen base salt sensitizer and a process for their manufacture employing the crude aqueous reaction product of nitrogen base and oxidizing acid.

Background of invention

Water-bearing explosives have found wide acceptance in recent years. These products typically comprise an oxidizing component, usually predominantly ammonium nitrate, and a fuel component dispersed or dissolved in an aqueous medium which is normally thickened or gelled. The high strength, high velocity water-bearing explosives used where premium performance is required additionally contain a high explosive, e.g., TNT, or a metallic fuel, e.g., aluminum, as at least part of the fuel component. Not only do such materials act as fuels, but also they increase explosive strength and, particularly in the case of high explosives and finely divided metals, also increase sensitivity.

Use of the aforementioned high explosives and metallic additives presents some problems. First, such additives are expensive and, thus, use of such products is often restricted on a purely economic basis. However, without such additives, products of relatively low explosives strength result. Second, the aforementioned metallic and high explosive additives are usually solids which must be dispersed through the explosives during manufacture and maintained dispersed throughout storage and use. Segregation of metallic and high explosive constituents adversely affects explosive properties and, in the case of high explosive sensitizers, may create a safety hazard. Finally, incorporation of insoluble solid high explosives and metallic fuels in water-bearing explosives is more difficult and expensive than the incorporation of corresponding liquid or soluble components.

Summary of invention

This invention provides improved high-performance water-bearing explosives of low cost. For water-bearing explosives, the products of this invention has a surprisingly high detonation velocity and brisance end, thus, are particularly adapted for hard shooting conditions. These advantageous properties are obtained with the products of this invention over a wide range of densities including those as high as 1.4 g./cc. or higher. Preferred products of this invention contain sensitizers which are liquid or, if solid, soluble or readily dispersable in the aqueous phase of the explosives, and, hence, have inherent advantages in manufacture and storage. More specifically, this invention provides an improvement in water-bearing explosives comprising an inorganic oxidizing salt component, a fuel component and water, said improvement comprising incorporating in said explosives a sensitizer component comprising at least one salt of an inorganic oxidizing acid, preferably nitric acid, and a base selected

2

from the group consisting of (a) acyclic nitrogen bases having no more than two hydrogen atoms bonded to the basic nitrogen and up to three carbons per basic nitrogen and (b) phenyl amines, said salt having an oxygen balance more positive than -150%, said sensitizer component comprising, other than said salt, less than about 50% by weight of high explosive sensitizer.

"Oxidizing" and "fuel" components are used herein in their conventional sense to refer to materials in the explosives which have positive and negative oxygen balances, respectively. "Oxygen balance" as used herein refers to the percent excess or deficiency of oxygen required for complete combustion and is calculated as the molecular weight of oxygen required or given off in complete combustion divided by the molecular weight of the material in question. "Sensitizer" as employed herein refers to a material which when removed from an explosive in small (e.g., a few percent), incremental amounts substantially reduces the sensitivity of the explosive at its critical diameter at a given temperature of test.

Description of preferred embodiments

The nitrogen base salts employed in this invention can be derived from inorganic bases such as hydrazine but preferably are derived from aliphatic amines and phenyl amines. Phenyl amines as used herein refers to compounds having one carbocyclic aromatic ring to which is bonded at least one, and preferably one or two, primary amino groups. Salts of primary, secondary and tertiary amines meeting the aforementioned requirements can be used. Although the base moiety can bear substituents other than carbon, hydrogen and the base nitrogen inert with the system, those consisting of carbon, hydrogen and the aforementioned basic nitrogen are preferred. Because of availability, low cost, ease of handling and manufacture and excellent explosive properties of the products of this invention made therefrom, salts of saturated aliphatic amines of up to three carbons are preferred. The oxidizing acid moiety can be that of any of the strong inorganic oxidizing acids, preferably mineral acids, and such as, for example, salts of nitric, nitrous, chloric, and perchloric acids. Those acids having an oxygen balance of at least about +10% are preferred. Nitrates are particularly preferred because of their ready availability and excellent sensitizing effect.

Examples of salts which can be used in the sensitizing component include inorganic salts such as hydrazine nitrate, dinitrate, and perchlorate; salts of aliphatic amines such as monomethylamine nitrate, nitrite, chlorate, and perchlorate, ethylenediamine dinitrate and diperchlorate, dimethylamine nitrate, trimethylamine nitrate, ethylamine nitrate, propylamine nitrate, guanidine nitrate and urea nitrate and salts of phenyl amines such as aniline nitrate, chlorate and perchlorate, p-chloroaniline nitrate and phenylenediamine dinitrate. Of the aforementioned salts monomethylamine nitrate, trimethylamine nitrate and ethylenediamine dinitrate are particularly preferred because of the ease of formulation of explosives therewith and the outstanding explosive properties including velocity and strength of the resulting products. Mixtures of the aforementioned salts can be used as well as mixtures of one or more of such salts with other similar salts having an oxygen balance more negative than -150%, for example, cyclohexylamine nitrate and diethylamine dinitrate. Normally, in such salt mixtures, the overall oxygen balance of the salt should be more positive than -150%.

The nitrogen-base salts can be incorporated in the explosives of this invention in substantially pure form; however, they can be, and preferably are, provided as a crude reaction mixture of the base substantially neutral-

ized with oxidizing acid, either formed separately in aqueous medium then blended with the remainder of the constituents of the explosive or formed in situ in the presence of one or more of such constituents. Thus, a preferred embodiment of this invention provides an improvement in the process for preparing water-bearing explosives which comprises blending oxidizing and fuel components with water, which improvement comprises blending with the ingredients of said explosive the product obtained by neutralizing one or more of the aforementioned nitrogen bases with one or more of the aforementioned oxidizing acids.

A characteristic feature of the explosives of this invention is that they require none of the conventional high explosive sensitizers or metallic-fuels characteristically required for premium performance in high velocity, high strength water-bearing explosives. Thus, although metals such as finely divided aluminum or high explosives such as TNT, PETN, RDX, HMX, or mixtures thereof such as pentolite (PETN/TNT) and Composition B (TNT/RDX) can be used as a minor part of the sensitizer component, they are not required and, in the preferred case, are avoided. If such conventional high explosives are employed, they constitute less than about 50% of the total weight of sensitizer. Some of the amine salts used in the compositions of this invention are high explosives, i.e., detonating explosives per se. However, both high explosive salts as well as those that are not explosives per se, so long as they meet the aforementioned criteria, can be used alone or in combination in the sensitizer component of the subject products.

The total amount of nitrogen-base salt used varies with the particular composition and can range from 5 to 90% by weight of the total composition. In general, the amount of salt decreases as the amount of water used is reduced and as the amount, if any, of auxiliary sensitizer is increased or as a lower strength product is desired. Preferably, about 10 to 50% of the salt sensitizer is used. Depending on its oxygen balance, the amine salts in addition to being the primary sensitizer, are a part of the oxidizing or fuel component, normally the latter.

In its broad aspects the improvement of this invention can be applied to any of the known general types of inorganic salt based water-bearing explosives having a continuous phase comprising water, and the explosives of this invention can contain the conventional ingredients normally employed in such water-bearing explosives in the amounts generally used therein. As the primary oxidizing ingredients, the compositions of this invention usually contain at least about 20% by weight of inorganic oxidizing salt. Examples of inorganic oxidizing salts include ammonium, alkali metal and alkaline earth metal nitrates and perchlorates as well as mixtures of two or more such salts. Examples of such salts are ammonium nitrate, ammonium perchlorate, sodium nitrate, sodium perchlorate, potassium nitrate potassium perchlorate, magnesium nitrate, magnesium perchlorate and calcium nitrate. Preferably, when an inorganic oxidizing salt is used as the oxidizing component, such component contains at least 45% of at least one salt which is highly soluble in water at room temperature, that is, at least as soluble as ammonium nitrate, and preferably, the aqueous phase in the compositions contains a substantial portion of oxidizing salt, for example, 40 to 70% by weight thereof at room temperature. Inorganic oxidizing salt mixtures containing at least about 50% by weight of ammonium nitrate and at least 5% by weight of sodium nitrate are particularly preferred.

The nitrogen base salt sensitizer can provide substantially all of the fuel component. Often, however, it is desirable to include one or more of the conventional fuels as auxiliary fuels. Auxiliary fuel or fuels used in the compositions of this invention can be varied widely, provided that in the composition in which any particular fuel is used, the fuel is stable, that is, prior to detonation, during

preparation and storage, the fuel is chemically inert with the system. In addition to the aforementioned high-explosive auxiliary sensitizers examples of auxiliary fuels are sulfur and carbonaceous nonexplosive fuels such as finely-divided coal and other forms of finely-divided carbon and solid carbonaceous vegetable products such as cornstarch, wood-pulp, sugar, ivory nut meal and bagasse. Examples of auxiliary metallic fuels are aluminum and iron, and alloys of such metals such as aluminum-magnesium alloys, ferrosilicon, ferrophosphorous, as well as mixtures of the aforementioned metals and alloys. Preferably, the total amount of fuel is adjusted so that the total composition has an oxygen balance of about from -25 to +10% and, except for those compositions containing the aforementioned heavier metallic fuels such as ferrophosphorus and ferrosilicon, preferably the oxygen balance is between about -10 and +10%.

As is conventional in water-bearing explosives, the compositions of this invention contain at least about 5% by weight of water. The water-bearing compositions to which this invention is directed generally contain less than about 50% by weight of water and, preferably, on the order of about 10 to 30% by weight of water based on the total composition.

Conventional materials also can be used to thicken or gel the aqueous phase. Of such materials, galactomannans, especially guar gum, are particularly preferred. Usually about from 0.1 to 5% of such galactomannan based on the total weight of composition is employed. Galactomannans also preferably are crosslinked with an oxidizing agent such as an alkali metal dichromate either alone or in combination with a soluble antimony compound. Guar gum in combination with polyacrylamide is often preferred for pourable explosives.

As previously indicated, the compositions of this invention are preferably prepared using the crude reaction product obtained by neutralizing nitrogen base with oxidizing acid in aqueous medium. The product is conveniently blended with a concentrated substantially saturated solution of the oxidizing components optionally with thickeners incorporated therein, then optional additives such as auxiliary fuels and sensitizers blended therewith. Finally, crosslinking agents are added just prior to packing, in the case of packaged products, and just prior to loading into the borehole in the case of pump-truck products. Alternately, the nitrogen base salt can be formed in situ in the presence of other ingredients of the explosive, particularly the oxidizing component. With ammonium nitrate based explosives, preferably pH is adjusted to about from 4 to 7. Water content can conveniently be controlled by the concentration of the oxidizing acid added to neutralize the nitrogen base.

In the following examples which further illustrate this invention parts and percentages are by weight unless otherwise indicated. Monomethylamine nitrate is indicated by MMAN and ethylenediamine dinitrate by EDAN. PAT designates potassium antimony tartrate. AN is ammonium nitrate.

EXAMPLES 1-3

Water-bearing explosives of the compositions shown in Table 1, in parts, are prepared in a mixer from the materials listed by the following sequence of steps:

(1) Ammonium nitrate liquor (about 80% ammonium nitrate), solid ammonium nitrate if required, and aqueous solution of amine nitrate of 70-74% concentration are combined, the mixture heated to 130 to 140° F. (54-60° C.) and the heated mixture transferred to a suitable mixing vessel.

(2) A premixed combination of sodium nitrate and guar gum is added and mixed for 3½ minutes until thickening is observed.

(3) The auxiliary fuels and carbonaceous non-explosive fuels are added and the blend mixed until the fuels are uniformly incorporated.

(4) Crosslinking agents are added; the composition is mixed for several minutes and discharged into polyethylene bags.

TABLE 1

Example	1	Control 2	Control 3
MMAN.....	10.0	10.0	3.33
EDAN.....			6.67
AN.....	41.4	51.4	43.4
Water.....	19.6	19.6	19.6
Sodium nitrate.....	15.0	15.0	15.0
Aluminum.....	4.0	4.0	2.0
Formamide.....	4.0	4.0	4.0
Coal.....	4.0	4.0	3.0
Detonation Results:			
Diameter (in.).....	3	3	3
Velocity (m./sec.).....	4,650	4,500	3,225
° F.....	75	75	75
Diameter (in.).....	2	2	2
Velocity (m./sec.).....	3,700	3,550	2,550
° F.....	38	38	38

In addition to the ingredients listed the compositions also contain, per hundred pound weight, 0.7–0.9 lb. of guar gum, 0.25 lb. of stearic acid and crosslinking agents for the guar gum. The densities of these compositions range from 1.10 to 1.20 g./cc.

The polyethylene bags containing the explosive composition are initiated at 35–40° F. (–1.67 to 4.44° C.). Detonation velocity is measured by placing the composition in cardboard containers having the indicated diam-

In order to determine the detonation velocities given in Table 2, samples of the compositions of the examples of 5-inch diameter are initiated with a conventional 1 pound cast TNT primer.

EXAMPLES 14–21

Water-bearing explosive compositions are prepared from the materials listed in Table 3, in parts, by the following sequence of steps:

(1) The amine nitrate and half of the required ammonium nitrate are added to the water and heated to about 140–149° F. (60–65° C.).

(2) The remaining amount of ammonium nitrate and the sodium nitrate and/or sulfur, if required, are premixed with the guar gum and then added to the heated ammonium nitrate, water and amine nitrate mixture. This composition is mixed for 4 minutes.

(3) The crosslinkers, 0.1 part of 1% K₂Cr₂O₇ and .07 part of 5% PAT, are added and the mixture is mixed for 30 seconds.

(4) The final mix is tested for sensitivity by pouring it into an 8-oz. jar of 2¼ inch diameter which is placed on a cylindrical lead block 2½ inches x 4 inches. A 50 g. RDX pellet is used for priming the unconfined 300-gram mixes. In the table, D indicates the composition propagates a detonation at the specified temperatures.

TABLE 3

Examples.....	14	15	16	17	18	19	20	21
Ammonium nitrate.....	42.7	54.1	71.0	54.2	73.0	48.0	66.7	69.1
Water.....	15.0	15.0	15.0	15.0	15.0	10.0	15.0	10.0
Amine nitrate.....	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
(Amount of amine nitrate).....	24.6	30.0	13.0	29.8	11.0	30.0	17.5	20.2
(O. B. percent of amine nitrate).....	–74	–34	–105	–26	–133	+8	–75	–74
Sodium nitrate.....	15.0							
Sulfur.....	2.0					5.0		
Refined mineral oil.....						1.0		
Guar gum.....	0.7	0.7	1.0	1.0	0.7	1.0	0.75	0.7
Density, g./cc.....	1.3	1.4	1.3	1.3	1.1	1.42	1.3	1.5
O. B., percent.....	–7	–0.4	–0.6	0.0	–0.8	+0.3	–0.6	–1
Detonation results.....	D	D	D	D	D	D	D	D
° F.....	77	35	70	70	77	29	77	77

- 1 Monoethylamine nitrate.
2 MMAN.
3 Trimethylamine nitrate.
4 EDAN.
5 Aniline nitrate.
6 Hydrazine nitrate.
7 p-Phenylenediamine dinitrate.

eter and at the indicated temperature. The compositions are detonated with a conventional primer and the results, as shown in Table 1, give the velocity in meters/second.

In a like manner compositions of this invention are obtained by substituting 10 parts of monomethylamine perchlorate for the monomethylamine nitrate used in Example 1.

EXAMPLES 4–13

Water-bearing explosives are prepared in a rotary mixer from the materials shown in Table 2, in parts, by the general procedures described in Examples 1–3.

TABLE 2

Examples.....	4	5	6	7	8	9	10	11	12	13
AN.....	33.0	35.2	22.2	22.2	22.2	22.2	31.0	35.0	28.8	27.2
Water.....	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	8.8	15.0
MMAN.....	20.0		15.0	15.0	45.0	15.0	20.0	30.0	20.6	30.0
EDAN.....	10.0	30.0	30.0	30.0		30.0	15.0			
Sodium nitrate.....	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	19.3	15.0
Oil.....	1.0	2.0								
Bagasse pith.....	2.0									
Sulfur.....	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.6	2.0
Ferrophosphorus.....									19.3	10.0
Coal.....	2.0							2.0		
Microballoons of Phenol-HCHO-resin.....								1.0		
Guar gum.....	1.0	.8	.8	.8	.8	.8	.8	.8	.6	.8
Density, g./cc.....	1.35	1.35	1.35	1.35	1.35	1.35	1.35	1.35	1.70	1.45
Velocity (m./sec.).....	4,900	4,400	6,100	5,900	4,000	6,000	4,950	6,300	5,100	4,350

We claim:

1. In water-bearing explosives comprising an inorganic oxidizing salt component, a fuel component and water and having a continuous thickened or gelled aqueous phase, the improvement which comprises including in said explosives a sensitizer component comprising at least one nitrogen-base salt of an inorganic oxidizing acid and a base selected from the group consisting of (a) acyclic nitrogen bases having no more than two hydrogen atoms bonded to the basic nitrogen and up to three carbons per basic nitrogen, and (b) phenyl amines, said nitrogen-base salt having an oxygen balance more positive than about

—150%, said sensitizer component, other than said nitrogen-base salt therein, comprising less than about 50% by weight of high-explosive sensitizer.

2. An explosive of claim 1 wherein said nitrogen-base salt is the salt of an amine and nitric acid.

3. An explosive of claim 2 wherein said nitrogen-base salt is at least one salt of nitric acid and an amine consisting of carbon, hydrogen and basic nitrogen.

4. An explosive of claim 3 wherein said sensitizer consists essentially of at least one nitrogen-base salt of an aliphatic amine and nitric acid.

5. An explosive of claim 4 wherein said sensitizer consists essentially of a mixture of at least two of said nitrogen-base salts.

6. An explosive of claim 3 wherein said nitrogen-base salt is a saturated aliphatic amine nitrate of up to three carbon atoms.

7. An explosive of claim 6 wherein said nitrogen-base salt is monomethylamine nitrate.

8. An explosive of claim 6 wherein said nitrogen-base salt is ethylenediamine dinitrate.

9. An explosive of claim 6 wherein said nitrogen-base salt is trimethylamine nitrate.

10. An explosive of claim 3 wherein said nitrogen-base salt is aniline nitrate.

11. A gelled water-bearing explosive of claim 3 comprising, based on the total weight thereof, at least about 20% of said inorganic oxidizing salt component, about from 10 to 50% of said nitric acid-amine salt component, and about from 10 to 30% by weight of water.

12. An explosive of claim 11 wherein said inorganic oxidizing salt component consists essentially of inorganic oxidizing salt at least 50% by weight of which is ammonium nitrate.

13. An explosive of claim 12 wherein said nitric acid-amine salt component is monomethylamine nitrate.

14. An explosive of claim 12 wherein said nitric acid-amine salt component is ethylenediamine dinitrate.

15. In the process for making water-bearing explosives which comprises blending an inorganic oxidizing salt component, a fuel component and water, the improvement which comprises blending in said explosive as a sensitizer the reaction mixture obtained by reacting at least one inorganic oxidizing acid with at least one base selected from the group consisting of (a) acyclic nitrogen bases having no more than two hydrogen atoms bonded to basic nitrogen and up to 3 carbons per basic nitrogen and (b) phenyl amines in water to yield a nitrogen-base salt, said nitrogen-base salt having an oxygen balance more positive than —150%.

16. A process of claim 15 wherein said nitrogen-base salt is formed in said aqueous medium then blended with the remainder of the constituents of said explosive.

17. A process of claim 15 wherein said nitrogen-base salt is formed in water in the presence of at least one other constituent of said explosive.

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