United States Patent

[11] 3,617,404

[72] Inventor **William M. Lyerly**
Hagerstown, Md.

[21] Appl. No. **836,676**
[22] Filed **Feb. 14, 1969**
[45] Patented **Nov. 2, 1971**

[73] Assignee **E. I. du Pont de Nemours and Company**
Wilmington, Del.

[54] **SLURRYXPLOSIVES CONTAINING THE COMBINATION OF NITROGEN-BASE SALT AND HARD SOLID PARTICLES AS SENSITIZER**
15 Claims, No Drawings

[52] **U.S. Cl.** **149/29,** 149/19, 149/22, 149/38, 149/39, 149/47, 149/56, 149/60, 149/62, 149/67, 149/69, 149/75, 149/78, 149/80, 149/92

[51] **Int. Cl.** **C06c 19/04,** C06c 19/04

[50] **Field of Search** 149/19, 22, 29, 38, 39, 47, 56, 60, 69, 62, 67, 75, 78, 80, 92

[56] **References Cited**

UNITED STATES PATENTS

3,235,424	2/1966	Butler	149/38
3,275,485	9/1966	Egly	149/38 X
3,390,028	6/1968	Fee et al.	149/39
3,390,031	6/1968	Albert	149/38 X
3,401,067	9/1968	Fee et al.	149/92 X

Primary Examiner—Leland A. Sebastian
Attorney—James J. Flynn

ABSTRACT: A water-bearing slurry explosive containing inorganic oxidizing salt, fuel, water and thickener together with nitrogen-base salt and solid particles having a hardness of at least 4 on the Mohs scale and that have an acoustic impedance at least two times that of the matrix of the slurry explosive.

SLURRYXPLOSIVES CONTAINING THE COMBINATION OF NITROGEN-BASE SALT AND HARD SOLID PARTICLES AS SENSITIZER

BACKGROUND OF THE INVENTION

In recent years, blasting agents, particularly those of the type known as water gels or slurry explosives have gained considerable commercial acceptance, Generally, the slurry explosives comprise an inorganic oxidizing salt, predominantly ammonium nitrate, a thickening agent for the liquid, water and fuel. Although water-bearing slurry explosives have been used extensively in blasting operations, their use in commercial blasting has been somewhat restricted primarily because many products do not have a sufficiently high detonation velocity, satisfactory sensitivity and ability to propagate a detonation in intermediate or relatively small diameter boreholes. Such properties in water-bearing explosives are extremely important and form the basis for optimum performance. Accordingly, there is a need for water-bearing explosive compositions of sufficient sensitivity that they will reliably detonate and propagate a detonation under adverse conditions of low temperatures in relatively small diameter boreholes and that have a high velocity of detonation.

SUMMARY OF THE INVENTION

This invention provides an improvement in water-bearing blasting agents in that the density, velocity of detonation and ability to sustain detonation are increased so that said compositions propagate in small diameter boreholes. Thus, more specifically, this invention provides a water-bearing slurry explosive composition of improved sensitivity and having a high velocity of detonation containing inorganic oxidizing salt, fuel, water and thickener, wherein the improvement comprises including in said water-bearing explosive a sensitizer comprising:

A. about from 15 to 60 percent by weight based on the total composition of at least one nitrogen-base salt of an inorganic oxidizing acid and a base selected from the group consisting of (1) acyclic nitrogen bases having no more than two hydrogen atoms bonded to the basic nitrogen and up to three carbon atoms per basic nitrogen, and (2) phenyl amines, said nitrogen-base salt having an oxygen balance more positive than about −150, and

B. about from 1 to 20 percent preferably 3 to 10 percent by weight of solid particles having a hardness value of at least about 4, based on Mohs scale, and that have an acoustic impedance at least about two times, and preferably at least five times, that of the slurry explosive matrix, said solid particles being distributed substantially uniformly throughout said composition.

The compositions of this invention can be prepared by heating a mixture of the nitrogen-base salt, water and inorganic oxidizing salt, such as ammonium nitrate, to 150° to 170° F. in a mixer in order to blend the ingredients. Fuel, usually coal and/or sulfur, and the aforementioned solid, hard particles that increase sensitivity and velocity of detonation having the properties stated hereinabove are added, and the ingredients thoroughly mixed. A thickening agent, for example guar gum, is added, alone or admixed with inorganic oxidizing salt, e.g. sodium nitrate or additional ammonium nitrate, to the slurry. Subsequently, a conventional cross-linking agent, such as borax, can be added to thicken the composition if a self-complexing thickening agent was not employed, and the composition is then either packaged or pumped directly to a borehole. The compositions are readily detonatable with conventional primers even in relatively small diameter, e.g., four inch or less boreholes with high-detonation velocities.

"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" are used herein refers to the present excess or deficiency of oxygen required for complete combustion and is calculated as the gram molecular weight of oxygen required or given off in complete combustion divided by the gram 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 reduced the sensitivity of the explosive at its critical diameter at a given temperature of test. By acoustic impedance is meant the product of the density time the velocity of sound in said composition and by matrix of the slurry explosive is meant the slurry explosive less the solid, hard particles.

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 are 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. The base moiety can bear substituents other than carbon, hydrogen and the base nitrogen but the aforementioned 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, especially alkyl amines, having up to four carbon atoms are preferred. The oxidizing acid moiety can be that of any of the strong inorganic oxidizing acids, preferably mineral acids, such as salts of nitric, nitrous, chloric and perchloric acids. Those acids having an oxygen balance of at least about +10 percent are preferred. Nitrates are particularly preferred because of their ready availability and excellent sensitizing effect.

Representative 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, ethanolamine nitrate, guanidine nitrate and urea nitrate and salts of phenylamines such as aniline nitrate, chlorate and perchlorate, p-chloroaniline nitrate and phenylenediamine dinitrate. The nitrogen-base salts particularly preferred are monomethylamine nitrate, ethanolamine nitrate and ethylenediamine dinitrate because of their ease of formulation of explosives therewith and the outstanding explosive properties including velocity, sensitivity 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 positive than −150 percent.

The nitrogen-base salts can be incorporated in the explosive composition in substantially pure form or as a crude reaction mixture of the base substantially neutralized with the 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. The amount of nitrogen-base salt used in the water-bearing slurry explosive composition, said composition usually containing about from 6 to 30 percent, and preferably 10–25 percent, water, is about from 15 to 60 percent by weight of the total composition and, under most conditions, the velocity of detonation and sensitivity are quite adequate if the composition contains about from 20 to 55 percent nitrogen-base salt.

Dense, solid particles of materials having a hardness value of at least about 4, and generally from 4 to 10, based on Mohs scale, are used in the slurry explosive composition of this invention. The solid particulate material must be present in the slurry explosive of this invention, together with the nitrogen-base salt, in amounts of from about 1 to 20 percent, preferably 3 to 10 percent, and most preferably 3 to 8 percent, by weight, to attain the improvement in velocity of detonation and sen-

sitivity. The particle size of said solid material varies within rather wide limits, e.g. smaller than 5 mesh to greater than 425 mesh. Generally, the smaller particle sizes are preferred, for example, particles that are for the most part less than about 150 mesh. Secondly, the solid hard particles must have an acoustic impedance of at least two times, and preferably at least five times, that of the slurry explosive matrix. The higher the acoustic impedance generally produces the best results. The acoustic impedance is a characterizing property of the hard, dense particles, and it is defined as the product of the density times the velocity of sound of the material on which acoustic impedance is being determined. Accordingly, to determine if the material is suitable the acoustic impedance of the slurry matrix, i.e., the slurry explosive without the solid hard particles, is measured and then the acoustic impedance of the solid particles is measured. To be suitable in the present composition the particles must have an acoustic impedance of at least about two times that of the slurry explosive matrix. Representative hard, dense particles that are used in the explosive composition all having hardness values on the Mohs scale of greater than 4 are sand, ferrophosphorus, ferrosilicon, silicon carbide, glass, phosphor bronze, pyrite, quartz, marble and hematite. These materials acoustically impede the velocity of sound and establish discontinuities in the velocity of sound in said explosive when the explosive is detonated. This appears to result in the creation of "hot spots" in the explosive composition which, in combination with the nitrogen-base salt, e.g. monomethylamine nitrate, increases both the sensitivity and velocity of detonation of the novel slurry explosive, in that it will propagate at higher velocities and in smaller diameters under any given set of conditions than will a similar formulation not containing the hard, dense particles.

An inorganic oxidizing salt, conventionally used in water-bearing explosives, is incorporated in the present explosive composition. Soluble inorganic oxidizing salts include the nitrates, perchlorates and chlorates of ammonia and the alkali metals and alkaline earth metals thereof. In general, for economical reasons, ease of handling and overall sensitivity and other explosive properties the inorganic oxidizing salt can comprise 75 percent by weight of the total composition but usually is present in quantities of up to about 55 percent. Examples of inorganic oxidizing salts are sodium nitrate, calcium nitrate, potassium nitrate, magnesium nitrate, sodium perchlorate, potassium perchlorate, ammonium nitrate, ammonium perchlorate and magnesium perchlorate. Ammonium nitrate in amounts of from 10 to 55 percent is preferred and, most preferably, is used in combination with 10 to 25 percent sodium nitrate based on the weight of the composition.

The fuel added to the nitrogen-base salt—solid particle-containing water-bearing composition can be any conventional fuel used in water slurry explosive compositions. Such fuels include nonexplosive fuels and metallic fuels. Nonexplosive fuels include nitro aromatic compounds such as mono- and dinitrotoluenes, sugars, carbonaceous materials such as carbohydrates, starches, finely divided coal and other forms of finely divided carbon and sulfurous fuels including sulfur. In general, up to about 25 percent and preferably from 2 to 20 percent by weight of such carbonaceous fuels are used. Finely divided coal or sulfur, alone or in combination, are the fuels of choice from both an economic and functional standpoint.

The metallic fuels that can be used in the present composition include light metals such as aluminum, magnesium, zinc and boron, both singly and in combination. The amount of metallic fuel used varies with the particular metal employed and although such fuel is not necessary for the successful operation of the invention and such modification is not preferred, metallic fuels can be present in amounts of from 1 to 25 percent, by weight. Although high explosives and self-explosives can be used as a fuel component their inclusion in the compositions in major amounts is not required and, in many cases, not desirable. In any event, organic nitrates, nitro compounds and nitramines such as TNT, PETN, RDX, HMX and smokeless powder can be added to the composition. In those compositions in which a self-explosive fuel is employed it is used, preferably, in amounts less than about 25 percent by weight, based on the weight of the composition.

A crystal habit modifier, such as those described in U.S. Pat. No. 3,397,097, can be employed in the water-bearing explosive compositions of this invention. The crystal habit modifier is usually added to the slurry explosive when it is at a temperature above the crystallization point of the oxidizing salt(s) in solution. Representative crystal habit modifiers include surfactants such as anionic surfactants, especially higher alcohol sulfonic esters, sodium lauryl sulfate and sodium stearyl sulfate; aliphatic amide sulfonates, sodium stearyl amide, and alkyl-aryl sulfonates, sodium dodecylbenzene sulfonate. The amount of crystal habit modifier, or surfactant, used in the composition is within the range of about from 0.1 to 3 percent, or more, and generally at least about 0.5 percent.

The compositions of this invention, which usually contain from 6 to 30 percent water, and preferably 10 to 25 percent, are thickened. "Thickened" as used herein refers to compositions in which the viscosity of the aqueous phase has been materially increased, e.g., to 20,000 cps. or more, as gelled products including those which are cross-linked. The explosive compositions can vary in consistency from pourable, pumpable, semifluid solutions, slurries and dispersions to moldable, tough plastic masses. Thickening agents that can be used in the present invention are those conventionally used in water-bearing explosives and generally are used in amounts of from 0.1 to 10 percent, and preferably from 0.1 to 2 percent, by weight of the composition. Representative thickening agents include tree exudates such as gum arabic, and ghatti; seaweed colloids such as agar-agar and Irish moss; seed extracts such as locust bean, locust kernel, guar and quince seed gums; starches and modified starches such as dextrines and British gums; polyacrylamides and modified polyacrylamides; high-molecular weight polyethylene oxides, as well as mixtures of two or more of the above thickening agents. Of these galactomannans such as guar and locust bean gum, and especially guar gum, are preferred. When the thickening agent is galactomannan, particularly guar gum, about from 0.75 to 1 percent of the galactomannan is usually employed. The galactomannan can be a self-complexing guar gum, for example EX-FC-50 and EX-FC-DP supplied by Stein-Hall Company or a noncomplexing guar gum such as Stein-Hall's Jaguar 100 in which no cross-linking agent is incorporated. However, when a noncomplexing guar gum is used usually small portions, e.g., about 0.001 to 1 percent by weight of the total composition, of conventional cross-linking agents, e.g. borax, can be employed for gelling or thickening the slurry explosive. Carbonaceous thickening agents such as guar gum, serve the dual function of fuel and thickener and can comprise all or part of the soluble fuel.

For a clearer understanding of the invention, the following specific examples are given. These examples are intended to be merely illustrative of the invention and are not to be considered limitations thereof. Unless otherwise indicated, parts are by weight.

The explosive compositions illustrated in table I were prepared by heating a mixture of nitrogen-base salt, inorganic oxidizing salt and water to 150° to 170° F. in a mixer until the ingredients are blended. The crystal habit modifier, that is the surfactant sodium lauryl sulfate, ("Duponol") was added to the mixture along with the hard, solid particles, (Examples B to F), fuel constituents, e.g. sulfur or coal, and the composition mixed to blend the ingredients. After the ingredients were thoroughly mixed a cross-linking agent was added to the mixer and thoroughly incorporated in the explosive composition.

TABLE I

Examples	A	B	C	D	E	F
MMAN [1]	30	30	30	30	30	30
Water	15	15	15	15	15	15
Sodium nitrate	15	15	15	15	15	15
Ammonium nitrate	32.6	26.6	35.6	34.1	31.6	29.1
Solid, dense particulate material:						
Sand		10				
FeP			1	2.5	5	7.5
Sulfur	2	2	2	2	2	2
Coal	4					
Duponol [2]						
Guar, self-complexing	0.6	0.6	0.6	0.6	0.6	0.6
Velocity—meters/sec. at 40–45° F. in 5-inch diameter column	0.8	0.8	0.8	0.8	0.8	0.8
	2,600	5,200	3,700	4,150	5,700	5,700

[1] Monomethylamine nitrate.
[2] Sodium lauryl sulfate.

NOTE.—Compositions detonated with one pound cast TNT primer.

From the above table it can be seen that the inclusion of hard, solid particulate material in combination with the nitrogen-base salt, as shown in Examples B to F, results in a significant increase in velocity of detonation at 40° to 45° F. in a 5-inch diameter column when compared with a similar composition that does not contain hard solid particles

The procedure described above was repeated using the ingredients shown in table II.

TABLE II

Examples	G	H	I	J	K	L	M
MMAN	20	20	20				30
EDAN				36		25	
EAN					32		
Water	18.7	15.1	15.1	18	15	19	19
TNT	15	15	15				
Sodium nitrate	15	15	15	7	14	15	15
Ammonium nitrate	28.7	22.3	17.3	28.4	30.4	33.4	25.4
Ferrophosphorus		10	15				
Ferrosilicon				8	6	5	
Silicon carbide							8
Sulfur	2	2	2	2	2	2	2
"Duponol"	0.6	0.6	0.6	0.6	0.6	0.6	0.6

NOTE.—EDAN=Ethylenediamine dinitrate; EAN=Ethanolamine nitrate.

Composition G failed to detonate in air, i.e. unconfined, at about 40° F. at a 4-inch diameter whereas Compositions H and I had detonation velocities of 5,442 and 5,255 m./sec. respectively, in air at 40° F. and at 4-inch diameters. Compositions J, K, L and M had detonation velocities in excess of 5,000 m./sec. in air at 40° F. and at 4-inch diameters.

The water-bearing slurry explosives of the present invention containing nitrogen-base salt and hard, dense particulate material results in a water-bearing explosive composition of improved sensitivity and velocity of detonation.

I claim:

1. A water-bearing explosive composition of improved sensitivity and having a high velocity of detonation containing inorganic oxidizing salt, fuel, water and thickener, wherein the improvement comprises including in said water-bearing explosive sensitizer comprising:

A. about from 15 to 60 percent by weight based on the total composition of at least one nitrogen-base salt of an inorganic oxidizing acid and a base selected from the group consisting of (1) acyclic nitrogen bases having no more than 2 hydrogen atoms bonded to the basic nitrogen and up to 3 carbon atoms per basic nitrogen and (2) phenyl amines, said nitrogen base salt having an oxygen balance more positive than about −150, and

B. about from 1 to 20 percent by weight of solid particles having a hardness value of at least about 4, based on Mohs scale, and that have an acoustic impedance at least 2 times that of the slurry explosive matrix, said solid particles being distributed substantially uniformly throughout said composition.

2. The product of claim 1 wherein the nitrogen-base salt is an aliphatic amine nitrate.

3. The product of claim 2 wherein the solid particles are sand, ferrophosphorus, ferrosilicon or silicon carbide.

4. The product of claim 2 wherein the aliphatic amin nitrate is ethanolamine nitrate.

5. The product of claim 2 wherein the aliphatic amine nitrate is alkylamine nitrate.

6. The product of claim 5 wherein the alkylamine nitrate is monomethylamine nitrate.

7. The product of claim 5 wherein the alkylamine nitrate is ethylenediamine dinitrate.

8. The product of claim 6 free of self-explosives.

9 The product of claim 6 wherein the inorganic oxidizing salt is ammonium nitrate or sodium nitrate or mixtures thereof.

10. The product of claim 9 containing 10 to 25 percent water.

11. The product of claim 9 wherein the solid particles are ferrophosphorus.

12. The product of claim 9 wherein the solid particles are sand.

13. The product of claim 9 wherein the solid particles are ferrosilicon.

14. The product of claim 9 wherein the solid particles are silicon carbide.

15. The product of claim 5 containing 3 to 10 percent by weight solid particles.

* * * * *