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3,496,040

**AQUEOUS AMMONIUM NITRATE SLURRY
EXPLOSIVE COMPOSITIONS CONTAINING
HEXAMETHYLENETETRAMINE**

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No Drawing. Filed Mar. 25, 1966, Ser. No. 537,306

Int. Cl. C06b 1/04

U.S. Cl. 149-43

6 Claims

ABSTRACT OF THE DISCLOSURE

Storage-stable aqueous slurry ammonium nitrate blasting explosives which contain no high explosive as sensitizer, although they have a water content of at least 15 weight percent, employ at least one weight percent hexamethylenetetramine as combined sensitizer and inhibitor or stabilizer. Preferred compositions for maximum strength comprise about 16 to 25 weight percent water, 40 to 55 weight percent ammonium nitrate, 10 to 20 weight percent aluminum particles, not more than 2 percent being smaller than 50 mesh (U. S. Standard) size, about 2 to 10 weight percent hexamethylenetetramine and sufficient water-soluble thickening agent to stabilize the composition against settling of solids.

The manufacture of explosives by combining ammonium nitrate with various oxidizable substances or fuels is an established practice. (See, for example, British Patent 449,909.) When used in suitable proportions, various oxidizable substances in combination with ammonium nitrate produce high explosion temperatures and in many instances high sensitivity in the explosive composition. Powered metals have been employed as fuels along with ammonium nitrate so as to obtain high explosion temperatures by means of the unusually large quantity of heat released in the formation of metal oxides. Aluminum and magnesium in particular have been recommended and commercially employed for this purpose. (See U. S. patent 2,499,321, for example.) The combination of from about 20 to 64 percent by weight of aluminum metal with water has also been recognized as a fuel capable of yielding very high oxidation temperatures. This is disclosed for example in U. S. Patent 3,034,874 of Emmons et al.

It has been recognized that the addition of water to certain ammonium nitrate explosive compositions has beneficial results, i.e. yielding more of a heaving and less of a shattering action. This is particularly desirable in explosives used in quarrying and blasting for strip mining. This effect is disclosed for example in U.S. Patent 2,463,709 of McFarland. However, when large amounts of water are used in proportion to ammonium nitrate, the sensitivity of the mixture is quite low, so that a self-sustaining detonation is difficult to obtain. For this reason, a sensitive high explosive such as nitroglycerin, TNT or nitrostarch is usually included in the composition. By way of illustration, U.S. Patent 1,386,478 of Waller discloses an explosive composition containing 14 percent

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ammonium nitrate, 15 percent water and 65 percent nitrostarch.

There have recently come into use several blasting explosive compositions containing principally ammonium nitrate, a particulate solid material such as aluminum, water and auxiliary sensitizers such as TNT, nitroglycerin or other high explosives. The ingredients of these compositions are usually stabilized against settling from suspension by use of a water-soluble gum or other protective colloid. Compositions of this type are disclosed in U.S. Patents 3,124,495, 2,860,041 and 3,153,606. Substantial benefits have been obtained from use of explosive compositions of this type because of their low cost, water resistance imparted by the colloid, high density and ease of handling. However, storage of these products presents certain problems. The water in the mixture has a tendency to react with the metal particles, releasing hydrogen gas and changing the surface characteristics of the metal. The stored explosive may then become too unreliable and dangerous for use. It has been proposed to stabilize these products by controlling the pH with buffers. However, mixing at the site is still practiced as the safest method of use, the particulate metal sometimes being mixed into the composition as the very last step. Phosphate salts, which may be employed to buffer the pH, have a tendency to reduce the sensitivity of the explosive mixture, requiring use of additional quantities of sensitizer. Control of pH by addition of ammonia, on the other hand, is preferable from the standpoint of sensitivity but because of volatility does not produce a lasting effect.

I have discovered that ammonium nitrate explosive compositions containing suspended metal can be made substantially free from gassing problems on standing and at the same time do not require the inclusion of a high explosive as a sensitizer.

The new aqueous suspension explosive compositions comprise:

- (a) At least 15 weight percent water in the form of an aqueous solution which is saturated with respect to ammonium nitrate;
- (b) At least 25 weight percent ammonium nitrate in suspended solid form, the total of both dissolved and suspended ammonium nitrate being at least 40 weight percent of the composition;
- (c) At least 0.5 weight percent of a finely divided solid fuel selected from the group consisting of metals, sulfur and combustible carbonaceous substances;
- (d) At least one weight percent hexamethylenetetramine, sufficient to improve the sensitivity of the explosive composition; and
- (e) A minor quantity of a water-dispersible thickening agent sufficient to stabilize the composition against settling of suspended solids.

Preferably, these compositions also contain from about 5 to 20 weight percent of a metal nitrate as an auxiliary oxidizing agent such as, for example, sodium nitrate, potassium nitrate or calcium nitrate.

The new compositions are unusual in several respects. They contain rather large percentages of water. The powdered fuel content, on the other hand, is considerably less

than that used in other gel explosives and there is no high explosive employed as an auxiliary sensitizer. The compositions containing aluminum powder are found to be adequately sensitive and to be free from gas formation in storage. The beneficial effects with regard to both sensitivity and storage stability appear to be attributable to the presence of hexamethylenetetramine in the compositions. It is considered proper therefore to refer to this compound as the combined sensitizer and inhibitor. The preferred type of aluminum powder employed is paint grade aluminum flake. This type of finely divided aluminum is treated to render the surface oil-wettable so that the powder is easily dispersed in drying oils or other organic liquids employed as paint vehicles. Stearic acid or other fatty acid or glyceride oil is commonly used to treat the surface of paint grade aluminum flake. The improved properties of the new explosive compositions appear to be at least partially attributable to the combined use of oil-wettable, water-repellent aluminum powder and hexamethylenetetramine. So that the nature of the invention may be fully understood, the following examples are presented by way of illustration.

EXAMPLE I

Several compositions were prepared containing 24 weight percent water, 10 weight percent sodium nitrate as auxiliary oxidizer, 0.5 weight percent paint grade aluminum powder as solid fuel and 0.8 weight percent guar gum as water-dispersible thickening agent. In these compositions the content of hexamethylenetetramine was arbitrarily varied from 2 weight percent to 8 weight percent and the balance of the composition consisted of ammonium nitrate.

Explosive charges of each composition were prepared and tested, unconfined except for a light waterproof container, employing a 30 gram pentolite booster in each charge. The diameters of the charges varied from one inch to eight inches, four charges being tested in each diameter for each composition. If one out of four identical charges failed to detonate, this was accepted as evidence of unreliable behavior and this diameter was recorded as a failure. The smallest diameter of charge in which there was no failure is indicated for each composition in the table below.

Composition:	Percent NH_4NO_3	Percent hexamethylenetetramine	Smallest detonatable charge
A.....	62.7	2	All failed.
B.....	62.7	2	Do.
C.....	60.7	4	8 inches.
D.....	60.7	4	6 inches.
E.....	58.7	6	5 inches.
F.....	58.7	6	4.5 inches.
G.....	56.7	8	Do.
H.....	56.7	8	3.5 inches.

EXAMPLE II

The procedure of Example I was repeated, with the exception that one weight percent of paint grade aluminum

flake was employed as the solid fuel. Results are summarized in the table below.

Composition:	Percent NH_4NO_3	Percent hexamethylenetetramine	Smallest detonatable charge
I.....	64.2	0	All failed.
J.....	62.2	2	8 inches.
K.....	60.2	4	2.5 inches.
L.....	60.2	4	2 inches.
M.....	58.2	6	Do.
N.....	58.2	6	1.5 inches.
O.....	56.2	8	1.25 inches.

These examples demonstrate clearly the ability of hexamethylenetetramine to improve the sensitivity of compositions which contain relatively low percentages of solid fuel.

EXAMPLE III

A single composition was prepared and tested as above, containing 67.4 weight percent ammonium nitrate, 10 weight percent sodium nitrate, 16 weight percent water, 0.6 weight percent guar gum and 2 weight percent paint grade aluminum powder. With only 4 weight percent hexamethylenetetramine in the composition, the detonatable diameter of the charge proved to be 2 inches. This indicates that although increasing the hexamethylenetetramine content improves sensitivity, doubling the powdered aluminum content does not produce a noticeable improvement.

When the hexamethylenetetramine content of compositions K and L was doubled in composition O, the sensitivity showed a great improvement. However, as shown above, when the aluminum content was doubled with respect to compositions K and L, no improvement was observed, even though water content was decreased and ammonium nitrate content was increased at the same time in order to improve the effectiveness of the aluminum.

EXAMPLE IV

An explosive composition was prepared containing 61.4 weight percent ammonium nitrate, 10 weight percent sodium nitrate, 6 weight percent powdered coal, 16 weight percent water, 6 weight percent hexamethylenetetramine and 0.6 weight percent guar gum. This composition had a critical detonatable diameter of 4.5 inches.

A second composition was prepared which was identical with the exception that the weight percent of ammonium nitrate was reduced to 47.4 and 14 weight percent granular aluminum was added. The critical detonatable diameter of the resulting composition was 3 inches, indicating that use of large proportions of granular aluminum has little effect on sensitivity of compositions which contain hexamethylenetetramine.

EXAMPLE V

Several explosive compositions of the high strength type, suitable for use in drill holes of two or three inches in diameter or larger, were formulated as shown in the following table.

Wt. percent water	Wt. percent Guar gum	Wt. percent ammonium nitrate	Wt. percent sodium nitrate	Wt. percent hexamethylenetetramine	Wt. percent granular Al	Wt. percent paint grade Al flake
23	0.6	42	14	4	15.4	1
23	0.6	42	14	4	15	1.4
23	0.6	42	14	4	15.6	0.8
23	0.6	42	14	4	15.2	1.2
23.6	1	63.4	5	4	-----	3
24	1	44	10	4	14	(1)

¹ 2 weight percent of powdered sulfur was substituted for the powdered aluminum.

EXAMPLE VI

Two compositions of a low density type suitable for use in seismic exploration were prepared as shown in the following table.

	Wt. percent Guar gum	Wt. percent NH ₄ NO ₃	Wt. percent NaNO ₃	Wt. percent hexa- methylene- tetramine	Wt. percent granular Al	Wt. percent Al powder	Wt. percent perlite (powder)
Wt. percent water:							
24.....	0.5	44	12	4	-----	10	6
20.....	0.9	48	12	4	7	2.1	6

With respect to the method of manufacture it is recommended that hexamethylenetetramine be dissolved in water, after which the ammonium nitrate and other water-soluble substances are added, then the thickening agent, followed by the insoluble solids.

In Examples I-III above, there are illustrated variations which demonstrate the effect of hexamethylenetetramine in various concentrations and in comparison with the effect of powdered aluminum.

Example IV illustrates one of the preferred types of compositions in which the finely divided solid fuel is powdered coal. This type of composition preferably contains at least 50 weight percent ammonium nitrate, about 5 to 20 weight percent of a metal nitrate as auxiliary oxidizing agent, about 2 to 15 weight percent powdered coal, about 4 to 10 weight percent hexamethylenetetramine, about 15 to 25 percent water and sufficient water-dispersible thickening agent to stabilize the composition. These compositions are cheap, easily handled with safety and are sufficiently sensitive and powerful for general blasting purposes.

Example V illustrates a type of composition which is preferred for high strength. This type of explosive contains about 40 to 55 weight percent ammonium nitrate, up to about 20 weight percent of a metal nitrate, about 2 to 10 weight percent hexamethylenetetramine, about 10 to 20 weight percent aluminum in finely divided solid form, not more than 2 weight percent being smaller than 50 mesh (U.S. Standard) size, about 16 to 25 weight percent water and sufficient water-soluble thickening agent to stabilize the suspension against settling of solids.

Example VI illustrates a low density type of composition suitable for use in seismic exploration. These compositions are essentially sensitive explosives of reduced power containing about 20 to 25 weight percent water, about 40 to 50 weight percent ammonium nitrate, about 10 to 15 weight percent of a metal nitrate, about 2 to 10 weight percent hexamethylenetetramine, about 5 to 15 weight percent finely divided aluminum, about 3 to 10 weight percent of a porous siliceous substance having a bulk density below that of solid ammonium nitrate and sufficient water dispersible thickening agent to stabilize the composition. Although these low density compositions are substantially reduced in explosive strength, the hexamethylenetetramine assures adequate sensitivity.

As shown by the illustrative examples, considerable variation is possible within the scope of the invention. Other variations not specifically illustrated may be made by those who are skilled in the art.

What is claimed is:

1. An aqueous suspension explosive composition comprising:

- (a) at least 15 weight percent water in the form of an aqueous solution which is saturated with respect to ammonium nitrate;
- (b) at least 25 weight percent ammonium nitrate in suspended solid form, the total of both dissolved and suspended ammonium nitrate being at least 40 weight percent of the composition;
- (c) at least 0.5 weight percent of a finely divided solid fuel selected from the group consisting of metals, sulfur and combustible carbonaceous substances;
- (d) at least one weight percent hexamethylenetetramine, sufficient to improve the sensitivity of the explosive composition; and

(e) a minor quantity of a water-dispersible thickening agent sufficient to stabilize the composition against settling of suspended solids.

2. A composition according to claim 1 which contains from about 5 to 20 weight percent of a metal nitrate selected from the group consisting of sodium nitrate, potassium nitrate and calcium nitrate.

3. A composition according to claim 1 in which the finely divided solid fuel is oil-wettable, water-repellent aluminum powder.

4. An aqueous suspension explosive composition comprising:

- (a) about 16 to 25 weight percent water;
- (b) about 40 to 55 weight percent ammonium nitrate;
- (c) about 10 to 20 weight percent aluminum in finely divided solid form, not more than 2 weight percent being smaller than 50 mesh (U.S. Standard) size;
- (d) about 2 to 10 weight percent hexamethylenetetramine; and
- (e) sufficient water-soluble thickening agent to stabilize the composition against settling of solids.

5. An aqueous suspension explosive composition comprising:

- (a) about 20 to 25 weight percent water;
- (b) about 40 to 50 weight percent ammonium nitrate;
- (c) about 5 to 15 weight percent finely divided aluminum;
- (d) about 2 to 10 weight percent hexamethylenetetramine;
- (e) about 3 to 10 weight percent of a porous siliceous substance having a bulk density below that of solid ammonium nitrate;
- (f) about 10 to 15 weight percent of a metal nitrate; and
- (g) sufficient water-dispersible thickening agent to stabilize the composition against settling of suspended solids.

6. An aqueous suspension explosive composition comprising:

- (a) from 15 to 25 weight percent water;
- (b) at least 50 weight percent ammonium nitrate;
- (c) about 2 to 15 weight percent powdered coal;
- (d) about 4 to 10 weight percent hexamethylenetetramine;
- (e) about 5 to 20 weight percent of a metal nitrate; and
- (f) sufficient water-dispersible thickening agent to stabilize the composition against settling of suspended solids.

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U.S. Cl. X.R.

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