

United States Patent [19]

Wilson et al.

[11] 3,816,191

[45] June 11, 1974

[54] **METHOD OF MAKING CALCIUM NITRATE
EXPLOSIVE COMPOSITION**

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[22] Filed: **May 30, 1972**

[21] Appl. No.: **257,830**

Related U.S. Application Data

[62] Division of Ser. No. 34,522, May 4, 1970.

[52] U.S. Cl. **149/41, 149/44, 149/46,**
149/61

[51] Int. Cl. **C06b 1/04**

[58] **Field of Search** 149/43, 41, 60, 61, 44,
149/46

[56]

References Cited

UNITED STATES PATENTS

3,450,582	6/1969	Sheeran et al.	149/61 X
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[57]

ABSTRACT

An explosive composition and method is provided containing a mixture comprising calcium nitrate, a water miscible organic fuel and water.

6 Claims, No Drawings

METHOD OF MAKING CALCIUM NITRATE EXPLOSIVE COMPOSITION

CROSS REFERENCE TO RELATED APPLICATION

This application is a division of application Ser. No. 34,522, filed May 4, 1970.

BACKGROUND OF THE INVENTION

Inorganic oxidizing salt based explosive compositions are well known in the art. Most of these compositions contain ammonium nitrate as the major inorganic oxidizing salt constituent. Other salts have been thought of as less potent or so sensitive and unstable as to be dangerous. In some compositions, a portion of the ammonium nitrate has been replaced by other inorganic oxidizing salts such as, for example, sodium nitrate, calcium nitrate, certain perchlorates and other inorganic oxidizing salts. These optional inorganic oxidizing salts have been employed for various purposes, such as economy, fluidizing properties, sensitivity enhancement and the like.

These inorganic oxidizing salt based explosive compositions vary from dry mixes to slurry mixtures containing water and/or other liquids, such as glycols, fuel oils and the like. A typical dry mix known in the art is ANFO which contains ammonium nitrate and fuel oil. Typical slurry explosive compositions contain inorganic oxidizing salts, normally a major portion comprising ammonium nitrate, water, a fuel and/or sensitizer and a thickening agent.

It has also been proposed to employ, in amounts up to about 16 percent by weight of these compositions, various organic solvent compounds as supplemental fuels and fluidizing agents, e.g., formaldehyde, ethylene glycol and the like. Waterless slurries containing a liquid organic fuel as a solvent for ammonium nitrate or ammonium perchlorate based explosive composition having a density greater than 1.8 grams per cubic centimeter, have also been suggested.

Specifically, in the past calcium nitrate has been considered as a less potent minor substitute for a portion of the ammonium nitrate in certain inorganic oxidizing salt based compositions.

An explosive composition has now been discovered comprising calcium nitrate, a water miscible organic fuel component and water. The unique composition can be employed as an explosive, as an explosive additive, and as a base mix for preparing other explosives. These novel compositions have certain unique favorable characteristics over other inorganic oxidizing salt based explosive compositions known in the art. Of the more important characteristics is better sensitivity and fluidity at lower temperatures, even without the presence of additional sensitizers and fuels such as self-explosives metals and the like. Also the compositions are characterized as being detonable at higher densities and in smaller diameters than prior ammonium nitrate based explosives.

SUMMARY OF THE INVENTION

The present invention comprises an explosive composition comprising from about 10 to about 100 percent of a mixture comprising, as percent by weight, calcium nitrate about 65-85 percent, a water miscible organic fuel about 15 to about 35 percent, and water

present in an amount such that the ratio, by weight, of water in the mixture to calcium nitrate in the mixture ranges from about 1/26 to about 2/1, and up to about 90 percent of an additional blasting agent or additives known in the explosives art.

The explosive composition contains up to about 90 percent of a blasting agent and/or additive such as, for example, additional inorganic oxidizing salts, fuels and sensitizers, thickening agents, density control agents and the like, in addition to the above defined mixture.

DETAILED DESCRIPTION OF THE INVENTION

As indicated, the present explosive composition comprises at least from about 10 to 100 percent so defined mixture. Preferably the explosive composition comprises from about 10 to about 40 percent by weight of the mixture.

Also, the mixture preferably comprises about a stoichiometric amount of said organic fuel and $\text{Ca}(\text{NO}_3)_2$ to produce N_2 , CO_2 and H_2O upon combustion of the mixture.

The organic fuel component employed in the mixture comprises water miscible organic compounds and mixtures thereof which contain at least one functional group selected from the group consisting of $=\text{O}$, $-\text{OH}$, $=\text{N}$, $=\text{NH}$, $-\text{NH}_2$, $=\text{S}$ and $-\text{SH}$ and which form a stable liquid solution in water at normal temperatures. Examples of groups of organic fuels which can be employed comprise certain amines, including primary and secondary; amides; alcohols including both mono- and polyhydric alcohols; alcohol ethers; carbohydrates (saccharides and polysaccharides); compounds which are hydroxy or polyhydroxy derivatives of hydrocarbons including monosaccharides and disaccharides, sulpho compounds including sulphoamino and sulphoamido compounds, aldehydes and various salts of such compounds. Specific compounds include, for example, n-octylamine, sodium alkyl aryl polyether alcohol sulfonates such as the compound $\text{CH}_3 - \text{C}(\text{CH}_3)_2 - \text{CH}_2 - \text{C}(\text{CH}_3)_2 - (\text{OCH}_2\text{CH}_2)_x\text{OH}$ in which x has an average value of SO_3Na about 20; N,N-dimethyl formamide, 1-hydroxy-2-methoxy-4-allyl benzene, formamide, dimethyl sulfoxide; ethylene carbonate; glycerol; acetonitrile; acetic acid, glyconitrile; ethylene glycol monomethyl ether; methanol; ethanol; furfuryl alcohol; diethylene glycol; sodium acetate; hexamethylene tetramine; hexamethylene tetramine mono and dinitrate; acrylonitrile; acetamide; glycine; ammonium gluconate; acrylamide; N,N-dimethyl acetamide; ethylene glycol; propylene glycol; urea; thiourea; formaldehyde; acetadehyde ammonia; methylacetyl carbinol; acetone cyanohydrin; 2-hydroxybutylaldehyde; pentylene glycol; benzylamine; butylamine; butyldiethanolamine; diacetone alcohol; diethylene-di-imide oxide ethanol; hexylene glycol; methyl glycerinate; 3-methylpyridine; thiodiglycol; triethanol amine; benzyl hydrazine, synthetic sugar like materials, sugar, molasses, and mixtures of compatible compounds. Polymers may also be employed as fuels and in some instances they will also serve as a thickening agent. Such polymers include, for example, polyamides, celluloses, guar, polyols, polyalkylamines, polyethyleneimines and other water soluble polymers containing the previously defined functional groups.

Preferred water miscible organic fuels include lower alcohols, glycols, polyglycols, saccharides, amines or

amides including, as examples, methanol, ethanol, ethylene glycol, propylene glycol, formamide, molasses, glycerol, mannitol, sorbitol and mixtures thereof.

By miscible it is meant that the organic fuel is normally soluble in the liquid phase of the mixture to the extent of at least about 2 percent by weight of the mixture.

The so defined mixture may be added to any of the blasting agents well known in the art to enhance certain characteristics thereof. Thus it may be added to inorganic oxidizing salts other than calcium nitrate including, for example, ammonium, alkaline earth and alkali metal nitrates, sulfates, chlorates and perchlorates. Specific examples of such salts include ammonium nitrate, sodium nitrate, ammonium perchlorate, barium nitrate, ammonium sulfate, sodium sulfate, sodium perchlorate, potassium perchlorate or mixtures thereof and the like. The inorganic oxidizing salts may be employed in particulate form, in solution or both.

In addition the explosive composition can contain sensitizers and/or fuels to alter or improve certain explosive characteristics of the composition. Well known sensitizers and/or fuels normally employed in inorganic oxidizing salts based explosive compositions can be employed in the present invention. These fuels and sensitizers comprise, for example, particulate metals, self-explosives and non-explosive water insoluble carbonaceous fuels and/or others such as sulphur and mixtures of two or more of these materials. They are employed in amounts sufficient to enhance the base explosive compositions in the manner desired. For example, metal may be employed in an amount to provide a weight ratio of metal to the base composition of up to 1/1 and more. The kind and size of the metal particles will effect the explosive composition in several different ways as is well known in the art. Finer metal, e.g. -200 mesh tends to sensitize the explosive composition to detonation while coarser metal tends to increase the power of the composition when exploded, but with less sensitizing effect. The use of such specific size metals is described in U.S. Pat. Nos. 3,307,986 and 3,432,371. The teachings of these patents are specifically incorporated herein by reference.

Particulate metals which can be employed include, for example, aluminum, magnesium, iron, silicon, titanium, aluminum alloys, silicon alloys, magnesium alloys, ferrosilicon, silicon carbide, ferrophosphorous, zinc, boron, and other like particulate metals which sensitize and/or function as a fuel in the explosive. Of particular importance are the light metals, e.g. aluminum, silicon, magnesium, beryllium, alloys thereof and the like. Generally the metals range in size from about -4 to about +325 mesh, U.S. Standard Sieve Series. For metals which react with materials in the explosive composition, e.g. nitrate solution, water, etc., certain inhibitors known in the explosives art may be employed to stabilize the composition; as examples of such inhibitors are ammonium or alkali metal phosphates and the like.

Self-explosives as used herein refer to those substances which, by themselves, are generally recognized in the art as an explosive and which usually can be detonated with a No. 6 or 8 blasting cap. Examples of self-explosives which can be employed include organic nitrates, nitro compounds and nitroamines such as TNT, pentaerythritoltetranitrate (PETN), cyclotrimethylenetrinitramine (RDX), cyclotetramethylene tetra-

tramine, tetryl, nitro starch and explosive grade nitro-cellulose as well as mixtures of the aforesaid and other self-explosives. The self-explosives can be employed in any of the conventional forms such as flake, pelleted, gelatinized or crystalline.

Examples of water insoluble carbonaceous non-explosive fuels and sensitizers which can be employed include finely divided coal and carbon, solid carbonaceous vegetable products such as corn starch, wood pulp, ivory nut meal and bagasse, organic liquids such as petrolic liquids, including hydrocarbon oils, crude oils, and crude oil fractions, fuel oils, fatty oils, vegetable oils and mixtures of two or more of these water insoluble carbonaceous non-explosive fuels.

Any grade of calcium nitrate, e.g., anhydrous or hydrated, may be employed in the present invention. Anhydrous grade, not containing any water, or mono, di tri, tetra fertilizer grade, or any other hydrated form may be employed. When hydrated calcium nitrate is employed the water of hydration is considered in calculating the water content of the mixture. Thus a portion of the water present in the mixture may come from water of hydration, water may be added separately or a combination of the two can be employed.

Thickening and/or gelling agents can also be employed in the present compositions. These agents are employed in amounts to provide a thickened free flowing pumpable to very stiff practically immobile composition. The physical characteristics desired depend mainly on the ultimate use of the explosive. For example, in water-containing boreholes very strong gels or viscous compositions are desired to prevent a leaching out and erosion of the explosive composition. Gelling and/or thickening agents are employed which will swell and/or can be crosslinked in the liquid system containing dissolved $\text{Ca}(\text{NO}_3)_2$, water, and the water miscible organic fuel. Examples of suitable gelling and thickening agents include synthetic polymers, e.g. polyethers, polyesters, polyacrylamide, polyamines, starches, metal alcoholates, polysaccharides, wheat flour, galactomannans, gums, such as guar, karaya and the like. Specific thickening agents which may be employed include cellulose acetate, polyalkylene glycol, hydroxyalkyl cellulose, potato starch, wheat starch, corn starch, carboxymethyl hydroxyethyl cellulose, methyl cellulose, polyethylenimine carboxymethyl cellulose, polyvinyl alcohol, polyvinylpyrrolidone (PVP), sodium polystyrene sulfonate and the like. It has been found that cellulosic materials, e.g., carboxymethyl hydroxyethyl cellulose, methyl and ethyl cellulose, and the like are preferred in the present invention. Examples of thickeners which provide a thickening and suspending of solids by their physical presence include magnesium oxide, asbestos fibers, cotton fibers, glass fibers, wood fibers and the like.

Various density control agents can also be employed in the present invention. These materials are employed to decrease the density of the explosive and/or sensitize the composition and/or alter the energy release of the explosive composition and/or provide compositions which can be more readily exploded under elevated pressures and/or low temperatures. Density control agents include void containing materials, gas generating compounds, gaseous bubbles stabilized with gum and the like. Suitable void-containing materials include, for example, hollow spheres prepared from metals, clays, glass, thermoplastics, resins and other like

materials. Also naturally occurring void-containing materials such as ground corn cobs, bagasse, can be employed in the explosive. The carbonaceous thickening, gelling and density control agents also provide additional fuel for the explosive composition. Suitable gas generating compounds include certain carbonates and the like.

The compositions of the present invention range from dry substances to very thick or very fluid materials.

Exemplary of specific blasting agents which can be employed in the present invention include ANFO, and those blasting agents taught in U.S. Pat. Nos. 3,307,986; 3,456,589; 3,446,681; 3,432,371; 3,287,189; 3,260,632; 3,124,495; 3,400,026; 3,397,097 and other like inorganic oxidizing salt based compositions known in the art.

The use of the mixture to prepare aqueous slurries permits the preparation of slurries containing smaller amounts of water. This has the advantage of preparing slurries which remain more fluid at lower temperatures.

One preferred composition of the present invention comprises the following constituents as percent by weight: from about 5 to about 25 percent by weight of calcium nitrate; from about 10 to about 25 percent of a water miscible organic fuel; from about 3 to about 8 percent of water, and from about 50 to about 85 percent of ammonium nitrate. Optionally up to about 60 percent by weight of a metallic fuel may be employed. Also, an effective amount of a thickening or gelling agent may be employed to stabilize and waterproof the explosive. Other inorganic oxidizing salts, as well as self-explosive sensitizers, density control agents and the like may also be employed to alter various characteristics of the explosive composition.

One method for preparing the explosive composition comprises dissolving ammonium nitrate in a water miscible organic fuel, preferably gelled or thickened, adding solid ammonium nitrate to the gelled or thickened mixture and then adding slaked or unslaked lime. The lime will react in situ to produce $\text{Ca}(\text{NO}_3)_2$, water, and ammonia, giving a slurry containing the above-defined constituents. Other constituents which may be added include, particulate metals, density control agents and the like. For example, a slurry explosive is prepared as follows: A polar organic liquid such as formamide is thickened with about 2 percent of methyl cellulose. To about 18 parts by weight of the thickened liquid is added about 20 parts by weight of ammonium nitrate and the mix allowed to come to equilibrium, i.e. the thickened liquid becomes saturated with ammonium nitrate. To the saturated thickened liquid is then added about 56 parts by weight of additional ammonium nitrate and about 5 parts by weight of CaO or $\text{Ca}(\text{OH})_2$. The resulting slurry will contain about 1.6 or 3.2 percent water (depending on whether CaO or $\text{Ca}(\text{OH})_2$ is employed). Particulate metal such as aluminum may be blended into the slurry if desired.

EXAMPLE 1

Three different compositions containing the following constituents as percent by weight were prepared.

TABLE I

Constituent	Mix (% by Weight)			
	A	B	C	D
Formamide	13	19		8
Methanol			15	
*Na ₂ EDTA				5
Ca(NO ₃) ₂ ·4H ₂ O	20	20	20	20
NH ₄ NO ₃	46.5	60.5	64.5	46.5
Particulate Al				
(-20 +60 mesh)	20.0	—	—	20.0
Gum (guar)	0.5	0.5	0.5	0.5

*Na₂EDTA is the sodium salt of ethylenediaminetetracetic acid. All the compositions contained about 6 percent water derived from the tetrahydrate of calcium nitrate. They were all observed to have good to excellent fluidity at room temperature. The four compositions were placed in a deep freeze at -20°F for about four hours. At the end of this time period Mixes A and B were solid while mix C was still fluid, and mix D, although stiff, was still workable.

EXAMPLE 2

In this example a 100 gram composition was prepared in the following manner. To 16 grams of formamide was added 74 grams of ammonium nitrate and 10 grams of CaO . A reaction was evident with moderate odor of ammonia observed. The resulting composition was very fluid.

EXAMPLE 3

Four compositions were prepared containing the constituents, as percent by weight as set forth in the following table. 306 grams of gelled formamide were first prepared for use in the composition. The formamide was prepared by mixing 6 grams of methyl cellulose to 300 grams of formamide and allowing the mixture to gel. A weighed amount of each composition was then tested in a standard small lead block test. In this test a weighed sample of the composition was placed in a small container and placed on top of a steel driving plate which was centered over a cylindrical lead block supported by a heavy piece of steel as a base. The deformation, i.e. reduction in height, of the lead block, in inches, upon detonation of the composition is taken as a measure of the detonability and brisance of the charge. The weight of each sample tested and the resultant deformation (ΔH) in inches is also set forth in the table.

TABLE II

Constituent	Mix No. (Per Cent by Weight)			
	1	2	3	4
NH ₄ NO ₃ (prilled)	82	59	75	72
Formamide (gelled)	18	20	18	18
Ca(NO ₃) ₂ ·H ₂ O		20		
Gum Thickener		1	2	
CaO			5	
*Gelled NH ₄ NO ₃ solution				10
Density (gm/cc)	1.0	1.0	0.9	1.1
Wt. of sample tested (grams)	140	140	129.5	155.5
ΔH (inches)	0.3699	0.2167	0.4368	0.2037

*Prepared by dissolving 60 grams NH₄NO₃ in 40 grams H₂O and thickening with 1 gram of guar gum

EXAMPLE 4

In this example various amounts of a calcium nitrate dihydrate-formamide mixture was added to NH₄NO₃ and NH₄NO₃-metal compositions and the resulting mixes tested in a standard lead block test similar to that employed in the previous example. The compositions, densities of the composition and resulting lead block deformations (ΔH in inches) is set forth in the following table.

TABLE III

Composition No.	NH ₄ NO ₃ *	Ca(NO ₃) ₂ ·2H ₂ O*	Formamide*	Particu- late* Al	Density (gm/cc)	ΔH (inches)	ΔH Density
1.....	100				1.08	0.06	0.056
2.....	90			10	1.07	1.08	1.01
3.....	90	7	3		1.05	.52	.495
4.....	80	14	6		1.13	.73	.64
5.....	70	21	9		1.11	.80	.72
6.....	60	28	12		1.08	1.05	.97
7.....	80	7	3	10	1.07	1.21	1.13
8.....	60	21	9	10	1.16	.95	.82

* All constituents are shown as percent by weight of the total.

As demonstrated the addition of the formamide/Ca(-NO₃)₂·2H₂O mixture improved the performance of both NH₄NO₃ and NH₄NO₃ metal mixtures.

EXAMPLE 5

In this example various mixtures of Ca(NO₃)₂·2H₂O and formamide were tested in a lead block test similar to that described in the previous examples. The following table lists the compositions, density and deformation (ΔH in inches).

TABLE IV

Composition No.	Constituent (% by Weight) Formamide	Ca(NO ₃) ₂ ·2H ₂ O	Density (gm/cc)	ΔH inches
1	32.5	67.5	1.11	0.63
duplicate	32.5	67.5	1.10	0.75
2	27.5	72.5	1.12	0.81
duplicate	27.5	72.5	1.25	0.90
3	35.0	65.0	1.07	0.10
4	25.0	75.0	1.18	0.91
5	30.0	70.0	1.12	0.82

What is claimed is:

1. A method of preparing an explosive composition containing calcium nitrate, water and a liquid water miscible organic fuel which comprises:

- preparing a mixture of ammonium nitrate and said liquid water miscible organic fuel, and
- reacting slaked or unslaked lime with said mixture of ammonium nitrate and liquid water miscible organic fuel by mixing said lime therewith to form a mixture of calcium nitrate, water and liquid water miscible organic fuel said slaked or unslaked lime being provided in an amount sufficient to provide the quantity of calcium nitrate desired in said explosive composition.

2. The method as defined in claim 1 including thickening the ammonium nitrate and liquid water miscible organic fuel prior to reacting it with the slaked or unslaked lime by adding a thickening or gelling agent thereto.

3. The method as defined in claim 2 wherein sufficient ammonium nitrate, slaked or unslaked lime, liquid water miscible organic fuel, and additional water if necessary are mixed and reacted together to form a mixture comprising from about 10 to about 100 percent by weight of a mixture comprising from about 65 to about 85 percent by weight of calcium nitrate, from about 15 to about 35 percent by weight of a liquid water miscible organic fuel, and water in an amount to provide a weight ratio of water to calcium nitrate ranging from about 1/26 to about 2/1.

4. The method as defined in claim 1 wherein sufficient ammonium nitrate, slaked or unslaked lime, liquid water miscible organic fuel, and additional water, if necessary, are mixed and reacted to form an explosive composition comprising from about 5 to about 25 percent by weight calcium nitrate; from about 10 to about 25 percent liquid water miscible organic fuel; from about 3 to about 8 percent water; and from about 50 to about 85 percent by weight of ammonium nitrate.

5. The method as defined in claim 4 including thickening the ammonium nitrate and liquid water miscible organic fuel by adding a thickening or gelling agent thereto prior to reacting it with slaked or unslaked lime.

6. The method as defined in claim 4 including mixing with said explosive composition during the manufacture thereof up to about 60 percent by weight of a particulate metallic fuel component.

* * * * *