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Wade

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[54] **WATER-IN-OIL EMULSION TYPE EXPLOSIVE COMPOSITIONS HAVING STRONTIUM-ION DETONATION CATALYSTS**

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[21] Appl. No.: **295,565**

[52] **U.S. Cl.** **149/2,** 149/21, 149/41, 149/47, 149/60, 149/61, 149/70, 149/71, 149/73, 149/76, 149/78, 149/83, 149/85, 149/92

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

[58] **Field of Search** 149/2, 41, 46, 47, 149/60, 61, 73, 62, 70, 71, 76, 21, 92, 82, 83, 85

[56] **References Cited**

UNITED STATES PATENTS

3,039,903	6/1962	Enoksson	149/61 X
3,296,094	1/1967	Gehrig	149/47
3,356,547	12/1967	Berthmann et al.	149/62 X
3,447,979	6/1969	Bluhm et al.	149/61 X
3,453,155	7/1969	Sheeran et al.	149/61 X
3,459,608	8/1969	Ludolphy et al.	149/61 X
3,617,406	11/1971	Young	149/41
3,674,578	7/1972	Cattermole et al.	149/2
3,447,978	6/1969	Bluhm	149/44 X

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[57] **ABSTRACT**

A water-in-oil emulsion explosive composition comprising a carbonaceous fuel, an inorganic oxidizer, a detonation sensitizer, water, an emulsifier, and an occluded gas is further sensitized by the incorporation of strontium compounds which are soluble in the aqueous phase. The sensitized materials can be detonated with a No. 6 cap at diameters as low as 1 inch and with densities as high as 1.25 grams/cc.

18 Claims, No Drawings

WATER-IN-OIL EMULSION TYPE EXPLOSIVE COMPOSITIONS HAVING STRONTIUM-ION DETONATION CATALYSTS

This invention relates to water-in-oil emulsion type explosive compositions containing a detonation catalyst sensitizer. Specifically, the invention relates to inorganic oxidizer salt explosives of the aqueous slurry type containing an improved sensitizer-catalyst system. Furthermore, the invention relates to explosives having high energy, high sensitivity, high detonation rate properties, and unexpectedly high densities.

The invention relates to water-in-oil emulsion type blasting agents exemplified by Bluhm, U. S. Pat. No. 3,447,978, and Cattermole, U. S. Pat. No. 3,674,578, which have many advantages over conventional slurry blasting compositions but which are particularly disadvantaged in that they are not cap-sensitive. These materials, therefore, require a booster in order to effect their detonation. The use of metal ion and inorganic metal compounds as a catalyst-sensitizer system for such explosive compositions was first described in my copending patent application, U. S. Ser. No. 69,433, now U. S. Pat. No. 3,715,247.

I have now found that water-in-oil emulsion explosive compositions can be prepared which retain all the advantages of the emulsion blasting agents described in the above-cited patents but which, in addition, are cap-sensitive without the use of an explosive ingredient, in diameters as low as 1 inch and sometimes smaller, at densities as high as 1.25 grams/cc., at temperatures lower than 20° F., and which can be stored over extended periods of time (at least 3 months). Therefore, it is not necessary to employ a booster to detonate the compositions of the present invention which are even more sensitive than those described in my earlier patent. The compositions of this invention, however, have excellent water resistance and safety characteristics in that they have high resistance to burning, impact, friction, rifle bullets, and static. They do not initiate headaches as do compositions employing nitroglycerin, and they have unexpectedly high velocities (typically, 17,000 feet per second) in 1-inch diameters and unexpectedly high detonation pressures (typically, 90-100 kilobars).

The greatly enhanced sensitivity of the compositions of the invention is brought about without the addition of ingredients which are cap-sensitive in themselves. Unexpectedly, it has been discovered that, while metal ions of Group 2A of the periodic table of elements, such as beryllium, magnesium, calcium, and barium, do not effectively sensitize water-in-oil emulsion type explosives, strontium ion is particularly unique in that it does. Therefore, the incorporation of water-soluble strontium compounds in low concentrations in the aqueous phase of the water-in-oil type explosive slurries of the invention has been found to sensitize the slurries to a No. 6 blasting cap.

It is an object of the present invention, therefore, to present a water-in-oil slurry type explosive composition or blasting agent which comprises inorganic oxidizing salts, water, water-insoluble organic fuel that forms a continuous oil phase, a lipophilic emulsifier, and from about 4 percent to about 47 percent by volume of occluded gas at 70° F. and atmospheric pressure, and a small amount of water-soluble strontium metal compound.

The cap-sensitive compositions of this invention comprise about 1 percent to about 10 percent (all percentages herein are by weight) of a carbonaceous fuel, 55–87 percent oxidizer salt, 0.4–4.0 percent strontium ion catalyst, 10–25 percent water, 0.5–2.0 percent lipophilic emulsifier, and sufficient gas to give the composition a density of about 0.9 to about 1.4 grams/cc. (4–48 percent by volume). Preferred compositions which are cap-sensitive in 1-inch diameters comprise about 2–6 percent carbonaceous fuel, about 60–80 percent oxidizer salt, about 1–10 percent strontium salt, about 15–20 percent water, about 0.75–1.25 percent lipophilic emulsifier, and sufficient gas to give the composition a density ranging from 0.9–1.25 grams/cc.

In addition, the composition can contain a gelling agent which greatly increases storage stability. The preferred amount for gelling agents is about 0.25 percent to about 2.0 percent. Suitable gelling agents include polyacrylamide, interpolymers of methyl vinyl ether and maleic anhydride and their salts, guar gum, etc.

The compositions may also contain up to about 10 percent auxiliary fuel, such as sulfur, sugar, urea, formaldehyde, dimethyl formaldehyde, aluminum, or magnesium, preferably aluminum, aluminum alloys, or sulfur for greatest sensitivity. Up to about one-third of the water may be replaced with a water soluble fuel, such as ethylene glycol; low molecular-weight alcohol, such as methanol, ethanol, or propanol; however, water is preferred because of its economy and because it is a better solvent for the oxidizing salts. Other optional ingredients include glycerin, formamide, dimethyl formamide, sugar, and water-soluble alkyl amines, such as ethylene diamine and methyl amine.

The carbonaceous fuel is a water-immiscible, emulsifiable fuel which is liquefiable at a temperature up to about 200° F., and preferably between 110° F. and about 160° F., to facilitate aeration and packaging. Waxes having melting points of at least 80° F., and preferably in the range of about 110° F. to about 200° F., are usually suitable; examples include waxes derived from petroleum, such as petrolatum wax, microcystalline wax, and paraffin wax; mineral waxes, such as ozocerite and montan wax; animal waxes, such as spermacetic wax; and insect waxes, such as beeswax and Chinese wax. A modified, highly cohesive microcystalline wax having a melting point of about 114°–119° F. and identified as the trademark "Indra 2119" sold by Industrial Raw Materials Corporation and a similar wax sold by the same company under the trademark "Indra 1153" having a melting point of about 150°–155° F. are preferred as they give good sensitivity and stability.

For greater sensitivity, it is preferred to use a carbonaceous fuel, such as 100 percent wax. However, up to about 60 percent of the wax can be replaced with an oil to increase long-term storage stability. Examples of suitable oils include the various petroleum oils, DNT, and various vegetable oils; a highly refined mineral oil sold by Atlantic Refining Company under the trademark "Atreol 34" is preferred if a stabilizing oil is employed.

The oxidizer may be about 20 percent to about 95 percent ammonium nitrate (AN), about 5 percent to about 40 percent other inorganic nitrate, up to about 60 percent of an organic amine salt of an inorganic oxidizing acid, and up to about 30 percent inorganic chlorate or inorganic perchlorate. The oxidizer which is preferred for greatest sensitivity comprises about

55–80 percent ammonium nitrate (AN), about 5–15 percent sodium nitrate (SN), about 10–20 percent ethylene diamine dinitrate (EDDN), and about 5–10 percent ammonium perchlorate (AP). Examples of other suitable inorganic nitrates include sodium nitrate, which is preferred for greatest sensitivity, potassium nitrate, lithium nitrate, calcium nitrate, magnesium nitrate, barium nitrate, zinc nitrate, and organic amine nitrates, nitrites, chlorates, perchlorates, such as monomethylamine nitrate (MMAN), nitrite, chlorate and perchlorate, ethylene diamine dinitrate, diperchlorate, and dichlorate, dimethylamine nitrate, trimethylamine nitrate, ethylamine nitrate, propylamine nitrate, ethanolamine nitrate, guanidine nitrate, urea nitrate, and salts of phenylamine, such as aniline nitrate, chlorate and perchlorate, p-chloroaniline nitrate, and phenylene diamine dinitrate. Of the above-mentioned salts, saturated aliphatic amine nitrates containing up to three carbon atoms, for example, monomethylamine nitrate, trimethylamine nitrate, ethylene diamine dinitrate, and ethanolamine nitrate are particularly preferred because of the ease of formulation of explosives therewith and the outstanding explosive properties, such as velocity and strength of the resulting compositions. Mixtures of the aforementioned salts can be used; and, generally, in such salt mixtures, the overall oxygen balance of the salt should be more a positive than minus 150 percent. Examples of suitable chlorates include sodium chlorate, potassium chlorate, calcium chlorate, and lithium chlorate. Suitable perchlorates include ammonium perchlorate, preferred because of greater weight strength, sodium perchlorate, calcium perchlorate, potassium perchlorate, lithium perchlorate, magnesium perchlorate, barium perchlorate, and zinc perchlorate.

The strontium ion detonation catalyst is introduced as a water-soluble organic or inorganic strontium salt. Preferably, the strontium is introduced as an oxidizing salt, such as strontium nitrate, strontium chlorate, strontium perchlorate, strontium nitrite, and the like. However, any water-soluble strontium salt, such as strontium chloride, bromide, acetate, bromate, cyanide, dichromate, iodide, hydroxide and oxide are suitable.

The emulsifier is a water-in-oil emulsifier such as those derivable from sorbitol by esterification with removal of one molecule of water, such as sorbitan, fatty acid esters, for example, sorbitan monolaurate, sorbitan monooleate, sorbitan monopalmitate, sorbitan monostearate, and sorbitan tristearate. Other useful materials comprise mono- and diglycerides of fat-forming fatty acids, as well as polyoxyethylene sorbitol esters, such as polyoxyethylene sorbitol, beeswax derivative materials and polyoxyethylene(4)lauryl ether, polyoxyalkylene(2)ether, polyoxyethylene(2stearyl ether, polyoxyalkylene oleyl/laurate, oleyl acid phosphate, substituted oxazolines, and phosphate esters and mixtures thereof.

The gas may be in the form of occluded air or in a gas-entrapping material such as phenol-formaldehyde or urea-formaldehyde hollow microspheres, expanded perlite, or hollow glass microspheres. The function of the gas is to reduce the density to within the range of .8–1.4 grams/cc.; and, therefore, any gas, such as nitrogen, CO_2, carbon monoxide, argon, hydrogen and helium, methane, propane, freon, and the like can be used. If a combustible gas-entrapping material or combustible gas is used, it should be included in the calculation for the total fuel.

The compositions of this invention are preferably made by premixing the water, the inorganic oxidizer, the detonation catalyst, and a second premix of the carbonaceous fuel and the emulsifier. The two premixes are heated, the first until the salts are completely dissolved (about 120°–205° F.), and the second until the carbonaceous fuel has liquified (about 120° F. or more). The premixes are then blended together and emulsified, after which the air or gas or gas-entrapping material is incorporated therein until the density is lowered to the required range. Additional details and alternatives for the preparation of emulsion blasting agents can be found in the Bluhm U.S. Pat. No. 3,447,978 and my copending application, Ser. No. 69,433, filed Sept. 3, 1970, now U. S. Pat. No. 3,715,247, which are herein incorporated by reference. In the continuous manufacture of the compositions, it is preferred to prepare an aqueous solution containing all the ingredients with the exception of the organic fuel in one tank and thereafter pumping into a mixing device where it is emulsified with hot fuel liquids heated to just above their congealing point, pumped from a second tank. The emulsion is then aerated and packaged through a Bursa filler or any other conventional device in desired diameters.

The effectiveness of the presence of strontium ion in compositions of the present invention is demonstrated in the following examples:

EXAMPLES 1 – 6

The blasting agents of Examples 1 through 6 are prepared by making a premix of water, the inorganic oxidizer, and the detonation catalyst at 160° F. and a second premix of the carbonaceous fuel and the emulsifier at 130° F. The first premix is then slowly added to the second premix with vigorous agitation to obtain a water-in-oil emulsion. The agitation is continued with cooling to occlude air until the density is lowered to the desired range. In Example 5, hollow glass microspheres sold under the trademark "Corcel" by the Interpace Corporation can be added in place of the occluded air. The compositions are then extruded or tamped into high-density polyethylene tubes which are sealed with plastic caps and stored at 70° F. until detonated. Other packaging materials such as paper, cardboard, and plastics such as polyethylene film are suitable.

Table I lists the compositions in terms of their concentration in percent by weight, their density at the time of detonation, their diameter at the time of detonation, their detonation temperature, and the standard blasting cap size required for detonation.

The wax referred to is a microcrystalline wax having melting points of 153° F. and 114°–119 F., sold under the trademarks "Indra 1153" for Examples 1–3 and "Indra 2119" for Examples 4–6 by Industrial Raw Materials Corporation, respectively. The oil referred to in Examples 1 through 6 is a highly refined mineral oil sold by Atlantic Refining Company under the trademark "Atreol 34."

The emulsifier in Examples 1 through 6 are mono- and diglycerides of fat-forming fatty acids or sorbitan monooleate sold by ICI America Inc. under the trademarks "ATMOS 300" and "SPAN 80," respectively.

The gelling agent referred to in Example 6 is guar gum sold by Stein Hall Company under the name "Jaquar EXCW."

The air-entrapping material of Example 5 is "Corcel" sold by the Interpace Corporation, which comprises hollow glass agglomerate particles.

When detonated, the compositions described can be expected to have a detonation velocity ranging between 16,000 and 20,000 feet/second.

TABLE I

Formulations (percent by wt.)	Examples					
	1	2	3	4	5	6
Wax	4.5	4.5	4.5	2.0	2.0	2.0
Oil	0.5	0.5	0.5			
AN	60.2	60.2	60.0	44.0	31.7	34.4
SN	10.0	10.0	10.0	10.0	10.0	10.0
EDDN				10.0	10.0	20.0
AP	10.0	10.0	4.0	10.0	10.0	10.0
Emulsifier	1.0	1.0	1.0	1.0	1.0	1.0
Water	16.8	16.8	17.0	20.0	20.0	17.0
Gelling agent						.6
Sulfur						2.0
Air-entrapping material					3.0	
Sr^{++} ion	(1.2)	(1.2)	(1.2)	(0.55)	(2.0)	(4.90)
$Sr(NO_3)_2$	3.0	3.0	3.0			
$SrCl_2$				1.0		
$Sr(OAc)_2$					5.0	
$Sr(OH)_2$						5.5
Density, g./cc	1.15	1.15	1.08	1.14	0.95	1.12
Diameter, inches	1	1.25	2	1	1	1
Cap size	8	8	6	8	6	6
Det. temp., ° F	70	70	70	70	70	70

What is claimed is:

1. A cap-sensitive water-in-oil emulsion explosive composition comprising:
   - *a.* about one percent to about 10 percent of a water-immiscible, emulsifiable carbonaceous fuel liquifiable at a temperature up to about 200° F., selected from the group consisting of petrolatum, microcrystalline, paraffin, mineral, animal, and insect waxes, petroleum oils, and vegetable oils;
   - *b.* about 55 percent to about 87 percent of an oxidizer comprising about 20 percent to about 95 percent ammonium nitrate, about 5 percent to about 40 percent of an other inorganic nitrate, up to about 60 percent of a salt formed by reacting organic amines with an inorganic oxidizing acid, and up to about 30 percent inorganic chlorate or perchlorate;
   - *c.* about 10 percent to about 25% water;
   - *d.* about .5 percent to about 2 percent water-in-oil emulsifier;
   - *e.* sufficient occluded gas or gas-entrapping material to give the composition a density of about 0.9 to about 1.25 grams/cc.; and
   - *f.* about 0.4 – 4 percent strontium ion including that present in said other inorganic nitrate as a detonation catalyst sensitizer in the form of a water-soluble strontium salt.

2. A composition of claim 1 wherein said other inorganic nitrate is sodium nitrate.

3. A composition of claim 1 wherein said strontium salt is an oxidizing salt of strontium selected from strontium nitrate, strontium chlorate, and strontium perchlorate.

4. A composition of claim 1 wherein said detonation sensitizer is a strontium chloride, acetate, bromide, or hydroxide.

5. A composition of claim 1 wherein said oxidizer comprises about 55 percent to about 80 percent ammonium nitrate, about 5 percent to about 15 percent sodium nitrate, about 10 percent to about 35 percent ethylene diamine dinitrate, and about 5 percent to about 10 percent ammonium perchlorate.

6. A composition of claim 1 wherein up to about 10 percent of an auxiliary fuel is included.

7. A composition of claim 6 wherein said auxiliary fuel is aluminum or sulfur.

8. A composition of claim 1 wherein about .25 percent to about 2 percent of a gelling agent is included.

9. A composition of claim 8 wherein said gelling agent is guar gum.

10. A cap-sensitive water-in-oil emulsion explosive composition comprising:
   - *a.* about 2 percent to about 6 percent water-immiscible, emulsifiable fuel which is liquifiable at a temperature between about 110° F. and about 160° F., selected from the group consisting of petrolatum, microcrystalline, paraffin, mineral, animal, and insect waxes, petroleum oils and vegetable oils;
   - *b.* about 60 percent to about 80 percent of an oxidizer comprising about 20 percent to about 95 percent ammonium nitrate, about 5 percent to about 40 percent of an other inorganic nitrate, up to about 60 percent ethylene diamine dinitrate, up to about 40 percent alkylamine nitrate or alkanolamine nitrate, and up to about 30 percent inorganic chlorate or perchlorate;
   - *c.* about 15 percent to about 20 percent water;
   - *d.* about .75 percent to about 1.25 percent emulsifier;
   - *e.* sufficient occluded gas or gas-entrapping material to give the composition a density of about 1.05 to about 1.25 grams/cc.; and
   - *f.* about 1 percent to about 10 percent including that present in said other inorganic nitrate of a detonation catalyst sensitizer comprising a water-soluble inorganic salt selected from the group consisting of strontium nitrate, strontium chloride, strontium chlorate, strontium perchlorate, strontium acetate, strontium hydroxide, and strontium bromide.

11. A composition of claim 10 wherein said oxidizer comprises about 55 percent to about 80 percent ammonium nitrate, about 5 percent to about 15 percent sodium nitrate, about 10 percent to about 35 percent ethylene diamine dinitrate, and about 5 percent to about 10 percent ammonium perchlorate.

12. A composition of claim 10 wherein said gas is in the form of occluded air bubbles.

13. A composition of claim 10 wherein said gas is in a gas-entrapping material.

14. A composition of claim 10 wherein said composition includes up to about 10 percent auxiliary fuel.

15. A composition of claim 14 wherein said auxiliary fuel is aluminum or sulfur.

16. A composition of claim 15 wherein about 0.25 – 2 percent of a gelling agent is included.

17. A composition of claim 16 wherein said gelling agent is guar gum.

18. A composition of claim 1 wherein said gas-entrapping material is selected from the group consisting of expanded perlite, and hollow microspheres of phenol-formaldehyde, urea-formaldehyde, and glass.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,765,964 Dated October 16, 1973

Inventor(s) Charles Gary Wade

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

Column 1, line 44, "90-100" should read --90-110--.

Column 4, line 57, "114°-119F." should read --114°-119°F.--.

Column 5, lines 20-25 in Table I under Example column 6, "(4.90)" should read --(4.0)--.

Signed and sealed this 3rd day of December 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

PO-1050
(5/69)

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