Aug. 15, 1972 R. H. EVANS 3,684,594
AQUEOUS EXPLOSIVE COMPOSITIONS HAVING REVERSIBLE FLUENT-NONFLUENT PROPERTIES
Filed May 15, 1970

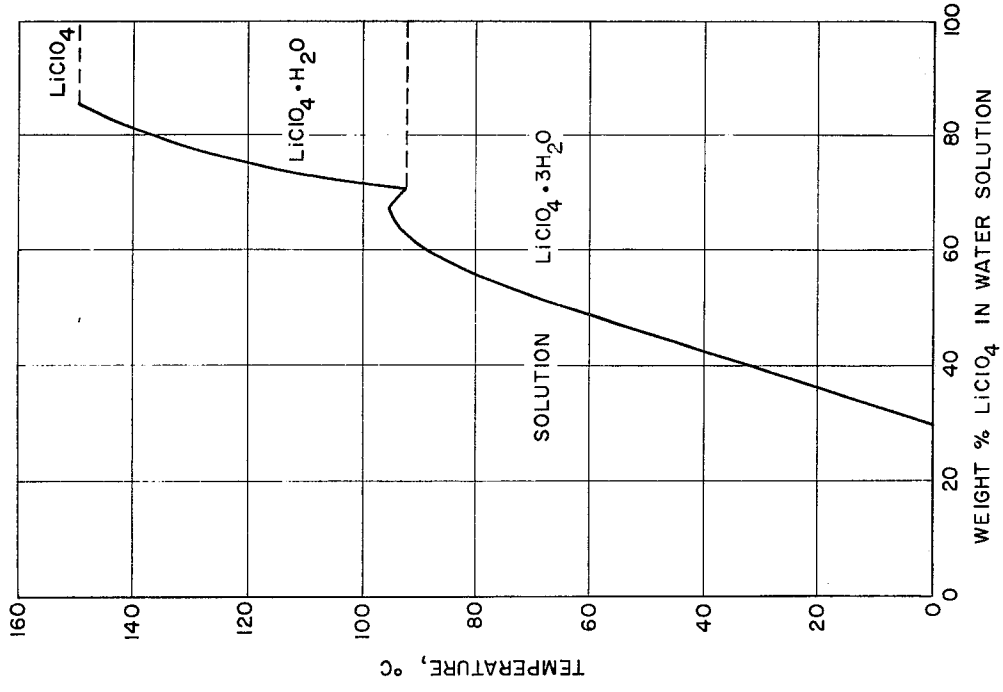


FIG. 2

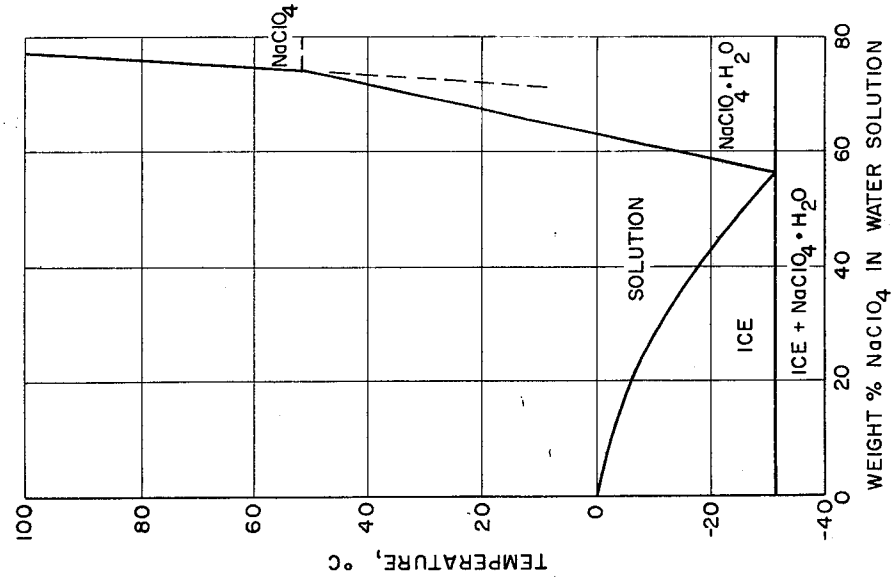


FIG. 1

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AQUEOUS EXPLOSIVE COMPOSITIONS HAVING REVERSIBLE FLUENT-NONFLUENT PROPERTIES

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U.S. Cl. 149—38 12 Claims

ABSTRACT OF THE DISCLOSURE

Aqueous exposive compositions having a density of 1.8 grams/cc. or greater and having reversible fluent-nonfluent properties are provided. These aqueous explosive compositions employ metal perchlorates, capable of forming a hydrate with water, as the oxidizer. Fluent-nonfluent reversibility is achieved by processing the aqueous compositions at temperatures above a temperature at which a hydrate of the perchlorate will dissociate releasing water enabling preparation of a fluent explosive slurry composition. The fluent exposive slurry composition is then cooled to a temperature at which a hydrate forms and the previously released water is combined with the metal perchlorate as a hydrate forming a nonfluent explosive slurry composition.

This invention relates to a new class of high energy, high density explosive compositions comprising water, a metallic perchlorate capable of forming a hydrate with water, and a moderate amount of a fuel and/or sensitizing agent. In another aspect this invention relates to the process for preparing high energy, high density explosive compositions which have reversible fluent-nonfluent properties as a result of hydrate formation and dissociation.

Explosive compositions of the slurry type employing an inorganic oxidizer salt as the oxidizing agent have had wide use in the explosives industry in recent years. These compositions are generally comprised of an inorganic oxidizer salt, water, a sensitizing agent, and a thickening agent. The thickening agent is employed in an amount sufficient to impart consistency to the slurry and to prevent settling of any of the various solid ingredients in the slurry. In many inorganic oxidizer salt compositions, the principal oxidizer salt employed is ammonium nitrate. The exposives art has long recognized that other inorganic oxidizing salts and in particular, metal perchlorates, are effective oxidizing agents. Metal perchlorates have been employed in limited quantities in explosive compositions principally because in dry form and mixed or in contact with fuels, the perchlorates are hazardous, being particularly sensitive to shock, friction and heat. The explosives art has also recognized the advantages of explosive compositions that can be processed as a fluent slurry and then converted into a stable nonfluent composition after uniform mixing of the composition has taken place and the slurry has been transferred to a suitable receiving means. In order to achieve this result, gelling agents, thickening agents and polymers are commonly added to slurry compositions to convert the slurry from the fluent to the nonfluent state. Other means of converting exposive compositions both commercial and military from the fluent to the nonfluent state depend upon crystalline melting or freezing, upon changed solubility of products with temperature or upon the viscosity changes with temperature.

It is an object of this invention to provide an explosive composition employing metal perchlorates as the oxidizing agent which can be safely processed as a fluent aqueous slurry and which can be converted to the nonfluent state without the necessity of using gelling agents, thickening agents, or crosslinkable polymers and crosslinking agents.

It is another object of this invention to provide explosive slurry compositions having high energy densities which can be converted from the fluent to the nonfluent state as a result of hydrate formation and dissociation.

Other objects of this invention will, in part, be obvious and will, in part, appear hereinafter. For a complete understanding of the nature and objects of this invention, reference is made to the following detailed description.

In accordance with this invention an aqueous explosive composition is provided having a density of at least 1.8 grams per cc., said explosive composition comprising a metal perchlorate oxidizer selected from the group consisting of sodium perchlorate, lithium perchlorate, magnesium perchlorate, strontium, perchlorate, calcium perchlorate, aluminum perchlorate, and mixtures thereof; water, and a metal fuel and/or a sensitizing agent, said explosive composition comprising by weight from about 25% to about 90% of a metal perchlorate oxidizer, from about 3% to about 15% water, from about 0% to about 40% metallic fuel, and from 0% to about 60% sensitizing agent. The cumulative total of metallic fuel and sensitizing agent in the explosive composition of this invention comprises at least about 20% by weight of the composition. The ratio of metal perchlorate oxidizer to water in the explosive composition is maintained within the compositional range in which substantially all the water in explosive composition can be chemically bound to the metal perchlorate when the metal perchlorate is converted from its state of hydration in the fluent slurry to a higher state of hydration by a reduction in the temperature of the slurry.

The explosive compositions of this invention are prepared by a process which has as its first step the admixing of water and a metal perchlorate oxidizer which will form a hydrate with water at a temperature above the dissociation temperature of a hydrate which will form upon cooling and at which temperature there is provided sufficient uncombined water permitting addition of solid ingredients to the admixture to form a uniform and fluent slurry composition. The fluent slurry is stable to settling of solid ingredients since it has a high density of about 1.8 grams per cc. or above which effectively prevents settling out of solid ingredient additives employed. The resulting homogeneous and fluent explosive compositions is transferred to a suitable receiving means and cooled to a temperature at which the metal perchlorate hydrate forms a higher state of hydration than its state of hydration during mixing whereby a nonfluent explosive composition is formed. In the process of this invention some metal perchlorate can be and usually is dissolved in the water during the mixing process. Thus, in the case of sodium perchlorate, mixing of solid ingredients is generally carried out with most of sodium perchlorate in solution in water. In this condition the sodium perchlorate is in a non-hydrated state. Cooling of the admixture to below the dissociation temperature of sodium perchlorate monohydrate permits the water in the admixture to be chemically combined whereby the slurry is converted to the nonfluent state. In the case of a metal perchlorate where more than one state of hydration exists such as lithium perchlorate or aluminum perchlorate, it can be necessary to cool the fluent slurry to a temperature which is below the dissociation temperature of one or more of the possible hydrates of the perchlorate in order to combine substantially all the water present so that a nonfluent slurry results. The hydrate dissociation temperature is the minimum temperature at which the hydrate loses or starts to lose its water of hydration. Hydrates often do not have sharply defined dissociation temperatures and often dissociate over a temperature range.

The foregoing process can also be described with reference to FIGS. 1 and 2 in which FIG. 1 is a phase diagram of the system sodium perchlorate-water and FIG. 2 is a

phase diagram of the system lithium perchlorate-water. In the system sodium perchlorate-water the principal hydrate of sodium perchlorate that forms is sodium perchlorate monohydrate. Thus when preparing explosive compositions of this invention employing the sodium perchlorate-water system it is necessary to maintain the temperature of the aqueous slurry composition of sodium perchlorate above the dissocation temperature of sodium perchlorate monohydrate. In this system mixing of the slurry is carried out with the sodium perchlorate present in an unhydrated state. When employing the lithium perchlorate-water system to prepare the explosive compositions of this invention it is generally preferable to mix water and the lithium perchlorate at a temperature above the dissociation temperature of lithium perchlorate trihydrate. Thus, the solid ingredients can be admixed to form a fluent slurry in which the lithium perchlorate is present as a monohydrate. It is necessary to provide sufficient water in this composition so that the lithium perchlorate monohydrate and uncombined water provide sufficient liquid to permit dispersing of the desired amount of solid ingredients throughout the slurry during mixing. The amount of free water in the slurry composition is within the limits of water which can be combined with the lithium perchlorate when the lithium perchlorate is converted from the monohydrate to the trihydrate upon cooling to the dissociation temperature of the trihydrate or below.

Table I below contains a listing of metal perchlorates which can be employed in this invention, the predominate hydrates which will form with these metal perchlorates, a mixing temperature zone in which the perchlorate-hydrates lose their water of hydration and in which temperature zone a fluent slurry composition can be formed, and a dissociation temperature for the perchlorate hydrates at which temperature or below the perchlorate will form the hydrate designated and in which temperature range a nonfluent slurry can be formed in accordance with this invention. For almost all applications of the slurry compositions and process of this invention the slurry will be cooled to a temperature below the dissociation temperature of the perchlorate hydrate in its highest state of hydration to convert the slurry from a fluent to a nonfluent condition.

TABLE I

Metal perchlorate hydrate	Dissociation temperature, ° C.	Mixing temperature range, ° C.
$NaClO_4.H_2O$*	50	>50
$LiClO_4.H_2O$		
$LiClO_4.3H_2O$	93	95–100
$Mg(ClO_4)_2.2H_2O$		
$Mg(ClO_4)_2.4H_2O$		
$Mg(ClO_4)_2.6H_2O$	80	>80–100
$Ca(ClO_4)_2.4H_2O$	<85	85–100
$Sr(ClO_4)_2.2H_2O$		
$Sr(ClO_4)_2.4H_2O$	95	>95–100
$Al(ClO_4)_2.6H_2O$	<120	121–170
$Al(ClO_4)_2.9H_2O$	<85	86–125
$Al(ClO_4)_3.15H_2O$	<75	77–80

*A trihydrate of sodium perchlorate is known but is generally considered unstable.

The following examples more fully illustrate this invention. All parts and percentages are by weight unless otherwise specified.

EXAMPLE 1

About 35 parts of sodium perchlorate, and 10 parts of water are added to a paddle type mixer and mixed slowly at 60° C. The water dissolves about 85% of the sodium perchlorate. To the resulting admixture comprising a fluent slurry of sodium perchlorate particles in aqueous sodium perchlorate solution is added 17.5 parts of cyclotrimethylenetrinitramine (RDX), and 37.0 parts of particulate aluminum in which at least 97% of the particles are smaller than 44 microns in their largest dimension. The slurry temperature is maintained at 60° C. or above during the entire mixing process. The aqueous sodium perchlorate solution provides sufficient liquid to maintain the admixture in the form of a fluent explosive composition. After sufficient mixing the fluent explosive composition is poured into a polyethylene bag and is cooled to a temperature below the sodium perchlorate-hydrate dissociation temperature. Under these temperature conditions, the sodium perchlorate chemically binds the water in the composition in the form of a crystalline monohydrate. This hydrate formation removes the "free" water from the fluent slurry with the result that a solid nonfluent explosive composition is formed.

A small charge of the nonfluent explosive composition prepared as described in Example 1 is tested for stability and initiation sensitivity. The test values are within limits normally considered safe for processing. Results of the testing are given below.

Impact test—No reaction on impact of a 2 kilogram drop weight from a height of 64 centimeters.

Sliding friction test—No reaction to sliding friction at 8 feet per second and at a pressure of 22,000 p.s.i.

Thermal stability—No exotherm below 210° C.

Critical diameter—<1.0 inch; detonation rate 5100 meters/sec. Detonation is accomplished with a blasting cap containing 0.95 gram of pentaerythritol tetranitrate. Detonation propagation rate is measured and the rate is 5100 meters/second.

EXAMPLES 2–7

The following examples illustrate additional explosive compositions of this invention. These compositions are prepared following the procedure set forth in Example 1 with the exception that the processing temperature at which these compositions are mixed varies as specified in Table II.

TABLE II

Example Number	2	3	4	5	6	7
Composition, wt. percent:						
$NaClO_4$	30		60	40	30	30
$LiClO_4$	20					
$Mg(ClO_4)_2$						
$Sr(ClO_4)_2$		56				
Si (5μ)			30			
Ferro silicon (12μ)				20		
Al (12μ)		38			30	30
Al (38μ)	38					
RDX [1]				30	30	
HMX [2]						30
H_2O (pH 5.0)	10	6	10	10	10	10
Formamide	2					
Mixing temperature, ° C. (fluent slurry)	95–100	95–100	>70	>70	>70	>70
Cooling temperature, ° C. (non-fluent slurry)	≥93	≥95	≥50	≥50	≥50	≥50
Critical diameter (inches)				2.0	1.0	1.0
Detonation rate (meters/sec.)				5,500	6,200	5,850

[1] Cyclotrimethylenetrinitramine (Type E).
[2] Cyclotetramethylenetetranitramine (Class B).

The explosive composition of Example 2 is a fluent mixture between 95 and 100° C. This composition solidifies with the formation of the trihydrate of lithium perchlorate at a temperature of 93° C. or below, see FIG. 2. In this example it is not believed that the monohydrate of sodium perchlorate takes part in the hydrate hardening of the mixture since the water in the mixture is utilized principally in forming the trihydrates of lithium perchlorate and possibly some monohydrates of lithium perchlorate at temperatures above the dissociation temperature of the sodium perchlorate hydrate, see FIG. 1.

The explosive composition of Example 3 is a fluent slurry between 95 and 100° C. but hardens on cooling below 95° C. to a nonfluent slurry where the di, tetra and other hydrates of strontium perchlorate are formed.

The explosive composition of Examples 4–7 are all fluent above 70° C. and harden upon cooling to 50° C. or below to a nonfluent slurry as a result of the sodium perchlorate-hydrate formation. No attempt is made to detonate the explosive composition of Example 4 but the explosive compositions of Example 5 detonates at a diameter of less than about 20 inches, and the explosive composition of Examples 6 and 7 detonate at a diameter of less than 1.0 inch.

The metal perchlorates which can be employed in the explosive composition of this invention are all capable of forming one or more hydrates with water. When preparing the fluent-nonfluent compositions of this invention it is necessary to maintain the perchlorate-water ratio within a compositional range within which a hydrate will form in order to take advantage of hydrate formation to achieve heat reversible fluent-nonfluent compositions. This compositional range varies with different metal perchlorates depending on the predominate hydrates which can be formed which hydrates are set forth in Table I. Metal perchlorates can be added to water in forming a fluent slurry as either anhydrous or hydrated salts. In generals, particle size of the metal perchlorates can range from about 10 to about 200 mesh (U.S. Standard Sieve Series).

High energy metallic fuels which can be employed in the explosive composition of this invention include metals and alloys of metals. Illustrative materials of this class include aluminum, boron, magnesium, silicon, titanium, zirconium, and alloys such as ferrosilicon, aluminum/magnesium, silicon carbide, and the like. These metallic fuels are generally employed as small particles having a particle size range from about 7μ to about 50μ. A preferred high energy metallic fuel for use in the explosive composition of this invention is aluminum. When employing aluminum in these compositions it is preferable to maintain the water admixed in the slurry composition at a pH of about 6.0 or below and preferably at a pH of about 5.0 or below. By making the water slightly acidic the metallic aluminium remains passive to attack water present within the composition with the result that the compositions are stable for long periods of time.

When employing a metallic fuel such as magnesium, it is preferable to employ an alkaline buffer in the water, which passivates the magnesium from attack by water present within the composition. Other means to passivate metals such as coating of the metals employed to prevent attack of the metals by water are known and generally can be employed as long as the passivating material is compatible with the ingredients of the explosive composition.

Sensitizing agents which can be employed in the explosive composition of this invention include pentaerythritol tetranitrate (PETN), trinitrotoluene (TNT), cyclotrimethylenenitramine (RDX) cycloetramethylenetetranitramine (HMX), nitrophenols, and the like.

The explosive composition of this invention can optionally contain from 0% to about 5.0% of an organic fuel which functions as both a solvent for the metal perchlorate and as a sensitizing agent. The organic fuels which can be employed are solvents for the metal perchlorate salts and will form a solid solvate with the metal perchlorate salts. Illustrative solvents for the metal perchlorate oxidizer salts of this invention include low molecular weight amines such as ethylamine, propylamine, butylamine, pentylamine, cyclohexylamine, mixtures thereof, and the like; amides such as formamide, dimethylformamide, acetamide, urea, N-methyl propionamide, N-ethyl propionamide, N-propylpropionamide, acetanilide, mixtures thereof, and the like; polyhydric alcohols, ethylene glycol, propylene glycol, polyethylene glycol, polypropylene glycol, polyethylene glycol monoethylether, polyethylene glycol dimethylether and the like.

The explosive compositions of this invention can be employed as blasting agents, as conventional explosives and as military explosives. When employed as a blasting agent these compositions can be stored in polyethylene bags and used for blasting in dry or wet bore holes. The explosive compositions of this invention are particularly useful in military explosives. These compositions can be mixed, charged to a munition and cooled to a homogeneous solid explosive mass. If desired, these compositions can be removed from a munition by heating the munition to a temperature above the hydrate dissociation temperature of the explosive at which temperature water will be released from the hydrate permitting the explosive composition to be removed from the munition.

In the explosive compositions of this invention the water solvent replaces relatively non-energetic carbonaceous fuels and allows for a larger incorporation of high energy metal fuels, thus increasing the overall energy of the explosive. The increased energy density and inherently lower costs of these solvated perchlorate explosive make these explosive compositions highly advantageous particularly where it is desirable to convert the slurry from the fluent to nonfluent state and vice versa.

What I claim and desire to protect by Letters Patent is:

1. An explosive composition having a density of at least 1.8 grams per cc., said explosive composition consisting essentially of by weight from about 25% to about 90% of a metal perchlorate oxidizer selected from the group consisting of sodium perchlorate, lithium perchlorate, lithium perchlorate, magnesium perchlorate, chlorate, magnesium perchloride, strontium perchlorate, and mixtures thereof; from about 3% to about 15% water, from about 0% to about 40% metallic fuel, and from 0% to about 60% organic sensitizing agent, the cumulative total of metallic fuel and organic sensitizing agent in the composition comprising at least 20% by weight of the composition, and the ratio of metal perchlorate oxidizer(s) to water in the explosive composition being within the compositional range in which substantially all of the water in the explosive composition is chemically bound to the metal perchlorate(s) in the form of a perchlorate-hydrate(s) at a temperature below a dissociation temperature of the perchlorate hydrate(s) at which temperature said explosive composition is nonfluent.

2. The explosive composition of claim **1** containing from 0% to about 5.0% of organic fuel solvent.

3. An explosive composition having the density of at least 1.8 grams per cc. said explosive composition consisting essentially of sodium perchlorate, water, a metallic fuel, and a sensitizing agent, said composition comprising by weight from about 25% to about 75% sodium perchlorate, from about 6% to about 15% water, from about 5% to about 40% metallic fuel, and from about 2% to about 60% sensitizing agent, the cumulative total of metallic fuel and sensitizing agent in the composition comprising at least 20% by weight of the composition, and the ratio of metal perchlorate oxidizer to water falling within the compositional range in which sub-

stantially all of the water in the slurry can be chemically bound to the sodium perchlorate in the form of a hydrate.

4. The explosive composition of claim 3 in which the metallic fuel is aluminium and in which the sensitizing agent is cyclotrimethylenetrinitramine.

5. The explosive composition of claim 4 containing from about 0% to about 5.0% organic fuel solvent.

6. The process of preparing as explosive composition consisting essentially of by weight from about 25% to about 90% of a metal perchlorate oxidizer, selected from the group consisting of sodium perchlorate, lithium perchlorate, magnesium perchlorate, strontium perchlorate, calcium perchlorate, aluminum perchlorate, and mixtures thereof, from about 3% to about 15% water, from about 0% to about 40% metallic fuel, and from 0% to about 60% organic sensitizing agent, said process comprising:

(a) admixing water and a metal perchlorate oxidizer at a temperature above a dissociation temperature of a hydrate which can be formed from the water-metal perchlorate admixture to form a fluent slurry,

(b) while maintaining the temperature of the slurry above the dissociation temperature of a perchlorate-hydrate which can be formed, admixing metallic fuel and organic sensitizing agent to the fluent slurry in an amount such that the cumulative weight of these components comprises at least 20% by weight of the resulting slurry composition, said resulting slurry being homogeneous and fluent,

(c) transferring said fluent explosive composition into a receiving means, and

(d) cooling the explosive composition to below the dissociation temperature of the perchlorate hydrate at which temperature the fluent slurry is converted to the nonfluent state.

7. The process of claim 6 in which the metal perchlorate oxidizer is sodium perchlorate, the temperature of admixing water and sodium perchlorate oxidizer is above 50° C. the resulting explosive composition being cooled to a temperature below about 50° C. to form a nonfluent composition.

8. The process of claim 6 in which the metal perchlorate oxidizer is the lithium perchlorate, the temperature of admixing water and lithium perchlorate is between about 95° C. and 100° C., the resulting explosive composition being cooled to a temperature below about 93° C. to form a nonfluent explosive composition.

9. The process of claim 6 in which the metal perchlorate oxidizer is magnesium perchlorate, the temperature of admixing water and magnesium perchlorate is between about 80° C. and 100° C., the resulting explosive composition being cooled to a temperature below about 80° C. to form a nonfluent explosive composition.

10. The process of claim 6 wherein the metal perchlorate oxidizer is strontium perchlorate, the temperature of admixing water and strontium perchlorate is between about 95° C. and 100° C., the resulting explosive composition being cooled to a temperature below about 95° C. to form a nonfluent explosive composition.

11. The process of claim 6 wherein the metal perchlorate oxidizer is calcium perchlorate, the temperature of admixing water and calcium perchlorate is between about 85° C. and 100° C., the resulting explosive composition being cooled to a temperature below about 85° C. to form a nonfluent exposive composition.

12. The process of claim 6 wherein the metal perchlorate oxidizer is aluminum perchlorate, the temperature of admixing water and aluminum perchlorate is between above 77° C. and 175° C., t he resulting explosive composition being cooled to a temperature below about 75° C. to form a nonfluent explosive composition.

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U.S. Cl. X.R.

149—40, 42, 44, 77, 78, 83, 85, 92

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,684,594 Dated August 15, 1972

Inventor(s) Richard H. Evans (Case 1)

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 1 of the Abstract of Disclosure
Page 1, line 1 of the Abstract of Disclosure
" exposive " should read -- explosive --.

Column 1, line 60 of the printed patent
Page 2, line 31 of the application, " exposive "
should read -- explosive --.

Column 3, Table 1 last column corresponding to
Page 6 of the application, " 121-170 ",
" 86-125 " and " 77-80 " should read -- 121-175 --,
-- 86-120 -- and -- 77-85 --.

Column 4, Table II opposite "Cooling Temperature,
°C. (non-fluent slurry)" corresponding to Page 9
of the application, " $\geq$93, $\geq$95, $\geq$50, $\geq$50, $\geq$50, $\geq$50 "
should read -- $\leq$93, $\leq$95, $\leq$50, $\leq$50, $\leq$50, $\leq$50 --.

Column 5, line 56 of the printed patent
Page 11, line 16 of the application, insert " by "
between -- attack water --.

In the Claims, Column 6, Claim 1, line 46, delete
" lithium perchlorate ". Claim 1, line 47, delete
" chlorate, magnesium perchloride, ". Claim 1, line
47 after "strontium perchlorate," insert -- calcium
perchlorate, aluminum perchlorate, --.

Column 7, Claim 4, line 4, " aluminium " should read
-- aluminum --.

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,684,594 Dated August 15, 1972

Inventor(s) Richard H. Evans (Case 1) - 2 -

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

Column 7, line 8, Claim 6, " as " should read -- an --.

Column 8, Claim 11, line 21, " exposive " should read -- explosive --.

Column 8, Claim 12, line 25, " above " should read -- about --.

Signed and sealed this 9th day of January 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents