United States Patent Office

3,312,578

Patented Apr. 4, 1967

3,312,578

SLURRIED BLASTING EXPLOSIVES WITH CROSS-LINKING DELAY AGENT

Joseph Francis McLean Craig, Beloeil, Quebec, Errol Linton Falconer, St. Hilaire, Quebec, Stanton Evan Jack, Kingston, Ontario, and Gordon Towell, Otterburn Heights, Quebec, Canada, assignors to Canadian Industries Limited, Montreal, Quebec, Canada, a corporation of Canada

No Drawing. Filed July 1, 1965, Ser. No. 468,967

Claims priority, application Canada, Sept. 13, 1963, 884,511

10 Claims. (Cl. 149—38)

This application is a continuation in part of our copending application, Ser. No. 390,755 filed Aug. 19, 1964, entitled, "Slurried Blasting Explosives."

The present invention relates to improved slurried blasting explosive compositions which consists essentially of one or more organic explosives and one or more inorganic oxygen-supplying salts slurried in an aqueous solution of said inorganic oxygen-supplying salts. Thus water, for example, in an amount between about 5 and 25% by weight, is an essential ingredient of such explosive compositions. This invention also relates to processes for the preparation of such explosive compositions.

The above slurried explosives are now well known and some of them containing trinitrotoluene (TNT), ammonium nitrate (A.N.) and water are described, for example, in United Kingdom Patent No. 869,155. They have found wide acceptance and use in recent years, particularly in open-pit mining, quarrying and construction operations. They are safe to use because of their insensitivity to blasing cap detonation, economical and, because of their high borehole loading density characteristics, very powerful.

As is well known in the art, addition of finely divided metal such as aluminum or magnesium or alloys thereof to explosive mixtures composed of an oxygen-supplying salt and an organic explosive, greatly enhances the power of the explosive mixtures.

Such explosive mixtures containing aluminum are described, for example, in the aforementioned United Kingdom Patent 869,155. It can be demonstrated that explosive slurries devoid of aluminum and containing about 25% by weight of particulate TNT and about 40% by weight of A.N. produce a power, measured in terms of pure TNT=10, of 10.8. When the composition of these slurries is altered so as to contain about 17% by weight of finely divided aluminum, the final composition being in approximate parts by weight, 17 percent of aluminum, 20 percent of particulate TNT and 48.2 percent of A.N., the remainder being water, the power measured in terms of pure TNT=10 is found to be 17.6. It can be seen, therefore, that these aluminum-containing slurried explosive compositions, because of their substantial increase of power over ordinary slurries, are most desirable for use in the field.

It has been found, however, that slurried explosive compositions comprising inorganic oxygen-supplying salts, particulate organic explosives and finely divided aluminum or other suitable metal have very poor storage properties, even when containing gelling agents such as the mannogalactans proposed in Canadian Patent No. 617,006 dated Mar. 21, 1961. Even over short periods of time the gel characteristics of the slurries tend to be destroyed, which results in rapid segregation of the slurries into solids and a supernatant liquid layer. This segregation, which does not normally occur in slurry compositions which, while containing a mannogalactan gelling agent, do not contain finely divided aluminum or alloys of aluminum, appears to be due to a chemical interaction between the metal ions and the gelling agent which breaks down the gel consistency of the mixture. This, in turn, results in the rapid segregation referred to above. This segregation, of course, destroys the homogeneity of the mixture, making it subject to failure to propagate in boreholes in the field. Furthermore, a homogeneous gelled slurry presents excellent resistance to water which may be present, for example, in boreholes as has been described in the aforementioned Canadian Patent 617,006. However, when segregation of the slurries occurs, resistance to water attack and penetration is reduced and this in turn reduces the sensitivity of the composition and can result in detonation failure in use. Consequently, factory-manufactured aluminum or aluminum alloy-containing explosive slurries have proven attractive to the trade only under conditions of very short-term storage at relatively low ambient temperatures, the latter factory having some tendency to reduce the segregation of the solid and liquid ingredients.

To overcome the problem of segregation of ingredients in aluminum or aluminum alloy-containing slurry explosives, some users have resorted to the on-site mixing of the slurries followed by immediate loading into boreholes. However, even this procedure may permit segregation of ingredients to take place in the boreholes unless charged boreholes are detonated without delay. Furthermore, this on-site mixing of the slurries can normally only be justified on an economic basis by the large users of explosives. The small user of explosives who is unable to support the cost of on-site mixing and raw material storage facilities, and yet wishes to take advantage of the additional power and low cost of aluminum-containing explosive slurries, must resort to the use of a factory-manufactured and packaged product.

It is the primary object of this invention to provide an improved slurried explosive composition containing finely divided aluminum or alloys thereof which is resistant to segregation of its ingredients over long periods of storage and which resists attack and penetration by water. Other objects of the invention will appear hereinafter.

The improved slurried blasting explosive composition of this invention comprises at least one inorganic oxygen-supplying salt, at least one particulate organic explosive, a gel-forming or thickening polysaccharide, finely divided metal from the group consisting of aluminum and aluminum alloy, water and a metal chromate, selected from the group consisting of sodium and potassium dichromate, in an amount ranging from 0.01% to 0.10% by weight, and zinc chromate and barium chromate in an amount ranging from 0.01% to 2.0% by weight.

When the slurry contains a gel-forming or thickening polysaccharide of the self-cross-linking type, the amount of zinc chromate should preferably not exceed 0.1% by weight since otherwise there may be a syneresis effect and the composition may tend to segregate to some extent on storage. Also, when TNT is employed as the organic explosive, some darkening in colour of the TNT and evolution of ammoniacal fume may occur.

The composition may also advantageously contain a cross-link delaying agent in an amount ranging from 0.002% to 0.1% by weight of the composition.

It has indeed been surprisingly discovered that the addition of the above metallic chromates in the amounts indicated to an aluminum or an aluminum alloy-containing explosive slurry has the desirable effect of overcoming, or at least reducing, the tendency for this type of slurry to separate into solid and liquid layers on storage and, at the same time, providing a cross-linking action with the gel-forming polysaccharide, thereby producing a cohesive slurry much more resistant to water attack and penetration than possible heretofore.

It has also been surprisingly discovered that the addition of a cross-link delaying agent in the amounts indicated has the advantageous effect of delaying the cross-linking action of the metallic chromate ion on the polysaccharide, thereby permitting the slurry to remain extremely free-flowing for a period sufficiently long to enable easy packaging. Suitable cross-link delaying agents are metal oxalates, metal citrates, oxalic acid, citric acid, tartaric acid and gluconic acid or a mixture thereof.

The invention thus renders possible the preparation of useful and powerful aluminum or aluminum alloy-containing slurries in explosive factories under controlled and safe conditions, which slurries may be stored for long periods of time without segregation of the solid and liquid ingredients.

Preferred slurried blasting explosive compositions of this invention contain from 20 to 80 percent by weight of at least one inorganic oxygen-supplying salt, from 3 to 50 percent by weight of at least one particulate organic explosive, from 5 to 35 percent by weight of finely divided aluminum or aluminum alloy, from 0.2 to 2.0 percent by weight of a gel-forming or thickening polysaccharide, from 0.01 to 2.0 percent by weight of zinc chromate, from 0.002 to 0.1 percent by weight of a cross-link delaying agent and from 5 to 25 percent by weight of water.

A very suitable inorganic oxygen-supplying salt for inclusion in the explosive composition of this invention is ammonium nitrate. It is in some cases advantageous to replace some, suitably up to 50 percent, or all of the ammonium nitrate by other metal nitrates such as sodium, barium, potassium and calcium nitrates. The particle size of the inorganic oxygen-supplying salts is not critical and powdered, granulated, prilled or crystalline forms may be used or all or part of the salts may be predissolved in all or part of the water.

The organic explosives suitable for use in the blasting agents of this invention are described herein as "particulate." By "particulate" it is intended to exclude liquid explosives such as nitroglycerine and nitroglycol and to indicate that the explosive should be in a powdered, granular, flaked or pelleted form. A very suitable organic explosive is TNT although a large class of organic explosives that can be made in particulate form is suitable for use in this invention either as such or in admixture with TNT or each other, but in many cases they prove more expensive than TNT. This class includes pentaerythritol tetranitrate (PETN), tetryl, cyclotrimethylenetrinitramine (R.D.X.), pentolite (being a mixture of approximately equal parts of TNT and PETN) and composition B (being a mixture of about 60 percent by weight of R.D.X. and

about 40 percent by weight of TNT, plus a little wax). Smokeless powder is also considered as an organic explosive for the purpose of this invention.

The aluminum or aluminum alloy suitable for use in the explosive composition of this invention must be in a finely divided form and may most suitably range from a fine dust to a form not coarser than that which will pass through a size 10 Tyler mesh screen.

The gel-forming or thickening polysaccharides are preferably mannogalactans such as guar gum or carob seed gum.

The slurried explosive composition of this invention may be prepared in any suitable type of mixing equipment, but preferably the mixer should have no rapidly moving parts and should have a folding action combined with a lifting of material from the bottom of the mixer to the top. The conventional "ribbon type" mixer is particularly suitable for this purpose. A preferred mixing procedure is to mix together the dry inorganic oxygen-supplying salt, the metal chromate and water and then add the finely divided aluminum or aluminum alloy. After a few minutes of mixing, the particulate organic explosive may be added and dispersed and the cross-link delaying agent added. The gelling or thickening agent may then be added as a dry powder or mixed with a small quantity of ethylene glycol or glycerine as a dispersion medium and the whole composition mixed until homogeneous. The desired final temperature of the mixture should be from 50° to 140° F. in order that the slurry can be packaged satisfactorily. To achieve the desired final temperature it may be necessary that the water ingredient be added hot or as a hot solution of the inorganic oxygen-supplying salt, or a heated mixer may be used.

The following tables and example illustrate the improved explosive composition of this invention but it is to be understood that the invention is not limited in scope to the embodiments described. In the tables and example all parts and percentages are by weight of the total composition.

The compositions shown in Table I were prepared in the aforedescribed manner, ethylene glycol being used as dispersion medium for the thickening agent, and placed in glass cylinders 20" high. The inches of segregated fluid at the top of the column after storage at 90° C. are shown for the times indicated. Mix No. 10 containing no metal chromate is included to illustrate the high rate of segregation of the compositions of the prior art.

TABLE I

Mix No.	1	2	3	4	5	6	7	8	9	10
Formula Composition (parts):										
Ammonium nitrate	48.8	48.6	48.4	48.9	48.9	48.9	51.6	48.7	48.6	48.7
Sodium nitrate	8.0	8.0	8.0	8.0	8.0			8.0	8.0	8.0
Barium nitrate						8.0	8.0			
Water	11.5	11.5	11.5	11.5	11.5	11.5	13.5	11.5	11.5	11.8
Aluminum powder (98 percent purity)	10.0	10.0	10.0	10.0	10.0	10.0	20.0	10.0	10.0	10.0
TNT	20.0	20.0	20.0	20.0		20.0		10.0	20.0	20.0
PETN							5.0			
Composition B					20.0					
Smokeless powder								10.0		
Ethylene glycol	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Guar gum (fast gelling)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Zinc chromate	0.2	0.4	0.6				0.4	0.2	0.4	
Sodium dichromate				0.1	0.1					
Potassium dichromate						0.1				
Tartaric acid	0.01	0.02	0.03	0.02	0.02	0.02	0.02			
Citric acid								0.09		
Gluconic acid									0.02	
Segregation in 20" column stored at 90° F.:										
Inches of segregation	Nil	Nil	Nil	Nil	⅛	Nil	Nil	Trace	Nil	1½
Length of storage in days	30	34	30	31	28	28	28	37	31	11

The Table II illustrates the cross-linking delaying effect produced by the addition of the cross-link delaying agents.

The times in minutes from the addition of the gel-forming agent until the onset of cross-linking are shown. The compositions used were the same as that shown as Mix No. 1 in Table I and were prepared in the same manner except that beaker-size laboratory batches only were used and the cross-link delaying agent was varied as indicated. The viscosity of the composition was determined at 3 to 5 minute intervals after the addition of the gel-forming agent by means of a Brookfield Viscosimeter, the onset of cross-linking being marked by a sudden change in viscosity reading.

the aluminum slurry loaded per hole was 25 percent less than had been the practice with the 25 percent TNT slurry. Despite the lower weight of aluminum slurry (Mix No. 1) used, it was found that the fragmentation of the ore in the ensuing blast was much greater than had been obtained previously. The higher power of the aluminum slurry also resulted in greater throw of the muck-pile which combined with the better fragmentation made for easier handling by the shovel. Complete progagation in all charged boreholes resulted.

TABLE II

Cross-link delaying Agent	Time in minutes from addition of guar to onset of cross-linking			
	Citric Acid	Tartaric Acid	Gluconic Acid	None
0.1%		More than 122 min	More than 180 min	
0.9%	75 min			
0.07%	40 min			
0.05%	32 min	90 to 160 min		
0.025%		110 min	More than 96 min	
0.125%		95 min		
0.00325%		56 min		
None				13 to 30 min.

Table III illustrates the effects of using various proportions of zinc chromate in slurries containing self-cross-linking guar gum. The compositions shown in the table comprised 37.5% of ammonium nitrate, 8.0% of sodium nitrate, 20.0% of trinitrotoluene, 17.0% of finely divided aluminum, 0.9% of glycol and 16.0% of water. The percentages of self-cross-linking guar gum and zinc chromate in the examples are shown under appropriate headings in the table. The examples were prepared and placed in glass cylinders 20" high The depth of segregated fluid on the top of the column after storage at 85–90° F. is shown for the time indicated. Observations of the final condition of the compositions are indicated under the heading "comments."

TABLE III

Mix No.	Self-cross linking guar gum, percent	Zinc chromate, percent	Days storage at 85–90° F.	Segregation in 20" column	Comments
11	0.6		25	5/8"	Considerable darkening, stickiness, NH_3 odor.
12	0.6	0.1	33	Nil	Slight syneresis, slight darkening.
13	0.6	0.03	14	Nil	No syneresis or colour change.
14	0.6	0.01	15	Nil	Do.
15	0.6	0.003	7	2"	Moderate darkening.
16	0.6	0.001	7	3"	Do.

As can be seen from the table, those compositions which contained less than 0.01% of zinc chromate exhibited undesirable properties of segregation or excessive colour change. The composition of Mix No. 12, while containing the preferred upper level of 0.1% by weight of zinc chromate, showed no segregation of ingredients and only slight syneresis and colour change.

The following example illustrates the increased power and reliable propagation of the improved slurry blasting explosive of this invention.

Example

In a trial at an iron ore quarrying operation, a factory-manufactured slurry having the composition shown as Mix No. 1 in Table I (containing 10 percent aluminum) and made one month before the date of trial, was substituted for a slurry containing 25 percent by weight of TNT, inorganic nitrates and water. The drill pattern and borehole diameter were unchanged but the weight of

What we claim is:

1. A slurried blasting explosive composition resistant to segregation of its ingredients over long periods of storage, comprising at least one inorganic oxygen-supplying salt, at least one particulate organic explosive, a thickening polysaccharide, a finely divided metal selected from the group consisting of aluminum and alloys thereof, water, a metal chromate selected from the group consisting of sodium chromate and potassium dichromate in an amount ranging from 0.01 percent to 0.1 percent by weight and zinc chromate and barium chromate in an amount ranging from 0.01 percent to 2.0 percent by weight and a cross-link delaying agent selected from the group consisting of metal oxalates, metal citrate, oxalic acid, tartaric acid, gluconic acid and citric acid.

2. An explosive composition as in claim 1 wherein the components are present in the following proportions, by weight: 20 to 80% oxygen-supplying salt, 3 to 50% particulate organic explosive, 0.2 to 2% polysaccharide in the form of a gel-forming mannogalactan, 5 to 35% finely divided metal, 5 to 25% water.

3. An explosive composition as in claim 1 wherein the cross-link delaying agent is present in an amount from 0.002% to 0.1% by weight.

4. An explosive composition as in claim 1 wherein the inorganic oxygen-supplying salt is selected from the group consisting of nitrates of ammonium, sodium, barium, potassium, calcium and mixtures thereof.

5. An explosive composition as in claim 1 wherein the particulate organic explosive is selected from the group consisting of trinitrotoluene, composition B, pentolite, pentaerythritol tetranitrate, cyclotrimethylene-trinitramine, smokeless powder and mixtures thereof.

6. An explosive composition as in claim 1 wherein the

polysaccharide is selected from the group consisting of guar flour, self-cross-linking guar gum and carob seed gum.

7. An explosive composition as in claim **1** wherein the finely divided metal has a particle size not greater than 10 standard Tyler mesh size.

8. An explosive composition as in claim **1** wherein the components are present in the following proportions by weight: 20 to 80% oxygen-supplying salt, 3 to 50% particulate organic explosive, 0.2 to 2% self-cross-linking polysaccharide, 0.01 to 0.1% zinc chromate, 5 to 35% finely divided metal and 5 to 25% water.

9. A process for preparing the slurried blasting explosive of claim **1** comprising: first mixing the inorganic oxygen-supplying salt, the metal chromate, the water and the finely divided metal; incorporating the particulate organic explosive and the cross-link delaying agent; adding the polysaccharide; and mixing further to form a homogeneous slurry.

10. A process as in claim **9** wherein the polysaccharide is added in the form of a dispersion in a liquid selected from the group consisting of ethylene glycol and glycerine.

References Cited by the Examiner

UNITED STATES PATENTS

2,904,420	9/1959	Holker	149—46 X
3,155,552	11/1964	Vriesen	149—37 X
3,214,307	10/1965	Logan et al.	149—41 X

CARL D. QUARFORTH, *Primary Examiner.*

S. J. LECHERT, Jr., *Assistant Examiner.*